BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1937.

New electronic theory of organic reactions. H. F. Tseou (Separate, Hangchow, 223 pp.; cf. A., 1936, 960).—An extension of previous theory and a survey of the literature of theory of org. reactions. The position of an element in the periodic table is determined by the condition of the electrons in the outermost sphere and there is an equilibrium point at which the electrons of an element would have no tendency to be displaced either inwards or outwards. C is supposed to be an element slightly to the left of this point but its position may be moved either farther to the right or left depending on whether it is joined to an element which repels electrons strongly or to one which attracts them. In doubly and trebly bound C and also in cyclic compounds the octets of electrons are more compact. In every chemical reaction there is involved a complicated system of electron displacements of the reacting mols., and the at. radius of an element can by no means be a const. quantity but is different in different compounds. With this formulation the facts in org. chemistry are accounted for. The theory finds substantial proofs in different physical measurements. F. R. S.

Catalytic isomerisation of *n*-hexene and octene in presence of zinc chloride and phosphoric acid. A. D. Petrov and M. A. Tschelzova (Compt. rend. Acad. Sci. U.R.S.S., 1937, **15**, 79—84).—Branched-chain hydrocarbons containing a quaternary C are much less readily chlorinated by $SbCl_5$ in $CHCl_3$ than those with only *tert.* C (cf. A., 1935, 1102). In absence of $CHCl_3$, chlorination is much more extensive. Octan-β-ol when heated with $ZnCl_2$ affords a mixture of Δ^{α}- (I) and Δ^{β}-octene (II), which when heated at 325—350° for 25 hr. in presence of $ZnCl_2$ and then hydrogenated affords 12% of *iso*-compounds (III). Higher yields of (III) are obtained at pressures of 50 atm. and in <1·5 hr. in presence of $ZnCl_2$ or H_3PO_4. (I) and (II), individually, similarly afford isomerides hydrogenated to products containing 46·8% of (III). Δ^{α}-Hexene after isomerisation and hydrogenation gives 23% of (III). J. L. D.

Completion of Krafft's proof of the structure of cetene. S. L. Langedijk and P. L. Stedehouder (Rec. trav. chim., 1937, **56**, 526—528).—Cetene is Δ^{α}-*n*-hexadecene since its dibromide (I) is converted by 0·9*N*-EtOH–KOH at 180—200° first into Δ^{α}-*n*-hexadecinene (II) (ppt. with $AgNO_3$–EtOH), isomerised by prolonged treatment into Δ^{β}-*n*-hexadecinene (III) (no Ag compound). (III) is unchanged by solid KOH at 190°/75 mm., conditions under which (I) affords (II). J. W. B.

Determination of the constitution of hydrocarbons of the C_nH_{2n-2} series. A. E. Favorski and M. D. Bone (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 499—504).—Oxidation of allene hydrocarbons with $KMnO_4$ yields unsaturated glycols which isomerise at once to ketols, which are further oxidised to acids, giving no differentiation between the acetylenic and allene type. With O_3, diozonides are formed which decompose to CO_2 and dicarboxylic acids, from the nature of which the structure of the allene may be deduced. J. D. R.

Characteristics of hydrocarbons of the C_nH_{2n-4} series with conjugated double and triple linkings. A. I. Zacharova (Sci. Rep. Leningrad State Univ., 1936, **2**, No. 2, 162—195).—COMeEt is added gradually to a suspension of KOH in Et_2O saturated with C_2H_2 at −10°, C_2H_2 is passed for 8 hr., and H_2O is added, when OH·CMeEt·C:CH is obtained in 70% yield. This gives CHMe:CMe·C:CH (I) when passed over $MgSO_4$ at 230°. (I) and KOH in MeOH (120°; 12 hr.) give *β-methoxy-γ-methyl-*$\Delta^{\alpha\gamma}$*-pentadiene* (II), b.p. 45—46°/15 mm., converted by heating with 1% H_2SO_4 (25—30°; 8 hr.) into CHMe:CMe·COMe, and by O_3 in $CHCl_3$ into MeCHO, $AcCO_2Me$, and HCO_2H. (I) and KOH in EtOH yield similarly *β-ethoxy-γ-methyl-*$\Delta^{\alpha\gamma}$*-pentadiene* (III), b.p. 54—55°/15 mm., which reacts analogously to (I) with 1% H_2SO_4, and gives *β-ethoxy-γ-methylpentane*, b.p. 140—142°, on hydrogenation (Pd–Ni). A *dimeride* of (I), b.p. 74—75°/10 mm., is obtained as a by-product of the prep. of (II) or (III); it yields $H_2C_2O_4$, COMeEt, and AcOH with $KMnO_4$, and is probably $(CMeEt:C:C:)_2$. R. T.

Photochemical oxidation, sensitised by bromine, of carbon tetrabromide to carbonyl bromide and bromine in solution in carbon tetrachloride. W. Koblitz, H. Meissner, and H. J. Schumacher (Ber., 1937, **70**, [*B*], 1080—1086).—The rate of Br-sensitised photochemical oxidation of CBr_4 in CCl_4 has been examined by measurement of the O_2 absorbed at 14° and 0·3° with light of λ 436 mμ. With relatively high [Br] the complete change may be nearly represented by $2CBr_4 + O_2 = 2COBr_2 + 2Br_2$. Even with high [$CBr_4$] the quantum yield of the change is <1 mol. per *hν*. Br is feebly restrictive, O_2 weakly accelerating, to the change. $COBr_2$ has no influence. The temp. coeff. between 0° and 14° is about 1·2 per 10°. The course of the change is approx. expressed, $QA = [CBr_4]/0{\cdot}11 + 0{\cdot}06[Br_2]/[O]_2 + [CBr_4]$. The energy required to separate the first Br from CBr_4 is ⩾50 kg.-cal. H. W.

Halogenation of ethylenes. I. Roberts and G. E. Kimball (J. Amer. Chem. Soc., 1937, **59**, 947—948).—Contrary to usual statements, free rotation about the C:C linking is not to be expected in

CRR'Hal·CR''R'''. Since the ionisation potentials of C and halogen are similar, an equally probable structure is $Hal^+<^{CRR'}_{CR''R'''}$, in which the halogen acts as donor of two electrons to form a co-ordinate link with the C; the actual structure of the ion is intermediate between the two. Reaction of an ethylene with halogen involves first formation of such an ion, which then adds Hal^- by a "three-atom" reaction; this gives *trans* addition. If, however, R and R'' are similarly charged, *e.g.*, CO_2^-, the force of repulsion may suffice to cause rotation before the second step of addition occurs; this leads to *cis* addition. This mechanism is shown to accord with experiment.

R. S. C.

Addition of hydrogen bromide to allyl bromide in the presence of various substances. VI. Homogeneity of the catalytic action of oxygen. Theory of the oxygen effect. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1937, **12**, 173—176).—CH_2:CH·CH_2Br and HBr react in the presence of O_2 in an identical manner and to the same extent whatever is the surface area at which reaction occurs. It is suggested as an interpretation of earlier results (cf. this vol., 224) that O_2 catalyses the formation of $CH_2(CH_2Br)_2$ and not CHMeBr·CH_2Br in the above reaction.

J. L. D.

Preparation of aliphatic dihalogeno-compounds of high mol. wt. J. VON BRAUN and E. KAMP (Ber., 1937, **70**, [*B*], 973—978).—The prep. of long-chained dihalogeno-paraffins according to the scheme, Br·$[CH_2]_n$·Br → OPh·$[CH_2]_n$·Br → OPh·$[CH_2]_{2n}$·OPh → Hal·$[CH_2]_{2n}$·Hal fails when n is large owing to the difficulty of the final step. This difficulty disappears when the corresponding alkyl ethers are used but the b.p. of Br·$[CH_2]_n$·Br and OAlk·$[CH_2]_2$·Br are inconveniently close; it is completely avoided by use of hydroaromatic ethers. $CH_2(CH_2·CH_2·OPh)_2$ is reduced (Ni) by H_2 at about 200°/100 atm. to αε-*dicyclohexyloxypentane* (I), b.p. 180—184°/10 mm., with some *cyclo*hexyloxypentane and *cyclo*hexanol (II). (I) and fuming HBr at 100° yield Br·$[CH_2]_5$·Br and *cyclo*hexyl bromide. OPh·$[CH_2]_{10}$·OPh, b.p. 215—225°/0·05 mm., best obtained from OH·$[CH_2]_{10}$·OH, is hydrogenated to ακ-*dicyclohexyloxydecane* (III), b.p. 168—170°/0·05 mm., mixed with *n*-decane, (II), and *cyclo*hexyl decyl ether. (III) gives Br·$[CH_2]_{10}$·Br (IV), m.p. 28°. (IV) and NaOPh in EtOH give unchanged material, OPh·$[CH_2]_{10}$·OPh, and OPh·$[CH_2]_{10}$·Br; the latter is converted by Na in Et_2O into Ph decyl ether, κ-phenoxy-Δ^{α}-decene, and *diphenoxyeicosane*, m.p. 92—93°, from which impure dibromoeicosane is isolated.

H. W.

1 : 2- and 1 : 4-Addition. II. Nitrogen tetroxide and trimethylethylene [*iso*amylene]. A. MICHAEL and G. H. CARLSON (J. Amer. Chem. Soc., 1937, **59**, 843—849; cf. this vol., 244).—N_2O_4, alone or in light petroleum, functions as O·NO_2 + NO, since with CMe_2:CHMe it gives 43·2—47·6 and 35·2—39·2%, respectively, of bis(*iso*amylene nitrosate) (I). In Et_2O it functions mainly as O·NO + NO_2, since in this solvent it yields about 35% of γ-nitro-β-methylbutan-β-ol nitrite (II), m.p. 60°, and 0·15—8·2% of (I). In both cases the yields are relatively independent of temp. and thus of the equilibrium, $N_2O_4 \rightleftharpoons 2NO_2$. In neither case could the other products be identified. As usually obtained, (I) is blue; distillation in steam gives a colourless product, removing about 25% of a blue oil, b.p. 43—47°/2 mm. (C 48·72, H 7·25, N 12·58%), which is not the monomeric form of (I). (I) is identified by reaction with NaSPh and NaSEt in EtOH to give $NaNO_3$ and the *thio-ethers*, NO·CHMe·CMe_2·SR, R = Ph, m.p. 90° (PhNCO additive *compound*, m.p. 113—114°), and Et, m.p. 60° (PhNCO additive *compound*, m.p. 122°), respectively. (II) and NaSPh in EtOH give the *thio-ether*, NO_2·CHMe·CMe_2·SPh, an oil, stable to H_2O_2–AcOH, but oxidised by CrO_3 to the *sulphone*, m.p. 102—103°.

R. S. C.

Catalytic oxidation of organic compounds by carbon dioxide. I. Oxidation of *iso*amyl alcohol in presence of oxide and salt catalysts. A. M. RUBINSTEIN, K. P. PREOBRASHENSKAJA, and L. S. TSCHERNOMORSKAJA. **II. Oxidation of different alcohols.** A. M. RUBINSTEIN and N. F. LUKASCHINA. **III. Mechanism of oxidation of alcohols.** A. M. RUBINSTEIN and N. M. NAGIEV (Sci. Rep. Moscow State Univ., 1936, No. 6, 287—297, 299—305, 307—319).—I. The yields of CH_2Pr^{β}·CHO (I) and CH_2Pr^{β}·CO_2H (II) obtained under optimum conditions by passing *iso*-C_5H_{11}·OH (III) in a stream of CO_2 over a no. of catalysts are: U_3O_8 at 450°, 72·9 and 12·3, MoO_3–pumice at 450°, 59·3, and 18·2, $Ca(VO_3)_2$ (IV) at 600°, 58·6 and 3·7, $Sn(VO_3)_2$ at 450°, 56 and 30·4, and MoO_3–V_2O_5–pumice at 400°, 40·8 and 37·9%. Except in the case of (IV) the optimum temp. are the same as for oxidation by air in presence of the same catalysts. The optimum rates of flow of CO_2 are determined for each catalyst.

II. (III)–CO_2 mixtures yield chiefly CH_2:$CHPr^{\beta}$ (V) in presence of V_2O_5 at 550°, and $Bu^{\beta}OH$–CO_2 mixtures give chiefly CH_2:CMe_2 with MoO_3 at 350—500°. CH_2Ph·OH and CO_2 afford PhCHO 54% and BzOH 32·5% with MoO_3 at 400°.

III. The gaseous products obtained by passing (III), (III)–H_2O, (III)–CO_2, or (III)–CO_2–H_2O mixtures over MoO_3–asbestos at 350—500° contain chiefly H_2, together with (V), CO, and CO_2, the yield of (V) being greatest, and of H_2 least, when (III) alone is passed over the catalyst. The ratio (I)/(II) in the liquid product falls with increasing temp. Under the conditions of the experiment, HCO_2H (VI) yields CO and H_2. The reaction of oxidation of alcohols by CO_2 is represented: $CH_2R·OH + CO_2 \rightarrow R·CHO + (VI)$; $(VI) \rightarrow CO + H_2$; $R·CHO + H_2O \rightarrow CHR(OH)_2 \rightarrow R·CO_2H + H_2$; $CHR(OH)_2 + CO_2 \rightarrow R·CO_2H + (VI)$.

R. T.

Photochemical peroxide formation. VIII. Oxidation of glycol by molecular oxygen in ultra-violet light. IX. Oxidation of paracetaldehyde by molecular oxygen in ultra-violet light. R. CANTIENI (Z. wiss. Phot., 1937, **36**, 116—118, 119—120).—VIII. $(CH_2·OH)_2$ forms a peroxide OH·CH_2·CH_2·O_2H with O_2 in ultra-violet light. Further action of the peroxide with activated $(CH_2·OH)_2$ gives CO_2, H_2O, and $(CH_2·OH)_2$. The reaction is similar to the photochemical oxidation of glycerol (A., 1936, 1091).

IX. Paracetaldehyde forms a peroxide when mixed with O_2 and exposed to ultra-violet light. The amount of peroxide produced varies linearly with time at first, but later decreases owing to decomp. A. J. M.

Acidimetric determination of glycerol (and erythritol) by periodates. M. L. Malaprade (Bull. Soc. chim., 1937, [v], **4**, 906—910).—The solution is neutralised to Me-red, treated with an excess of $NaIO_4$ for 20 min. and then with conc. aq. KNO_3 (which ppts. KIO_4). The liberated HCO_2H ($2NaIO_4 + C_3H_8O_3 \rightarrow 2CH_2O + HCO_2H + 2NaIO_3 + H_2O$) is determined by titration with a strong base. With KIO_4 the procedure is simpler. The method is exact in presence of EtOH or $(CH_2{\cdot}OH)_2$. Weak bases and acids weaker than HCO_2H must be absent, but strong bases and acids do not interfere provided that they have no reducing or pptg. action towards $NaIO_4$. Under similar conditions erythritol affords $2HCO_2H$. H. W.

Synthesis of ethyl *iso*butyl ether. E. M. Marks, D. Lipkin, and B. Bettman (J. Amer. Chem. Soc., 1937, **59**, 946—947).—$EtOBu^{\beta}$ is obtained in 70% yield from dry $Bu^{\beta}OH$, Na, and Et_2SO_4 at 120—130°. Use of KOH instead of Na gives a 22·5% yield; 50% aq. KOH gives no ether. OEt·CHMeEt is obtained in 48% yield by use of Na. R. S. C.

Oxidation of ethyl mercaptan and ethyl disulphide by bromine in the presence of water. H. A. Young (J. Amer. Chem. Soc., 1937, **59**, 811—812).—The following reactions are proved to occur in CCl_4–H_2O mixtures: $EtSH + 3Br_2 + 3H_2O \rightarrow EtSO_3H + 6HBr$; $Et_2S_2 + 5Br_2 + 6H_2O \rightarrow 2EtSO_3H + 10HBr$. Br vapour very rapidly oxidises EtSH to Et_2S_2. R. S. C.

Rate of oxidation of ethyl disulphide by bromine. H. A. Young and M. B. Young (J. Amer. Chem. Soc., 1937, **59**, 812—816).—Et_2S_2 removes Br or I from the aq. layer of CCl_4–H_2O mixtures, indicating complex formation, but the reaction is reversible. A kinetic study shows that the initial rate of reaction is given by $dBr_2/dt = k \times [Et_2S_2(Br_2)_2]$, k being dependent on the rate of shaking. It is suggested that the first steps are: (fast) $Et_2S_2 + 2Br_2 \rightarrow 2EtSBr_2$; (slow) $EtSBr_2 + H_2O \rightarrow EtSO + 2H^{\cdot} + 2Br^-$, followed by formation of $EtSO_2Br$ and $EtSO_3H$. The reaction is catalysed by $H^{\cdot}$; when EtSH reacts with Br, the first reaction is formation of Et_2S_2 and HBr, and subsequent reaction is, therefore, abnormally fast. R. S. C.

Formation of organo-metalloidal and similar compounds by micro-organisms. V. Methylated alkyl sulphides. Fission of the disulphide link. F. Challenger and A. A. Rawlings (J.C.S., 1937, 868—875).—The prep. of the following reference substances is described: *MeSEt dimercurichloride*, m.p. 127—128°; *benzylmethylethylsulphonium picrate*, m.p. 100·5—101°; *MeSPr$^{\alpha}$ mercurichloride*, m.p. 163·5—165°; *benzylmethyl-n-propylsulphonium picrate*, m.p. 95—95·5°; *MeSEt platinochloride*, m.p. 121·5—122·5°. When $(EtS)_2$ is treated with excess of saturated aq. $HgCl_2$, 70% yields of SEt·HgCl,$HgCl_2$ (I), m.p. 151°, and with $(Pr^{\alpha}S)_2$ SPr$^{\alpha}$·HgCl,$HgCl_2$, m.p. 139°, are obtained, the products being identical with those from the corresponding mercaptans. With EtSH and $HgCl_2$, $(EtS)_2Hg$, m.p. 76—77°, SEt·HgCl, m.p. ≠260°, and (I) may be obtained at will and with Pr$^{\alpha}$SH the corresponding compounds, m.p. 65—66°, 182°, and 138—139°, respectively. Neither SR·HgCl,$HgCl_2$ nor SR·HgCl liberates any mercaptan when warmed with NaOH in an air stream. When $(EtS)_2$, $(Pr^{\alpha}S)_2$, EtSH, and Pr$^{\alpha}$SH are added to cultures of *Penicillium brevicaule* (*Scopulariopsis brevicaulis*), Saccardo, and the gases produced are absorbed in $HgCl_2$, ppts. are obtained which on treatment with NaOH in a stream of air yield MeSEt and MeSPr$^{\alpha}$. Negative results were obtained when $(PhS)_2$ and $(CH_2Ph{\cdot}S)_2$ were added to the cultures. P. W. C.

Determination of ββ-dichlorodiethyl sulphide. L. Buruiană (Z. anal. Chem., 1937, **109**, 107—110).—$(C_2H_4Cl)_2S$ in EtOH is pptd. by 5 parts of 24% aq. Na_2HgI_4 at 30—40°. The oily ppt. is collected by centrifuging in a graduated tube, and its vol. is measured. Hydrolysis products are not pptd. by Na_2HgI_4. J. S. A.

Unsaturated sulphides derived from the chloroethylenes. N. W. Cusa and H. McCombie (J.C.S., 1937, 767—770).—NaSPh with $(CHCl{:})_2$ in EtOH affords *diphenylthiolethylene*, b.p. 235—242°/760 mm., m.p. 62°. $(CH_2Cl{\cdot}CHCl)_2S$ when distilled at ordinary pressure yields *dichlorodivinyl sulphide* (I), b.p. 75—80°/15 mm., converted by NaSPh in EtOH into *di(phenylthiol)divinyl sulphide* (II), m.p. 78°, converted by NaOEt into an *isomeride* of (II), m.p. 138°. (I) with β-$C_{10}H_7{\cdot}OH$ and Na in EtOH yields *di-(β-naphthyloxy)divinyl sulphide*, m.p. 151—152°. C_2HCl_3 with NaSPh in EtOH affords *Ph αβ-dichlorovinyl sulphide* (III), b.p. 145—150°/22 mm., converted by NaOMe into *Ph α-chloro-β(?)-methoxyvinyl sulphide*, b.p. 160—165°/20 mm., by Cl_2 in CCl_4 into *Ph ααββ-tetrachloroethyl sulphide*, b.p. 175—182°/20 mm., and by NaOH in aq. EtOH into NaSPh and glycollic acid. C_2HCl_3 with NaSEt in EtOH affords mixtures of *Et dichlorovinyl sulphide*, b.p. 77—80°/30 mm., with *chlorodi(ethylthiol)ethylene* and *tri(ethylthiol)ethylene*. NaSPh with C_2Cl_4 in EtOH yields *s-dichlorodiphenylthiolethylene*, m.p. 71—72°, the Cl of which is very resistant to further substitution. SNa·$C_2H_4{\cdot}OH$ and C_2Cl_4 in EtOH, followed by treatment with $SOCl_2$, afford isomeric *compounds*, $C_6H_6Cl_4S_2$, (*a*) b.p. 145—147°/30 mm., and (*b*) m.p. 72—73°. J. D. R.

Enzymic ester syntheses.—See A., III, 269.

Constitution of peptides. I. Structure of organic acids. Raman bands of the acidic function in acids and their derivatives. C. Sannié and U. Poremski (Bull. Soc. chim., 1937, [v], **4**, 880—893).—Comparison of the Raman spectra of aldehydes, ketones, and esters with those of acids, homogeneous or dissolved in non-polar solvents, shows that the band at 1730 cm.$^{-1}$ attributed to the double linking C:O appears in acids at 1650 cm.$^{-1}$ This is not due to a displacement such as is frequently caused by substitution and the phenomenon can be explained only by the existence of two different forms of acids. The same doubling is observed in solutions of acids in

polar solvents, the relative intensity of the two bands being a function of the concn. of acid. The two forms of the acid are thus in an equilibrium dependent on the polarity of the solvent, the concn., and the temp. Since the mol. associations of acids also depend on these factors it is reasonable to attribute 1650 to the existence of associated mols. The frequency appears to be due to the vibration of a system of 2 atoms rather than to that of the entire complex or of the group O·C·O. 1650 may therefore be due to C:O deformed by the production of particular linkings of the type of the "H bond" of Latimer and Rodebush between doubly linked O and OH of the CO_2H of the associated mol. or to the existence of a "H bond" itself. Association of acids is comparable with the phenomena of "chelate structure" by which the infra-red and Raman spectra of aldehydes, *o*-hydroxybenzoic acids, and OH-acids are explained. In all these cases the internuclear distances of the O atoms (2·65 A.) are very close and appear to justify such a view. H. W.

Rates of reaction of aliphatic acid halides. R. Leimu (Ber., 1937, **70**, [*B*], 1040—1053).—Among fatty acid halides AcCl reacts most rapidly and EtCOCl least rapidly with $CH_2Cl·CH_2·OH$ (I), $CH_2Ph·OH$ (II), or *cyclo*hexanol (III) in dioxan. Higher chlorides are somewhat less active than AcCl. The rate of alcoholysis corresponds with the strength of the *n*-acids, but this does not appear to be a general regularity. Branching in the C chain, particularly at $C_{(\alpha)}$, greatly diminishes the rate of reaction with (I) but the effect is much less obvious with (II) or (III). With alkoxyacetyl chlorides the rate of reaction has a relative minimum when O is in the β-position to CO. Similar regularities are observed in the behaviour of chlorides of Cl-acids, the rates for the α-, β-, and γ-derivatives being about = 20 : 2 : 3. The α-compounds are characterised by high rate of reaction and small temp. coeff. which diminishes as the rate of reaction increases. The greater rate is connected with a smaller energy of activation of alcoholysis. The theory of induced alternating polarities cannot be used in explanation of the behaviour of fatty acid chlorides towards alcohols. $COCl_2$ is characterised by a very high rate of alcoholysis and its relatively low temp. coeff. $ClCO_2Et$ reacts so slowly with (I) in dioxan that the rate cannot be measured satisfactorily. $ClCO_2Et$ and $ClCO_2Pr^{\alpha}$ react at about the same rate with MeOH, $ClCO_2Me$ more and $ClCO_2Pr^{\beta}$ much less rapidly. The greatest rate is observed with $ClCO_2CH_2·CH_2Cl$. AcBr and (I) react very rapidly and the change has a small temp. coeff. The following new or revised data are recorded for various chlorides: dl-α-*methylbutyryl*, b.p. 118·0—118·3°/761 mm.; β-*methylbutyryl*, b.p. 117·8°/766 mm.; $CCl_3·COCl$, b.p. 117·9°/754 mm., from $CCl_3·CO_2H$ and $SOCl_2$ in C_6H_6; dl-α-*chloropropionyl*, b.p. 110·7—111·2°/760 mm.; αα-*dichloro*-, b.p. 117·4—117·8°/753 mm., dl-αβ-*dichloro*-, b.p. 43—44°/10 mm., and ββ-*dichloro*-, b.p. 43—44°/10 mm., *-propionyl*; γ-*chlorobutyryl*, b.p. 35—36°/12 mm.; *methoxy*-, b.p. 50—51°/69 mm., *ethoxy*-, b.p. 49—50°/37 mm., and n-*propoxy*-, b.p. 44—44·5°/12·5 mm., *-acetyl*-; β-*methoxy*-, b.p. 27—27·5°/3 mm., and β-*ethoxy*-, b.p. 28—28·5°/2 mm., *-propionyl*; γ-*methoxy*-, b.p. 46—47°/7 mm., and γ-*ethoxy*-, b.p. 35°/10 mm., *-butyryl*; δ-*methoxy*-, b.p. 51—51·5°/3 mm., and δ-*ethoxy*-, b.p. 64—66°/4 mm., *-valeryl*. H. W.

Kinetics of thermal decomposition of potassium formate. A. A. Balandin, L. C. Freidlin, and D. N. Vaskevitsch (Sci. Rep. Moscow State Univ., 1936, No. 6, 321—345).—HCO_2K (I) yields chiefly K_2CO_3 (II) at 370—425°, and chiefly $K_2C_2O_4$ (III) at 440—475°; both reactions proceed simultaneously at 425—440°. The energy of activation of the former reaction is 10 times that of the latter. The ratio (II)/(III) of the product falls when <27% of glass is added to the (I), and then rises rapidly to a max. for 10 : 1 glass–(I) mixtures, at 440°; the ratio is at a min. for 0·8 : 10 (III)–(I), or 3 : 10 (II)–(I) mixtures, at 405°. The process is represented as 2(I) → OH·CH(OK)·CO_2K (IV) → (III) + H_2; (IV) → (II) + CH_2O; CH_2O → CO + H_2. R. T.

Alkylacetylenes and their addition compounds. XX. Reactions of alkenyl esters derived from alkylacetylenes. S. J. Slanina and G. F. Hennion (J. Amer. Chem. Soc., 1937, **59**, 855—857; cf. A., 1936, 1490).—Esters, $RCO_2·CR':CH_2$, are readily cleaved by various reagents to the ketone, COMeR, and appropriate second fragment. β-Acetoxy-Δ$^{\alpha}$-heptene (I) with HBr at 0° gives an unstable additive compound, yielding AcBr, AcOH, COMe·C_5H_{11}, and a substance, b.p. 140—150°/23 mm.; β-acetoxy-Δ$^{\alpha}$-hexene (II) gives AcBr, COMeBu, and a substance, b.p. 130—140°/23 mm. β-Chloroacetoxy-Δ$^{\alpha}$-hexene and HCl at 10° give $CH_2Cl·COCl$ and COMeBu. With NaOMe or *p*-$C_6H_4Me·SO_3Me$ in NaOH (I) yields MeOAc and COMe·C_5H_{11}, and with Na in liquid NH_3 gives COMe·C_5H_{11}, but it is stable for 1 hr. in liquid NH_3 alone at −34°. With I in liquid NH_3 (II) gives CHI_3. R. S. C.

Preparation of angelic acid. H. P. Kaufmann and K. Küchler (Ber., 1937, **70**, [*B*], 915—916).—Tiglic acid (I) is converted into its dibromide and thence into β-bromoangelic acid. This is debrominated in neutral or acid solution to (I), whereas in alkaline solution, particularly with Na–Hg, it affords angelic acid in 70% yield. H. W.

Geometrical isomerism of halogen substituted ethylenic acids. II. Addition of hydrogen bromide to tetrolic acid. V. O. Mochnatsch and A. I. Stoliarov (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 559—564).—CMe:C·CO_2H with aq. HBr (saturated at 0°) at 25° or at 40° affords a mixture of αβ-dibromobutyric acids but aq. HBr (saturated at 25°) at 18—20° gives a mixture of β-bromocrotonic acids separated by fractional crystallisation from H_2O into the β-bromocrotonic acid, m.p. 94·4° (*Na* and *Ca* salts), and, from the mother-liquor, its stereoisomeric *form*, m.p. 80—81° (*Ca* salt). J. W. B.

***n*-Fatty acids and certain of their derivatives.**—See A., I, 289.

Fats. XXXV. Diene synthesis with fats. IV. Determination of the diene value by iodometry. Diene values of various fats and their interpretation. H. P. Kaufmann, J. Baltes, and H. Büter (Ber., 1937, **70**, [*B*], 903—907; cf. A., 1936, 966).—Maleic anhydride (I) can be determined in $COMe_2$ or

in solvents not miscible with H_2O by addition of KI–KIO_3 and an excess of 0·1*N*-$Na_2S_2O_3$; after 2 hr. 0·1*N*-I ≡ 0·1*N*-$Na_2S_2O_3$ is added and the liberated I is titrated with 0·1*N*-$Na_2S_2O_3$. The method is applied to the determination of the "diene val." of fats, which is more accurate when effected in sealed vessels than under a reflux condenser; the presence of the additive products and of other components of the fat is immaterial. The examples of $\Delta^{9\lambda}$-octadecadienoic acid and α-elæostearic acid are cited. The "diene val." is an excellent method for the determination of the content in oils of acids with conjugated double linkings but several oils have "diene vals." although, as far as is known, they are not derived from such acids. The possibility of re-esterification of (I) appears excluded and it must therefore be assumed that all oils which have a diene val. contain compounds which can react with (I). The free fatty acids derived from such oils have no diene vals. so that either the unsaponifiable matter is responsible for the action or the diene-fatty acids are changed under the mildest conditions of hydrolysis. Experiments with linseed oil suggest the presence of previously unrecognised, unsaturated compounds of very labile nature. H. W.

Catalysed polymerisation in monolayers of drying oils.—See A., I, 369.

Action of periodic acid on lactic and pyruvic acid. P. Fleury and (Mlle.) S. Boisson (Compt. rend., 1937, **204**, 1264—1266; cf. A., 1933, 376).—0·05—0·025*N*-Lactic acid (I) with HIO_4 (0·4—0·1*N*) during 1 hr. at 100° affords MeCHO (1 mol.), CO_2, and H_2O following the reduction of 1 mol. of HIO_4. (I) is very slowly oxidised completely but the amount of aldehyde present decreases only slowly, because CH_2O is formed by the action of hot HIO_4 on MeOH, a secondary product of the main reaction. $AcCO_2H$ with hot HIO_4 easily affords AcOH, which resists further oxidation. J. L. D.

Determination of lactic acid in presence of methylglyoxal. E. Bauer and F. Ziegler (Z. physiol. Chem., 1937, **247**, 1—5).—To the mixture of lactic acid (I) and AcCHO (II) containing H_2SO_4 and $MnSO_4$ a tenfold excess of H_2O_2 is added to destroy (II); the mixture is boiled for 20 min., most of the excess of H_2O_2 is destroyed with $KMnO_4$ or $NaHSO_3$, and (I) is determined by titration with 0·01*N*-I in the usual way. With biological material the method is best applied after deproteinisation. W. McC.

Oxidation of some polyhydroxylic and polyethylenic higher fatty acids by aqueous alkaline permanganate solutions. T. G. Green and T. P. Hilditch (J.C.S., 1937, 764—767).—With $KMnO_4$ in aq. NaOH, the isomeric pairs of θι-dihydroxy-stearic and -palmitic acids afford suberic acid (I); εξ-dihydroxystearic acid yields undecoic and glutaric acid, whilst the isomeric μν-dihydroxybehenic acids yield decane-αω-dicarboxylic acid. Similarly, θιλμ-tetra- and θιλμοπ-hexahydroxystearic acids afford (I) and azelaic acid, also formed from α- and β-elæostearic acids. J. D. R.

Diels–Alder diene synthesis. R. Delaby (Bull. Soc. chim., 1937, [v], **4**, 765—791).—A lecture.

Dieneometry and the diene value of fats. H. P. Kaufmann (Ber., 1937, **70**, [*B*], 900—902).—The procedure of Ellis and Jones (B., 1937, 152) has no advantage over that of the author (A., 1936, 966) and the term "M.A. val." has no advantage over "diene val." H. W.

Halogenometric determination of fumaric acid. E. Szegedy (Z. anal. Chem., 1937, **109**, 95—107).—An aq. solution of fumaric acid, free from other substances and exactly neutralised (phenolphthalein), is treated in a stoppered flask with an excess of 0·1*N*-Br in *N*-KBr. After 2 hr. in the dark, KI in 0·1*N*-HCl is added, and the liberated I is titrated with $Na_2S_2O_3$. Sources of error in the bromometric titration are discussed. J. S. A.

Contact isomerisation of methyl maleate. R. J. Levina (Sci. Rep. Moscow State Univ., 1934, No. 3, 183—185).—Me_2 maleate is converted into Me_2 fumarate by passing over Pd–asbestos at 205—206° in CO_2. R. T.

Structure of glutaconic acids and esters. IX. α-Methyl- and α-ethyl-glutaconic acids. F. S. Fitzgerald and G. A. R. Kon (J.C.S., 1937, 725—727).—*trans*-α-Methyl-Δ^{β}-propene-αγ-dicarboxylic acid (I) with AcCl at 110° followed by hydration (cold H_2O) yields *cis*-α-*methyl*-Δ^{α}-*propene*-αγ-*dicarboxylic acid* (II), m.p. 125—126° (*Me*$_2$ ester, b.p. 82—85°/2 mm.). (I) in EtOAc with O_3 affords $H_2C_2O_4$ and Me α-formylpropionate, whilst (II) gives $AcCO_2Me$. Similarly, *trans*-α-ethyl-Δ^{β}-propene-αγ-dicarboxylic acid gives a non-homogeneous *cis*-acid, $H_2C_2O_4$ being the only identifiable product from O_3 on both the *cis*- and *trans*-acids in EtOAc. J. D. R.

Vinylene homologues of glutaconic acid. C. Grundmann (Ber., 1937, **70**, [*B*], 1148—1153).—Oxalocrotonic acid is converted by warm 3% H_2O_2 into glutaconic acid (yield 75%). Similar treatment of oxalosorbic acid (I) gives $\Delta^{\alpha\gamma}$-*pentadiene*-αε-*dicarboxylic acid* (*Me*$_2$ ester, b.p. 120—122°/2 mm., m.p. 39—40°), identical with the piperylenedicarboxylic acid obtained by Willstätter by degradation of the tropine alkaloids. Treatment of (I) with excess of H_2O_2 in alkaline solution leads to *trans-trans*-muconic acid. Condensation of the higher polyenedicarboxylic esters with $Et_2C_2O_4$ is greatly improved by use of KOEt and C_5H_5N in the complete absence of moisture. The esters are hydrolysed by 2*N*-NaOH and MeOH under N_2 at room temp. The following substances are thus obtained: *oxalo-octatrienoic acid*, m.p. >360° after much softening at 230—240°, oxidised to $\Delta^{\alpha\gamma\epsilon}$-*heptatriene*-αη-*dicarboxylic acid*, m.p. 199°; *oxalo-decatetraenoic acid*, m.p. >360° after softening at 250°, oxidised to $\Delta^{\alpha\gamma\epsilon\eta}$-*nonatetraene*-αι-*dicarboxylic acid*, m.p. 215° when rapidly heated, m.p. >360° after gradual softening when heated slowly. H. W.

***dl*- and active methyldiglycollic acids and their derivatives.** M. Godchot and P. Vieles (Bull. Soc. chim., 1937, [v], **4**, 937—944; cf. A., 1936, 823).—Et_2 methyldiglycollate (Et α-carbethoxymethoxypropionate) of whatever degree of optical activity (dependent on that of the technical Et lactate used in its prep.) is transformed by NH_3–H_2O at 0° into *dl*-methyldiglycolldiamide (I), m.p. 126° (*Hg* deriv-

ative), which cannot be resolved into its optical antipodes by spontaneous crystallisation. (I) is hydrolysed by 10% NaOH to dl-*methyldiglycollic acid*, m.p. 61° (in sealed capillary) (*anhydride*, $O<\begin{matrix}CHMe\cdot CO\\CH_2\cdot CO\end{matrix}>O$, b.p. 118°/28 mm.; *dianilide*, m.p. 92°). H. W.

Catalytic oxidation of ascorbic acid.—See A., I, 368.

Vitamin-*C* [and scorbamic acid]. F. Micheel and R. Mittag (Z. physiol. Chem., 1937, **247**, 34—42; cf. this vol., 180).—Scorbamic acid (I), decomp. about 100°, yields with air, and especially with benzoquinone, a red dye catalytically reduced by H_2 to a colourless leuco-compound but not to (I). The dye is probably produced by irreversible condensation of 1 mol. of (I) with 1 mol. of dehydroscorbamic acid. Improved methods of preparing aminotetronic acid and 2-deoxy-*l*-ascorbic acid are described. W. McC.

Isomerisation of 2 : 3-dimethylascorbic acid. W. N. Haworth, E. L. Hirst, F. Smith, and W. J. Wilson (J.C.S., 1937, 829—834).—Dimethylascorbic acid (I) with aq. $Ba(OH)_2$ isomerises to iso*dimethylascorbic acid* (II), b.p. 175°(bath)/0·03 mm., $[\alpha]_D^{22}$ −18° in MeOH, showing no selective absorption, and converted quantitatively into the amide of (I), from which (II) may be regenerated by aq. $Ba(OH)_2$. (II) when heated at 120°/0·1 mm. yields in some cases (catalytic impurity) (I), whilst heating with MeOH–HCl affords 2-*methylascorbic acid* (III), a syrup, $[\alpha]_D$ +10° in H_2O, converted by CH_2N_2 into 2 : 3-*dimethyl*-l-*ascorbic acid monohydrate* (IV). *l*-Ascorbic acid (V) with CH_2N_2–Et_2O affords mainly 3-methylascorbic acid, but also small quantities of monomethylhetero-ascorbic acid (?1-methyl) (VI), formerly (cf. A., 1934, 1333) described as 2-methylascorbic acid, hydrolysed by H_2O to (V), and converted by CH_2N_2 into a Me_2 derivative which with H_2O yields (III). (I) with CPh_3Cl in C_5H_5N affords 6-*triphenylmethyl*-2 : 3-*dimethyl*-l-*ascorbic acid* (VII), m.p. 156°, $[\alpha]_D$ +35° in $CHCl_3$, and an isomeric *substance* (VIII), m.p. 178°, $[\alpha]_D$ +31° in $CHCl_3$, also produced by isomerisation of (VII) with MeOH–NH_3. (VII) and (VIII) with HCl–$CHCl_3$ yield (IV), with MeI–MeOH–Ag_2O give *triphenylmethyltrimethyl*-l-*ascorbic acid*, m.p. 131°, $[\alpha]_D$ +31·5° in $CHCl_3$, and with HCl–$CHCl_3$ at −5° give 2 : 3 : 5-*trimethyl*-l-*ascorbic acid* (IX), m.p. 69—70°, $[\alpha]_D$ −11·4° in H_2O (*mono*-p-*nitrobenzoate*, m.p. 118°), isomerised by $Ba(OH)_2$ to iso*trimethyl*-l-*ascorbic acid* (X), b.p. 115° (bath)/0·01 mm., m.p. 38°, $[\alpha]_D^{15}$ −34·9° in H_2O (*amide*, m.p. 115°, $[\alpha]_D^{16}$ −35·4°), showing no selective absorption in H_2O. When boiled with MeOH–HCl, (X) affords (III), methylated by CH_2N_2 to (IX). J. D. R.

Acetone derivatives of gluconic acid. W. N. Haworth, E. L. Hirst, and K. A. Chamberlain (J.C.S., 1937, 795—797).—Ca gluconate H_2SO_4, $COMe_2$, and $CuSO_4$ afford a mixture of *di*- (I), m.p. 154°, $[\alpha]_D^{18}$ +11° in EtOH, and *tri*-iso*propylidenegluconic acid* (II), m.p. 111°, $[\alpha]_D^{18}$ +31° in EtOH, hydrolysed (MeOH–HCl) to (I). (I) with MeI–Ag_2O in MeOH yields *Me* 2-*methyldi*iso*propylidenegluconate*, b.p. 105°/0·02 mm., m.p. 44°, $[\alpha]_D^{19}$ +41° in H_2O, which is hydrolysed (HCl) to 2-*methyl*-γ-*gluconolactone*, a syrup, $[\alpha]_D$ +45°, converted by MeOH–NH_3 into 2-*methylgluconamide*, m.p. 139°, $[\alpha]_D^{18}$ +39° in H_2O. *X*-Ray examination of (II) shows it to be probably either the 1 : 2, 3 : 4, 5 : 6- or the 1 : 2, 3 : 5, 4 : 6-$[CMe_2]_3$ compound. J. D. R.

***allo*Mucic acid.** F. L. Humoller and W. F. McManus (J. Amer. Chem. Soc., 1937, **59**, 945—946). —Priority of Posternak (A., 1936, 55) for the prep. of this acid is acknowledged (cf. this vol., 49). R. S. C.

Constitution and reactions of thiocarbonyl tetrachloride. III. Reaction with primary alkylamines and phenols. J. M. Connolly and G. M. Dyson (J.C.S., 1937, 827—828).—*n*-Heptyl- and allyl-amine in Et_2O with K_2CO_3 in H_2O and $CSCl_4$ in Et_2O afford respectively S-n-*heptyl*- and S-*n*-allyl-*aminotrichloromethylthiol*, both oils, decomp. 170°. NH_2R with $CSCl_4$ in ligroin yields $NHR\cdot S\cdot CCl_3$, converted by excess of NH_2R and HCl into $NR{:}C(NHR)_2,HCl$, also prepared by methylation (Me_2SO_4) of $CS(NHR)_2$ followed by heating with NH_2R. Thus are prepared *triallyl*-, m.p. 176°, *tribenzyl*-, m.p. 201°, and *tri*iso*amyl*-, m.p. 206°, *-guanidine hydrochloride*. $OPh\cdot S\cdot CCl_3$ with NaOEt in EtOH affords *S*-ethoxytrichloromethylthiol, b.p. 155° (decomp.), also prepared from $CSCl_2$ and NaOEt in Et_2O–EtOH, converted by excess of NaOEt into Et_4 orthocarbonate, b.p. 158°. Similarly are prepared S-*iso*butoxytrichloromethylthiol, b.p. 181° (decomp.), and Bu^{β}_4 orthocarbonate, b.p. 238°. J. D. R.

Thetines and selenetines. E. Bilmann and K. A. Jensen (Bull Soc. chim., 1936, [v], **3**, 2310—2318).—$CHMeBr\cdot CO_2Et$ (I) when treated with Me_2S in the hot or cold yields SMe_3Br, m.p. 201—202° (sealed tube; cf. lit.), and *Et* α-*methylthiopropionate* (II), b.p. 173—175°/773 mm. and 70—72°/14 mm., also obtained from (I) and a suspension of NaSMe in Et_2O. The prep. of solid NaSMe by treatment of NaOEt–EtOH with MeSH and then Et_2O is described. (II) when treated with MeI in the hot or cold yields SMe_2I, m.p. 213—214° (sealed tube; cf. lit.), and $CHMeI\cdot CO_2Et$. $CHMeBr\cdot CO_2H$ (III) with Et_2S in the cold during 17 days gives *diethylpropiothetine hydrobromide*, $CHMe(SEt_2\}Br)\cdot CO_2H$, m.p. 105—105·5° (decomp.), but with Me_2S (or Et_2S) at 100° SMe_3Br (or SEt_3Br) and $SMe\cdot CHMe\cdot CO_2H$. Similarly, (I) and Me_2Se gives *trimethylselenonium bromide*, m.p. 197—198° (sealed tube). (III) with R_2Se (R = Me or Et) gives mixtures of $CHMe(SeR_2\}Br)\cdot CO_2H$ and SeR_3Br. All atempts to prepare propiothetinates and propioselenetinates failed. H. G. M.

Inhibition of photochemical reactions by nitric oxide.—See A., I, 370.

Kinetics of polymeric aldehydes. IV. Mechanism of the process of dissolution of polyoxymethylenes. J. Löbering (Ber., 1937, **70**, [*B*], 967—970).—Determination of the rate of dissolution of polyoxymethylene Me_2 ethers shows that the long chains are dissolved and then become degraded in the solution; with polyoxymethylenes a similar process is very probable. H. W.

β-Heptyl- and β-nonyl-acraldehydes. R. Delaby (Bull. Soc. chim., 1936, [v], **3**, 2375—2382).—Acraldehyde (I) with n-C_7H_{15}·MgBr–Et_2O gives *vinyl-n-heptylcarbinol*, b.p. 99—101°/11·5 mm., 114—116·5°/25 mm. (*acetate*, b.p. 122—123°/24 mm.), converted by PBr_3–C_5H_5N into *α-bromo-Δ$^\beta$-decene*, b.p. 118—121°/17·5 mm. (corresponding *α-acetoxy-* (II), b.p. 132—134°/18 mm., and α-iso*butoxy-*, b.p. 147—148°/18 mm., -compounds), which with $(CH_2)_6N_4$ in $CHCl_3$ yields a *quaternary ammonium salt* (III), C_7H_{15}·CH:CH·CH_2·N:$(N_3C_6H_{12})$}Br. Hydrolysis of (II) with NaOH gives *Δ$^\beta$-decenol*, b.p. 117—118°/11 mm., oxidised by $K_2Cr_2O_7$–H_2SO_4 to *Δ$^\alpha$-decenal*, b.p. 106—108°/12 mm. (*semicarbazone*, m.p. 168·5°), also obtained by hydrolysis of (III). Similarly, *vinyl-n-nonylcarbinol*, b.p. 131·5—132°/13·5 mm., prepared from n-C_9H_{19}·MgBr–Et_2O and (I), is converted into *α-bromo-Δ$^\beta$-dodecene*, b.p. 142—144°/12·5 mm.; this with $(CH_2)_6N_4$ in $CHCl_3$ gives a quaternary NH_4 *compound*, hydrolysed to Δ$^\alpha$-dodecenal, b.p. 108—109°/1 mm. (semicarbazone, m.p. 165·5—166°; cf. A., 1932, 721).

H. G. M.

Preparation of alkoxyaldehydes by oxidation of glyceryl α-ethers with periodic acid. L. Palfray and S. Sabetay (Bull. Soc. chim., 1937, [v], **4**, 950—951).—Agitation of a mixture of glyceryl α-CH_2Ph ether, KIO_4, H_2SO_4, and H_2O emulsified by CH_3·$[CH_2]_{11}$·O·SO_3Na at room temp. gives CH_2O and benzyloxyacetaldehyde, b.p. 115°/15 mm. (semicarbazone, m.p. 120°).

H. W.

Acid character of monoximes. A. Gandini and (Signa.) C. Straneo (Gazzetta, 1937, **67**, 104—113).—p_H of aq. solutions of various aliphatic and aromatic aldoximes and ketoximes, and of alicyclic ketoximes, is determined potentiometrically. Alkaline p_H of monoximes is due to impurities (NH_2OH, NH_3); the highly purified oximes are slightly acid, in accordance with the normal formulæ. Absorption spectra are also determined.

E. W. W.

Study of the α- and β-aldoses and their solutions by bromine oxidation and mutarotation measurements. H. S. Isbell and W. W. Pigman (J. Org. Chem., 1937, **1**, 505—539).—When α- and β-pairs of sugars have the O-ring on the right in the projection formulæ, the more dextrorotatory member is termed α; when the O-ring is on the left, the less lævorotatory member is termed β. All aldoses thus termed β are oxidised by Br more rapidly than are the α-isomerides. The O-ring of pentoses is not in the plane of the C atoms and the mol. as a whole is asymmetric; the configuration of the ring in pentoses is allotted by comparison with hexoses. Assignment of structures on the above system is discussed in detail. The rate of oxidation of equilibrium solutions of sugars is at first that of the β- and later that of the α-form; the amounts of α- and β-forms present in the mixture, calc. from the rates of oxidation, are compared with the amounts calc. from [α] on the assumption that only α- and β-forms are present. The approx. correspondence of the two methods shows that the equilibrium mixture contains mainly α- and β-forms, but possibly also other forms, particularly for galactose (I), arabinose (II), talose (III), and ribose (IV); part of the equilibrium mixture of (IV), however, is oxidised more rapidly than the β-form, which may thus be incorrectly designated. The rate of oxidation of the equilibrium mixture from $(d$-gulose$)_2$,$CaCl_2$,H_2O (V) indicates existence of 32% of the unknown β-form. At 0° and 20° mutarotation of α- and β-*d*-glucose and -mannose, α-*d*-gulose,$CaCl_2$,H_2O (V), α- and β-*d*-lyxose, α-*l*-rhamnose, α- and β-lactose, and β-maltose is a first-order reaction, that of α- and β-*d*-(I), α- and β-*l*-(II), β-*l*-(II),$CaCl_2$,$4H_2O$, *d*-mannose,$CaCl_2$,H_2O, α-*d*-(III), and *l*-(IV) is complex. Temp. coeffs. are determined for the mutarotation of 20 sugars; α- and β-forms mutarotate 8·34 and 5·32 times, respectively, faster at 20° than at 0°. Mutarotations occurring when equilibrium mixtures of (I), (II), and (III) are cooled give maxima, showing that constituents other than the α- and β-forms are present. [α] of a freshly prepared solution of α- and β-*d*-(I) in proportions corresponding with the equilibrium [α] decreases to a min. and then returns to the original val., which proves conclusively the presence of other modifications. The following approx. contents of α-form in the equilibrium mixtures are calc.: *d*-glucose 37, *d*-mannose 69, *d*-(I) 31, *d*-(III) 56, (V) 18·5, *l*-(II) 32·4 (26·5), *d*-xylose 32, *d*-lyxose 80, *d*- and *l*-ribose 89, *l*-rhamnose 69, lactose 37, maltose 37.

R. S. C.

Oxidation of carbohydrates in acid solution. M. R. Everett and F. Sheppard (Univ. Oklahoma Med. School, Dept. Biochem., 1937, 66 pp.).—Results are recorded of a study of the oxidation of many carbohydrates by Br–H_2O in acid solution, identification of the products being based on the Sumner/Folin–Wu ratios of glucose equivs., mol. optical rotations, and ratios and mols. of acid/reducing material. The stages of oxidation of aldoses are (1) formation of monocarboxylic lactones, (2) production of dicarboxylic and keturonic acids (I), and (3) oxidation of (I). Ketoses are partly changed to *l*-keturonic acids (II). Sugar alcohols and non-reducing glucosides are first converted into ketoses and then partly oxidised to (II). Bromide retards all stages of oxidation, particularly (2), hence more (I) is formed in dil. solutions of sugar. Buffers accelerate all stages and cause production of mixtures of (I). Increased temp. does not invariably cause the same acceleration of the several reactions. With ketoses, α-glucosides (III), methylpentoses (IV), and *d*-glucosamine, oxidation is not distorted; with other aldoses, reducing disaccharides, and β-glucosides (V), a greater formation of non-reducing acids occurs. Oxidation paths are determined by substitution at $C_{(1)}$, *cis–trans*-isomerism of the intermediate C atoms, and substitution at $C_{(6)}$. The first is manifested in the great differences between α- and β-glucosides, the second determines the relationship of isomeric sugars, whilst the third becomes important for (IV) and dicarboxylic acids. A biological significance of *cis–trans*-isomerism is indicated. Oxidation of glucosides provides a chemical method for distinguishing between α- and β-isomerides in solution. With hexosides, colour tests suffice to detect this difference but optical activity is applicable to all glucosides. Only reducing (III) capable of forming bionic lactones exhibit appreciable changes of rotation during oxidation; these are ≪ the marked changes of (V). (III)

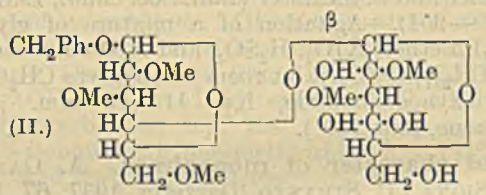
and (V) differ in rates of hydrolysis and oxidation mechanisms. (V) follow the rapid oxidation paths of their component units; the *sec.*-OH of (III) are more slowly oxidised without hydrolysis. At higher temp. these reactions become more nearly identical for the two series. The effects of αβ-isomerism extend to linkings in anhydro-sugars and polysaccharides. Complications appear in the former when both ordinary ring structures and glucosidic O bridges are present so that some resemble (III) and others (V). *cis–trans*-Isomerism of cyclic C atoms exerts its influence on oxidation *via* ring stability and lactone equilibria. Content of (I) and mol. optical rotations of oxidised sugar solutions are predictable from this isomerism. Optimal conditions for the formation of (I) are provided by perfectly compensated types of cyclic *trans* isomerism; minimal conditions by complete *cis* arrangement. (I) are formed from pentoses through furanose and γ-lactone modifications, from hexoses through pyranose and δ-lactone, and from heptoses through ε-oxide form and ε-lactone. In many respects the oxidation of carbohydrates by HNO_3 resembles that by Br but the latter is advantageous for analytical studies. Unoxidised anhydro-sugars of the α-*d*-glucosan series show the same remarkable behaviour with analytical reagents as do their reducing polymerides. H. W.

Dibenzylidene-glucose and -glycuronic acid from 6-benzoyldiethylmercaptoglucose. Synthesis of another dibenzylideneglucose from 4 : 6-benzylideneglucose. P. E. Papadikis (J. Amer. Chem. Soc., 1937, **59**, 841—843).—Diethylmercaptoglucose 6-benzoate (modified prep.), m.p. 114°, $[\alpha]_D^{23}$ +47·23° in $CHCl_3$, with $ZnCl_2$ in PhCHO gives (?1 : 2 : 3 : 5-)*dibenzylideneglucose* 6-*benzoate*, m.p. 156°, stable to Fehling's solution, hydrolysed by hot KOH–EtOH or cold NaOMe–$CHCl_3$ to (?1 : 2 : 3 : 5-)*dibenzylideneglucose* (I), m.p. 163°, which with NaOBr in aq. C_5H_5N gives a little *dibenzylideneglycuronic acid*, m.p. 175°. Dry 4 : 6-benzylideneglucose and P_2O_5 in PhCHO give a non-reducing *dibenzylideneglucose*, m.p. 163°, different from (I). R. S. C.

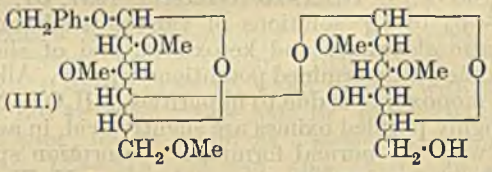
Glucose 2 : 3 : 6-tri-*p*-toluenesulphonate. K. Hess and L. Kinze (Ber., 1937, **70**, [*B*], 1139—1142).—1-α-Bromoglucose 4-acetate 2 : 3 : 6-tri-*p*-toluenesulphonate (I), obtained by fission of starch *p*-toluenesulphonate by HBr–AcOH, is smoothly converted by a large excess of AgOAc in warm AcOH into β-*glucose* 1 : 4-*diacetate* 2 : 3 : 6-*tri*-p-*toluenesulphonate*, two *forms*, m.p. 140—142° and 150—151°, respectively, $[\alpha]_D^{20}$ +17·6° in $CHCl_3$, +39·3° in C_6H_6, +19° in $COMe_2$. *Glucose* 4-*acetate* 2 : 3 : 6-*tri*-p-*toluenesulphonate* (II), $[\alpha]_D^{20}$ +24·6° in $CHCl_3$, +60·0° in C_6H_6, +27·8° in $COMe_2$, obtained from (I), H_2O, and a large excess of Ag_2O, is a mixture of the α- and β-forms which could not be isolated individually; addition of $AgNO_3$, application of Schlubach's method, or use of dry TlOH did not give improved results. Treatment of (II) with Ac_2O containing KOAc or NaOAc gives a mixture of *glucose* 1 : 4-*diacetate* 2 : 3 : 6-*tri*-p-*toluenesulphonates* (III), m.p. 86—93° (indef.), $[\alpha]_D^{20}$ +65·2° in C_6H_6, +48·9° in $CHCl_3$, which could not be separated into individuals. (I) is readily transformed by $HgCl_2$ in boiling C_6H_6 into 1-α-*chloroglucose* 4-*acetate* 2 : 3 : 6-*tri*-p-*toluenesulphonate*, m.p. 173—174°, $[\alpha]_D^{20}$ +80·7° in $CHCl_3$, +70·3° in $COMe_2$, +132·2° in C_6H_6 [also derived from (II) and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at room temp.], which does not react with mol. Ag, Na powder, or Ag_2O. Treatment of (III) with NaI in $COMe_2$ at 90° and then at 115° leads to 6-*iodo*-β-*glucose* 1 : 4-*diacetate* 2 : 3-*di*-p-*toluenesulphonate*, m.p. 189—190° (decomp.), $[\alpha]_D^{20}$ +13·0° in $CHCl_3$, +22·1° in C_6H_6, +10·1° in $COMe_2$. H. W.

Partly methylated disaccharides. I. K. Hess, H. von Hammerstein, and W. Gramberg (Ber., 1937, **70**, [*B*], 1134—1138).—Benzylcellobioside is shaken with $ZnCl_2$ and PhCHO and the product is poured into light petroleum; the powdery residue is treated with C_5H_5N (to remove $ZnCl_2$) and, after removal of the solvent, with abs. EtOH, thus giving *benzylidene*-β-*benzylcellobioside* (I), $[\alpha]_D^{20}$ −47·0° in MeOH, −47·8° in C_5H_5N. Removal of :CHPh from (I) can be effected with 0·001*N*-H_2SO_4 at 100° or by 0·01*N*-HCl–MeOH. (I) in small quantities with Ag_2O and MeI affords *benzylidenepentamethyl*-β-*benzylcellobioside*, m.p. 140°, $[\alpha]_D^{20}$ −53·2° in $CHCl_3$, −48·0° in MeOH, −45·8° in $COMe_2$, hydrolysed to 2 : 3 : 6 : 8 : 10-*pentamethyl*-β-*benzylcellobioside* (II), m.p. 140°, $[\alpha]_D^{20}$

(II.)



(III.)



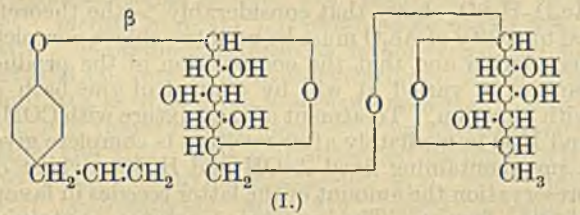
−42·2° in $CHCl_3$, −42·5° in MeOH. Treatment of acetobromomaltose with $CH_2Ph{\cdot}OH$ and Ag_2CO_3 and hydrolysis of the product with NH_3–MeOH at 0° yields β-benzylmaltoside, transformed by PhCHO and $ZnCl_2$ into *benzylidene*-β-*benzylmaltoside*, m.p. (indef.) 110—116°, $[\alpha]_D^{20}$ +27·3° in MeOH, +21·0° in $CHCl_3$, +31·0° in $COMe_2$. This is methylated to *benzylidenepentamethyl*-β-*benzylmaltoside*, m.p. 132—133°, $[\alpha]_D^{20}$ +33·0° in MeOH, +29·6° in $COMe_2$, +38·4° in $CHCl_3$, hydrolysed to 2 : 3 : 6 : 8 : 10-*pentamethyl*-β-*benzylmaltoside* (III), m.p. 103—104°. H. W.

Anthranol-β-*d*-glucoside. J. H. Gardner and T. F. McDonnell (J. Amer. Chem. Soc., 1937, **59**, 857—858).—Anthrone, acetobromoglucose, and KOH in aq. $COMe_2$ give *anthranol*-β-d-*glucoside tetra-acetate*, m.p. 205—205·2°, converted by $Ba(OH)_2$ in aq. EtOH at 60° into the free *glucoside*, $+H_2O$, m.p. 204—206°, which is hydrolysed by 0·05*N*-HCl (1 hr.; to anthrone) or -KOH (30 min.; to anthrone and dianthrone) and by 9% aq. borax (64% in 1 hr.). Barbaloin is thus not an anthranol glucoside. R. S. C.

Glucoside of *Belamcanda chinensis* (L.,) Leman (*Pardanthus chinensis*, Ker.), shekanin (tectoridin). C. Mannich, P. Schumann, and W. H. Lin (Arch. Pharm., 1937, **275**, 317—328).—Shekanin

(I), m.p. 257° (decomp.), $[\alpha]_D^{20}$ −29·4° (Ac_6 derivative, m.p. 182°, $[\alpha]_D^{20}$ − 34·9° in C_6H_6), isolated in 1·5% yield from the rhizome of this plant by EtOH, is proved to be identical with tectoridin (isolated from *Iris tectorum* with $[\alpha]_D^{20}$ −29·95°) by hydrolysis to glucose and tectorigenin (II), m.p. 230° (decomp.) (Ac_3, m.p. 190°, and Bz_3 derivative, m.p. 230°; *Me*$_2$ *ether*, m.p. 188°, and its *Ac* derivative, m.p. 213—214°). The *Me ether*, m.p. 230°, of (I) with 38% HCl gives the 4′-*Me ether* (III), m.p. 191—192°, of (II). With HBr–AcOH (II) gives 5 : 6 : 7 : 4′-*tetrahydroxy*-iso*flavone*, m.p. about 270° (*Ac*$_4$ derivative, m.p. 217—220° after sintering), with 65% HNO_3 gives picric acid, and with KOH gives iretol, *p*-OH·C_6H_4·CH_2·CO_2H, and HCO_2H. KOH converts (III) into iretol and *p*-OMe·C_6H_4·CH_2·CO_2H. R. S. C.

Synthesis of lusitanicoside (chavicol-β-rutinoside), the glucoside from *Cerasus lusitanic*, Lois. G. Zemplén and A. Gerecs (Ber., 1937, **70**, [*B*], 1098—1101).—Rutinose hepta-acetate (β-l-*l*-rhamnosido-6-*d*-glucose β-hepta-acetate) in $CHCl_3$ is converted by HBr in AcOH at 0° into α-*acetobromo-rutinose* [α-*acetobromo*-β-l-*l*-*rhamnosido*-6-*d*-*glucose*], m.p. 130·5—131°, $[\alpha]_D^{18}$ +90·68° in $CHCl_3$, which is converted by chavicol and KOH in $COMe_2$–H_2O into *chavicolrutinoside hexa-acetate*, m.p. 171·5°, $[\alpha]_D^{18}$ −48·43° in $CHCl_3$. This is hydrolysed by NaOMe



(I.)

in abs. MeOH to *chavicol*-β-*rutinoside*, m.p. 188·5°, $[\alpha]_D^{18}$ −73·86° in H_2O, identical with the lusitanicoside of Héressey *et al.* (A., 1932, 662), which is therefore (I). H. W.

Ring structure of xylal. W. N. Haworth, E. L. Hirst, and C. S. Woolvin (J.C.S., 1937, 780—782).—Xylal diacetate deacetylated and methylated (Me_2SO_4 and NaOH followed by MeI and Ag_2O) affords *dimethylxylal* (I), b.p. 73°/17 mm., $[\alpha]_D^{19}$ −180° in $CHCl_3$. (I), oxidised in H_2O by BzO_2H in Et_2O, followed by methylation (NaOH–Me_2SO_4 and MeI–Ag_2O) and hydrolysis (HCl), affords trimethyl-lyxose and -xylose, proving the pyranose structure of xylal. J. D. R.

Polysaccharides. XXIV. Yeast mannan. W. N. Haworth, E. L. Hirst, and F. A. Isherwood (J.C.S., 784—791).—Extraction of yeast with aq. NaOH, followed by formation of a $Cu(OH)_2$ complex, decomp. of this by HCl, and repeated pptn. by EtOH from H_2O yields *yeast mannan*, (I), $(C_6H_{10}O_5)_n$, $[\alpha]_D^{24}$ +89° in H_2O {*acetate* (II), by Ac_2O–C_5H_5N, $[\alpha]_D^{24}$ +62° in $CHCl_3$}. *Methylated mannan*, $[\alpha]_D^{24}$ +85° in $CHCl_3$ [from (I) or (III) by Me_2SO_4–NaOH], is hydrolysed by 1% HCl in MeOH at 150° to tetramethylmethyl-mannopyranoside (III), b.p. 120—125°/0·07 mm., 2 : 3 : 4-*trimethylmethylmannoside* (IV), b.p. 145—155°/0·1 mm., and 3 : 4-*dimethylmethylmannoside* (V), b.p. 138—145°/0·04 mm., the proofs of these structures being as follows. (III) is hydrolysed (H_2SO_4) to tetramethylmannose, recognised as the anilide and mannonolactone. (IV) is hydrolysed (H_2SO_4), at a rate indicating a pyranoside structure, to 2 : 3 : 4-trimethylmannose (VI), which is oxidised (Br–H_2O) to 2 : 3 : 4-trimethylmannonolactone, b.p. 135°/0·02 mm., m.p. 91—92°, $[\alpha]_D^{20}$ +138° in H_2O. (VI) is oxidised (HNO_3) to 2 : 3 : 4-*trimethylmannosaccharic acid* (*diamide*, m.p. 191°). (V) is hydrolysed (H_2SO_4; rate indicates a manno-pyranoside structure) to 3 : 4-*dimethylmannose monohydrate*, (VII), m.p. 107—109°, $[\alpha]_D$ +3° in H_2O, oxidised (Br–H_2O) to 3 : 4-*dimethyl-mannonolactone*, m.p. 157—158°, $[\alpha]_D^{20}$ +174° in H_2O, the rate of hydrolysis of which indicates a δ-structure, converted by NH_3–MeOH into 3 : 4-*dimethylmannon-amide*, m.p. 140°, $[\alpha]_D^{20}$ +22° in H_2O, which with NaOCl yields NaCNO, indicating a free OH at $C_{(2)}$. (VII) yields an *osazone* with no loss of OMe, and with MeOH–HCl the [α] is unaltered, showing substitution at $C_{(4)}$. The structural unit of yeast mannan consists, therefore, of three mannose residues; one is attached by its reducing group to another, and thus forms a terminated side-chain, one is attached at $C_{(1)}$ and $C_{(6)}$ to the other two, and the third is attached to other residues at $C_{(1)}$, $C_{(2)}$, and $C_{(6)}$. J. D. R.

Polysaccharides. XXV. α-Amylodextrin. W. N. Haworth, E. L. Hirst, H. Kitchen, and S. Peat (J.C.S., 1937, 791—795; cf. A., 1935, 1355).—Starch, with β-amylase from wheat, at 38° affords maltose and α-amylodextrin (I), $[\alpha]_D^{20}$ +167° in H_2O, which yields an acetate (II) with Ac_2O–C_5H_5N or with Ac_2O–AcOH–Cl_2–SO_2. Three specimens of methylated amylodextrin, from (I) by NaOH–Me_2SO_4 and from two specimens of (II) by deacetylation and methylation, yield, by the end-group method of assay, 9·8, 10·5, and 10·4%, respectively, of tetramethylglucose, indicating a chain length of 11—12 glucose units. It is considered that this represents genuine α-amylodextrin, which is not identical with that formerly described (*loc. cit.*), where a length of 16—17 units was found. J. D. R.

Mol. wt. of limit-dextrin. K. Myrbäck (Svensk Kem. Tidskr., 1937, **49**, 145—152).—The diffusion of limit-dextrin in NaCl aq. gives vals. for *M* from 2240 to 3300, in agreement with those calc. from the reducing power. The material is homogeneous and does not show any ageing effects. M. H. M. A.

Degradation of methylated inulin to hexamethyldifructosan. W. N. Haworth, E. L. Hirst, and F. A. Isherwood (J.C.S., 1937, 782—784).—Drastic methylation of deacetylated inulin acetate or dimethylinulin leads to methylated inulin with strongly negative [α]. Fully methylated inulin, $[\alpha]_D^{20}$ −55° in $CHCl_3$, after boiling for 50 hr. with MeI–Ag_2O–MeOH is unchanged, but the presence of HI in the MeI affords *hexamethyldifructosan*, b.p. 180°/0·1 mm., $[\alpha]_D^{20}$ +59·3°, hydrolysed (H_2SO_4) to 3 : 4 : 6-trimethylfructofuranose. The strong positive [α] of the methylated inulin of Irvine and Steele (cf. J.C.S., 1930, **117**, 1474) is, therefore, due to depolymerisation. J. D. R.

White oak cellulose. C. D. Bird and G. J. Ritter (J. Amer. Chem. Soc., 1937, **59**, 802—803).—White oak holocellulose (I) resembles that from maple

and spruce, contains OMe 1·64, Ac 3·07, and pentosans 23·4%, and yields 1·56% of CO_2. Extracted white oak wood contains lignin (OMe 22·44%) 23·4, OMe 6·44, Ac 2·37, and pentosans 18·7%, and yields 1·2% of CO_2. R. S. C.

Decomposition of ethers and esters of cellulose with sodium in liquid ammonia. P. Schorigin and N. N. Makarova-Semljanskaja (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 509—511).—Benzylcellulose with Na in liquid NH_3 yields cellulose and $(CH_2Ph)_2$. The reaction product of trimethylcellulose and Na in liquid NH_3, treated with CO_2, gives a small yield of an acidic cellulose, indicating that a Na-cellulose with a C–Na structure is formed. Under similar conditions, cellulose acetate is completely deacetylated. J. D. R.

Nitration of cellulose. A. Bouchonnet, F. Trombe, and G. Petitpas (Bull. Soc. chim., 1937, [v], **4**, 894—904).—HNO_3–H_2O with <33% H_2O yields stable cellulose nitrates but causes hardening and considerable diminution in the final val. of the product. These drawbacks can be overcome by use of HNO_3 containing alkali nitrates, sulphates, or phosphates, whereby products of high N content are obtained. Similar results are attained by the action of conc. HNO_3 on cellulose nitrates of lower N content obtained by means of HNO_3–H_2SO_4 or HNO_3–salts. H. W.

Highly polymerised compounds. CLIV. Cellulose acetates and celluloses. H. Staudinger and G. Daumiller (Annalen, 1937, **529**, 219—265).—The highly polymerised nature of the insol. cellulose triacetates (I) obtained by the action of Ac_2O–C_5H_5N on cotton or ramie is established by their hydrolysis to celluloses (II) of the same high mol. wt. as the initial materials. Only strongly degraded (II) of degree of polymerisation <500 yield sol. acetates. Attempts to obtain more freely sol. esters by causing irregularity in structure by use of a mixture of acylating reagents did not lead to the desired result. Treatment of (I), re-pptd. from Schweitzer's reagent, with C_5H_5N until all the H_2O is displaced and then with C_5H_5N–Ac_2O gives eucolloidal (II), sol. in $C_2H_2Cl_4$ or *m*-cresol and with more difficulty in $CHCl_3$, freely sol. in HCO_2H, in which they suffer degradation. They do not age. A continuous series of polymeric-homologous triacetates similar to the trinitrates is thus available. Investigation of the viscosity of (I) in $CHCl_3$ and *m*-cresol shows that the polymeric homologues of very varied method of prep. have the same K_m const. Also, from the simplest to the most complex (I) the same relationship maintains between mol. wt. and sp. viscosity of equally conc. dil. solutions. All the acetates therefore have the same structure and the same form and are thus polymeric-homologous products. From the osmotically determined mol. wts. and the η_{sp}/c vals. the K_m const. for cellite are calc. in $COMe_2$ and *m*-cresol; they are > those of (I) in *m*-cresol. Revision of the K_m consts. for (II) indicates the necessity of doubling the mol. wt. hitherto adopted; its degree of polymerisation is ≯2000, in harmony with investigation of the mol. wt. of cellulose nitrate. The K_m consts. for (II) and its derivatives do not differ very greatly from one another but are widely different from those of starch and its derivatives. The viscosity relationships of (II) show that eu-, meso-, and hemicolloidal products have the same structure and that in all of them the glucose residues are united straight, unbranched chains. The K_m consts. are very close to those calc. for products of extended thread form which contain rings in the chain. The conversion of (II) into polymeric-analogous products establishes the macromol. structure of the most complex members by the classical methods of org. chemistry. H. W.

Reversibility of the viscosity of solutions of cellite in acetic acid. K. Hess and W. Philippoff (Ber., 1937, **70**, [*B*], 1143—1148).—1% solutions of cellite in AcOH are diluted to 0·05% and again conc. to 1%, whereby the sp. viscosity of the original solution is again attained. The reversibility indicates that the apparent rupture of cellulose acetates observed osmometrically by Hess and Ulmann is not attributable to fission of the bridges by a type of hydrolysis. H. W.

Preparation of cellulose acetates. L. Clément and C. Rivière (Bull. Soc. chim., 1937, [v], **4**, 869—880).—Bleached cotton linters is immersed in a mixture of AcOH and H_2SO_4 at 18—20°, whereby hydrocellulose is produced and there appears to be a temporary fixation of H_2SO_4 probably as an additive compound. Treatment of the product with AcOH–Ac_2O–H_2SO_4 shows that considerably > the theoretical quantity of Ac_2O must be used to achieve complete acetylation and that the composition of the product cannot be varied at will by control of the bath as with nitration. Treatment of the mixture with $COMe_2$ and H_2O immediately after reaction is complete gives a ppt. containing fixed AcOH and H_2SO_4, whilst on preservation the amount of the latter recedes in favour of the former. The primary acetates containing much OAc appear to be mixtures of cryst. and amorphous phases, the former of which disappears during progressive hydrolysis, and when the solubility of the product in $COMe_2$ is complete, the *X*-ray diagram is ill-defined and without rings. Further hydrolysis leads to cryst. cellulose. Halogen acids are much more effective catalysts of hydrolysis than are H_2SO_4 or $HClO_4$, which are of about equal merit. Generally, good accelerators of hydrolysis are poor catalysts of acetylation. The quantity of H_2O used has a profound influence on the products of hydrolysis. With < the theoretical quantity hydrolysis is observed, but the proportion of residual SO_3 is considerable. With about the theoretical amount, hydrolysis of SO_4 becomes pronounced whilst that of OAc remains regular and without considerable variations. With double the quantity a great variation is not observed with respect to OAc whilst the amount of SO_4 remains const., whereas a larger proportion of H_2O causes further removal of AcOH accompanied, apparently, by a fresh fixation of H_2SO_4. H. W.

Effect of pressure on the reactions between amines and alkyl halides in acetone.—See A., I, 366.

Action of liquid ammonia on organic halogeno-compounds. J. von Braun [with R. Lute, K. C. Warne, W. Pinkernelle, W. Rohland, A. Pohl, F. Dengel, and H. Arnold] (Ber., 1937, **70**,

[*B*], 979—993).—The yield of primary amine from org. halogeno-compounds is greater when liquid NH_3 is used than with NH_3–H_2O or NH_3–EtOH and increases very greatly with increasing mol. wt. of halide independently of constitutional details. The method is very advantageous for the prep. of ether-bases, *sec.* primary and *tert.*-primary diamines, monoacylated diamines, decarboxypeptides, and quinoline derivatives with 2-CH_2Cl whereby nuclear Cl is little affected. With compounds $Cl{\cdot}[CH_2]_n{\cdot}Cl$ spiran formation is observed when the val. of *n* is suitable; otherwise diamines are mainly produced. With very reactive halogen the formation of imino- rather than amino-compounds is observed.

$C_5H_{11}Br$ and liquid NH_3 at room temp. afford $C_5H_{11}{\cdot}NH_2$ (about 10%) and about 80% of $NH(C_5H_{11})_2$, possibly containing $N(C_5H_{11})_3$. $C_8H_{17}Br$ gives $C_8H_{17}{\cdot}NH_2$ (45%) and $NH(C_8H_{17})_2$ (43%), whilst $C_{12}H_{25}Br$ yields almost 90% of $C_{12}H_{25}{\cdot}NH_2$. CH_2PhCl and liquid NH_3 give $CH_2Ph{\cdot}NH_2$ (53%) and $NH(CH_2Ph)_2$ (39%), whereas with NH_3–EtOH the yields of $CH_2Ph{\cdot}NH_2$, $NH(CH_2Ph)_2$, and $N(CH_2Ph)_3$ are respectively 9%, 35%, and 48%. 1-$C_{10}H_7{\cdot}CH_2Cl$ gives α-$C_{10}H_7{\cdot}CH_2{\cdot}NH_2$ and *di-α-naphthylamine*, b.p. 230—235°/0·3 mm., m.p. 55° (*hydrochloride*, m.p. 230°; *picrate*, m.p. 206°; *NO*-derivative, m.p. 132°). *Tri-α-naphthylamine*, m.p. 178° (*hydrochloride*, m.p. 199°; *picrate*, m.p. 211°), is obtained by use of NH_3–EtOH. 9-Bromophenanthrene is converted by Mg and $(CH_2O)_3$ into 9-phenanthrylcarbinol, which with conc. HCl at 100° gives 9-*phenanthrylmethyl chloride*, m.p. 102° (more readily obtained from phenanthrene, CH_2O, and HCl); this is transformed by liquid NH_3 into 9-aminomethylphenanthrene, m.p. 107° (yield 70%) [*hydrochloride*, m.p. 277° (slight decomp.); *picrate*, m.p. 236°], and *di*-9-*phenanthrylmethylamine*, m.p. 193° (*hydrochloride*, m.p. 239°; *NO*-compound, m.p. 268°). With NH_3–EtOH *tri*-9-*phenanthrylmethylamine*, m.p. 163° (*hydrochloride*, m.p. 229°; *picrate*, m.p. 190° after softening at 170°), is obtained. $OPh{\cdot}[CH_2]_2{\cdot}NH_2$ and $OPh{\cdot}[CH_2]_3{\cdot}NH_2$ are obtained in 65% and 71% yield respectively from $OPh{\cdot}[CH_2]_2{\cdot}Br$ and $OPh{\cdot}[CH_2]_3{\cdot}Br$. NH_2Ph is transformed by a large excess of $C_2H_4Br_2$ at 100° into non-distillable $NHPh{\cdot}[CH_2]_2{\cdot}Br$, which with conc. HCl at 100° affords β-*chloroethylaniline*, b.p. 91—94°/1 mm. The latter and liquid NH_3 afford $NHPh{\cdot}[CH_2]_2{\cdot}NH_2$ (65%) and di-β-anilinoethylamine, b.p. 215—225°/0·1 mm. [*hydrochloride*, m.p. 233°; $(NO)_3$-compound, m.p. 99°]. $NPhMe{\cdot}[CH_2]_2{\cdot}Br$ similarly affords β-*methylanilinoethylamine* (I), b.p. 100—112°/0·3 mm. (*picrate*, m.p. 174°; *hydrochloride*, m.p. 205°; *Ac* derivative, m.p. 88°), and *di*-β-*methylanilinoethylamine*, b.p. 200—202°/0·3 mm. (*hydrochloride*, m.p. 204°). The *NO*-derivative, m.p. 140°, of (I) is transformed by successive treatment with $NaHSO_3$ and HCl into β-*methylaminoethylamine*, b.p. 115—117° (*hydrochloride*, m.p. 132°; *picrate*, m.p. 223°). $NPhEt{\cdot}[CH_2]_2{\cdot}Br$ affords β-*ethylanilinoethylamine*, b.p. 148—150°/20 mm. (*hydrochloride*, m.p. 153°; *picrate*, m.p. 166°; *Ac* derivative, b.p. 180—185°/0·5 mm., m.p. 100°), and *di*-β-*ethylanilinoethylamine*, b.p. 223—230°/12 mm. (*hydrochloride*, m.p. 203°; *picrate*, m.p. 176°). $NPhMe{\cdot}[CH_2]_3{\cdot}Cl$ yields *γ-methylanilinopropylamine*, b.p. 112—115°/0·3 mm. (*hydrochloride*, m.p. 189°; *picrate*, m.p. 152°; *Ac* derivative, b.p. 168—172°/0·2 mm., and its *NO*-derivative, m.p. 114°), and *di-γ-methylanilinopropylamine*, b.p. 220—222°/0·3 mm. [hygroscopic *hydrochloride*; *picrate*, m.p. 166°; *Ac* derivative, b.p. 250—255°/0·3 mm., and its $(NO)_2$-derivative, m.p. 161°]. *γ-Methylaminopropylamine*, b.p. 138—139° (*hydrochloride*, m.p. 185°; *picrate*, m.p. 227°), and *di-γ-methylaminopropylamine*, b.p. 122°/15 mm., m.p. 22° (*picrate*, m.p. 175°; *hydrochloride*, m.p. 275°), are described. $NHBz{\cdot}[CH_2]_4{\cdot}Cl$ gives benzoylputrescine, b.p. 186°/0·7 mm. (yield about 70%), and *di-δ-benzamidobutylamine*, b.p. 290°/0·3 mm., m.p. 87° (*hydrochloride*, m.p. 230°), and $NHBz{\cdot}[CH_2]_5{\cdot}Cl$ affords benzoylcadaverine, b.p. 202°/0·5 mm., with *di-ε-benzamidoamylamine*, m.p. 69° (*hydrochloride*, m.p. 199°).

3 : 4 -Dichloro-2-chloromethylquinoline and liquid NH_3 afford 3 : 4-*dichloro-2-aminomethylquinoline*, m.p. 104—106° (yield 72%) (*hydrochloride*, m.p. 239°; *picrate*, m.p. 185°; *Ac* derivative, m.p. 170°), and *di*-3 : 4-*dichloro-2-quinolylmethylamine*, decomp. 162—165° (*hydrochloride*, m.p. 218—220°); with NH_3–EtOH at 100° only the *sec.* base is obtained. 3-Chloro-4-anilino-2-chloromethylquinoline yields 3-*chloro*-4-*anilino*-2-*aminomethylquinoline*, m.p. 155° [*hydrochloride*, m.p. 214°; *picrate*, m.p. about 170°; *Ac* derivative (+1H_2O), m.p. 189°], and *di*-3-*chloro*-4-*anilino*-2-*quinolylmethylamine*, m.p. 232° (*hydrochloride*, m.p. 225—230°; *NO*-derivative, m.p. 119°). $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt$-*p* is transformed by contact with PCl_5 and $POCl_3$ into 3-*chloro*-4-p-*phenetidino*-6-*ethoxy*-2-*chloromethylquinoline*, m.p. 118—120° (*hydrochloride*, m.p. 231°; *picrate*, m.p. 155°), which yields 3-*chloro*-4-p-*phenetidino*-6-*ethoxy*-2-*aminomethylquinoline*, m.p. 110—112° (*hydrochloride*, m.p. 185°; *Ac* derivative, m.p. 143°), and *di*-3-*chloro*-4-p-*phenetidino*-6-*ethoxy*-2-*quinolylmethylamine*, m.p. 214—216° (*hydrochloride*, m.p. 206°; *Ac* compound, m.p. 160—162° after slight softening).

$Cl{\cdot}[CH_2]_{11}{\cdot}Cl$ gives almost exclusively $NH_2{\cdot}[CH_2]_{11}{\cdot}NH_2$. $Br{\cdot}[CH_2]_5{\cdot}Br$ affords mainly dipiperidinium bromide with very small amounts of piperidine and cadaverine. Similarly $Br{\cdot}[CH_2]_4{\cdot}Br$ give chiefly dipyrrolidinium bromide with some pyrrolidine and 1-Δ^{γ}-*butenylpyrrolidine*, b.p. 152—154° (*picrate*, m.p. 107°; hygroscopic *methiodide*, m.p. 178°). $Br{\cdot}[CH_2]_3{\cdot}Br$ affords $NH_2{\cdot}[CH_2]_3{\cdot}NH_2$ and *di-γ-aminopropylamine*, b.p. 210—230°. $(CH_2Cl)_2$ gives $(CH_2{\cdot}NH_2)_2$ and $NH(CH_2{\cdot}CH_2{\cdot}NH_2)_2$; with $(CH_2Br)_2$ the yield of primary amine is lower and compounds, $NH_2{\cdot}[CH_2]_2{\cdot}[NH{\cdot}CH_2{\cdot}CH_2]_n{\cdot}NH_2$, are produced.

Ph_2, CH_2O, and HCl give only $(CH_2Cl)_2$ derivatives whereas HBr affords 4 : 4′-*dibromomethyldiphenyl*, m.p. 170°, in almost 50% yield. This with liquid NH_3 gives 4 : 4′-*diaminomethyldiphenyl*, m.p. 135° (*picrate*, m.p. 222°; Ac_2 derivative, m.p. 272°; Bz_2 compound, m.p. 243°). H. W.

Synthesis of ethylenic amines. R. Paul and H. Cottin (Bull. Soc. chim., 1937, [v], 4, 933—937).—Ethylenic amines are best obtained by reduction of the corresponding nitriles with Na and abs. EtOH. Δ^{γ}-Pentenonitrile, b.p. 145°, obtained in 60% yield by passage of NH_3 and $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CN$ over SiO_2

at 480—500°, gives *α-amino-Δ$^{\delta}$-pentene*, b.p. 105—106°/767 mm. (*hydrate*, b.p. about 93°; *platinichloride*, decomp. 160°; *picrate*, m.p. 115—116°; *H oxalate*, m.p. 129—130°). α-Cyano-α-allyl-Δ$^{\gamma}$-pentenoic acid passes at 110—120° into *α-allyl-Δ$^{\gamma}$-pentenonitrile*, b.p. 85°/14 mm., 186°/760 mm., reduced to *α-amino-β-allyl-Δ$^{\delta}$-pentene*, b.p. 84—85°/20 mm., 168°/764 mm. (*platinichloride*, decomp. 142—143°; *picrate*, m.p. 138—139; *H oxalate*, m.p. 137°). *β-Allyl-Δ$^{\delta}$-pentenyl bromide*, b.p. 74—75°/17 mm., obtained with some *δ-bromo-β-allylamyl bromide*, b.p. 113—114°/13 mm., by gradual addition of $(CH_2{:}CH{\cdot}CH_2)_2CH{\cdot}CH_2{\cdot}OH$ and C_5H_5N to PBr_3, affords *β-allyl-Δ$^{\delta}$-hexenonitrile*, b.p. 90—91°/14 mm., whence *α-amino-γ-allyl-Δ$^{\epsilon}$-hexene*, b.p. 86—18°/23 mm. (*picrate*, m.p. 124°). H. W.

Highly polymerised compounds. CLVI. Polyammonium compounds of high mol. wt. H. Staudinger and H. von Becker (Ber., 1937, **70**, [*B*], 879—888).—Simple relationships between viscosity and chain length as with homopolar mol. compounds are not observed with proteins, the sp. viscosity of which varies within wide limits with the [H$^{\cdot}$] and electrolytic addenda. Solutions of proteins which obey Einstein's law contain approx. spherical mols.; proteins which give highly viscous solutions of low concn. and with which the viscosity is not ∝ concn. have extended mols. Solutions of Na polyacrylate (heteropolar mol. colloid as model for proteins) do not obey the Hagen–Poiseuille law mainly on account of cluster formation of the thread ions. The polyammonium bromides obtained by Gibbs *et al.* (A., 1933, 381) from $NMe_2{\cdot}[CH_2]_3{\cdot}Br$ can be separated by dialysis into less and more viscous fractions the sp. viscosity of which diminishes with increasing concn. Cluster formation is impeded by the presence of HBr and in presence of sufficient electrolyte they behave like homopolar mol. colloids. A more perfect model of the proteins is afforded by polyammonium polyacrylate, which resembles a globulin in its insolubility in dil. NaOH or HCl and its ready solubility in 1·5*N*-NaCl containing a trace of H$^{\cdot}$ or OH′. The relative viscosity of its solutions in 1·5*N*-NaCl containing NaOH or HCl (compared with that of a similar solution of NaCl) is independent of [H$^{\cdot}$] or [OH′]. H. W.

Betaines. IV. Mechanism of racemisation of salts of ethyl propiobetainate. E. Bilmann, K. A. Jensen, and H. B. Jensen (Bull. Soc. chim., 1936, [v], **3**, 2295—2305; cf. A., 1935, 331).—(−)-, m.p. 130—131°, $[\alpha]_D^{15}$ −19·64° in EtOH, and (+)-*Et propiobetainate iodide*, m.p. 130—131°, $[\alpha]_D^{20}$ +19·78° in EtOH (prep. described), are racemised at the same speed by a mixture of (+)-NN-*diethyl-β-methylbutylamine*, b.p. 150—151°/765 mm., $[\alpha]_D^{20}$ +17·96°, and its *iodide*, which, as in the case of other *tert.*-amines and their salts, has a considerable influence on the velocity. Racemisation by means of the weak base PEt_3 occurs very slowly. (+)-, m.p. 157—157·5°, $[\alpha]_D^{20}$ +19·60° in EtOH, and (−)-*trimethyl-α-phenylethylamine iodide*, m.p. 156·5—157°, $[\alpha]_D^{20}$ −19·60°, prepared by methylation of the appropriate amine, are not racemised by NaOEt–EtOH during 2 months, whilst *Et* (+)-*α-dimethylaminopropionate*, b.p. 155·5—156·5°/767 mm., $[\alpha]_D^{20}$ +5·58°, but not Et *d*-α-aminopropionate, is racemised by NaOEt–EtOH, but more slowly than the betainate. These results support the view that racemisation involves the formation of an intermediate enolate ion. H. G. M.

Reactions of amino- and imino-acids with formaldehyde. M. Levy and D. E. Silberman (J. Biol. Chem., 1937, **118**, 723—734).—Changes of p_H (H electrode) during the titration in presence of alkali of *dl*-alanine, *dl*-valine, *l*-aspartic acid, *l*-tryptophan, *dl*-sarcosine, and *l*-hydroxyproline with CH_2O show that NH_2-acids may react with 1 or 2 mols., NH-acids with only 1. Similar measurements with asparagine and CH_2O, and measurements of the rate of disappearance of NH_2-N, show that the product of this reaction is a pyrimidine derivative. A. Li.

Highly polymerised compounds. CLVII. Measurements of the viscosity of amino-acids. H. Staudinger and H. von Becker (Ber., 1937, **70**, [*B*], 889—900).—The same relationships between sp. viscosity and chain length are not observed with acylated NH_2-acids and their esters (containing an acyl group of high mol. wt.) as with purely homopolar compounds; the observed viscosity is > that calc. by an increment. This is attributed to the influence of the many $CO{\cdot}NH_2$ linkings. It is not therefore possible to calculate the chain length in a simple manner from measurements of viscosity as with hydrocarbons and esters. By the addition of the requisite acid chloride to $NH_2{\cdot}CH_2{\cdot}CO_2Et$,HCl in $CHCl_3$–C_5H_5N the lauryl, m.p. 61·5°, *myristyl*, m.p. 70°, palmityl, m.p. 77·5°, and *stearyl*, m.p. 82·5°, derivatives of $NH_2{\cdot}CH_2{\cdot}CO_2Et$ are obtained. Analogously, sarcosine Et ester gives palmityl, m.p. 33·5°, and *stearyl*, m.p. 35—37°, compounds whilst *lauryl*, m.p. 132°, *myristyl*, m.p. 133°, *palmityl*, m.p. 133·5°, and *stearyl*, m.p. 134°, derivatives are obtained from glycylglycine Et ester. $NH_2{\cdot}CH_2{\cdot}CO_2H$ or the requisite acid chloride in presence of aq. NaOH afford the lauryl, m.p. 119·5°, *myristyl*, m.p. 122°, palmityl, m.p. 123·5°, and stearyl, m.p. 124·5°, derivatives. Sarcosine give the *palmityl*, m.p. 61·5°, and *stearyl*, m.p. 67—68°, compounds whilst palmityl, m.p. 113°, and stearyl, m.p. 113·5°, derivatives are obtained from alanine. H. W.

Synthesis of *dl*-alanine in improved yield from α-bromopropionic acid and aqueous ammonia. W. C. Tobie and G. B. Ayres (J. Amer. Chem. Soc., 1937, **59**, 950).—Details are given for obtaining a 65—68% yield in this synthesis. R. S. C.

Colour reactions of sarcosine and alanine with ferric salts. III. J. V. Dubský and A. Langer (Coll. Czech. Chem. Comm., 1937, **9**, 137—149).—The following complex *salts* are prepared, usually by evaporation of aq. solutions of the Fe^{III} salt with sarcosine (*S*), *dl*-alanine (*A*), or glycine (*G*): $FeCl_3$,*A* + H_2O, m.p. 115°, decomp. 134°; $FeCl_3$,$FeCl_2(OH)$,3*A* + $4H_2O$, m.p. 70°, decomp. 105°; $FeCl_3$.2*S* + $0{\cdot}5H_2O$, m.p. 65°; $FeBr_3$,$FeBr_2(OH)$,2*S* + H_2O, decomp. 135°; $FeBr_3$,$FeBr_2(OH)$.3*S*; $FeBr_3$,$FeBr(OH)$,4*S* + $2H_2O$, decomp. 135°; $FeCl_3$,$FeCl_2(OH)$,2*A* + $4H_2O$, m.p. 116°, decomp.

123°; $FeCl_3$,$FeCl_2(OH)$,3*A* + $2H_2O$, decomp. 120°; $FeCl_3$,2*A* + $2H_2O$, decomp. 126°; $FeBr_3$,$FeBr_2(OH)$,2*A* + H_2O; $FeBr_3$,$FeBr_2(OH)$,4*A* + H_2O, decomp. 145°; $FeCl_3$,$FeCl_2(OH)$,3*G* + $3H_2O$, decomp. 120°; $FeCl_2(OH)$,*G* + $2H_2O$, decomp. 115°; $FeCl_2(OH)$,2*G* + $1{\cdot}5H_2O$; $FeCl_3$,$FeCl_2(OH)$,2*G* + $2H_2O$; $FeCl_2$,$FeCl_2(OH)$,3*G* + $4H_2O$; $FeCl_3$,$FeCl_2(OH)$,2*G* + $6H_2O$, darkens 120°, decomp. 170°; 2$FeCl_3$,3HCl,3*G*, m.p. 95°; $FeCl_2$,HCl,*G*, m.p. 96—140°; 2$FeCl_3$,HCl,*G* + $4H_2O$. J. W. B.

Dideuterovaline and dideuteroleucine. C. R. Kinney and R. Adams (J. Amer. Chem. Soc., 1937, **59**, 897—898).—$CMe_2Br{\cdot}CH(OEt)_2$, b.p. 80°/28 mm., gives *isobutenaldehyde Et₂ acetal*, b.p. 136—139°, reduced by H_2–PtO_2 to *iso*butaldehyde Et_2 acetal, b.p. 135—136°/745 mm., and by D_2–PtO_2 in EtOAc to *αβ-dideuteroisobutaldehyde Et₂ acetal*, b.p. 133—135°/747 mm., which with NH_4Cl–KCN gives *βγ-dideuterovaline*, m.p. 273° (decomp.) (1·5—2° < *dl*-valine); this acid contains 25% < the theoretical amount of D, due to loss during enolisation of the aldehyde. Similarly are obtained *αβ-dideuteroisovaleraldehyde Et₂ acetal*, b.p. 164—165°/740 mm., *iso*valeraldehyde Et_2 acetal, b.p. 167—168°/750 mm., and *βγ-dideuteroleucine*, m.p. 271° (decomp.) (2° < *dl*-leucine) (93·5% pure; enolisation much less probable). R. S. C.

Photographic chemistry of cystine. A. Steigmann (Phot. Ind., 1937, **35**, 357—358; cf. A., 1936, 873).—A general method for producing new compounds containing labile S consists in heating together cystine, in H_2O, with $CH_2Br{\cdot}CO_2H$ (or other halogenofatty acids), NaOH (or other alkali or aldehydes), with or without CH_2O. Thus two new *compounds* (or mixed compounds) formed from the above substances, with and without CH_2O, are named "cystiformin" and "cysticin" respectively; in emulsions they desensitise strongly, but show no other notable properties. J. L.

Selenium-substituted amino-acids. III. Inactive selenocystine. A. Fredga (Svensk Kem. Tidskr., 1937, **49**, 139—145; cf. this vol., 235).—Study of the variation with time of the solubility of (+)- (I) and (−)-selenocystine, singly and as equimol. mixture, indicates the production of the *meso*-form in the solution. The *hydrochloride* and *hydrobromide* of (I), r-*selenocystine hydrochloride*. (−)-*cystine hydrobromide*, and r-*cystine hydrochloride* are described. M. H. M. A.

Acid amides. K. von Auwers (Ber., 1937, **70**, [*B*], 964—967).—According to present chemical and physical evidence, acid amides are typical tautomeric compounds which in the liquid condition give mixtures of the $\cdot CO{\cdot}NH_2$ and $\cdot C(OH){:}NH$ forms. According to peculiarities of their components, the position of equilibrium can be greatly, under conditions almost completely, displaced in one or other direction. H. W.

Photochemical properties of the keto-imino-linking.—See A., I, 370.

Transposition of the functional group carboxyl in the form of an ester. J. Miliotis (Bull. Soc. chim., 1936, [v], **3**, 2365—2367).—Transposition of carboxyl as ester occurs in the Hofmann degradation of Et oxamate with Br–KOH, the products being $OEt{\cdot}CO{\cdot}NH_2$, only in small amount owing to evolution of NH_3 towards the end of the reaction, and EtOH. H. G. M.

Decarboxypeptides and their derivatives. III. J. von Braun, F. Dengel, and A. Jacob [in part, with A. Bahn] (Ber., 1937, **70**, [*B*], 994—1001; cf. A., 1930, 73).—Examination of a series of decarboxypeptides shows them to be physiologically inactive when containing NH_2, NHMe, or NHEt but productive of cramp and lowering of temp. when higher alkyl groups are present; the activity appears to attain a max. with groups of medium size. Peptides which are not composed entirely of natural protein components appear physiologically inactive whatever the magnitude of the alkyl group. $CHMeBr{\cdot}COBr$ and pyrrolidine in dry Et_2O give 1-*α-bromopropionylpyrrolidine*, b.p. 112—114°/0·2 mm., which with the requisite primary amine afford 1-*α-ethylaminopropionylpyrrolidine* (*N-ethylalanyldecarboxyproline*), b.p. 90—95°/0·2 mm. (*hydrochloride*, m.p. 210°; *picrate*, m.p. 174°), and 1-α-iso*amylaminopropionylpyrrolidine*, b.p. 130—135°/0·2 mm. (*hydrochloride*, m.p. 201°; *picrate*, m.p. 147°). Addition of $NH_2{\cdot}[CH_2]_3{\cdot}NH_2$ in Et_2O to $CH_2Cl{\cdot}COCl$ affords *αγ-dichloroacetamidopropane*, m.p. 125°, transformed by liquid NH_3 at room temp. into *αγ*-diamino-acetamidopropane (*hydrochloride*, m.p. 165°). *αγ-Diethylaminoacetamidopropane*, b.p. 221°/0·5 mm. (*hydrochloride*, m.p. 158°), and *αγ-di*iso*amylaminoacetamidopropane* (*hydrochloride*, m.p. 158°) are described. *Di-α-aminopropionamidopropane* (very hygroscopic *hydrochloride*, m.p. 227°) its *Et₂*, b.p. 200—204°/0·4 mm., m.p. 45° (*hydrochloride*, m.p. 120°), and *di*-iso*amyl*, b.p. 219—221° (0·2 mm. *hydrochloride*, m.p. 122°), derivatives have been prepared. Putrescine and $CH_2Cl{\cdot}COCl$ in Et_2O–CH_2Cl_2 give *αδ-dichloroacetamidobutane*, m.p. 131°, which gives *αδ-diaminoacetamidobutane*, m.p. 108° (very hygroscopic *hydrochloride*; *Et₂* derivative, m.p. 58°, and its *hydrochloride*, m.p. 198°; *di*iso*amyl* compound, b.p. 220°/high vac., m.p. 42—43°, and its *hydrochloride*, m.p. 248°). *Di-α-bromopropionamidobutane*, m.p. 175°, gives *di-α-ethylaminopropionamidobutane* (*hydrochloride*, m.p. 67°) and the corresponding *Pr₂* (*hydrochloride*, m.p. 80°), *Bu^{n}₂*, (*hydrochloride*, m.p. 58°), *di*iso*amyl* (*hydrochloride*, m.p. 56°), and *didecyl* compounds, b.p. about 270°/high vac., m.p. 75—77°. *αε-Dichloroacetamidopentane*, m.p. 121°, gives *αε-diaminoacetamidopentane*, m.p. 91° (*hydrochloride*, m.p. 207°; *Et₂* derivative, m.p. 227—229°/0·5 mm., m.p. 39—41°, and its *hydrochloride*, m.p. 201°; *di*iso*amyl* compound, b.p. 250—252°/0·1 mm., and its *hydrochloride*, m.p. 180°). *Di-α-bromopropionamidopentane*, m.p. 135°, gives non.-cryst. *di-α-aminopropionamidopentane* (very hygroscopic *hydrochloride*, m.p. 123° after softening at 105°; *Et₂* derivative, b.p. 230°/0·4 mm. and its *hydrochloride*, m.p. 100°; *di*iso-*amyl* compound, b.p. 242°/0·3 mm., m.p. 26°, and its very hygroscopic *hydrochloride*, m.p. 110°). NH_2Et and $CHBrEt{\cdot}COBr$ afford *α-bromobutyrethylamide*, b.p. 125—128°/16 mm., m.p. 63°, whence *α-ethylamino-*, b.p. 120—122°/13 mm., m.p. 43° (*hydrochloride*, m.p. 113°), and α-iso*amylamino-*, b.p. 147—152°/16 mm. (*hydrochloride*, m.p. 84°), *-butyrethylamide*. *α-Ethyl-*

amino-, b.p. 177—180°/1 mm. (*hydrochloride*, m.p. 235°), and α-iso*amylamino-*, b.p. 180—182°/0·3 mm. (*hydrochloride*, m.p. 153—155°), are derived from α-*bromo-γ-phenylbutyrethylamide*, m.p. 68—69°. α-*Bromo-γ-phenylbutyryl chloride*, b.p. 122—125°/1 mm., tends to lose HBr when distilled. p-*Nitrobenz-β-phenylethylamide*, m.p. 151°, is reduced (Pd in MeOH) to p-*aminobenz-β-phenylethylamide*, m.p. 151° (*hydrochloride*, m.p. 265°). *Di*-p-*nitrobenzamidobutane*, m.p. 260°, affords αδ-*di*-p-*aminobenzamidobutane*, m.p. 243° (*Ac*$_2$ derivative, 299°). Tyramine and *p*-NO_2·C_6H_4·COCl yield *mono-*, m.p. 175°, and *di-*, m.p. 193°, *-nitrobenzoyldecarboxytyrosine* which are reduced to the corresponding NH_2-, m.p. 214°, and $(NH_2)_2$-, m.p. 248°, -compounds. H. W.

Carbonyl cyanide. I. R. Malachowski, L. Jurkiewicz, and J. Wojtowicz (Ber., 1937, **70**, [*B*], 1012—1016).—$CO(CH{:}N{\cdot}OH)_2$ is transformed by Ac_2O at 100° into the *diacetate*, m.p. 80—81° after softening at 75—77°, which passes at 110°/12 mm. into AcOH and *acetoximinoacetonitrile* (I), b.p. 110°/9 mm., m.p. (indef.) about 90°. (I) is readily hydrolysed by H_2O to CO_2, HCN, and AcOH. It is transformed by EtOH into *Et acetoximinoacetate*, b.p. 113°/8 mm., also obtained from Et oximinoacetate and Ac_2O at 90°. At 160° (I) yields AcOH and *carbonyl cyanide*, b.p. 65·5° (corr.)/740 mm., m.p. −36° to −35°, which does not tend to polymerise and can be kept unchanged in vessels of resistant glass in absence of moisture. It reacts immediately and explosively with cold H_2O giving HCN and CO_2. With cold EtOH it yields $CN{\cdot}CO_2Et$. H. W.

Action of halogen compounds of arsenic and phosphorus on acetylenic carboxylic acids. I. Addition of arsenic chloride to tetrolic acid. V. O. Mochinatsch and V. S. Bagniuk (Compt. rend. Acad. Sci., U.R.S.S., 1937, **14**, 553—558).—$CMe{\equiv}C{\cdot}CO_2H$ and $AsCl_3$ at 110—115° afford the normal *adduct*, $AsCl_2{\cdot}CMe{:}CCl{\cdot}CO_2H$, but at 120—130° decarboxylation occurs to give, after KOH-treatment, α-*chloro*-β-*arsinoxy*-Δ^{α}-*propene*. At 140° the product is α-*chloro*-Δ^{α}-*propenyl*-β-*arsine*, m.p. 91·5—92°. At 150—155° $CEt{\equiv}C{\cdot}CO_2H$ with $AsCl_3$ gives $AsO{\cdot}CEt{:}CHCl$; at lower temp. mixtures containing mainly the arsinoxy-acid are obtained. J. W. B.

Phosphetines and arsenetines. E. Bilmann and K. A. Jensen (Bull. Soc. chim., 1936, [v], **3**, 2306—2309).—$CHMeBr{\cdot}CO_2Et$ (I) when treated with PEt_3, alone or in Et_2O, gives *Et propiotriethylphosphetinate bromide*, $CHMe(PEt_3\}Br){\cdot}CO_2Et$, m.p. 113—114°. Similarly, *d*-$CHMeBr{\cdot}CO_2Et$ (II) yields a partly active *product*, instantly racemised by NaOEt–EtOH, rapidly by NEt_3–EtOH, and slowly by EtOH. $CHMeBr{\cdot}CO_2H$ and PEt_3 in an atm. of CO_2 yield *propiotriethylphosphetinate hydrobromide*, $CHMe(PEt_3\}Br){\cdot}CO_2H$. *Et propiotrimethylphosphetinate bromide*, m.p. 124—125°, and a partly active *form*, $[\alpha]_D^{20}$ +10·03° in EtOH, were similarly prepared. (II) with PPr_3 gives only r-*Et propiotripropylphosphetinate bromide*. By similar methods (I) with $AsEt_3$ gives *Et propiotriethylarsenetinate bromide*, $CHMe(AsEt_3\}Br){\cdot}CO_2Et$, m.p. 69—70°, the same inactive form being also obtained from (II). H. G. M.

Organic derivatives of silicon. F. S. Kipping (Proc. Roy. Soc., 1937, **A**, **159**, 139—147).—Bakerian lecture. G. D. P.

Electronegative series of organic radicals. A. N. Nesmejanov and K. A. Kotscheschkov (Sci. Rep. Moscow State Univ., 1934, No. 3, 283—289).—Two reactions take place between SnX_2 (X = Cl, Br) and HgR_2 in EtOH, viz., $HgR_2 + SnX_2 \rightarrow SnR_2X_2 + Hg$, and $HgR_2 + SnX_2 + 2EtOH \rightarrow 2RH + (OEt)_2SnX_2$. Domination of the latter over the former increases in proportion to the electronegative character of R, in the series of diminishing electronegativity R = ·$CH(CO_2Et)_2$, *p*-$NH_2{\cdot}C_6H_4$, *p*-$OH{\cdot}C_6H_4$, *o*-$OMe{\cdot}C_6H_4$, β-$C_{10}H_7$, *o*-, *p*-C_6H_4Me, *p*-C_6H_4I, *p*-C_6H_4Br, *p*-C_6H_4Cl, *p*-C_6H_4F, Ph, *p*-$C_6H_4{\cdot}CO_2Et$, CH_2Ph. This series is practically identical with that of Kharasch (A., 1927, 165). It is concluded that the reactions do not involve ionisation of the substrate. R. T.

Mechanism of formation of mercuri-organic compounds through diazo-compounds. A. N. Nesmejanov (Sci. Rep. Moscow State Univ., 1934, No. 3, 291—296).—Liberation of Hg is not an intermediate phase of the reaction $PhN_2Cl,HgCl + 2Cu \rightarrow HgPhCl + 2CuCl + N_2$, as Cu may be replaced by Ag, which cannot displace Hg. In addition, Cu may be replaced by Cu-bronze, Al, Fe, Zn, Mg, or $SnCl_2$. $CHN_2{\cdot}CO_2Et$ and $HgCl_2$ yield $Hg[CCl(HgCl){\cdot}CO_2Et]_2$, $CH_2Cl{\cdot}CO_2Et$, and N_2. R. T.

Oxidation of non-electrolytic *cis*-bivalent platinum compounds with sulphuric acid.—See A., I, 374.

Ethylene compounds of platinum. A. Gelman (Sci. Rep. Leningrad State Univ., 1936, **2**, No. 2, 5—47).—C_2H_4 is passed through aq. K_2PtCl_4 for 15 days at room temp., and aq. $Pt(NH_3)_4Cl_2$ is added, when $[Pt,C_2H_4,Cl_3]_2[Pt(NH_3)_4]$ is pptd. This reacts with K_2PtCl_4 to yield $K[Pt,C_2H_4,Cl_3],H_2O$ (I), identical with that obtained by Zeise from Na_2PtCl_4 and EtOH. $[Pt,C_2H_4,NH_3Cl_2]$ reacts with HCl to afford $NH_4[Pt,C_2H_4,Cl_3]$, and with $CS(NH_2)_2$ (II) to give $PtCl_2$,4(II) (III), indicating its *cis* configuration. An attempted prep. of the *trans*-isomeride by Jörgensen's method was unsuccessful. (I) in dil. HCl and C_5H_5N yield cis-$[Pt,C_2H_4,C_5H_5N,Cl_2]$ (IV), converted by HCl into $C_5H_5NH[Pt,C_2H_4,Cl_3]$, by (II) into (III), and by excess of C_5H_5N into *trans*-$[Pt(C_5H_5N)_2Cl_2]$. (I) and $[Pt(C_5H_5N)_4]Cl_2$ give $[Pt,C_2H_4,Cl_3][Pt(C_5H_5N)_4]$. The *salts* $[Pt,C_2H_4,(C_5H_5N),Br_2]$, $C_5H_5NH[Pt,C_2H_4,Br_3]$, and $[Pt,C_2H_4,Br_3]_2[Pt(NH_3)_4]$ are described. The stability of salts of the series $[Pt,C_2H_4,R,X_2]$ rises in the series R = (II) < NH_3 < C_5H_5N < quinoline, and X = CN < CNS < NO_2 < I < Br < Cl. R. T.

Inertness of *cyclo*pentane hydrocarbons with respect to dehydrogenation catalysis. E. M. Tarasova (Sci. Rep. Moscow State Univ., 1934, No. 3, 173—182).—2-Methyl*cyclo*pentanone and MgEtI yield cis-trans-1-*methyl*-2-*ethyl*cyclo*pentan*-2-*ol*, b.p. 55—61°/11 mm., converted by distillation from anhyd. $H_2C_2O_4$ into a mixture of 1-*methyl*-2-*ethyl*-Δ^1- and -Δ^2-cyclo*pentene* (cis-trans), from which

1-methyl-2-ethyl*cyclo*pentane (I) is obtained by hydrogenation. 1-Methyl-2-*n*-propyl*cyclo*pentane (II) is prepared analogously from 1-*methyl*-2-n-*propyl*-Δ^2-cyclo*pentene*, b.p. 144—148°. (I), (II), and ethyl-, *n*-propyl-, and *n*-butyl-*cyclo*pentane are not dehydrogenated by passage over C–Pt in H_2 or CO_2 at 300°. Under similar conditions, 1 : 4-dimethyl*cyclo*hexane yields *p*-xylene. (I) and Br in presence of $AlBr_3$ yield tetrabromo-*p*-xylene. R. T.

Estimation of *cyclo*pentadiene and indene and their polymerisation in carbon tetrachloride solution. D. L. Hammick and (Miss) D. Langrish (J.C.S., 1937, 797—801).—*cyclo*Pentadiene (I) and indene (II) can be determined in dil. (up to 0·05*M*) solution in CCl_4 with Br in CCl_4; polymerisation of (I) in CCl_4 is bimol., and much faster than that of (II), the rate of polymerisation of both in CCl_4 being retarded by MeCN and stopped in pure MeCN or CCl_4 without O_2. The polymerisations are considered to be autoxidation processes. J. D. R.

Influence of substituents on the velocity of catalytic dehydrogenation of *cyclo*hexane derivatives. II. A. A. Balandin and N. I. Schujkin (Sci. Rep. Moscow State Univ., 1936, No. 6, 281—286).—The velocity of dehydrogenation of methyl-*cyclo*hexane at 200—250° (Ni–Al_2O_3 catalyst) is slightly > that of *cyclo*hexane. R. T.

Influence of solvent on the course of chemical reactions. XIV. Aromatic hydrocarbons. K. Lauer [with Y. Abiko] (Ber., 1937, **70**, [*B*], 1127—1133).—Measurements are recorded of the dissociation consts. of PhOH and α- and β-$C_{10}H_7$·OH in H_2O by colorimetric determination of [H·] in partly neutralised solutions and of these and 1- and 2-anthrol in 25 vol.-% EtOH with thymolphthalein as indicator. Determinations are also based on solubility. The dipole moments of the anthrols have been measured in C_6H_6. The simple aromatic phenols differ slightly but appreciably in electrolytic dissociation, the extent of which corresponds conversely with the dipole moment. The product dissociation const. × (dipole moment)^2 is const. The cause of the relationship is the polarisability of aromatic hydrocarbons which causes the formation of cationoid positions in the polynuclear members. In the cases of $C_{10}H_8$ and anthracene the influence of cationoid polarity on the properties of substituents can be studied without interference from effects due to the surrounding field. H. W.

Isomerisation of *m*-xylene and hexahydro-*m*-xylene during bromination. R. J. Levina (Sci. Rep. Moscow State Univ., 1936, No. 6, 267—268).—The chief product of bromination of *m*-xylene or hexahydro-*m*-xylene in presence of $AlBr_3$ is tetrabromo-*p*-xylene. R. T.

Bromination of aromatic compounds in presence of beryllium and ether. R. Pajeau (Compt. rend., 1937, **204**, 1202—1204).—Be, Br, and Et_2O form a loose complex, $BeBr_2(Et_2O)_2$ (I), which catalyses brominations as follows. C_6H_6 gives *p*-$C_6H_4Br_2$, alkylbenzenes give tribromoalkylbenzenes, dialkylbenzenes give tetrabromodialkylbenzenes, Ph_2 yields 4 : 4′-dibromodiphenyl, CH_2PhCl yields *p*-C_6H_4Br·CH_2Br, and dihydric and alkyl-phenols yield Br_4-derivatives. Bromination of PhOH and nitrophenols is not affected by (I), and proceeds normally. J. D. R.

Metal halide catalysts for hydrocarbon reactions. A. V. Grosse and V. N. Ipatiev (J. Org. Chem., 1937, **1**, 559—566).—C_2H_4 ethylates C_6H_6 (up to C_6Et_6) in presence of HCl and the following salts, the figures being the no. of mols. of C_2H_4 reacting at the stated temp./>1 atm. in presence of 1 mol. of salt: $BeCl_2$ 200° 50, BF_3 25° 35, $AlCl_3$ 75° 75, $TiCl_4$ 170° 5, $ZrCl_4$ 100° 90, $NbCl_5$ 75° 25, $TaCl_5$ 75° 60, $HfCl_4$, $ThCl_4$, $EtCl_5$. Reaction is by way of EtCl, for, if much HCl is used, EtCl is detected in the product. R. S. C.

Polymerisation of styrene as revealed by the Raman effect.—See A., I, 283.

Kinetics of polymerisation reactions.—See A., I, 366.

Thermal polymerisation reactions.—See A., I, 366.

Mechanism of thermal polymerisation and polycondensation.—See A., I, 366.

Chlorobromide of styrene. E. Urion and L. Namias (Bull. Soc. chim., 1936, [v], **3**, 2333—2337).—Styrene (I) when treated with an equimol. mixture of Cl_2 and Br gives about 10% of CHPhCl·CH_2Cl, about 20% of CHPhBr·CH_2Br (II), and 65—70% of *α-chloro-β-bromoethylbenzene* (III), m.p. 27·5—28°, which with cold KOH–EtOH gives *α-chlorostyrene*, b.p. 73°/16 mm., hydrolysed to COPhMe. The rate of addition of BrCl to (I) is of the same order as that of Cl_2 and Br. The fusion diagram of (II) and (III) is given. H. G. M.

Action of diazo-compounds on unsaturated compounds. Determination of mono- and polymeride of phenylbutadiene. A. P. Terentiev and M. E. Zegelman (Sci. Rep. Moscow State Univ., 1936, No. 6, 257—261).—CHPh:CH·CH:CH_2 (I), but not its dimeride, combines with diazotised *p*-NO_2·C_6H_4·NH_2. The reaction of polymerisation is one of the second order. C_5H_5N reacts with (I), and is not a suitable solvent for studying velocity of polymerisation. R. T.

Nitronic ester of phenylcyanonitromethane. F. Arndt, L. Loewe, and H. Işik (Rev. Fac. Sci. Istanbul, 1937, **2**, 139—141).—CN·CPh:NO·OAg and MeI give the *O*-Me ether (I), m.p. 40—41°, also obtained from CN·CPh:NO_2H and CH_2N_2 in Et_2O. Contrary to Hantzsch (A., 1907, i, 500) (I) decomposes at 90°. (I) with HI–AcOH liberates 2 I and is converted into CN·CPh:N·OH. J. W. B.

Units of affinity of the elements. J. Gnezda (Separate, Zagreb, 1937, 17 pp.; cf. A., 1933, 450).—In accord with the author's theory, when $CHPh_3$ is kept for 3 months in excess of PhMe, the *compound*, $C_{40}H_{37}$ (= $CHPh_3$ + 3PhMe − 3H), m.p. 90—93°, is formed. With mesitylene, $CHPh_3$ yields a similar *compound*, $C_{28}H_{25}$, m.p. 91—93·5°. The theory also indicates that 8 Cl- and 10 Hg-"viravals" remain unsaturated in $HgCl_2$, and this is said to explain the existence of certain additive compounds. The effects

of various oxides on aq. rosaniline hydrochloride, decolorised by Mg, are in accord with the theory. The neutral character of triazole and the acidity of tetrazole are explained. Complex structures for various other compounds are developed. J. W. S.

Isomerism of triphenylmethane. M. V. Gaverdovskaja-Juschkevitsch (Sci. Rep. Moscow State Univ., 1936, No. 6, 263—266).—CPh_3·OH yields stable $CHPh_3$, m.p. 92°, when reduced in presence of C–Pt at 300°, and "unstable $CHPh_3$," m.p. 81°, at 150—180°; the structure, $CPh_2{:}C<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CH_2$ is assigned to the latter. R. T.

Action of aluminium chloride on diphenyl. J. K. Juriev and R. J. Levina (Sci. Rep. Moscow State Univ., 1934, No. 3, 203—207).—The chief product obtained by passing Ph_2 over $AlCl_3$ at 250—300° is C_6H_6, with *cyclo*hexane and methyl*cyclo*pentane. R. T.

Accelerated and retarded autoxidation of tetraphenyl-*p*-xylylene [tetraphenylquinodimethane]. Action of antioxidants. G. Wittig and H. Köhne (Annalen, 1937, **529**, 142—161).—LiC_6H_4Ph and *p*-$C_6H_4(CO_2Me)_2$ in Et_2O give ωω′-*dihydroxy*-ωωω′ω′-*tetradiphenylyl*-p-*xylene*, m.p. 289—291° (*Li*$_2$ derivative), converted by HCl–$CHCl_3$–AcCl into the *dichloride*, m.p. 265—266° (decomp.), which with Naturkupfer-*C* in xylene (CO_2) at 100° gives *tetra*-p′-*diphenylylquinodimethane* (I), *p*-$C_6H_4[{:}C(C_6H_4Ph)_2]_2$, m.p. 338—341° (decomp.). *p*-$C_6H_4(:CPh_2)_2$ (II) absorbs 1 O_2 in C_6H_6 to give a *peroxide*, OH·O·$[CPh_2{\cdot}C_6H_4{\cdot}CPh_2{\cdot}O_2]_n$·H ($n = 10$), m.p. 168—171° (decomp.), sol. in conc. H_2SO_4 with orange-red halochromy and gradually converted thereby into *p*-$C_6H_4(CPh_2{\cdot}OH)_2$, m.p. 166—168°, and reduced by $ZnCl_2$–HCl–AcOH and a trace of I to *p*-$C_6H_4(CHPh_2)_2$, m.p. 172°. The val. of *n* given above is only an average; in CCl_4 a *peroxide* is formed, in which the average val. of $n = 4$. (I) in $CHCl_3$ gives an analogous *peroxide*, m.p. about 250° (decomp. from about 170°), in which $n = 2$. The rate of peroxide formation of (I) in five solvents is determined. Mixtures of PhCHO and (I) absorb O_2 at a rate intermediate between those of PhCHO and (I) alone; (I) is preferentially oxidised and thus acts as an antioxidant for PhCHO. Polyenes, $CPh_2{:}CH{\cdot}[CH{:}CH]_x{\cdot}CH{:}CPh_2$, also act as antioxidants for PhCHO; their effectiveness is of the same order as that of (II) and increases with increasing *x* (max. with $x = 6$, owing to more rapid oxidation of the dodecahexaene). These effects are explained by assumption of a complex, RCHO···O:O···C:C. *p*-$C_6H_4(OH)_2$ delays oxidation of (II), but is itself fairly rapidly oxidised and thus soon loses its efficacy. Oxidation of a mixture of *p*-OH·C_6H_4·OMe and (II) gives the *substance*, *p*-*p*′-OMe·C_6H_4·O·$CPh_2{\cdot}C_6H_4{\cdot}CPh_2$·O·OH, m.p. 152—153° (decomp.). *p*-$C_6H_4(OMe)_2$ is not an antioxidant for (II). The presence of the terminal OH in the peroxides is proved by reaction with MgMeI. R. S. C.

Decomposition of hexavinylethane derivatives into radicals. G. Wittig and H. Kosack (Annalen, 1937, **529**, 167—184).—The tendency of symmetrical C_2H_6 derivatives to form the following free radicals is shown to be: $CPh_2{:}CH{\cdot}CPh_2{\cdot} < (CPh_2{:}CH)_2CPh{\cdot} < (CPh_2{:}CH)_3C$. Free radicals are not formed if accumulation of vinyl substituents can be avoided by the allylic rearrangement. $CH(C_6H_4Ph)_2$·OH and H_2SO_4–MeOH give *di*(*diphenylyl*)*methyl Me ether*, m.p. 125—127°, which with Na–K in dioxan gives the *K* derivative, converted by EtOH into $CH_2(C_6H_4Ph)_2$ and by $(CMe_2Br)_2$ in ligroin into ααββ-tetradiphenylylethane, m.p. 276—279°, which is stable at 300°. $CHPh(CH_2Bz)_2$ and LiPh give *ααγεε-pentaphenylpentaαγ-diol*, m.p. 133—134°, which in boiling AcOH gives *ααγεε-pentaphenyl-*$\Delta^{\alpha\delta}$*-pentadiene*, m.p. 168—169°, stable to LiPh, but giving with $KCPhMe_2$ a green *K* derivative, which with $(CMe_2Br)_2$ affords *phenyldi*-(ββ-*diphenylvinyl*)*methyl* (I); this radical is monomeric when solid, since it is green, but becomes colourless in a few hr. and later resinifies, whilst its solution is very rapidly decolourised in air; with benzoquinone it slowly gives the *ether* (II), *p*-$C_6H_4[O{\cdot}CPh(CH{:}CPh_2)_2]_2$, m.p. about 140° with dissociation, and it reacts slowly with N_2Ph_4. $CHPh{:}CH{\cdot}CH(CH_2Bz)_2$ could not be obtained from COPhMe and $CPh_2{:}CH{\cdot}CHO$. $CH(CH_2{\cdot}CO_2Me)_3$ and LiPh give *tri*-(β-*hydroxy*-ββ-*diphenylethyl*)*methane* [*ααεεβ′β′-hexaphenyl-γ-ethylpenta-αεβ′-triol*], m.p. 227—228°, unaffected by LiPh, but converted by $KCPhMe_2$ into the violet *K* derivative, which with $(CMe_2Br)_2$ gives *tri*-(ββ-*diphenylvinyl*)*methyl*, black, which behaves with O_2 as does (I) and with benzoquinone gives, more rapidly than does (I), the *ether* [as (II)], m.p. 167—172°, which is less stable than is (II). Ph·$[CH{:}CH]_2$·COPh and COPhMe in KOH–aq. EtOH give *cinnamylidenediacetophenone*, m.p. 84—85°, and *dicinnamylidenetriacetophenone*, m.p. 254—255°; the former product with 2 mols. of LiPh gives *ε-keto-ααγβ′-tetraphenyl-γ-vinylpentan-α-ol*, m.p. 146—147°, or with 4 mols. the diglycol, which could not be purified, but was dehydrated by hot AcOH to *ααεε-tetraphenyl-γ-styrylpentamethylene oxide*, m.p. 191—192° [also obtained from $CHPh{:}CH{\cdot}CH(CH_2{\cdot}CO_2Me)_2$]; this is further dehydrated by hot HCl–AcOH to give *styryldi*-(ββ-*diphenylvinyl*)*methane* [*ααγγβ′-pentaphenyl-γ-vinyl-*$\Delta^{\alpha\delta}$*-pentadiene*], m.p. 141—142°, which with LiPh gives a violet *Li* derivative; this with MeOH gives *ααεεβ′-pentaphenyl-γ-ethylidene-*$\Delta^{\alpha\delta}$*-pentadiene*, m.p. 130—131°, with I gives the dimeride, *ααεζκκβ′β′β″β″-decaphenyl-*βι-*divinyl-*$\Delta^{\alpha\gamma\iota\iota}$*-decatetraene*, m.p. 180° (decomp.), and does not react with $(CMe_2Br)_2$. The tetraene has only slight tendency to dissociate in boiling xylene; the Li derivative is, therefore, $LiCHPh{\cdot}CH{:}C(CH{:}CPh_2)_2$, formed by allylic rearrangement, and the structures of the derived hydrocarbons follow. $CHPh{:}CH{\cdot}CPh_2{\cdot}OMe$ (modified prep.), m.p. 76—77°, and $CPh_2{:}CH{\cdot}CHPh{\cdot}OMe$ with K–Na both give a K derivative, which with $(CMe_2Br)_2$ gives the dimeride, m.p. 211—212°, believed to be *ααγδζζ-hexaphenyl-*$\Delta^{\alpha\epsilon}$*-hexadiene*. R. S. C.

Halogen derivatives of indene. J. von Braun and H. Ostermayer (Ber., 1937, **70**, [*B*], 1006—1008).—Gradual addition of 1-hydrindone (I) to PCl_5 suspended in C_6H_6 at 0°, distillation of the product, and treatment of it with quinoline in cold Et_2O leads to 1-*chloroindene* (II), b.p. 105°/15 mm., which is readily hydrolysed by 5% HCl to (I).

(II) absorbs Br in cold CS_2 and the product loses HBr when distilled and gives 1-*chloro*-2-*bromoindene* (III), b.p. 115°/0·1 mm., the constitution of which is established by its ozonisation to homophthalic acid. With Br in CS_2 (III) affords some 1 : 2-*dibromoindene* (IV), m.p. 133°, which is resistant towards Br. (I) and PBr_5 similarly afford 1-*bromoindene*, m.p. 42°, and some (IV). H. W.

Synthesis of 1 : 2 : 4-trimethyl-7-*iso*propylindene. W. G. Whittleston (J. Amer. Chem. Soc., 1937, **59**, 825—826).—*p*-Cymene, 40% CH_2O (not paraformaldehyde), $ZnCl_2$, and, best, a little $NiCl_2$, and gaseous HCl at 60° give 2-*methyl*-5-iso*propylbenzyl chloride*, b.p. 123—124°/20 mm., and thence by standard methods *Et*$_2$ 2-*methyl*-5-iso*propylbenzylmalonate*, b.p. 190—195°/9 mm., the corresponding *acid*, m.p. 165°, β-p-*cymylpropionic acid*, b.p. 190—195°/20 mm., m.p. 76·5°, 2-*methyl*-5-iso*propylbenzylmethylmalonic acid*, cryst., β-p-*cymyl*-iso*butyric acid*, b.p. 189—190°/12 mm., 2 : 4-*dimethyl*-7-iso*propylhydrindone*, b.p. 147—150°/9 mm., and (by MgMeI) 1 : 2 : 4-*trimethyl*-7-iso*propylindene*, b.p. 140—145° (slight decomp.)/10 mm., m.p. 99·5° (*picrate*, m.p. 88—89°). R. S. C.

Decomposition of tetralin peroxide. IV. Effect of sulphur and sulphur compounds.—See A., I, 316.

Irreversible catalysis of unsaturated cyclic hydrocarbons. Contact transformation of Δ^2-octahydronaphthalene. M. B. Turova-Pollak (Sci. Rep. Moscow State Univ., 1934, No. 3, 193—196).—*trans*-Δ^2-Octahydronaphthalene (I) yields $C_{10}H_8$ and *trans*-decahydronaphthalene when passed over Pd–asbestos at 200—205° in CO_2. *trans*-2-Hydroxydecahydronaphthalene yields (I) when heated with $NaHSO_4$ at 180—200° (3 hr.), and the *cis*-isomeride when heated with $ZnCl_2$. R. T.

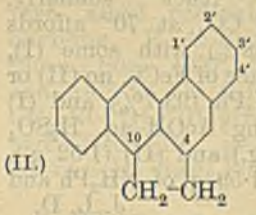
$\Delta^{9:10}$-Octahydronaphthalene. Isomerising action of zinc chloride in dehydration of 2-*cyclo*pentyl*cyclo*pentanol. N. I. Schujkin (Sci. Rep. Moscow State Univ., 1934, No. 3, 197—202).—2-*cyclo*Pentyl*cyclo*pentanol and $ZnCl_2$ (180°; 2 hr.) yield $\Delta^{1:9}$- and $\Delta^{9:10}$-octahydronaphthalene (I), which with HBr yields 9-bromodecahydronaphthalene, and this yields pure (I) when boiled with EtOH–KOH. R. T.

Dehydrogenation catalysis of condensed ring hydrocarbons. I. N. Titz and G. J. Bergo (Sci. Rep. Moscow State Univ., 1936, No. 6, 353—357).—Di- and octa-hydroanthracene yield anthracene when passed over C–Pt at 310°. Acenaphthene is not dehydrogenated under these conditions. R. T.

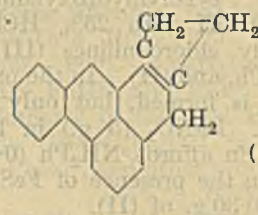
Action of aluminium chloride on octahydroanthracene. S. E. Michlina (Sci. Rep. Moscow State Univ., 1934, No. 3, 209—212).—The products obtained by distilling octahydroanthracene from $AlCl_3$ are tetradecahydroanthracene and tetrahydronaphthalene; the production of butadiene is postulated. R. T.

Friedel-Crafts reaction between oxalyl chloride and 1 : 2-benzanthracene. A. Dansi (Gazzetta, 1937, **67**, 85—88).—This reaction in CS_2 gives 1 : 2-*benzanthracene*-10-*carboxylic acid*, m.p. 220°, with 4 : 10-*oxalyl*-1 : 2-*benzanthracene*, m.p. 280—284°. The latter is oxidised ($KMnO_4$) and esterified (*Ag* salt and MeI) to *Me*$_2$ *anthraquinone*-1 : 2 : 4-*tricarboxylate*, m.p. 193°, and reduced (distillation in H_2 over Zn) to 4 : 10-*dimethylene*-1 : 2-*benzanthracene*, m.p. 130°. E. W. W.

4 : 10-Ace-1 : 2-benzanthracene. L. F. Fieser and A. M. Seligman (J. Amer. Chem. Soc., 1937, **59**, 883—887).—*γ-Keto*-*γ*-5-*hydrindylbutyric acid* (from hydrindene, succinic anhydride, and $AlCl_3$ in $C_2H_2Cl_4$–$PhNO_2$), m.p. 125—125·5°, with Zn–Hg in HCl–PhMe gives *γ*-5-*hydrindylbutyric acid*, m.p. 54·9—55·2°, the *chloride*, b.p. 170°/10 mm., of which with $AlCl_3$ in CS_2 gives 6 : 7-*trimethylene*-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 151—152°/2 mm., the structure of which is proved by oxidation to pyromellitic acid. Clemmensen reduction affords 6 : 7-*trimethylenetetrahydronaphthalene*, b.p. 104—106°/3 mm., which with BzCl gives 5-*benzoyl*-6 : 7-*trimethylenetetrahydronaphthalene* (I), b.p. 183—185°/0·5 mm., converted by Se at 290° in N_2 into impure 1-*benzoyl*-2 : 3-*trimethylenenaphthalene*, b.p. 215—220°/1·5 mm., which at 405° yields 4 : 10-*ace*-1 : 2-*benzanthracene* (II), m.p. 138·5—140° (*picrate*, m.p. 148—149°). CrO_3-oxidation of (II) gives 1 : 2-*benzanthraquinone*-4-*acetic acid*, m.p. 228—229·5°. When heated at 410° (I) affords 17—21% of (?) Δ^3-*dehydro*-3 : 4-*trimethylene*-2-iso*benzanthrene* (III), m.p. 144·5—145° (*picrate*, m.p. 136—137°; oxidised to phenanthrene-8 : 9-dicarboxylic anhydride), and 4% of 1′ : 2′ : 3′ : 4′-*tetrahydro*-4 : 10-*ace*-1 : 2-*benzanthracene*, m.p. 106—107° (*picrate*, m.p. 131—132°), dehydrogenated to (II) by Se. M.p. are corr. R. S. C.



(II.)



(III.)

Derivatives of pyrene. G. Lock (Ber., 1937, **70**, [*B*], 926—930).—Stepwise bromination of pyrene (I) is possible in CCl_4. 3-*Bromopyrene*, m.p. 95° [*picrate*, m.p. 172° (corr.)], is thus obtained. Its constitution is established by its conversion by CuCN in boiling quinoline into 3-*cyanopyrene*, m.p. 151·5° [*picrate*, m.p. 141° (corr.)], which is transformed by MgPhBr in Et_2O–C_6H_6 into 3-benzoylpyrene (picrate, m.p. 159°), identical with that described by Scholl and Seer (A., 1913, i, 58). Further bromination of (I) affords *dibromopyrenes*, m.p. 221—222° (corr.) and 176—177° (corr.), respectively, probably 3 : 8- and 3 : 10-derivatives. H. W.

Pyrene series. K. Dziewoński and L. Sternbach (Bull. Acad. Polonaise, 1937, **A**, 81—85).—Acetylation of pyrene ($AlCl_3$) yields 3-*acetylpyrene* (I), m.p. 94° (*picrate*, m.p. 160°; *phenylhydrazone*, m.p. 168°), the *oxime* of which, m.p. 198°, is converted by HCl in Ac_2O into 3-*acetamidopyrene*, m.p. 260°, hydrolysed to 3-aminopyrene. (I) when heated with S yields *bis*-4 : 3-*pyrenethiophenindigo*, m.p. > 400°, and with MgMeI followed by hydrolysis gives

3-iso*propenylpyrene*, m.p. 61·5—62·5° (*picrate*, m.p. 146—147·5°). A. Li.

Catalytic condensation of acetylene with aromatic amines. X. Intermediate products of condensation of acetylene with amines. N. Kozlov and O. Serko. **XI. Condensation of acetylene with aniline in presence of mercury salts.** N. Kozlov and G. Rodman (J. Gen. Chem. Russ., 1937, 7, 832—835, 836—838).—X. C_2H_2 and NH_2Ph in presence of $HgCl_2$ yield Schultz's and Eckstein's bases; NPh:CHMe is supposed to be an intermediate stage in their production.

XI. The above reaction may be catalysed by $HgSO_4$, Hg_2SO_4, or $HgNO_3$, but not by $Hg(CN)_2$. R. T.

Oxidation reaction occurring during reduction of aromatic nitro-compounds. K. G. Mizutsch (Compt. rend. Acad. Sci. U.R.S.S., 1937, **15**, 37—40; cf. A., 1936, 601).—NHPh·OH with warm aq. H_2SO_4 in CO_2 atm. affords azoxybenzene (I) and NH_2Ph, but mainly (85%) *p*-$NH_2·C_6H_4·OH$ (II). In the presence of $FeSO_4$, very little (II) is formed; NH_2Ph (68%) and (I) (30%) are the main products. *o*- and *p*-Tolylhydroxylamine react similarly. NHPh·OH with 25% HCl in CO_2 at 70° affords mainly chloroanilines (III) (88%) with some (I), NH_2Ph, and (II). In the presence of $FeCl_2$, no (II) or (III) is formed, but only NH_2Ph (93·7%) and (I) (6%). $PhNO_2$ (5 g.) in boiling AcOH–aq. H_2SO_4 with Sn affords NH_2Ph (0·44 g.) and (II) (1·52 g.), but in the presence of $FeSO_4$ 1·59 g. of NH_2Ph and only 0·30 g. of (II). J. L. D.

Condensations of aromatic amines with formaldehyde in media containing acid. VII. Polymeric states and structures of some anhydro-*p*-alkylaminobenzyl alcohols. W. S. Young and E. C. Wagner (J. Amer. Chem. Soc., 1937, **59**, 854—855; cf. this vol., 308).—The compounds $(·NR·C_6H_4·CH_2)_n$, in which R = Me, m.p. 209—212°, Et, m.p. 84—86°, *Pr*$^{\alpha}$, m.p. 106—108°, *Bu*$^{\alpha}$, m.p. 52—53°, iso*amyl*, m.p. 46—48°, and CH_2Ph, m.p. 162—163°, are found by cryoscopy to be trimeric in C_6H_6 (cf. Friedländer, A., 1903, i, 252). Much higher mol. wts. are found in camphor. The bases and, to a smaller extent, their hydrochlorides, are unstable. Structures are confirmed by reduction by Zn–H_2SO_4 to the base, NHPhR. M.p. are corr. R. S. C.

Action of primary aromatic amines on 1 : 6-dichlorodiethylenediamminocobaltic chloride. A. Ablov (Bull. Soc. chim., 1936, [v], **3**, 2270—2279; cf. A., 1936, 1241).—The following *compounds* have been obtained by interaction of praseo-1 : 6-dichlorodiethylenediamminocobaltic chloride (I) with the appropriate primary aromatic amine, all of which have a dissociation const. in H_2O < that of NH_2Ph: [Co en$_2$(*m*-$C_6H_4Me·NH_2$)Cl]X_2 [en = $(CH_2·NH_2)_2$; X = Cl, Br, I, and NO_3];
[Co en$_2$(*o*-$NH_2·C_6H_4·OMe$)Cl]X_2,$2H_2O$ (X = Cl, Br, and I; the nitrate has only 1 H_2O);
[Co en$_2$(*o*-$NH_2·C_6H_4·OEt$)Cl]X_2,$2H_2O$ (X = Cl and Br); [Co en$_2$(*p*-$NH_2·C_6H_4·OMe$)Cl]X_2 (X = Br, I, and NO_3; the chloride has 1 H_2O);
[Co en$_2$(*p*-$NH_2·C_6H_4·OEt$)Cl]Cl_2,H_2O (the corresponding nitrate has no H_2O); [Co en$_2$(*p*-$NH_2·C_6H_4F$)Cl]X_2 (X = Br, I, and NO_3; the chloride has 1 H_2O). Primary aromatic amines [*o*-$C_6H_4Me·NH_2$, *p*-$C_6H_4Cl·NH_2$, *o*-$C_6H_4(NH_2)_2$] with a dissociation const. < that of NH_2Ph cause isomerisation of (I) into the violeo-chloride. H. G. M.

Carbamide derivatives in the alkanolamine series. R. W. Charlton and A. R. Day (J. Org. Chem., 1937, **1**, 552—558).—The following *carbamides* are prepared from the appropriate alkanolamine with $NH_2·CO·NH·NO_2$ in H_2O or α-$C_{10}H_7·NCO$ in Et_2O or dioxan: β-*hydroxyethyl*- (I), m.p. 94—95° [O-p-*nitro*- (II), m.p. 183—184°, and -p-*amino-benzoate* (III), m.p. 203°; ON-*dicinnamoyl* derivative, m.p. 173·5—174° (absorbs $2H_2$ catalytically)]; β-*hydroxy*-n-*propyl*-, m.p. 119° (mixed mono- and di-*p*-nitrobenzoyl, m.p. 182—186°, ON-*di*-p-*aminobenzoyl*, m.p. 210—211°, O-p-*aminobenzoyl*, m.p. 149—150°, and ON-*dicinnamoyl* derivative, m.p. 179—179·5°); NN-di-β-hydroxyethyl- (OO-*di*-p-*nitro*-, *forms*, m.p. 140—140·5° and 152—153°, and -p-*amino-benzoate*, m.p. 172·5—172·8°); N-α-*naphthyl*-N′-β-*hydroxyethyl*- (IV), m.p. 186° [O-p-*nitro*-, m.p. 191° (decomp.), and -p-*amino-benzoate* (V), m.p. 193—193·5° (decomp.)], N-α-*naphthyl*-N-β-*hydroxy*-n-*propyl*-, m.p. 162° [O-p-*nitro*-, m.p. 218—221° (decomp.), and -p-*amino-benzoate*, m.p. 171°], and N-α-*naphthyl*-N′N′-*di*-β-*hydroxyethyl-carbamide*, m.p. 126—127°. αγ-*Dicarbamido*-, +H_2O, m.p. 86—87°, αγ-*di*-1-*naphthylcarbamido-propan*-β-*ol*, m.p. 171·5—172°, and 6-*carbamidothymol*, m.p. 179°, were also made. M.p. are corr. The structure of the *O*-esters is indicated by their failure to react with Na in C_6H_6 or PhMe and by the fission of (II) by NH_3–EtOH at 100° to *p*-$NO_2·C_6H_4·CO·NH_2$. (I), (III), (IV), and (V) are weak hypnotics; (II) and (IV) are toxic. R. S. C.

Influence of reaction conditions on the yields of isomerides in nitration of acetanilide. A. P. Terentiev and B. M. Kedrov (Sci. Rep. Moscow State Univ., 1936, No. 6, 213—234).—The content of *o*-$NO_2·C_6H_4·NH_2$ (I) in the product of nitration of NHPhAc rises from 6—7% when 100% H_2SO_4 is taken to 28% with 84% H_2SO_4; nitration does not proceed when the H_2SO_4 contains >16% of H_2O, whilst the use of 10% oleum leads to production of tarry products. Increasing the amount of 100% H_2SO_4 taken per g. of NHPhAc from 2 to 5 ml. greatly lowers the yield of (I), but further addition of H_2SO_4 does not further reduce it. The yield of (I) is slightly increased by raising the nitration temp. from −3° to 10°, whilst further rise to 40° has no effect. The *m*-$NO_2·C_6H_4·NH_2$ content of the product is independent of temp., concn. and amount of H_2SO_4 taken. Addition of AcOH or $HgSO_4$ does not affect the relative yields of (I) and *p*-$NO_2·C_6H_4·NH_2$. R. T.

Manufacture of aminomethylnaphthalenesulphonic acids.—See B., 1937, 420.

Manufacture of [sugar] derivatives of *o*-nitroanilines and *o*-phenylenediamines.—See B., 1937, 420.

Optically active tri*cyclo*hexanediaminecobaltic salts and ethylenediamine*cyclo*hexanediamine cobaltic salts.—See A., I, 289.

Diaryls and their derivatives. XIII. Azo-dyes from 6 : 6′-diamino-2 : 2′-dihydroxy-1 : 1′-dinaphthyl. J. S. Joffe (J. Gen. Chem. Russ., 1937, 7, 1022—1025).—2-β-*Hydroxynaphthalenecazo-*, m.p. 292°, and 2-(2″-*hydroxy*-3″-*carboxynaphthalene*)-*azo*-6 : 2′ : 6′-*trihydroxy*-1 : 1′-*dinaphthyl* are prepared by coupling with diazotised 6 : 6′-diamino-2 : 2′-dihydroxy-1 : 1′-dinaphthyl. R. T.

Action of mixed organo-magnesium compounds on the phenylhydrazones of aliphatic aldehydes. Preparation of *s*-alkylphenylhydrazines. P. Grammaticakis (Compt. rend., 1937, **204**, 1262—1263; cf. A., 1936, 837).—CHEt:N·NHPh (I) with MgPhBr affords *N*-phenyl-*N*′-α-phenylpropylhydrazine, also obtained from CHPh:N·NHPh and MgEtBr. (I) with MgEtBr gives N-*phenyl*-N′-α-*ethylpropylhydrazine*, b.p. 138°/12 mm. [*hydrochloride*, m.p. 185° (decomp.); *Ac* derivative, m.p. 93°; *PhNCO* derivative, m.p. 104°]. CHMe:N·NHPh with MgPhBr similarly affords N-*phenyl*-N′-α-*phenylethylhydrazine*, b.p. 190°/12 mm. [*hydrochloride*, m.p. 202° (decomp.); *Ac* derivative, m.p. 118°; *PhNCO* derivative, m.p. 187°], and with MgEtBr gives N-*phenyl*-N′-α-*methylpropylhydrazine*, b.p. 136°/12 mm. [*hydrochloride*, m.p. 195° (decomp.); *Ac* derivative, b.p. 177°/10 mm.; *PhNCO* derivative, m.p. 139°]. CH_2:N·NHPh with MgPhBr affords CH_2Ph·NH·NHPh. These hydrazines are oxidised in air to hydrazones. J. L. D.

Isomeric di- and tri-nitrophenylhydrazones. H. Brederеck and E. Fritzsche (Ber., 1937, **70**, [*B*], 802—809; cf. A., 1933, 154).—Further examples of isomeric di- and tri-nitrophenylhydrazones are given and reasons are advanced for considering them due to *cis–trans* isomerism. 5-Ethoxymethylfurfuraldehyde is converted by 2 : 4 : 6-$(NO_2)_3C_6H_4$·NH·NH_2 in boiling EtOH containing conc. HCl into 5-*ethoxymethylfurfuraldehyde*-2 : 4 : 6-*trinitrophenylhydrazone*, (I) m.p. 176—178°, (II) m.p. 152—154°. Interconversion occurs when (I) or (II) is boiled in AcOH. 5-*Methoxymethylfurfuraldehyde*-2 : 4 : 6-*trinitrophenylhydrazone* exists in two forms, m.p. 180—182° and 165—167°, respectively. Protracted treatment of (I) with boiling AcOH–Ac_2O yields 5-*acetoxymethylfurfuraldehyde*-2 : 4 : 6-*trinitrophenylhydrazone*, forms m.p. 198—199° and 205—207°, respectively. Isomeric forms are not obtained in the cases of *furfuraldehyde*-2 : 4 : 6-*trinitrophenylhydrazone*, m.p. 244—246°, or -*o*-nitrophenylhydrazone, m.p. 155—156°, 5-*ethoxymethylfurfuraldehyde*-*o*-*nitrophenylhydrazone*, m.p. 127—129°, *furfuraldehyde*-2 : 4-*dinitrophenyl*-N-*methylhydrazone*, m.p. 187—189°, 5-*ethoxymethylfurfuraldehyde*-2 : 4 : 6-*trinitrophenyl*-N-*methylhydrazone*, m.p. 116—118°, *pyrrole*-2-*aldehyde*-2 : 4-*dinitrophenylhydrazone*, m.p. 283—286° or *thiophen*-2-*aldehyde*-2 : 4-*dinitrophenylhydrazone*, m.p. 233—236°. Pyromucyl chloride gives *pyromuc*-2 : 4-*dinitrophenylhydrazide*, m.p. 211—212°, or *pyromuc*-2 : 4-*dinitrophenyl*-N-*furoylhydrazide*, m.p. 195—197°. *Pyromuc*-2 : 4-*dinitrophenyl*-N-*methylhydrazide* has m.p. 177—179°. H. W.

Alkylation of phenols with alcohols in presence of aluminium chloride. II. Alkylation with sec.- and *n*-alcohols. I. P. Tzukervanik and Z. N. Nazarova (J. Gen. Chem. Russ., 1937, 7, 623—631).—The following alkylphenols are obtained in good yield by heating the phenol with alcohols in presence of 2 mols. of $AlCl_3$ per mol. of alcohol: *p*-$C_6H_4Pr^{\beta}$·OH, *o*- and *p*-$C_6H_4Pr^{\beta}$·OMe, and 1 : 3 : 6-$C_6H_3MePr^{\beta}$·OH, with $Pr^{\beta}OH$ in light petroleum at 110—120°, *p*-CHMeEt·C_6H_4·OH, *p*-CHMeEt·C_6H_4·OMe, and *di*-sec.-*butylanisole*, b.p. 140—142°/11 mm., with CHMeEt·OH in ligroin at 140—150°, $CHEt_2$·C_6H_4·OH, and o-, b.p. 140—150°/30 mm., and p-α-*methylbutylphenol*, b.p. 150—156°/30 mm., from PhOH and CHMePr·OH (I) (50°; 4 hr.), sec.-*amyl*-, b.p. 223—230°, and *di*-sec.-*amyl*-*anisole*, b.p. 245—260°, from PhOMe and (I), $C_6H_3Et_2$·OH, *o*- and *p*-C_6H_4Et·OH, and *o*- and *p*-$C_6H_3Et_2$·OH, from PhOH and EtOH (120—140°; 6 hr.), *o*- and *p*-$C_6H_4Pr^{\alpha}$·OH from PhOH and $Pr^{\alpha}OH$, *o*- and *p*-$C_6H_4Bu^{\alpha}$·OH and $C_6H_3Bu^{\alpha}_2$·OH, from $Bu^{\alpha}OH$ and PhOH, $C_6H_4Bu^{\gamma}$·OH from $Bu^{\gamma}OH$ and PhOH, and a mixture of amylphenols from *iso*-C_5H_{11}·OH and PhOH. By-products of the type C_6H_4R·OR are obtained in all cases; they are readily converted into alkylphenols by boiling. R. T.

Migration of alkyl radicals. I. Transfer of *tert.* alkyl radicals from phenols to hydrocarbons. R. A. Smith [with J. Rosen] (J. Amer. Chem. Soc., 1937, **59**, 899—900).—*p*-$C_6H_4Bu^{\gamma}$·OH and $AlCl_3$ in hot C_6H_6 give PhOH and $PhBu^{\gamma}$. *p*-CMe_2Et·C_6H_4·OH gives similarly in the cold PhOH and $CPhMe_2Et$. *p*-CH_2Bu^{γ}·CMe_2·C_6H_4·OH in cold or hot C_6H_6 yields PhOH, $PhBu^{\gamma}$, and other products. R. S. C.

2 : 6-Dipropyl*cyclo*hexanols. G. Vavon and P. Anziani (Bull. Soc. chim., 1937, [v], **4**, 1080—1084).—2 : 6-Diallylphenol (cf. A., 1919, i, 266) with H_2–Pt gives 2 : 6-dipropylphenol and then, with H_2–Pt in AcOH, cis-cis-2 : 6-*dipropyl*cyclo*hexanol* (I), b.p. 119—120°/13 mm. (*H phthalate*, m.p. 95°; *H succinate*, m.p. 40°; *phenylcarbamate*, m.p. 95°), oxidised by CrO_3 to 2 : 6-dipropyl*cyclo*hexanone (II) (cf. A., 1932, 161). (II) with Na–EtOH affords cis-trans-2 : 6-*dipropyl*cyclo*hexanol* (III), m.p. 113° (*phthalate*, m.p. 160—163°; *H phthalate*, m.p. 87—88°; *H succinate*, m.p. 85°; *phenylcarbamate*, m.p. 150°). Ethers of (I) are hydrolysed less rapidly than those of (III) and hence have the *cis* configuration. (I) when heated with Na at 200° is partly converted into (III). J. L. D.

Oxidation of substituted phenols. Effect of iodine in the *o*- and *p*-positions. G. H. Woollett, F. M. Davis, C. N. Jones, and (Miss) M. Neill (J. Amer. Chem. Soc., 1937, **59**, 861—864).—*p*-I hinders, but does not entirely prevent, formation of diphenoquinones by oxidation of 2 : 6-substituted phenols; the % reduction of yield is approx. const. for different phenols. The formation of 3 : 5 : 3′ : 5′-tetraiodo-dipheno-4 : 4′-quinone (I) from $C_6H_2I_3$·OH and $K_3Fe(CN)_6$ is confirmed by reduction (N_2H_4) of the product to 3 : 5 : 3′ : 5′-*tetraiodo*-4 : 4′-*dihydroxydiphenyl*, m.p. 284° (decomp.), which re-forms (I) with CrO_3 or $FeCl_3$; it amounts to 2·1% of the crude product. 2 : 6-$C_6H_3I_2$·OH and CrO_3 give 31% of (I). 2 : 6-$(NHBz)_2C_6H_3$·OH and HIO_3, $KMnO_4$, or, best, $NaNO_2$ in AcOH, give 84% of 3 : 5 : 3′ : 5′-*tetrabenz-*

amidodipheno-4 : 4′-*quinone* (II), cryst. 4-*Iodo*-2 : 6-*dibenzamidophenol* [from $(NO_2)_2C_6H_3$·OH], m.p. 232° (decomp.) [*Bz* derivative, m.p. 253—254° (decomp.)], and CrO_3 give 11·3% of (II). R. S. C.

Decomposition of ethers with sodium in liquid ammonia. P. Schorigin and S. A. Skoblinskaja (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 505—508).—With Na in liquid NH_3, *o*-C_6H_4Me·OCPh$_3$ yields *o*-cresol and $CHPh_3$, CH_2Ph·OPh gives PhOH and dibenzyl, and Ph_2O affords PhOH. Di*iso*amyl ether is not attacked in 5½ days. J. D. R.

Diazo coupling of 5-hydroxy-6-methylhydrindene. L. F. Fieser and W. C. Lothrop (J. Amer. Chem. Soc., 1937, **59**, 945).—The statement that 5-hydroxy-6-methylhydrindene does not couple (A., 1936, 1503) is incorrect; the p-*nitrobenzeneazo*-, m.p. 230—232°, and *benzeneazo*-, m.p. 141—143°, -compounds are obtained in moderate yields in slightly, but in minute yields in conc., alkaline solution. R. S. C.

Manufacture of sulphonic acids of 3-hydroxyacenaphthene.—See B., 1937, 420.

Manufacture of 3 : 4 : 5 : 6-tetrahalogeno-*o*-aminophenols.—See B., 1937, 420.

Synthesis of iretol. R. E. Damschroder and R. L. Shriner (J. Amer. Chem. Soc., 1937, **59**, 931—933).—2 : 4 : 6-$(NO_2)_3C_6H_2$·OMe (from picryl chloride and NaOMe), *forms*, m.p. 50—51°, 56—57°, 58—59°, and (stable) 68—69°, with H_2 and very active PtO_2 or a large amount of Raney Ni in EtOH give 2 : 4 : 6-$(NH_2)_3C_6H_2$·OMe, m.p. 116·5—117·5° (corr.), converted by conc. HCl into iretol [2 : 4 : 6-$(OH)_3C_6H_2$·OMe], m.p. 187·5—188·5° (corr.), isolated in CO_2 and purified by sublimation in vac. R. S. C.

β-Phenyl sulphide. III. O. Hinsberg (Ber., 1937, **70**, [*B*], 936—939; cf. A., 1936, 602).—"β-Diphenylsulphonium hydroxide" can be obtained pure by taking advantage of its solubility in H_2O. When dried at 90° it has the probable composition, $SHPh_2$·OH,H_2O; it is an approx. 1 : 1 mixture of the α- and β-compounds. Its basic perchlorate is transformed by H_2O_2 in AcOH into a *perchlorate*, $C_{24}H_{27}O_9S_2Cl$, m.p. 76—78°, converted by KOH–EtOH into α-Ph_2S and β-Ph_2SO_2. Since these are not present in the initial material, the fundamental forms are α-OH·SPh:C_6H_6 and β-OH·SPh(:C_6H_6)$<^{O}_{O}$. The experiments explain the production of α-Ph_2S during the prep. of β-Ph_2S from purified basic perchlorate. H. W.

Pinacol rearrangement of *cis*- and *trans*-1 : 2-dimethyl*cyclo*hexane-1 : 2-diol. Relationship of the Walden inversion to the mechanism of molecular rearrangements. P. D. Bartlett and I. Pöckel (J. Amer. Chem. Soc., 1937, **59**, 820—825).—*cis*-1 : 2-Dimethyl*cyclo*hexane-1 : 2-diol gives solely 2 : 2-dimethyl*cyclo*hexanone (74%) under conditions (20% H_2SO_4) in which the *trans*-isomeride gives 1-acetyl-1-methyl*cyclo*pentane (78%). Assuming the ring to have an average planar configuration, that group migrates which is located in space near the opposite side of $C_{(1)}$ to that occupied by the OH which is to be replaced. This does not accord with loss of the OH before migration, nor with the "open sextet" theory; a modification of this theory is proposed. The formation of *iso*bornyl chloride (I) and acetate without the bornyl isomerides in the Wagner–Meerwein rearrangement necessitates a Walden inversion if (I) has the *exo*-structure; this is incompatible with the open sextet theory and with reaction by way of solvated carbonium ions. It is explained by a "push and pull" theory, thus: $A^+ + Cl{\cdot}C{\cdot}C{\cdot}C< + ClA \rightarrow ACl + >C{\cdot}C{\cdot}CCl + A^+$; the Cl-donor and acceptor may be Cl′ or HCl, which leads to a reaction of the 1·5 or second order; Meerwein's kinetic results are shown to fit either of these orders better than the first order which he favoured. R. S. C.

Preparation of *d*- and *l*-*iso*hydrobenzoin. F. Eisenlohr and L. Hill (Ber., 1937, **70**, [*B*], 942—947).—PhCHO is electrolytically reduced by a modification of Law's method (J.C.S., 1906, **89**, 512; 1907, **91**, 1753) to a mixture of much hydrobenzoin (I), m.p. 139—140°, and little *iso*-*hydrobenzoin* (II), m.p. 121—22°, accompanied by the (?)polymorphous forms, m.p. 103° and 93°, respectively. Gradual addition of Br to (I) and yellow P in CS_2 affords α-stilbene dibromide, transformed by KOAc in AcOH into (II). (II) is separated into its optical antipodes by selection of the crystals formed when its solution in Et_2O is allowed to evaporate slowly. *d*-*iso*Hydrobenzoin has $[\alpha]_D^{16}$ +95·46° (*c* = 1·598), $[\alpha]_D^{20}$ +94·0° (*c* = 2·000) in 96% EtOH, $[\alpha]_D^{19}$ +122° in C_6H_6, whilst the *l*-form has $[\alpha]_D^{17}$ −96·54° (*c* = 1·6004), $[\alpha]_D^{20}$ −93·5° (*c* = 2·000) in 96% EtOH, $[\alpha]_D^{19}$ −122° in C_6H_6. H. W.

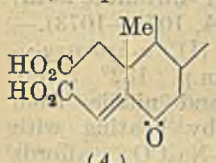
Hydrogenation of acetylenic compounds. XXVII. Hydrogenation of *s*-diphenylditolylbutinediol. J. S. Salkind and E. E. Martinson (J. Gen. Chem. Russ., 1937, **7**, 815—817).—COPh·C_6H_4Me-*p* and (:C·MgBr)$_2$ yield αδ-*diphenyl*-αδ-*di*-p-*tolyl*-Δ$^{\beta}$-*bulinene*-αδ-*diol*, m.p. 146°, which yields αδ-*diphenyl*-αδ-*di*-p-*tolylbutane*-αδ-*diol*, m.p. 176°, when hydrogenated in presence of Pt, and cis-, m.p. 96°, and trans-αδ-*diphenyl*-αδ-*di*-p-*tolyl*-Δ$^{\beta}$-*butene*-αδ-*diol*, m.p. 188—190°, in presence of Pd catalyst. R. T.

Enzymic hydrogenation of unsaturated compounds.—See A., III, 219.

Synthesis of vitamin-*A*. R. Kuhn and C. J. U. R. Morris (Ber., 1937, **70**, [*B*], 853—858).—β-Ionone-semicarbazone is converted by treatment with *o*-$C_6H_4(CO)_2O$ and steam into pure β-ionone, b.p. 128°/8 mm., which is condensed with Zn and $CH_2Br{\cdot}CO_2Et$ to Et β-ionylideneacetate, b.p. 162°/3 mm. Addition of this to the solution obtained by treatment of MgMeI in Et_2O with *o*-C_6H_4Me·NH_2 affords β-*ionylideneacet*-*o*-*toluidide* (I), which is partly cryst. at −40°. (I) is converted by PCl_5 in C_6H_6 into the *imidochloride*, which is added to a suspension of $CrCl_2$ in Et_2O, thus giving β-*ionylideneacetaldehyde* (II), $CH_2<^{CH_2{\cdot}CMe_2}_{CH_2-CMe}>C{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CHO$, b.p. 110° (bath)/$10^{-4}$ mm. (slight decomp.) (*semicarbazone*, m.p. 193—195°). (II) reduces warm Ag_2O–NH_3 and gives a reddish-brown ppt. with $SbCl_3$ in $CHCl_3$. Addition of CMe_2:CH·CHO to a solution of (II) in EtOH containing piperidine and AcOH gives the *aldehyde*,

$CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH_2\cdot CMe\end{matrix}>C[\cdot CH{:}CH\cdot CMe{:}CH]_2\cdot CHO$, which gives a bluish-green colour with $SbCl_3$ in $CHCl_3$ and is reduced by $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ to the corresponding alcohol, the identity of which with vitamin-*A* is shown by the mixed chromatographic adsorption test on Al_2O_3, and growth test on rats. H. W.

Oxidation of cholesterol with selenious acid. A. Butenandt and E. Hausmann (Ber., 1937, **70**, [*B*], 1154—1159).—Oxidation of cholesterol with SeO_2 in Ac_2O at 105—110° gives Δ^5-cholestene-3 : 4-diol diacetate (I), m.p. 165—166°, $[\alpha]_D^{20}$ +94·5° in $CHCl_3$, and Δ^4-*cholestene*-3 : 6-*diol diacetate* (II), m.p. 131—133°, $[\alpha]_D^{20}$ −18·5° in EtOH, hydrolysed respectively to 4-hydroxycholesterol (III), m.p. 174°, and Δ^4-*cholestene*-3 : 6-*diol* (IV), m.p. 255—256°. The authors agree with Rosenheim and Starling (this vol., 191) in interpreting the constitution of (I) and (III) but for the following reasons do not share the view that (II) and (IV) are the *trans*-isomerides of (I) and (III). (IV) suspended in AcOH is oxidised by CrO_3 (= 6 O) to the *ketodicarboxylic acid* (V), $C_{27}H_{42}O_5$, m.p. 185—187°, $[\alpha]_D^{20}$ +67·53° in $COMe_2$ (*Me*$_2$ ester, m.p. 137—138° after slight softening at 135°), which must be *A* since it is also obtained by oxidation of Δ^4-cholestene-3 : 6-dione. (V) is transformed by Zn dust in boiling AcOH into the *ketone*, $C_{26}H_{42}O_2$, m.p. 114—115°. (IV) with $Al(OPr^{\beta})_3$ in boiling $COMe_2$–C_6H_6 gives cholestan-3 : 6-dione, m.p. 169°. H. W.



(*A*.)

Unsaturated steroids. I. Constitution of cholesterilene. II. Preparation and properties of $\Delta^{2:4}$-cholestadiene. III. Titration of unsaturated steroids with thiocyanogen. H. E. Stavely and W. Bergmann (J. Org. Chem., 1937, **1**, 567—574, 575—579, 580—581).—I. Cholesterilene (I), m.p. 78—79°, $[\alpha]_D^{20}$ −97·5° in $CHCl_3$, prepared from cholesterol (II) by anhyd. $CuSO_4$, absorbs 2 Br, but gives no cryst. bromide, absorbs 1·97 O_2 from BzO_2H, with H_2–PtO_2 in EtOAc gives 80% of cholestane and 20% of coprostane, and with maleic anhydride in xylene at 135° gives abnormally the acid *adduct* (III), $C_{31}H_{48}O_4$, decomp. 240—245°. The cholestadiene, $[\alpha]_D$ −112° (IV), from *allo*- or *epiallo*-cholesterol and HCl is unaffected by Na–C_5H_{11}·OH, is hydrogenated (PtO_2) to 85% of cholestane and 15% of coprostane, and yields (III). The dienes (I) and (IV) have the same absorption spectrum and are thus both $\Delta^{3:5}$-cholestadiene. 7-Ketocholesteryl acetate and HCl–EtOH give 7-keto-$\Delta^{3:5}$-cholestadiene (*semicarbazone*, m.p. 198—200°), reduced by NaOEt at 200° to $\Delta^{3:5}$-cholestadiene, m.p. 78—79°, $[\alpha]_D^{21}$ −63·75° in $CHCl_3$, similar to the above dienes in absorption spectrum. Cholesterilenes recorded in the lit. fall into two groups with $[\alpha]$ −60° to −70° and − >100°, respectively; the nature of the isomerism is unknown.

II. When (II) and Al_2O_3 are heated at 200°/vac., a hydrocarbon, m.p. 72—74°, $[\alpha]_D^{23}$ −56·5°, is sometimes obtained; distillation at 240—270° gives $\Delta^{2:4}$-*cholestadiene* (V), m.p. 63°, $[\alpha]_D^{23}$ +114° in $CHCl_3$, hydrogenated (PtO_2) in EtOH to coprostane only, absorbing 2 O_2 from BzO_2H, yielding with maleic anhydride in hot C_6H_6 or, better, xylene at 135° an *isomeride*, m.p. 70—72°, $[\alpha]_D^{21}$ −77·8° in $CHCl_3$, and the acidic *adduct*, m.p. 268—270° (decomp.), reduced by Na–Hg to Δ^4-cholestene, m.p. 77—78°, $[\alpha]_D^{20}$ +66·9° in $CHCl_3$, and rearranged by HCl–EtOH to $\Delta^{3:5}$-cholestadiene. The ready change of the $\Delta^{2:4}$- into the $\Delta^{3:5}$-system is noted. The product, $[\alpha]$ +1·45°, obtained from (I) and Zn dust is probably a mixture of (I) and (V).

III. Titration with $(CNS)_2$ in AcOH discloses the following no. of ethylenic linkings: cholestanone 0·1, cholesteryl chloride 0·02 and benzoate 0·05, Δ^5-cholestene 0·1, cholestenone 0·11, sitosteryl acetate 0·04, stigmasteryl acetate 0·03, cholesterilene 0·99, $\Delta^{2:4}$-cholestadiene 0·95, and ergosteryl acetate 2·03. Δ^3-, but not Δ^4-, Δ^5-, or Δ^{22}-, linkings react and reaction thus indicates ethylenic linkings present in reactive positions. R. S. C.

Ether-soluble constituents of sarsaparilla root. I. J. C. E. Simpson and N. E. Williams (J.C.S., 1937, 733—738).—The sterol fraction on bromination of the mixed acetates gave (1) a sparingly sol. *bromoacetate*, m.p. 210—211°, debrominated to an acetate, m.p. 140—141°; free sterol, m.p. 170°, $[\alpha]_D^{17}$ −45·8°; *p-nitrobenzoate*, m.p. 203°, $[\alpha]_D^{17}$ −13·3°; *anisate*, m.p. 173·5—174·5, $[\alpha]_D^{17}$ −14·3°, all of which are identical with stigmasterol and its derivatives, and (2) the filtrate, which on debromination, saponification, conversion into the 3 : 5-dinitrobenzoates, and fractionation from *cyclo*hexane gave two products, (*a*) m.p. 207—209°, $[\alpha]_D^{17}$ −21·7°; corresponding free sterol, m.p. 135—135·5°, $[\alpha]_D^{17}$ −34·2°; acetate, m.p. 126—127°, $[\alpha]_D^{17}$ −34·7°; benzoate, m.p. 145—146°, $[\alpha]_D^{17}$ −14·2°, suggesting identity with β-sitosterol and its derivatives, (*b*) in minute amount, m.p. 215—217°; the free *sterol*, $C_{29}H_{50}O$, for which the name ε-sitosterol is proposed, has m.p. 143—144°, $[\alpha]_D^{17}$ −38·7° (*acetate*, m.p. 127—128°, $[\alpha]_D^{17}$ −44·7°). The remaining fractions of the Honduras root consisted largely of fats, waxes, and a mixture of paraffins, m.p. 57—59°, of mean formula $C_{18}H_{38} + CH_2$. The non-saponifiable fraction of this mixture gave on benzoylation a *substance*, m.p. 124·5—125°, apparently the dibenzoate of a dihydric phenol $C_{11}H_{14}O_3(OH)_2$, which may be identical with filixic acid of male fern. With Mexican root this fraction consisted 90% of a paraffin or mixture of paraffins, m.p. 61—62°, of mean formula $C_{23}H_{48}$, 9% of a tert.-*alcohol*, $C_{20}H_{42}O$, m.p. 82—82·5°, and 1% of a *substance*, $C_{29}H_{38}O_3$, m.p. 102—104°. P. W. C.

β-Œstradiol. B. Whitman, O. Wintersteiner, and E. Schwenk (J. Biol. Chem., 1937, **118**, 789—795).—Reduction of œstrone (Ni–Al + NaOH) yields two epimeric diols, separated by pptn. with digitonin, α-œstradiol, m.p. 176—178°, identical with the dihydrotheelin of MacCorquodale *et al.*, which predominates and has the greater œstrogenic activity, and β-œstradiol, m.p. 220—223° (3-*benzoate*, m.p. 156—157°; *diacetate*, m.p. 139—141·5°). All m.p. are corr. A. Li.

Silver-halogen complexes of benzoic acid. C. Prévost and J. Wiemann (Compt. rend., 1937, **204**, 989—991; cf. A., 1934, 292).—AgOBz with Cl_2, Br, or I in cold CCl_4 affords silver-halogeno-

benzoates which convert Δ^{α}-heptinine into the α-halogeno-derivatives. They also react with ethylenic compounds, and with *cyclo*hexene yield 2-*chloro*-, m.p. 50°, -*bromo*-, m.p. 64°, and -*iodo*-cyclo*hexyl benzoate*, m.p. 54°. J. L. D.

Action of thionyl chloride on aromatic amino-acids. R. Graf and W. Langer (J. pr. Chem., 1937, [ii], **148**, 161—169).—Previous failures to obtain *N*-thionylaminobenzoyl chlorides from the NH_2-acids and $SOCl_2$ (I) was due to decomp. during distillation. *o*-, *m*-, and *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ with (I) give, after removal of excess of (I) at > 120°, and distillation in vac., N-o-, m.p. 31—32°, b.p. 105—106°/0·8 mm., N-m- (II), m.p. 32—33°, b.p. 140°/12 mm., and N-p-*thionylaminobenzoyl chloride* (III), m.p. 40—41°, these are decomposed by H_2O or by MeOH to insol. *substances* of high mol. wt. accompanied by the hydrochlorides of the NH_2-acids, or of their esters. In Et_2O, with dry HCl, (II) and (III) give m-, decomp. about 270°, and p-*aminobenzoyl chloride hydrochloride* (IV), decomp. 250°. These are hydrolysed by H_2O, MeOH, or EtOH exclusively to the NH_2-acid or -ester hydrochloride; with $CH_2Cl{\cdot}CH_2{\cdot}OH$, (IV) gives *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2CH_2{\cdot}CH_2Cl$ m.p. 86°. *p*-$NHMe{\cdot}C_6H_4{\cdot}CO_2H$ and (I) give a product which with Et_2O–HCl forms p-*methylaminobenzoyl chloride hydrochloride*, m.p. 168—182°. p-*Ethyl*-, m.p. 100°, p-n-*propyl*-, m.p. 89—90°, p-n-*butyl*-, m.p. 112° (decomp.), and p-iso*amyl-aminobenzoyl chloride hydrochloride*, m.p. 105° (decomp.), are similarly prepared, and converted by MeOH into the Me esters. E. W. W.

Iodine value of cinnamic [acid] derivatives. A. Lespagnol and J. Bruneel (J. Pharm. Chim., 1937, [viii], **25**, 454—457).—$CHPh{:}CH{\cdot}CO_2H$, its Et, CH_2Ph, and cinnamyl esters, and $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ have low I vals., viz., about 29, 25, 4·5—6·7, 83·3—87, and 30, respectively. R. S. C.

***cis*-Cinnamic acids.**—See A., I, 291.

Amido- and imido-chlorides of non-aromatic acids. X. J. von Braun and H. Ostermayer (Ber., 1937, **70**, [*B*], 1002—1005; cf. A., 1934, 393, 1359).—Attempts to prepare acetylenic aldehydes by a process analogous to that leading from $>C{:}CH{\cdot}CCl{:}NR$ to $>C{:}CH{\cdot}CHO$ are hindered by the impossibility of avoiding addition of HCl during the action of PCl_5 on $CR{:}C{\cdot}CO{\cdot}NHR'$. Thus, *phenylpropiolanilide*, m.p. 128°, is converted by PCl_5 in cold C_6H_6 into β-*chlorocinnamphenylimidochloride* (I), b.p. 160—170°/0·1 mm., hydrolysed by H_2O to β-*chlorocinnamanilide*, m.p. 133°, and transformed by NH_2Ph in Et_2O into the *amidine*, $CPhCl{:}CH(:NPh){\cdot}NHPh$, m.p. 97°. Similarly *phenylpropiolethylamide*, m.p. 63°, gives β-*chlorocinnamethylimidochloride*, b.p. 140°/0·2 mm., whence β-*chlorocinnamethylamide*, m.p. 109°. Treatment of (I) with a suspension of $CrCl_2$ in Et_2O–HCl gives $CHPh{:}CH{\cdot}CHO$ (II) and β-chlorocinnamaldehyde, b.p. 125°/10 mm. (semicarbazone, m.p. 216°), whilst (II) is produced exclusively when an excess of $CrCl_2$ is used. α-Bromo-Δ^{α}-hexenoic acid, b.p. 134°/12 mm. (ozonised to $Pr^{\alpha}CHO$), and $SOCl_2$ give the corresponding *chloride*, b.p. 94°/14 mm., whence α-bromo-Δ^{α}-*hexenanilide*, m.p. 67°. This is converted by successive use of PCl_5 in C_6H_6 and much $CrCl_2$ into Δ^{α}-hexenaldehyde, whilst with a smaller proportion of $CrCl_2$ the crude α-Br-aldehyde is obtained. Reduction of a halogen atom vicinal to the ethylenic linking appears to depend on the presence of $\cdot CCl{:}NR$ since $CPhCl{:}CH{\cdot}CO{\cdot}NHPh$, $CPhCl{:}CH_2$, and 1-chloroindene are resistant to $CrCl_2$. H. W.

Formation of hydrocarbons by the thermal decomposition of α-ethoxy-acids. M. Meyer (Compt. rend., 1937, **204**, 1260—1261; cf. A., 1933, 377).—β-2-*Tetrahydronaphthyl-α-ethoxypropionic acid*, b.p. 165°/2 mm. (*amide*, m.p. 105°; *chloride*, b.p. 138°/3 mm.), when heated in presence of Pd affords 2-*tetrahydronaphthylacetaldehyde*, b.p. 161—162°/22 mm. (*semicarbazone*, m.p. 199—200°), and tetrahydro-2-methylnaphthalene; dehydrogenated (S) to give $2\text{-}C_{10}H_7Me$. Similarly, β-cinnamyl-α-ethoxypropionic acid gives propenylbenzene. J. L. D.

Influence of replacement of a β-hydrogen by methyl in α-hydroxy-γ-phenyl-Δ^{β}-butenoic acid. M. Girard (Compt. rend., 1937, **204**, 1071—1073).—Unlike the β-unsubstituted acid (I), α-*hydroxy-γ-phenyl-β-methyl-*Δ^{β}*-butenoic acid*, m.p. 132° (prep. through its *amide*, m.p. 161°, and nitrile from $CHPh{:}CMe{\cdot}CHO$), is unchanged by heating with alkali, does not react with I–Na_2CO_3, affords $\begin{matrix}CMe{\cdot}CHPh\\ CH\text{——}CO\end{matrix}>O$ with strong mineral acids (traces only with weak acids), but like (I) with I–$NaHCO_3$ it affords the γ-*lactone*, m.p. 80°, of β-iodo-αγ-dihydroxy-γ-phenyl-β-methylbutyric acid. J. W. B.

Isomerism of derivatives of *cyclo*hexane. R. D. Desai, R. F. Hunter, and G. S. Saharia (Nature, 1937, **139**, 718—719).—Both 3- and 4-methyl*cyclo*hexane-1-carboxylic-1-succinic acids have been isolated in two forms. There is no indication of isomerism with multiplanar forms. L. S. T.

Lichen substances. LXXIX. Components of *Cetraria islandica* (L.), Ach. II. Y. Asahina and M. Yasue (Ber., 1937, **70**, [*B*], 1053—1059).—Examination of new samples of *C. islandica* from Hokkaido gives in some instances solely *d*-protolichesteric acid (I) whereas from others l-allo*protolichesteric acid* (II), m.p. 107°, $[\alpha]_D^{16}$ −102·0° in $CHCl_3$, is obtained. The data recorded previously (A., 1936, 314) must be corr. for (II) and its derivatives (*pyrazoline* compound, $C_{21}H_{38}O_4N_2$, m.p. 67°, $[\alpha]_D^{26}$ −186·24° in $CHCl_3$; *dihydro*allo*protolichesteric acid*, m.p. 121—123° after softening at about 111°, $[\alpha]_D^{21}$ −57·24° in $CHCl_3$). Examination of Japanese *C. islandica* shows its components to be very heterogeneous whereas *C. islandica f. tenuifolia* from Japan, which invariably gives a positive *p*-$C_6H_4(NH_2)_2$ test, contains fumarprotocetraric acid alone or mixed with notable quantities of *l*-protolichesteric acid. Examination of European *C. islandica* and *crispa* confirms Zopf's opinion that lichesteric acid is not a primary component but is formed from protolichesteric acid during the extraction. Very mild treatment of *C. islandica f. tenuifolia* from Norway gives, however, a little *l*-lichesteric acid (III) and much (II). Specimens from Baden yielded a mixture

of (II) and (III) whereas another from Lausitz contained (I) almost exclusively. H. W.

Amino-acids. X. α-Methylamino-acids. Synthesis of *N*-methyl-3 : 4-dihydroxyphenylalanine and related compounds. T. H. Guerrero and V. Deulofeu (Ber., 1937, **70**, [*B*], 947—950; cf. this vol., 19).—Creatinine (I) and vanillin (II) when heated at 140° or boiled in piperidine afford 4-hydroxy-3-methoxybenzylidenecreatinine (III), m.p. 273°, whilst 4-*acetoxy*-3-*methoxybenzylideneacetylcreatinine* (IV), m.p. 217°, is obtained by acetylation of (III) or when (I) and (II) are heated with NaOAc and Ac_2O at 130°. Reduction of (III) or (IV) by Na–Hg in H_2O gives 4-*hydroxy*-3-*methoxybenzylcreatinine* (V), m.p. 231—233°, or 4-*hydroxy*-3-*methoxybenzylacetylcreatinine*, m.p. 174°. (V) is hydrolysed by boiling conc. $Ba(OH)_2$ to α-*methylamino*-β-4-*hydroxy*-3-*methoxyphenylpropionic acid*, m.p. 276—278° or m.p. 265—267° after darkening at 235° when slowly heated, converted by red P and HI (*d* 1·7) in Ac_2O into α-*methylamino*-β-3 : 4-*dihydroxyphenylpropionic acid*, m.p. 298—300° or m.p. 286—287° after darkening at 240—245° when slowly heated. H. W.

Catalytic oxidation of certain aromatic compounds. J. S. Salkind and V. V. Kesarev (J. Gen. Chem. Russ., 1937, **7**, 879—881).—A mixture of the vapour of the substance with air is passed over 9 : 1 V_2O_5–U_3O_8 on pumice at 400—420°, when 1- or 2-$C_{10}H_7Br$ or β-$C_{10}H_7$·OH yields *o*-$C_6H_4(CO_2H)_2$ (I) and BzOH, 1-$C_{10}H_7$·NO_2, or α-$C_{10}H_7$·NH_2 gives *o*-$C_6H_4(CO)_2NH$ and (I), C_5H_5N and quinoline give CO_2, H_2O, NH_3, NO, and H·CO_2NH_4, whilst carbazole is not oxidised at 500°. R. T.

(A) Action of hydrogen chloride on solutions in alcohol of substituted phthalamic acids. (B) Reaction of certain amines with alkylarylphthalamic acids. B. A. Porai-Koschitz (J. Gen. Chem. Russ., 1937, **7**, 604—610, 611—620).—(A) *N*-Arylphthalamic acids in EtOH yield the corresponding *N*-arylphthalimides when the solution is saturated with dry HCl. N-*o*- and -*p*-Tolyl-, α- and β-naphthyl-, *p*-hydroxyphenyl-, and p-*dimethylaminophenylphthalimide*, m.p. 218° (from p-*dimethylaminophenylphthalamic acid*, m.p. 157°), have been prepared by this reaction. Phenylnaphthalimide is obtained analogously from *N*-phenylnaphthalamic acid.

(B) The equilibrium *o*-CO_2H·C_6H_4·CO·NHR + NHR′R″ ⇌ *o*-CO_2H·C_6H_4·CO·NRR″ + NH_2R', in various org. solvents at room temp., is shown to exist in the cases R = R′ = R″ = Ph; R = R′ = Ph, R″ = Me; R = R′ = *o*-tolyl, R″ = Et; R = R′ = α-$C_{10}H_7$, R″ = Et. R. T.

Di-*n*-heptyl phthalate.—See A., I, 377.

Friedel–Crafts reaction of lactones. I. Synthesis of aromatically substituted acids from δ-chloro-γ-valerolactone. H. Beyer (Ber, 1937, **70**, [*B*], 1101—1113).—δ-Chloro-γ-valerolactone with $AlCl_3$ and C_6H_6 at 60—80° affords δ-phenylvaleric acid, m.p. 57—59°, *γδ-diphenylvaleric acid* (I), b.p. 180—182°/0·1 mm., *anthracene*-9 : 10-*dibutyric acid* (II), m.p. 248—250°/(vac.) after softening at 240°, and some anthraquinone (III). The intermediate formation of γ-chloro-δ-phenylvaleric acid is postulated. (I) [*Me* ester, b.p. 155—156°/0·1 mm.; *Et* ester, b.p. 165—166°/0·7 mm.; corresponding *chloride* (IV), not distillable without decomp.; *amide*, m.p. 70—71° (vac.); *anilide*, m.p. 112—113°; *carbamido*-derivative, m.p. 139—140° after softening at 135°] is also obtained from γδ-dibromovaleric acid, $AlCl_3$, and C_6H_6 at 60—70°. (IV) is transformed by $AlCl_3$ in CS_2 into 1-*keto*-4-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 165°/0·1 mm. (*semicarbazone*, m.p. 186—187°). (II) [Me_2 ester, m.p. 106—108° after softening at about 100°; Et_2 ester, m.p. 103—105° after softening at about 90°; *dihydrazide*, m.p. 258—259° (decomp.) after softening at 255°], which has an intense violet fluorescence, is hydrogenated (PtO_2 in AcOH at room temp.) to the non-fluorescent 1 : 2 : 3 : 4-*tetrahydroanthracene*-9 : 10-*dibutyric acid*, m.p. 230—232° after softening at 223° [Me_2 ester, m.p. 80—82° (decomp.) after softening at 75°; Et_2 ester, m.p. 92—93° after softening at 89°; *dihydrazide*, m.p. 250—252° (decomp.) after softening]. Ozonisation of (II) gives (III) and (·CH_2·CO_2H)$_2$. Addition of maleic anhydride to (II) at 260° gives the 9 : 10-*adduct*, m.p. 283—285° (decomp.) after softening at 280° (Me_2 ester, m.p. 187—189° after softening at 170°), which could not be hydrogenated. H. W.

Manufacture of chrysenecarboxylic acids.—See B., 1937, 420.

Synthesis of α-phenylparaconic acids. M. P. Gertschuk (J. Gen. Chem. Russ., 1937, **7**, 980—982).—Et_2 β-formyl-α-phenylsuccinate is reduced by Al to Et_2 phenylitamalate, which when distilled yields a mixture of cryst. (I), m.p. 92°, and liquid *Et*$_2$ *α-phenylparaconate* (II), b.p. 212—213°/15 mm. (I) or (II) gives *α-phenylparaconic acid*, m.p. 124° (+ 0·25H_2O, m.p. 102°), when hydrolysed with 10% HCl. R. T.

Electrolysis of aromatic acids. IV. Electrolysis of phthalic acid. V. M. Rodionov, V. M. Levtschenko, and V. C. Zvorikina. **V. Electrolysis of hemipinic acid.** V. M. Rodionov and V. C. Zvorikina (Bull. Soc. chim., 1937, [v], **4**, 463—473, 473—477; cf. this vol., 101).—IV. Anodic or cathodic electrolysis does not affect *o*-$C_6H_4(CO_2K)_2$. Electrolysis without a diaphragm or first anodically and then cathodically gives α-, m.p. 268—269°, and β-*di-dihydrophthalyl*, $(CO<\overset{C_6H_4}{O}>CH\cdot)_2$, m.p. 252°, phthalide, and a little *o*-CHO·C_6H_4·CO_2H (I) and BzOH. Probably (I) is first produced by way of peroxides, since cathodic reduction thereof gives the other products. BzOH is formed by loss of CO_2 from (I).

V. Electrolysis of K_2 hemipinate gives only small yields of *ψ*-meconine. R. S. C.

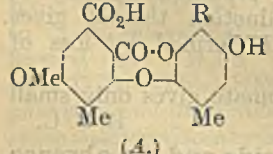
Enolisation of β-ketonic acids and the absence of their ketonic decompositions in accordance with Bredt's rule. J. Bredt (J. pr. Chem., 1937, [ii], **148**, 221—224).—Theoretical. The failure of 2 : 6-diketodiamontane-1 : 3 : 5 : 7-tetracarboxylic acid (this vol., 152) to lose CO_2 agrees with Bredt's rule that a β-ketonic acid is as stable as a γ- or other ketonic acid when it cannot give rise to an unsaturated

enolic form, and with the impossibility of a double linking being formed at a bridge-head. E. W. W.

αβ-Unsaturated aldehydes. III. The two *cyclo*citrylideneacetaldehydes. J. von Braun and P. Kurtz (Ber., 1937, **70**, [*B*], 1009—1012).—The possibility that cyclisation occurs during the prep. of citrylideneacetaldehyde (I) from citrylideneacetic acid (von Braun and Rudolph, A., 1934, 1335) is excluded by the observation that the properties of (I) differ from those of the cyclic compounds now prepared. (I) and the compound of Kuhn *et al.* (A., 1936, 316) are probably therefore *cis–trans*-isomerides. α-*cyclo*Citral, $CH_2<^{CH_2\cdot CMe_2}_{CH=CMe}>CH\cdot CHO$, b.p. 75·77°/10 mm., is converted by Zn and $CH_2Br\cdot CO_2Et$ into *Et* β-*hydroxy*-β-2 : 2 : 6-*trimethyl*-Δ^4-*cyclohexenylpropionate*, b.p. 147—152°/12 mm. The corresponding *hydroxy-acid*, m.p. 112—114°, is converted by Ac_2O and NaOAc at 100° into α-*cyclocitrylideneacetic acid*, b.p. 145—150°/0·05 mm., transformed by $SOCl_2$ into the corresponding *chloride* and thence by NH_2Ph in Et_2O into α-*cyclocitrylideneacetanilide*, b.p. 218—222°/0·05 mm. The latter is converted by the successive action of PCl_5 in C_6H_6 and of $CrCl_2$ in HCl–Et_2O into α-*cyclocitrylideneacetaldehyde*, b.p. 82·83°/0·1 mm., which resembles tetrahydroionone in odour. Similarly, β-*cyclo*citral, $CH_2<^{CH_2\cdot CMe_2}_{CH_2-CMe}>C\cdot CHO$, b.p. 90—92°/10 mm., is transformed into a mixture of hydroxy- and unsaturated ester from which β-*cyclocitrylideneacetic acid*, b.p. 146—150°/0·05 mm., is isolated. This is transformed into β-*cyclocitrylideneacetanilide*, b.p. about 220°/0·05 mm., whence somewhat impure β-*cyclocitrylideneacetaldehyde* which resembles β-ionone in odour. H. W.

Synthesis of benzylidene-ethylideneazine. S. A. Tebinov (J. Gen. Chem. Russ., 1937, **7**, 654—655).—PhCHO, MeCHO, and aq. N_2H_4 at 100° yield *benzylidene-ethylideneazine*, CHPh:N·N:CHMe, m.p. 89—90°, which does not reduce Ag_2O or Fehling's solution. R. T.

Lichen substances. LXXVIII. Psoromic acid. II. Y. Asahina and H. Hayashi [with, in part, M. Tasaka] (Ber., 1937, **70**, [*B*], 810—812; cf. A., 1933, 823).—Treatment of parinic acid with Ac_2O and C_5H_5N at 37° yields *acetylpsoromic acid*, $C_{20}H_{16}O_3$, m.p. 223°, converted by Ac_2O containing conc. H_2SO_4 into psoromic acid triacetate, m.p. 198—199°. Hypopsoromic acid (*A*, R = Me) is transformed by boiling 10% KOH into *hypoparellic acid*, m.p. 253° (decomp.), converted by short treatment with CH_2N_2 into the *Me* ester, m.p. 196—197°, by protracted treatment into the *Me ester Me*$_2$ *ether*, m.p. 135°, and by Me_2SO_4 into the *Me*$_2$ *ether*, m.p. 230°. Successive electrolytic and catalytic reduction of the latter substance leads to deoxyhyposalazinol Me_3 ether, thus establishing the structure of psoromic acid (*A*, R = CHO) from the analytical side. H. W.



(*A.*)

Reactions of *cyclo*hexanone with diazoethane. A. P. Giraitis and J. L. Bullock (J. Amer. Chem. Soc., 1937, **59**, 951).—*cyclo*Hexanone (I) and $CHMeN_2$ in Et_2O or Et_2O–MeOH give 2-methyl*cyclo*heptanone, reaction being faster than with CH_2N_2. CH_2N_2 does not react with *cyclo*heptanone (II), whilst with *cyclo*pentanone it gives a poor yield of (II) with a little (I). 2-Chloro*cyclo*hexanone with CH_2N_2 gives quantitatively a chloromethyl*cyclo*heptanone. R. S. C.

Synthesis of polyterpenoid compounds. III. J. W. Cook and C. A. Lawrence (J.C.S., 1937, 817—827; cf. Chuang *et al.*, A., 1936, 988).—*Et* 2-γ-*cyanopropyl*cyclo*hexanone*-2-*carboxylate*, b.p. 163—165°/0·7 mm., prepared from γ-iodobutyronitrile and Et *cyclo*hexanone-2-carboxylate, is hydrolysed to *octane*-αδ0-*tricarboxylic acid*, b.p. 280—290°/0·8 mm. (*Et* ester, b.p. 162—163°/1 mm.), and γ-2-keto*cyclo*hexylbutyric acid (p-*phenylphenacyl* ester, m.p. 78—79°; *Et* ester, b.p. 136°/0·4 mm.). γ-(2-Methyl-Δ^1-*cyclo*hexenyl)butyric acid (p-*phenylphenacyl* ester, m.p. 83—84°), obtained from MgMeI and Et γ-2-keto*cyclo*hexylbutyrate, is cyclised to 9-methyl-$\Delta^{4:10}$ or $^{5:10}$-1-octalone, m.p. 222—223° (decomp.) (2 : 4-*dinitrophenylhydrazone*, m.p. 133°), hydrogenated to 9-methyl-1-decalone [*oxime*, m.p. 108·5—111°; 2 : 4-*dinitrophenylhydrazone*, m.p. 159—160° (decomp.)]. *Et* β-Δ^1-cyclo*hexenylethylmethylmalonate*, b.p. 134—137°/0·5 mm., from β-Δ^1-*cyclo*hexenylethyl bromide and $CHMe(CO_2Et)_2$, is hydrolysed to the *acid*, m.p. 141·5—142·5°, which when heated affords γ-Δ^1-cyclo*hexenyl*-α-*methylbutyric acid*, b.p. 140—145°/0·8 mm. (p-*phenylphenacyl* ester, m.p. 88—90·5°); this is cyclised through the chloride and $SnCl_4$ to 2-*methyl*-$\Delta^{9:10}$-1-*octalone*, b.p. 129°/13 mm. [*semicarbazone*, m.p. 212° (decomp.); *oxime*, m.p. 160—161°; 2 : 4-*dinitrophenylhydrazone*, m.p. 219—220° (decomp.)], which is hydrogenated to 2-*methyl*-1-*decalone*, b.p. 109°/11 mm. [*semicarbazone*, m.p. 216—217·5° (decomp.); *oxime*, m.p. 152—153·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 223—224·5°]. Hydrolysis and decarboxylation of Et β-(4-methyl-Δ^1-*cyclo*hexenyl)propylmalonate gives in small yield γ-(4-*methyl*-Δ^1-cyclo*hexenyl*)*valeric acid*, b.p. 112—114°/0·14 mm., cyclised to 1 : 6-*dimethyl*-$\Delta^{9:10}$-4-*octalone*, b.p. 141°/13 mm. [*oxime*, m.p. 98—102°; *semicarbazone*, m.p. 163—165·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 217·5—219° (decomp.)]. Et γ-bromovalerate and Et 5-methyl*cyclo*hexanone-2-carboxylate form the keto-ester, hydrolysed to γ-(2-keto-4-methyl*cyclo*hexyl)valeric acid, b.p. about 160°/0·8 mm. (*semicarbazone*, m.p. 177—178·5°). γ-Δ^1-*cyclo*Hexenylbutyric acid is converted through the chloride and $AlCl_3$ into $\Delta^{9:10}$-1-octalone [2 : 4-*dinitrophenylhydrazone*, m.p. 266·5—267° (decomp.)]; the 2 : 4-*dinitrophenylhydrazone* of *trans*-1-decalone (I) has m.p. 222—222·5°. β-2-Keto*cyclo*hexylpropionic acid [*semicarbazone*, m.p. 181—182° (decomp.)] is hydrogenated to the *lactone* of β-2-hydroxy*cyclo*hexylpropionic acid, b.p. 145°/10 mm.

Methylation ($NaNH_2$–MeI) of (I) gives chiefly 2-methyl-1-decalone and some 9-Me compound with a methyl-1-decalone, isolated as the *oxime*, m.p. 139—139·5°. *cis*-2-Decalone (II) is chlorinated to 3-*chloro*-cis-2-*decalone*, m.p. 107—108°, converted

into the 3-*OH*-compound, m.p. 88—90°. $Et_2C_2O_4$ and (II) afford Et *cis*-2-ketodecalyl-3-glyoxylate (2 : 4-*dinitrophenylhydrazone*, decomp. 181—186°), converted into *Et* cis-2-*decalone*-3-*carboxylate*, b.p. 130°/0·7 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 169—170·5° (decomp.)]. This ester and MeI form *Et* 3-*methyl*-cis-2-*decalone*-3-*carboxylate*, b.p. 108·5—110°/0·4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 120—121·5°), dehydrogenated (Se) to 3-methyl-2-naphthol (III). Et *trans*-2-decalone-3-carboxylate [2 : 4-*dinitrophenylhydrazone*, m.p. 181·5—182° (decomp.)] is methylated to *Et* 3-*methyl*-trans-2-*decalone*-3-*carboxylate*, b.p. 113°/0·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 102·5—104°), dehydrogenated to (III). $CH_2Ph{\cdot}MgCH_2Cl$ and (II) give 2-β-*phenylethyl*-cis-2-*decalol*, m.p. 111—112°, dehydrated ($KHSO_4$) to 2-β-*phenylethyl*-cis-$\Delta^{2:3}$-*octalin*, b.p. 148—149°/0·9 mm., which is cyclised to dodecahydro-1 : 2-benzanthracene (IV), similarly prepared from *trans*-2-decalone (V). Dehydrogenation of (IV) affords 1 : 2-benzanthracene [2 : 7-*dinitroanthraquinone complex*, m.p. 252—253° (decomp.)], and its 5 : 6 : 7 : 8-H_4-derivative, *octahydro*-1 : 2-*benzanthracene*, m.p. 124·5—125·5°, and chrysene. Acetyl-Δ^1-*cyclo*hexene and (V) give 3-keto-Δ^4-hexadecahydro-1 : 2-benzanthracene (*trans* form), b.p. 192—195°/1·3 mm. [*semicarbazone*, m.p. 240·5—241·5° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 201·5—204° (decomp.)], and the *ketone* (cis *form*), m.p. 122—122·5° [*semicarbazone*, m.p. 258·5° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 172·5—179° (decomp.)], is similarly obtained from (II). These results show that the striking differences in the position of substitution in the stereoisomeric sterol ketones do not hold in the case of the 2-decalones, both *cis*- and *trans*- being attacked at position 3. The stability of the alternative Δ^1- and Δ^2-octalin systems present in the enolic forms of the ketones is influenced by the locking of this portion of the sterol mol. with the remainder of the ring system. F. R. S.

Fission of ketones with alkalis. I. Chloroacetophenones. G. Look and E. Böck (Ber., 1937, **70**, [*B*], 916—925).—Fission of chloroacetophenones with at least one free *ortho* position occurs, if at all, with production of the corresponding benzoic acid; the change is therefore similar to that caused by substitution of halogen in Me. If both *ortho* positions are occupied smooth scission to halogenobenzene and AcOH is observed. Di-*o*-substituted acetophenones therefore closely resemble di-*o*-substituted benzaldehydes. The substance is heated with 50% KOH at 150° in a Ni tube for 24 hr., then diluted with H_2O and extracted with Et_2O. The alkaline solution is acidified with H_3PO_4 and distilled with steam; the distillate is titrated with 0·1*N*-KOH. COPhMe gives a little BzOH whilst *o*-$C_6H_4Cl{\cdot}CO_2H$ is derived from *o*-C_6H_4ClAc. *m*-$C_6H_4Cl{\cdot}CHO$ is transformed into m-*chlorophenylmethylcarbinol*, b.p. 240—246° (corr.)/748 mm., oxidised by CrO_3 in AcOH to *m*-C_6H_4ClAc, which yields *m*-$C_6H_4Cl{\cdot}CO_2H$. *p*-C_6H_4ClAc affords *p*-$C_6H_4Cl{\cdot}CO_2H$. 2 : 6-$C_6H_3Cl_2{\cdot}CHO$ with MgMeI in Et_2O yields 2 : 6-*dichlorophenylmethylcarbinol*, b.p. 134—136°/13 mm., m.p. 34—35° (*benzoate*, m.p. 77°), oxidised to 2 : 6-*dichloroacetophenone*, m.p. 44°, which yields AcOH (= 81%); it is little affected by boiling 89% H_3PO_4. 2 : 6-$C_6H_3Cl_2{\cdot}CO_2H$ appears stable to 50% KOH. 3 : 5-*Dichlorophenylmethylcarbinol*, b.p. 136°/12 mm., m.p. 46°, gives 3 : 5-*dichloroacetophenone*, b.p. 134—136°/17 mm., m.p. 26° (*oxime*, m.p. 138°), whence 3 : 5-$C_6H_3Cl_2{\cdot}CO_2H$. 2 : 4-*Dichlorophenylmethylcarbinol*, b.p. 130—134°/11 mm. (p-*nitrobenzoate*, m.p. 113°), yields 2 : 4-$C_6H_3Cl_2Ac$, m.p. 29° (*oxime*, m.p. 148°). 2 : 3 : 6-*Trichlorophenylmethylcarbinol*, b.p. 149—155°/11 mm., m.p. 87—88° (*benzoate*, m.p. 106·5°), is oxidised to 2 : 3 : 6-*trichloroacetophenone*, m.p. 63°, which gives 1 : 2 : 4-$C_6H_3Cl_3$ in 82% yield. The conversion of 2 : 4 : 6-*trichlorophenylmethylcarbinol*, b.p. 158—163° (corr.)/17 mm., m.p. 76·5°, into 2 : 4 : 6-*trichloroacetophenone*, m.p. 51·5°, which gives 1 : 3 : 5-$C_6H_3Cl_3$ is described. *Pentachloroacetophenone*, m.p. 90°, affords C_6HCl_5 and AcOH (77·5%). H. W.

Polymethylbenzenes. XVI. Enolising action of magnesium methyl iodide upon hindered ketones. L. I. Smith and C. Guss (J. Amer. Chem. Soc., 1937, **59**, 804—806; cf. A., 1936, 323).—The no. of active H found and mols. of MgMeI added in the Grignard machine (A., 1928, 160) are, respectively, for aceto-phenone 0·025, 1·025, -*m*-xylene 0·05, 1·02, -mesitylene 1·03, 0, -durene 0·97, 0·04, -prehnitene 0·75, 0·27, and -*pentamethylbenzene*, b.p. 144—145°/8 mm., m.p. 84°, 0·93, 0·01, 3 : 5-diaceto-1·66, 0·44, and 5-aceto-ψ-cumene 0·25, 0·79, 2 : 4-diaceto-*m*-xylene (I) 0·16, 1·82, diaceto-mesitylene 1·82, 0·26, -durene (II) 1·62, 0·54, and -*prehnitene* (III), m.p. 113°, 1·68, 0·46. The large effect of Me *o*- to the CO is general, but Me in other positions also has some effect. The structure of (I) seems doubtful in view of its low result. Some (II) is formed in the prep. of (III) owing to demethylation of prehnitene by $AlCl_3$. R. S. C.

Reactions in the presence of metallic halides. I. β-Unsaturated ketone formation as a side-reaction in Friedel–Crafts acylations. N. O. Calloway and L. D. Green (J. Amer. Chem. Soc., 1937, **59**, 809—811).—In the reaction of C_6H_6, AcCl, and $AlCl_3$ in CS_2 evolution of HCl never ceases; some dypnone (I) is formed if the COPhMe : $AlCl_3$ ratio is $>1:1$. 2 mols. of COPhMe and 1 mol. of $AlCl_3$ in CS_2 at 40—50° give 73% of (I), which is also obtained with (?) $CPh_2{:}CH_2$ from COPhMe by $AlPh_3$. 1 mol. each of COPhMe, PhCHO, and $AlCl_3$, give 91% of chalkone. Reaction may occur by way of $AlR_2{\cdot}OR$. R. S. C.

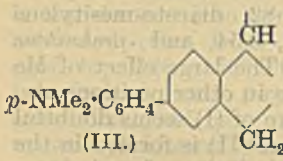
Application of the principle of vinylogy to unsaturated ketones. R. E. Christ and R. C. Fuson (J. Amer. Chem. Soc., 1937, **59**, 893—897).—The CH_2 in $:CH_2{\cdot}C{:}C{\cdot}C{\cdot}O$ is reactive, even if the C:C is in a ring and the CO is outside it. Thus, Δ^1-*tetrahydrobenzophenone* (prepared from *cyclo*hexene, BzCl, and $AlCl_3$ in CS_2), b.p. 147°/8 mm., gives (NaOEt) the 3-*benzylidene* derivative, m.p. 115°, and with KOEt and $Et_2C_2O_4$ the oxalo-*ester*

$$\begin{matrix} COR{\cdot}C{=\!=}CH \\ [CH_2]_3{\cdot}C{:}C(OK){\cdot}CO_2Et \end{matrix}$$ (I; R = Ph), m.p. 92° (enolic *K* salt and *acetate*, m.p. 92°). Δ^1-Tetrahydroacetophenone (modified prep.) condenses with PhCHO

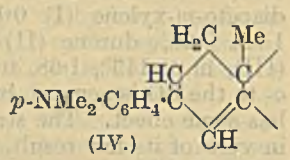
first at the Me, giving 1-*cinnamoyl*-Δ¹-cyclo*hexene* (II), m.p. 68°, which gives no CHI_3 and is also obtained from *cyclo*hexene and CHPh:CH·COCl. (II) and $Et_2C_2O_4$ give the *ester* (I; R = CO·CH:CHPh), m.p. 131—132° (*K* salt). Further treatment of the crude mixture of benzylidenecarvones with PhCHO yields an amorphous substance, probably the *dibenzylidene* derivative. R. S. C.

Indones. XIV. Partial dehalogenation of the 2 : 3-dichloro-3-phenyl-2-methylhydrindone of m.p. 111—112°. R. DE FAZI and F. PIRRONE (Gazzetta, 1937, **67**, 128—132).—In EtOH this compound (this vol., 153) is converted by $AgNO_3$ into a *compound*, $C_{16}H_{12}OCl$ [*sic*] (I), m.p. 125—126°, with an *isomeride* (II), m.p. 131—132°. With Cu, only (I) is obtained; with KI, a second *isomeride* (III), m.p. 153—155°, (I), a *compound* (IV), m.p. 143—144°, and 3-phenyl-2-methylindone (V). In $COMe_2$, aq. KOH gives (I) and (V). E. W. W.

Debromination of mono- and di-bromocholestanone. E. SCHWENK and B. WHITMAN (J. Amer. Chem. Soc., 1937, **59**, 949—950).—Debromination of bromo- (I) and dibromo-cholestanone (II) gives varying results according to the reagent used. With C_5H_5N (I) gives the pyridinium compound, m.p. 125—126°, and (II) gives the pyridinium *compound*, $C_{32}H_{49}ONBr$, decomp. >280°. With $NPhMe_2$ (I) gives cholestanone and (II) gives a *compound*, m.p. 230—232°, which couples with



(III.)



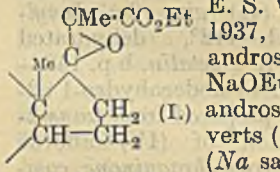
(IV.)

$NO_2·C_6H_4·N_2Cl$ and is (III) or, less probably, (IV). Similarly with KOPh (II) gives a compound, which couples and is probably the hydroxydiphenyl derivative. R. S. C.

Synthetic studies in the sterol and sexual hormone group. I. Synthesis of a 3-keto-10-hydroxyhexahydrochrysene and its methyl ether. C. K. CHUANG, Y. L. TIEN, and Y. T. HUANG (Ber., 1937, **70**, [*B*], 858—863).—Me δ-keto-η-*m*-methoxyphenyloctoate is cyclised by conc. H_2SO_4 at −15° to Me γ-6-methoxy-3 : 4-dihydro-1-naphthylbutyrate, b.p. 157—158°/0·3 mm., hydrolysed to the corresponding *acid*, m.p. 79—80°, which is dehydrogenated by S at 190—200° to γ-6-methoxy-1-naphthylbutyric acid (I), m.p. 150°. (I) is transformed by $SOCl_2$ in $CHCl_3$ followed by condensation with Et_2 α-acetylsodioglutarate into the non-cryst. *ester* $OMe·C_{10}H_6·[CH_2]_3·CO·CAc(CO_2Et)·[CH_2]_2·CO_2Et$, hydrolysed to δ-*keto*-η-6-*methoxy*-1-*naphthyloctoic acid*. The *Me* ester of this acid is transformed by NaOEt in Et_2O into β-6-*methoxy*-1-*naphthylethyl*cyclo*hexane*-2 : 6-*dione* (II), m.p. 168—170°, which has a pseudo-acidic character but does not give a colour with $FeCl_3$. Cyclisation of (II) with P_2O_5 in boiling C_6H_6 or with 80% H_2SO_4 at 100° affords 3-*keto*-10-*methoxychrysene* (III), m.p. 177—178°, (*oxime*, m.p. 263° in bath pre-heated to 250°), which decolorises $KMnO_4$ in AcOH and gives a red ppt. with Br in CCl_4. (III) is demethylated by HBr (*d* 1·49) in AcOH at 110° to 10-*hydroxy*-3-*ketochrysene*, m.p. 257—258° (decomp.) (bath preheated to 245°) [*oxime*, m.p. 287—288° (decomp.)], converted by 30% KOH and Me_2SO_4 into (III). H. W.

Projected synthesis of testosterone. R. ROBINSON (Chem. and Ind., 1937, 534).—Mainly polemical against Cook (cf. this vol., 292). Methyloctahydroindanone probably resembles a cholestanone rather than a β-decalone; a third ring has been added to this hydrindanone. R. S. C.

Condensation of dehydroandrosterone with ethyl α-chloropropionate. W. A. YARNALL and E. S. WALLIS (J. Amer. Chem. Soc., 1937, **59**, 951—952).—Dehydroandrosterone, $CHMeCl·CO_2Et$, and NaOEt give the *oxide* (I) and a little androstene-3 : 17-diol. NaOH converts (I) into the corresponding *acid* (*Na* salt) and a mixture of ketones, probably Δ⁵- and Δ⁵-*iso*-pregnenolone, formed by rearrangement. R. S. C.



(I.)

Constitution of artostenone, a ketonic sterol from *Artocarpus integrifolia*. M. C. NATH (Z. physiol. Chem., 1937, **247**, 9—22).—The unsaponifiable portion of the Et_2O extract of the juice of the fruit yields *artostenone* (I), $C_{39}H_{59}O$, m.p. 109°, $[\alpha]_D^{29}$ +19·86° in abs. EtOH, +23·44° in $CHCl_3$ [*oxime*, m.p. 175°; *semicarbazone* (II), m.p. 203—204° (decomp.); *Br*-derivative, $C_{30}H_{48}OBr_4$, m.p. 160°]. (I) with Pt–asbestos and H_2 at 65° gives *artostanone* (III) (dihydroartostenone), m.p. 106—107° (*oxime*, m.p. 192—194°), the double linking in the αβ-position to the keto-group being reduced, and with Na in EtOH or $C_5H_{11}·OH$ *artostenol*, m.p. 106—107° (*acetate*, m.p. 120—121°). (II) is only partly reduced by Na in EtOH but the semicarbazone of (III) gives *artostane*, $C_{30}H_{54}$, m.p. 101° [*picrate*, m.p. 163° (decomp.)]. (I) is not reduced by Zn–Hg. W. McC.

Pechmann's colouring matters. Synthesis of colours with different substituents. P. CHOVIN (Compt. rend., 1937, **204**, 1073—1075).—In agreement with earlier results (this vol., 150) it is shown that, in five further cases, the same substance is formed by condensation of either $COAr·CH_2·CO·CO_2H$–$COAr'·[CH_2]_2·CO_2H$ or $COAr'·CH_2·CO·CO_2H$–$COAr·[CH_2]·CO_2H$, and thus are prepared the *compounds* of general formula $Ar(C_8H_2O_4)Ar'$ where Ar, Ar' = Ph, β-$C_{10}H_7$, m.p. 297°; Ph, *p*-C_6H_4Br, m.p. 347°; *p*-C_6H_4Me, β-$C_{10}H_7$, m.p. 316°; *p*-C_6H_4Br, β-$C_{10}H_7$, m.p. 377°; *p*-C_6H_4Me, *p*-C_6H_4Br, m.p. 393°; and *p*-C_6H_4Br, *p*-C_6H_4Br, m.p. 432°. J. W. B.

Kinetics of the sulphuric acid condensation of *o*-benzoylbenzoic acid C. W. DEANE (J. Amer. Chem. Soc., 1937, **59**, 849—853).—Ring-closure of *o*-$C_6H_4Bz·CO_2H$ (modified purification), m.p. 127·2—128·5° (corr.), in 96%—fuming H_2SO_4 (up to 28% SO_3) is unimol., giving 97—99% yields of anthraquinone; it is catalysed positively by SO_3 and negatively by H_2O. Increase of the % SO_3 from 1·8 to 14% has little effect on the rate of ring-closure; this is ascribed

to H_2O formed at 75—85° thus: $H_2SO_4 \rightleftharpoons SO_3 + H_2O$. R. S. C.

Isomerisation of linalool under the influence of active silicate (floridin). G. V. Pigulevski, E. T. Kanetzkaja, and M. A. Platonova (J. Gen. Chem. Russ., 1937, **7**, 873—878).—*d*-Linalool and floridin at 95—102° yield *l*-terpineol, *l*-limonene, dipentene, terpin hydrate, and a dicyclic diterpene, b.p. 178—180°/6 mm., with 3 double linkings. R. T.

Certain transformations of linalool, connected with its stereoisomerism. I. I. Vanin and A. A. Tschernojarova (J. Gen. Chem. Russ., 1937, **7**, 885—892).—*d*-Linalool in $CHCl_3$ and PCl_5 yield *l*-linalyl chloride (I) and a dichloride (II) [by addition of HCl to (I)]; with PCl_3 only (I) is formed. (I) is converted by $NiCO_3$ at 130—140° into a monocylic terpene, b.p. 62—72°/6 mm., and (II) into dihydro-*p*-cymene. (I) gives β-pinene with Ag_2CO_3, and *l*-linalool with wet Ag_2O, or with KOH in MeOH at 15°. R. T.

Syntheses with aliphatic monoterpenes. T. Wagner-Jauregg and H. Arnold (Annalen, 1937, **529**, 274—287).—The effects of steric hindrance are very obvious during the production of acids $CHRR'\cdot CO_2H$ (R = *cyclo*hexyl, *cyclo*pentyl, or *cyclo*pentenyl and R' = geranyl, citronellyl, or dihydrocitronellyl) by the malonic synthesis. Introduction of the alkyl residue into $CH_2(CO_2Et)_2$ is satisfactorily effected in EtOH at 140° or in boiling xylene. Prolonged hydrolysis of esters $CRR'(CO_2Et)_2$ with boiling conc. alkali in many cases gives much Et H ester, the complete hydrolysis of which is effected only after decarboxylation. The following are described: *citronellyl chloride*, b.p. 93—95°/12 mm., and *bromide*, b.p. 103—105°/13 mm.; *geranyl chloride*, b.p. 103°/14 mm., and *bromide*, b.p. 110—112°/13 mm.; *Et*$_2$ cyclo*pentyl*-, b.p. 135—140°/12 mm., cyclo*pentenyl*-, b.p. 130—135°/2 mm., cyclo*hexyl*-, b.p. 137—140°/0·1 mm., *dihydrocitronellyl*-, b.p. 140—150°/1 mm., *citronellyl*-, b.p. 133—138°/0·2 mm., and *geranyl*-, b.p. 140—150°/0·25 mm., *-malonate*; *Et*$_2$ *citronellyl*cyclo*pentyl*-, b.p. 166—174°/0·15 mm., *dihydrocitronellyl*-cyclo*pentyl*-, b.p. 160—162°/0·15 mm., *geranyl*cyclo*pentyl*-, b.p. 159—167°/0·20 mm., *geranyl*cyclo*pentenyl*-, b.p. 160—167°/2 mm., *citronellyl*cyclo*hexyl*-, b.p. 178—188°/0·3 mm., *methylgeranyl*-, b.p. 160—170°/7 mm., and n-*hexylcitronellyl*-, b.p. 165—174°/0·3 mm., *-malonate*; *geranyl*cyclo*pentenyl*-, b.p. 160—165°/2·5 mm. (*Et* ester, b.p. 125—135°/2 mm.), *geranyl*cyclo*pentyl*-, b.p. 170—190°/0·2 mm. (*Et* ester, b.p. 154—165°/3 mm.; *CH*$_2$*Ph* ester, b.p. 200—210°/0·4 mm.; obtained from the acid and $CH_2Ph\cdot OH$ containing Zn dust), *citronellyl*cyclo*pentyl*-, b.p. 145—150°/0·3 mm. (*Et* ester, b.p. 145—150°/0·8 mm.), *citronellyl*cyclo*hexyl*-, b.p. 165—170°/0·4 mm. (*Et* ester, b.p. 148—150°/0·5 mm.; *CH*$_2$*Ph* ester, b.p. 211—216°/0·6 mm.), and n-*hexylcitronellyl-acetic acid*, b.p. 170—180°/0·4 mm. (*Et* ester, b.p. 168—172°/2 mm.); *CH*$_2$*Ph dihydrocitronellyl*cyclo*pentyl*-, b.p. 172—190°/0·8 mm., n-*nonyl*cyclo*hexyl*-, b.p. 190—200°/0·5 mm., and n-*octyl*cyclo*hexylethyl*-, b.p. 203—206°/0·3 mm., *-acetate*. Citronellal (I) and Mg *cyclo*hexyl bromide in Et_2O yield βζ-*dimethyl*-θ-cyclo*hexyl*-Δ^{β}-*octen*-θ-*ol* (cyclo*hexyl*-*citronellol*), b.p. 137—140°/0·4 mm. 1-*Citronellyl*-cyclo*hexan*-1-*ol*, b.p. 130—140°/0·5 mm., is derived from Mg citronellyl bromide and *cyclo*hexanone (II) in Et_2O. Addition of 35% NaOH to (I) and (II) in EtOH at −10° affords *citronellidene*cyclo*hexanone*, b.p. 127—135°/0·3 mm. *Methylgeranylbarbituric acid*, m.p. 166—167° (corr.) after softening at 158°, and its H_4-derivative, m.p. 221° (corr.), are devoid of soporific action. H. W.

Secondary alcohols from cineole. A. Gandini (Gazzetta, 1937, **67**, 113—119).—2-Ketocineole is reduced by Na–EtOH to a 2-*hydroxycineole*, m.p. 106—108° (*phenylurethane*, m.p. 86—86·5°), with a smaller quantity of an *isomeride*, m.p. 80° (*phenylurethane*, m.p. 145°), which is the main product when Pt–H_2 is used (cf. Vavon, A., 1926, 837). E. W. W.

Comparison of methods of bromination of terpenes. T. K. Gaponenkov (J. Gen. Chem. Russ., 1937, **7**, 994—995).—The highest yields of limonene tetrabromide are obtained by Godlewski's method (cf. A., 1899, i, 920). R. T.

Irreversible catalysis of dicyclic hydrocarbons. Contact transformation of carane. R. J. Levina (Sci. Rep. Moscow State Univ., 1934, No. 3, 187—192).—Carane is converted into cymene and menthane by passing over Pd–asbestos at 160—180° in a stream of CO_2. α-Fenchene and 1 : 3 : 3-trimethyl-Δ^4-*cyclo*hexene are not affected by similar treatment. R. T.

Preparation of camphorone and of two stereoisomeric dihydrocamphorols. R. Calas (Compt. rend., 1937, **204**, 984—986).—The *d*-camphorate when heated in vac. at 450° affords *dl*-2-methyl*cyclo*pentanone (5%), pulegenone (17%), and *dl*-camphorone (I) (65%). With Na in Et_2O–H_2O (I) gives a mixture, b.p. 82—84°/15 mm., of two alcohols, b.p. 83·2°/18 mm. and 83·3°/18 mm., which with *o*-$C_6H_4(CO)_2O$ afford *phthalates*, m.p. 114° (I) and 84° (II), respectively. Hydrolysis of the esters affords the alcohols, which with CrO_3 give dihydrocamphorone (cf. A., 1913, i, 348), indicating that the alcohols are saturated stereoisomerides. The *cis* form (I) is hydrolysed more slowly than the *trans* (II). J. L. D.

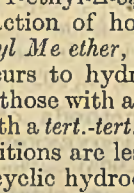
Stereoisomerism of *iso*camphanol (camphenilyl alcohol) and of ω-amino*iso*camphane. W. Hückel and K. Hartmann (Ber., 1937, **70**, [*B*], 959—963).—Oxidation of *dl*-camphene with $Pb(OAc)_4$ at 80° gives the *enol acetate* of *camphenilanaldehyde* (I), b.p. 111—113°/10 mm., and, apparently, a saturated *isomeride*, m.p. 101°. When warmed with KOH–EtOH (I) gives camphenilanaldehyde (II) (semicarbazone, m.p. 223°), also obtained mixed with some *iso*camphenylanic acid, m.p. 118°, but no camphenilone when (II) is ozonised in AcOH or moist C_6H_6. Reduction of (II) by Na and abs. EtOH affords preponderatingly iso*camphanol* I (III), m.p. 84° (*p-nitrobenzoate*, m.p. 109°; *H phthalate*, m.p. 139°). Hydrogenation (Pt-sponge in Et_2O) of (I) or (II) gives mainly iso*camphanol* II (IV), m.p. 101° (*p-nitrobenzoate*, m.p. 96°; *p-aminobenzoate*, m.p. 131°; *H phthalate*, m.p. 144°). The rates of hydrolysis of the esters of (III) and (IV) differ very greatly from one another. NH_2OH,HCl and (II) give a non-cryst.

oxime, reduced by Na and EtOH to ω-aminocamphane, which gives two *Bz* derivatives, m.p. 109° and m.p. 130·5°, respectively. H. W.

Addition of alcohols to double linkings. II. Ethers from unsaturated cyclic hydrocarbons and from the two pinenes. W. Treibs (Ber., 1937, **70**, [*B*], 589—594; cf. this vol. 157).—*cyclo*-Hexene is unaffected by prolonged action of boiling MeOH containing H_2SO_4 whereas 1-methyl-Δ¹-*cyclo*hexene gives 1-*methoxy*-1-*methyl*cyclo*hexane*, b.p. 149—150°, in >50% yield. 1-*Methoxy*-1-*ethyl*cyclo*hexane*, b.p. 165—167°, is derived similarly but in poorer yield from 1-ethyl-Δ-*cyclo*hexene. Menthene, obtained by the action of hot $H_2C_2O_4$ on menthol, affords tert.-*menthyl Me ether*, b.p. 200—201°. Addition of MeOH occurs to hydrocarbons containing a *sec.-tert.* but not to those with a *sec.-sec.* double linking. Homomenthene with a *tert.-tert.* double linking remains unchanged. Conditions are less favourable and more complicated with cyclic hydrocarbons containing two double linkings, owing to the tendency to the formation of a conjugated system and subsequent polymerisation. Carvene gives small amounts of an ether with 2 OMe, but is mainly dimerised. α-Phellandrene is completely dimerised, whilst the 5-ring hydrocarbon from piperitone oxide is rapidly converted into a mixture of polymerides. Gradual addition of α- or β-pinene to boiling H_2SO_4–MeOH (sulphonic acids, PCl_3, PCl_5, and certain anhyd. salts also accelerate addition) affords α-*terpineol Me ether*, b.p. 212°, which readily loses MeOH under the influence of hot, conc. HCO_2H, AcOH–H_2SO_4, or various anhyd. salts giving a doubly unsaturated, very unstable hydrocarbon, $C_{10}H_{16}$, b.p. 182—184°, apparently identical with that derived from α-terpineol. H. W.

Syntheses in the pinane group. II. Attempted synthesis of pinocamphone and synthesis of *trans-s*-homopinic acid. P. C. Guha, K. Ganapathi, V. K. Subramanian, and D. K. Sankaran (Ber., 1937, **70**, [*B*], 736—742; cf. A., 1936, 855).—Ketonopinone acould not be reduced to nopinone or nopinane by Zn dust and AcOH or HCl or by Clemmensen's method. Reduction of *cis*- or *trans*-Et_2 norpinate by Na and EtOH gives trans-1 : 1-*dimethyl*-2 : 4-*dihydroxymethyl*cyclo*butane* (I), b.p. 152—155°/15 mm. (yield 70—80%), oxidised by $KMnO_4$ in alkaline solution to *trans*-norpinic acid. (I) and PBr_3 in anhyd. $CHCl_3$ give trans-1 : 1-*dimethyl*-2 : 4-*dibromomethyl*cyclo*butane*, b.p. 100—102°/4 mm., re-converted into (I) by aq. $Ba(OH)_2$ and transformed by NaCN in EtOH–H_2O into trans-1 : 1-*dimethyl*-2 : 4-*dicyanomethyl*cyclo*butane* (II), b p. 142—145°/6 mm. Hydrolysis of (II) by 20% KOH yields trans-2 : 2-*dimethyl*cyclo*butane*-1 : 3-*diacetic acid* (trans-*s*-*homopinic acid*) (III), m.p. 120—121° [*anilide*, m.p. 216—217°; *Et*₂ ester (IV), b.p. 131—132°/4 mm.], converted by hot Ac_2O or by Ac_2O at 200° into the mixed *anhydride*, $OAc\cdot CO\cdot CH_2\cdot CH<\begin{matrix}CMe_2\\CH_2\end{matrix}>CH\cdot CH_2\cdot CO\cdot OAc$, which can be distilled unchanged, does not give an anilic acid or react with $NH_2\cdot CO\cdot NH\cdot NH_2$, and is converted by warm H_2O into (III). Distillation of (III) over $Ba(OH)_2$ does not appear to yield a ketone. The Dieckmann condensation of (IV) does not occur with Na in boiling C_6H_6 whereas in boiling xylene traces of a product are obtained which gives a brownish-red colour with $FeCl_3$ and yields a *Cu* derivative. H. W.

Syntheses in the thujane group. III. Synthesis of thujane. P. C. Guha and B. Nath (Ber., 1937, **70**, [*B*], 931—936; cf. A., 1936, 848, 850).—Gradual addition of Br to *l*-menthone in $CHCl_3$ in absence of light gives 2 : 4-dibromomenthone, m.p. 78—79°, $[\alpha]_D^{20}$ +199·2° in $CHCl_3$, in almost quant. yield. It is debrominated by Zn dust in EtOH to *methyl*iso*propyl*dicyclo*hexanone* (I), b.p. 205—208°/688 mm., $[\alpha]_D^{26}$ +25·13° (*semicarbazones*, m.p. 175—176°, $[\alpha]_D^{26}$ −52·5° in AcOH, and m.p. 150—151°, $[\alpha]_D^{26}$ −53·0° in AcOH, respectively), and 1-*methyl*-4-iso*propyl*-Δ¹·⁴-cyclo*hexadien*-3-*one* (II), b.p. 123—125°/14 mm., $[\alpha]_D$ ±0°. When heated or treated with HCl (II) passes into thymol. Reduction of (I) by Na and abs. EtOH gives menthol, whereas with Zn–Hg and HCl thujane, b.p. 156—157°, $[\alpha]_D^{20}$ +8·48°, and *p*-menthane are produced. Treatment of (I) with N_2H_4,HCl and KOAc in dil. MeOH affords the *ketazine* $(\cdot N{:}C_{10}H_{16})_2$, b.p. 175—177°/4 mm., m.p. 78—79°, $[\alpha]_D^{24}$ +102·5° in Et_2O, whereas the *hydrazone*, b.p. 123—125°/7—8 mm., $[\alpha]_D$ +2·38° (*CHPh* derivative, b.p. 162—165°/3—4 mm., $[\alpha]_D^{22}$ −21·6° in EtOH), is obtained from (I) and boiling 50% N_2H_4,H_2O. H. W.


(I.)

Diene value of essential oils. H. P. Kaufmann, J. Baltes, and F. Josephs (Ber., 1937, **70**, [*B*], 908—911).—The iodometric method of determining the diene val. is applied to phellandrene and myrcene, the additive products of which with maleic anhydride (I) are indifferent towards I. The compounds from ocimene and α-terpinene behave analogously. The use of the method with various essential oils containing these compounds shows that a sharp end-point of addition of (I) is reached with comparative rapidity. H. W.

Lucænol, a definite principle extracted from the seeds of *Lucœna glauca*, Benth. M. Masoré (Compt. rend., 1937, **204**, 890—891).—The seeds when extracted with H_2O give the substance *lucœnol*, $(C_4H_5O_2N)_x$, m.p. about 283—287° (decomp.), responsible for the coloration with $FeCl_3$. The mol. appears to contain phenolic, NH_2, and possibly CO_2H groups. The coloration with $FeCl_3$ is violet-blue in acid, deep red in alkaline, solution. F. A. A.

Lignin and related compounds. XXVII. Methylation and structure of methanol-lignin (spruce). J. Compton and H. Hibbert (Canad. J. Res., 1937, **15**, B, 38—45; cf. A., 1936, 995).—Crude methanol-lignin (I) (OMe 23%) is composed of two fractions, (i) (OMe 24%) removed by long extraction with Et_2O, or by its insolubility in 8—10% NaOH, and (ii) (OMe 21·6%), sol. in 8—10% NaOH and repptd. by cold 1% HCl. (I) with Me_2SO_4 and a slight excess of 7·5*N*-NaOH at 20—40° gives methylated lignins *A* and *B* (OMe 32·2 and 35·4%, respectively) (not acetylated by Ac_2O–C_5H_5N), whilst with a large excess of NaOH at 60°

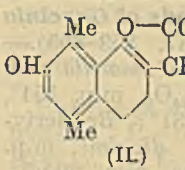
a product (OMe 37·2%) is obtained. Thus new OH groups are formed during methylation (probably from heterocyclic non-furan rings). Such degradation is markedly increased by rise of temp. and by increasing [NaOH], but is restricted by use of $COMe_2$ as solvent and by use of >5% excess of NaOH at 20°. When refluxed with 65% aq. MeOH–9% H_2SO_4, the OMe content (22·3%) of Et_2O-insol. (I) is reduced to 21·3% in 48 hr. and to 20·9% in 100 hr.

J. W. B.

Lignin. V. Preparation and sulphonation of the lignin from rye straw and pine wood. H. Friese [in part with H. Glassner] (Ber., 1937, **70**, [*B*], 1059—1071).—Treatment of rye straw with Ac_2O–AcOH (2·5 : 1) containing 6 vol.-% of H_2SO_4 give α-cellobiose acetate and an undefined mixture of sugar acetates corresponding with the presence of about 75% of carbohydrates. Treatment of the portion of the product sol. in H_2O with MeOH of varied concn. and ultrafiltration of the aq. solutions establishes the formation of ligninsulphonic acids. Similar treatment of pine meal indicates the presence of 65% of carbohydrates, a larger proportion of non-ultrafilterable matter, and a sol. portion similar to that derived from straw. Lignin obtained by use of superconc. HCl or 66% H_2SO_4 which does not contain carbohydrates is not dissolved by Ac_2O–AcOH–H_2SO_4. It appears therefore that a portion of the lignin at any rate is combined with polymeric carbohydrates in wood, but there is no reason to doubt the existence of lignin as such. The incomplete degradation of fir wood is described. H. W.

Lignin. VI. Sulphite liquors. H. Friese, V. Högn, and H. Wille (Ber., 1937, **70**, [*B*], 1072—1079).—The liquor is centrifuged and subjected to a short after-hydrolysis with 2—6 vol.-% H_2SO_4 at 100°. After removal of volatile acids the solution is neutralised with $CaCO_3$ and evaporated to dryness. The residue is divided into three fractions by treatment with boiling MeOH, 80% MeOH, and finally by ultrafiltration. These are acetylated. It is thus established that the contents of the liquor are (i) a complex, non-hydrolysable ligninsulphonic acid, possibly a mixture of isomerides of differing mol. size which can be separated by ultrafiltration, (ii) a mixture of free sugar derivatives largely derived from hemicelluloses, and (iii) lignin–carbohydrate compounds in which the lignin is sulphonated in varying degrees. Treatment of wood with $Ca(HSO_3)_2$ is regarded as causing sulphonation of the free lignin component, whereby it is rendered at least colloidally sol. in alkali; the combined lignin is also sulphonated and rendered sol. in H_2O. The acidity of the liquor is not sufficient to cause hydrolysis of the complex. The so-called hemicelluloses, in so far as they are not combined with lignin, are hydrolysed to small components. H. W.

α-Hydroxysantonin. Y. Asahina and T. Momose (Ber., 1937, **70**, [*B*], 812—819).—α-Hydroxysantonin (I), m.p. 286°, obtained from the urine of dogs to which santonin has been administered, is converted by boiling Ac_2O containing NaOAc into the acetate, m.p. 173°, from which it is regenerated by cold fuming HCl. It is not esterified when heated with AcOH at 155° for 1 hr. (I) can be sublimed unchanged in a high vac., but loses H_2O when heated with HCl or HCO_2H, giving the *lactone* (II), m.p. 244—246°, [α] ±0° in EtOH, (*Me ether*, m.p. 165—166°; *acetate*, m.p. 183°). (II) is transformed by 10% NaOH into α-1-keto-7-hydroxy-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydro-2-naphthylpropionic acid, m.p. 192—193° (*Me* ester, m.p. 138°), which is reduced (Na–Hg) to *r*-desmotroposantonin, m.p. 198—200° (acetate, m.p. 145°). (II) is reduced (Pd–C in AcOH) to *r-santonigenic acid*, m.p. 179—180° (*Me* ester, m.p. 98°), which is oxidised by $FeCl_3$ in 40% AcOH to *disantonic acid*, $C_{30}H_{38}O_6$, m.p. 265° (decomp.). (I) is converted by boiling 10% NaOH into the *diketone*, $C_{12}H_{16}O_2$, m.p. 106—107°, $[\alpha]_D^{22}$ −108·9° in EtOH [*dioxime*, m.p. 244—245° (decomp.); *monosemicarbazone*, m.p. 240° (decomp.); *enol acetate*, b.p. 134—135°/3 mm.], which could not be hydrogenated in AcOH or EtOH and remains unchanged when heated with fuming HCl at 100° or with H_2SO_4 (*d* 1·5). Oxidation by $KMnO_4$ at room temp. transforms the diketone into the *acid*, $C_7H_{11}(CO_2H)_3$, m.p. 164—165°.



(II)

H. W.

Manila elemi resin. M. Mladenovic (Monatsh., 1937, **70**, 276—280).—Elemi resin should properly be assigned to the resinol class since it is mainly composed of the alcohols, amyrin (I) and brein (II). Treatment of the resin by the customary methods yields an ethereal oil, (I), and elemic acid. The amorphous β-elemic acid of Tschirch is a mixture of various elemic acids and, after acetylation, gives Ac derivatives of the acids with α- (III) and β-amyrin (IV) acetate. Keeping a solution of the residue in EtOH for months results in the separation mainly of (I) and repeated slow evaporation of the mother-liquors gives a cryst. mixture of (I) and (II). Acetylation (Ac_2O–C_5H_5N) of the non-cryst. residue gives (III), (IV), and brein acetate, whilst the remainder appears to contain OH. The Ac val [calc. on (I)] indicates that (I) is present to the extent of about 70%. H. W.

Quassin. I. Preparation and purification of quassin and neoquassin; their molecular formulæ. E. P. Clark (J. Amer. Chem. Soc., 1937, **59**, 927—931).—Treatment of a hot-H_2O extract of quassia chips first with $Pb(OAc)_2$ and then with activated C, followed by percolation of the C with $CHCl_3$, gives 0·15—0·18% of a mixture, separated by crystallisation, of quassin (I), $C_{20}H_{21}O_4(OMe_2)$, m.p. 205—206°, $[\alpha]_D^{20}$ +40° in $CHCl_3$, and an isomeride, *neoquassin*, m.p. 225—226°, $[\alpha]_D^{20}$ +46·6° in $CHCl_3$. With 3·5% HCl (I) gives *semidemethoxyquassin*, $C_{20}H_{25}O_5$·OMe, m.p. 213°, sol. in aq. NaOH, but insol. in Na_2CO_3 or $NaHCO_3$, with constant-boiling HCl or HBr gives *quassinol*, $C_{20}H_{21}O_4(OH)_2$, m.p. 263° (decomp.), $[\alpha]_D^{20}$ +62·6° in $CHCl_3$ [*Ac* derivative, m.p. 236° (decomp.)], sol. in alkalis, with Ac_2O–NaOAc gives *anhydroquassin*, $C_{22}H_{28}O_5$, m.p. 196°, *dehydroquassin*, $C_{22}H_{28}O_6$, m.p. 254°, and picrasmin, and with CrO_3 yields an *isomeride*, m.p. 221°, $[\alpha]_D^{20}$ +35·1° in $CHCl_3$, which yields twice as much quassinol as does (I). Crystallo-optical data are recorded. R. S. C.

Reactions caused by "activated" alumina.— See A., I, 368.

Morellin, a constituent of the seeds of *Garcinia morella*. B. S. Rao (J.C.S., 1937, 853–855).— Extraction of the pericarp of seeds of *G. morella* with hot EtOH yields *morellin* (I), $C_{30}H_{34}O_6$, m.p. 154°, $[\alpha]_D$ −594° (*dihydrochloride*, m.p. 131°; *Br*$_4$-derivative, m.p. 138—139°, $[\alpha]$ −156°; *dioxime*, m.p. 148—149°; *mononitroguanylhydrazone*, m.p. 205·5°, $[\alpha]_D$ −748°; *tetra-acetate*, m.p. 178—179°, $[\alpha]_D$ −327°; *Me*$_2$ *ether*, m.p. 156°, $[\alpha]_D$ −242°, and its *dioxime*, m.p. 118°, $[\alpha]_D$ +241°, *diacetate*, m.p. 82—83°, and *Br*$_4$-derivative, m.p. 124°; *Me*$_3$ *ether*, m.p. 170—172°). (I) resinifies on prolonged boiling with EtOH or on keeping at 100° for several hr. and it is converted into an amorphous substance when dissolved in EtOH–KOH. A cryst. isomeride, iso*morellin*, m.p. 116°, $[\alpha]_D$ −561°, is obtained when an Et_2O solution of (I) is shaken with aq. KOH or when it is digested with AcCl in C_6H_6 solution in the presence of K_2CO_3. When fused with KOH, (I) gives *dl*-methylheptenol, phloroglucinol, AcOH, *iso*valeric, methylsuccinic, and homophthalic acids, and a di*tert.*-glycol, $C_{16}H_{22}O_2$, b.p. 130—140°/8 mm. (I) is probably related to mangostin from the pericarp of seeds of *G. mangostana*. P. W. C.

Chinese *Asarum*, *Asarum Blumei*, Duch, "Hsi-Hsin." Constitution of a neutral component. Huang-Minlon (Ber., 1937, **70**, [*B*], 951—958).—Extraction of the drug, which is free from alkaloids, with hot light petroleum affords *l*-asarinin (I), m.p. 121—122°, $[\alpha]_D^{18}$ − 122° in $CHCl_3$, identical with the product obtained from Korean *Asarum* (cf. A., 1935, 1433). (I) does not decolorise Br in $CHCl_3$ or $KMnO_4$ but gives an orange-yellow colour with $C(NO_2)_4$. It cannot be acetylated and does not give ketonic reactions. OH and OMe are absent. It is unchanged by boiling conc. KOH. Treatment of (I) with conc. HNO_3 in AcOH at room temp. gives *dinitro*-l-*asarinin*, m.p. 220—221°, $[\alpha]_D^{18}$ +32° in $CHCl_3$, and 4-nitro-1 : 2-methylenedioxybenzene. Prolonged treatment of (I) with boiling 10% HCl–EtOH causes isomerisation to *l*-sesamin, m.p. 121—122°, $[\alpha]_D^{18}$ −68·9° in $CHCl_3$, and produces small amounts of *substances*, m.p. 121—122°, 168—169°, and 184—185°, respectively. Similarly *d*-sesamin is isomerised to d-*asarinin*, m.p. 121—122°. dl-*Sesamin*, m.p. 126—127°, and dl-*asarinin*, m.p. 134—135°, are obtained by admixture of the requisite optical antipodes. Attempts to convert (I) into a $(OMe)_4$-compound are described. The constitution of (I) is discussed. H. W.

Hydrogenation of alcohols derived from furan. R. Paul (Bull. Soc. chim., 1937, [v], **4**, 846—854).— Furylalkylcarbinols (I) are obtained in good yield by the action of a considerable excess of the requisite Grignard reagent on furfuraldehyde at −15°. The product is decomposed by H_2O and extracted with Et_2O; the ethereal solution is vigorously shaken with conc. $NaHSO_3$ and then kept over K_2CO_3 to which a little NH_2Ph is finally added. The product is finally distilled under suitable low pressure. Hydrogenation of (I) in presence of Pt or Pd is accompanied by rupture of the nucleus at room temp.; with Ni this effect becomes more marked as the temp. of reaction is increased. With Raney Ni at 60—80°/50 atm., scission is entirely absent and the change is rapid; the small amount of unchanged (I) is removed, previous to distillation, by treatment of the product with Br in $CHCl_3$ at low temp. or with HCl (1 : 1). The following compounds are thus obtained: 2-*tetrahydrofurylmethylcarbinol*, b.p. 71°/16 mm. (*phenylurethane*, m.p. 83—84°; *acetate*, b.p. 84°/14 mm.); 2-*tetrahydrofurylethylcarbinol*, b.p. 82—84°/15 mm. (*phenylurethane*, b.p. about 200—202°/8 mm.; *acetate*, b.p. 90—91°/12 mm.); *tetrahydrofuryl*-n-*propylcarbinol*, b.p. 94—95°/14 mm. (*phenylurethane*, m.p. 75°); *phenyl*-2-*tetrahydrofurylcarbinol*, b.p. 147—148°/10 mm. (*phenylurethane*, m.p. 123—124°; *acetate*, b.p. 161—163°/11·5 mm.). H. W.

"Furanic" condensations. VII. Preparation of alcohols of the furan series by means of ethereal or individual organomagnesium compounds and their transformation into unsaturated substances and resins. V. V. Tschelincev [with A. S. Larionov] (Bull. Soc. chim., 1937, [v], **4**, 819—824; cf. A., 1936, 996).—Furfuraldehyde is transformed by MgEtI in Et_2O or, preferably, by MgEtI in C_6H_6–$NPhMe_2$ into 2-furylethylcarbinol (I), b.p. 181—183°; 2-furyl*iso*amylcarbinol (II), b.p. 202—204°/760 mm., is obtained similarly. (I) or (II) is dehydrated by MgI_2 or anhyd. $H_2C_2O_4$ to the corresponding alkylidene compound, which immediately passes into a hard, non-fusible plastic resin. H. W.

Interaction of mixed organomagnesium compounds with ethyl β-furylacrylate. N Maxim and (Mlle.) E. Georgescu (Bull. Soc. chim., 1936, [v], **3**, 2266—2270).—Et β-2-furylacrylate (I) with MgEtBr–Et_2O yields *γ-hydroxy-α-2-furyl-γ-ethyl-*Δ^{α}*-pentene*, b.p. 125°/16 mm. (*Bz* derivative, b.p. 193°/11 mm.). Similarly (I) with MgPrBr–Et_2O yields *γ-hydroxy-α-2-furyl-γ-propyl-*Δ^{α}*-hexene*, b.p. 130°/16 mm. (*Bz* derivative, b.p. 198°/12 mm.), with MgBu$^{\beta}$Cl–Et_2O yields *γ-hydroxy-α-2-furyl-ε-methyl-γ-*iso*butyl-*Δ^{α}*-hexene*, b.p. 143°/17 mm. (*Bz* derivative, b.p. 210°/18 mm.), with *iso*-C_5H_{11}·MgBr yields *γ-hydroxy-α-2-furyl-ζ-methyl-γ-*iso*amyl-*Δ^{α}*-heptene*, b.p. 174°/12 mm. (*Bz* derivative, b.p. 224°/8 mm.), and with MgPhBr yields *γ-hydroxy-α-2-furyl-γγ-diphenyl-*Δ^{α}*-propene*, m.p. 59°. Hydrolysis by KOH–H_2O of all the Bz derivatives gives the parent alcohols. Contrary to Thiele's hypothesis the organo-Mg compounds have reacted with the ester group and not with the conjugated system ·CH:CH·CO·. H. G. M.

Accelerators of vulcanisation.—See B., 1937, 592.

Synthesis of furfurylidene-ethylideneazine. S. A. Tebinov (J. Gen. Chem. Russ., 1937, **7**, 656—657).—Furfuraldehyde, MeCHO, and aq. N_2H_4 at 100° yield *furfurylidene-ethylideneazine*, m.p. 109°. R. T.

Oxidation of acetylene-γ-glycols. 3 : 4-Diketo-2 : 2 : 5 : 5-tetraphenyltetrahydrofuran. P. A. Tichomolov and A. E. Drushinin (J. Gen. Chem. Russ., 1937, **7**, 869—8 2).—$(OH·CPh_2·C:)_2$ in AcOH and CrO_3 yield 3 : 4 *diketo*-2 : 2 : 5 : 5-*tetraphenyltetrahydrofuran* [*phenylhydrazone*, m.p. 134°; *mon-*

oxime, m.p. 216° (decomp.); *compound* with *o*-$C_6H_4(NH_2)_2$, m.p. 249—250°]. R. T.

Natural coumarins. XXVII. Fraxidin and *iso*fraxidin. E. Späth and Z. Jerzmanowska-Sienkiewiczowa (Ber., 1937, **70**, [*B*], 1019—1020).—The mother-liquors left after isolation of fraxinol (this vol., 254) contain *fraxidin*, m.p. 196—197° (vac.), identified as 8-hydroxy-6 : 7-dimethoxycoumarin, and iso*fraxidin* (I), m.p. 148—149°. The methylation of (I) to 6 : 7 : 8-trimethoxycoumarin and its difference from the known hydroxydimethoxycoumarins of the 6 : 7 : 8-series prove it to be 7-*hydroxy*-6 : 8-*dimethoxycoumarin*. H. W.

Natural coumarins. XXVIII. Marmelosin. E. Späth, P. K. Bose, W. Gruber, and N. C. Guha (Ber., 1937, **70**, [*B*], 1021—1023).—Marmelosin (I), obtained from the fruits of *Aegle marmelos* (Dikshit and Dulb, A., 1932, 1035), is proved by its isomerisation to *allo*imperatorin, the identity of the Me ethers of (I) and imperatorin (II), and the characteristic fission with AcOH containing a little H_2SO_4 to be identical with (II). H. W.

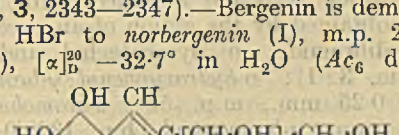
Natural coumarins. XXIX. Constitution of osthenol. E. Späth and J. Bruck (Ber., 1937, **70**, [*B*], 1023—1024).—Treatment of the residues left from the extracts of *Angelica* root after removal of angelicin and osthol (I) with CH_2N_2 leads to the isolation of further quantities of (I), thus disclosing the presence of *osthenol* [7-*hydroxy*-8-*γ*-*methyl*-Δ^{β}-*butenylcoumarin*], m.p. 124—125°, the direct isolation of which is also described. H. W.

Natural coumarins. E. Späth (Ber., 1937, **70**, [*A*], 83—117).—A lecture.

Synthetic coumarins. I. Coumarins derived from resacetophenone. R. R. Agarwal and S. Dutt (J. Indian Chem. Soc., 1937, **14**, 109—112).—Condensation of resacetophenone with the appropriate reagent gives 7-*hydroxy*-6-*acetyl*-, m.p. 139°, 7-*hydroxy*-6-*acetyl*-4-*methyl*-, m.p. 147° (*Ac* derivative, m.p. 120—121°; *oxime*, m.p. 205°; *semicarbazone*, m.p. 183°; *phenylhydrazone*, m.p. 146—147°), 7-*hydroxy*-6-*acetyl*-3 : 4-*dimethyl*-, m.p. 168°, 7-*hydroxy*-6-*acetyl*-4-*methyl*-3-*ethyl*-, m.p. 122°, 7-*hydroxy*-6-*acetyl*-4-*methyl*-3-iso*propyl*-, m.p. 108°, and 7-*hydroxy*-6-*acetyl*-3-*benzyl*-4-*methyl*-*coumarin*, m.p. 176°, and 7-*hydroxy*-4-*methylcoumarin* 6-*styryl ketone*, m.p. 141°. F. R. S.

Norbergenin. A. E. Tschitschibabin, A. V. Kirsanov, and G. A. Arbusov (Bull. Soc. chim., 1936, [v], **3**, 2343—2347).—Bergenin is demethylated by 48% HBr to *norbergenin* (I), m.p. 276—278° (decomp.), $[\alpha]_D^{20}$ −32·7° in H_2O (*Ac*$_6$ derivative,

(I.)



m.p. 214—218°, $[\alpha]_D^{20}$ −22·8° in C_6H_6), which also exists in an amorphous form and in another cryst. form with $0{\cdot}5H_2O$. With CH_2N_2 (I) gives dimethylbergenin, also obtained from bergenin, and on demethylation gives (I). This confirms the assigned constitution (I). In H_2O or EtOH with $FeCl_3$ (I) gives a deep blue coloration which turns brick-red with NaOH. Alkaline solutions of (I) become yellow in presence of atm. O_2 but are decolorised again on acidification. H. G. M.

Hydrogen cyanide synthesis of aromatic aldehydes. I. Dibenzfuran-3-aldehyde. L. E. Hinkel, E. E. Ayling, and J. H. Beynon (J.C.S., 1937, 778—780).—*Dibenzfuran*-3-*aldehyde* (I), m.p. 68° (*phenylhydrazone*, m.p. 162°; *NH$_2$Ph* derivative, m.p. 131°; *semicarbazone*, m.p. 240°; *oxime*, m.p. 129°), prepared from dibenzfuran, $C_2H_2Cl_4$, HCN, and $AlCl_3$, is oxidised ($KMnO_4$) to the -carboxylic acid and condenses with benzoin to 3-*dibenzfuroyl*-3-*dibenzfurylcarbinol*, m.p. 130°. The carbinol is oxidised (HNO_3) to *bis*-3-*dibenzfuryl ketone*, m.p. 236—237°, which is transformed (KOH) into *bis*-3-*dibenzfurylglycollic acid*, m.p. 248°. With NaOAc–Ac_2O (I) yields β-*dibenzfuran*-3-*acrylic acid*, m.p. 239—240° (*Me* ester, m.p. 130°), with $CH_2(CO_2H)_2$ forms *dibenzfuryl*-3-*methylenemalonic acid*, m.p. 213° (decomp.), and with NMe_2Ph gives 3-*dibenzfuryl*-pp′-*bis*(*dimethylamino*)*diphenylmethane*, m.p. 172°, oxidised to an intense green dye. F. R. S.

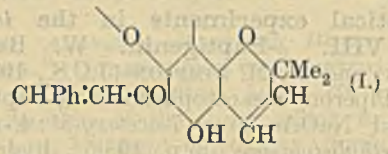
Synthetical experiments in the *iso*flavone group. VIII. ψ-Baptigenin. W. Baker, R. Robinson, and N. M. Simpson (J.C.S., 1937, 805—807).—ω-Piperonylresacetophenone (ψ-baptigenetin), Ac_2O, and NaOAc give 7-*acetoxy*-3′ : 4′-*methylenedioxy*-2-*methyl*iso*flavone*, m.p. 198·5°, hydrolysed to the -*hydroxy*- compound, m.p. 253—254·5°, which forms the -*benzyloxy*- derivative, m.p. 186°. Condensation of this compound with PhCHO affords 7-*benzyloxy*-3′ : 4′-*methylenedioxy*-2-*styryl*iso*flavone*, m.p. 199—200·5°, oxidised ($KMnO_4$) to 7-*benzyloxy*-3′ : 4′-*methylenedioxy*iso*flavone*-2-*carboxylic acid*, m.p. 179—181°, which with HBr–AcOH is converted into ψ-baptigenin, identical with the natural product (cf. Späth *et al.*, A., 1930, 611; Mahal *et al.*, A., 1935, 90). F. R. S.

Synthesis of brazilin and hæmatoxylin. V. H. Appel, W. Baker, H. Hagenbach, and R. Robinson (J.C.S., 1937, 738—744).—Resorcinol and Et indanedionecarboxylate (HCl) give 7-*hydroxy*-1′-*ketoindeno*(2′ : 3′ : 3 : 4)*coumarin*, m.p. above 340°, of which the *Me ether*, m.p. 270°, is reduced (Zn–AcOH) to the H_2-derivative, m.p. 185—187°, and with NaOH affords 2′-*hydroxy*-4′-*methoxy*-3-*phenylindan*-1-*one*, m.p. 141·5° (*semicarbazone*, m.p. 213—214°; *Me ether*, m.p. 89°). Veratroyl chloride and resorcinol Me_2 ether ($AlCl_3$) yield 2-*hydroxy*-4 : 3′ : 4′-*trimethoxybenzophenone*, m.p. 140—141°. 7-Methoxy-4-veratryl-, m.p. 151—153°, and 161—163°, obtained from the OH-derivative, is reduced to the -*dihydrocoumarin*, m.p. 82—83°, and to a product which is hydrolysed and esterified to *Et* β-*veratryl*-β-(2-*hydroxy*-4-*methoxyphenyl*)*propionate*, m.p. 113—115°. The ester is converted into β-*veratryl*-β-(2-*benzyloxy*-4-*methoxyphenyl*)*propionic acid*, m.p. 104—105°, which could not be made to undergo ring-closure. ω-Veratroylresacetophenone 4-veratrate in AcOH–HCl gives 7-*veratroyloxy*-3′ : 4′-*dimethoxyflavone*, m.p. 219°, and with the appropriate metallic chloride yields

9-*keto*-7-*veratroyloxy*-4′ : 5′-*dimethoxybrazylium zinci-chloride*, *stannichloride*, and *ferrichloride*; the stanni-chloride is oxidised ($KMnO_4$) to veratric acid and hemipinic acid. Pæanol, from resacetophenone and Me_2SO_4, with veratroyl chloride forms O-*veratroyl-pæanol*, m.p. 158—159°, which in presence of $NaNH_2$ gives ω-*veratroylpæanol*, m.p. 162—163°, forming brilliant red solutions with metallic chlorides.

F. R. S.

Rottlerin. I. A. McGookin, F. P. Reed, and A. Robertson (J.C.S., 1937, 748—755).—Rottlerin (I), $C_{33}H_{30}O_9$ or $C_{31}H_{30}O_8$, m.p. 212° (cf. Perkin, J.C.S., 1893, **63**, 975 *et seq.*; Dutt, A., 1925, 1296; Hoffmann *et al.*, A., 1933, 397), is a highly reactive substance, difficult to obtain pure; some of the results of previous authors have not been confirmed. It gives a Ac_6 derivative (?), m.p. 213°, and is oxidised ($KMnO_4$) to BzOH; there is one cinnamyl residue and not two Ph residues. With KOH (I) affords phloroglucinol, CHPh:CH·CO_2H, BzOH, and AcOH, and with NaOH–Zn, CH_2Ph·CH_2·CO_2H and *C*-methyl- and -dimethyl- but no -trimethyl-phloroglucinol, are obtained. Hydrogenation of (I) yields the H_4-compound and *perhydrorottlerin* (II), m.p. 178°. $Ba(OH)_2$ and (I) lead to rottlerone (III), m.p. 236°, and



(I.)

some BzCHO; (III) is reduced to the H_4-compound (IV), m.p. 172—173° (*Ac* derivative, m.p. 214—215°), methylated to the *Me* derivative, m.p. 102° (*oxime*, m.p. 188°). *Perhydrorottlerone*, m.p. 166°, may be obtained by reduction of (III) or from (II) and NaOH. Hydrolytic fission of (IV) affords CH_2Ph·CH_2·CO_2H and 5 : 7-dihydroxy-2 : 2-dimethylchroman. It is suggested that (I) contains the unit shown and that the results disprove the structure suggested by Dutt *et al.* (A., 1928, 643).

F. R. S.

Pyrenium salts. XXVII. 2 : 4-Diarylnaphtha-pyrenium salts. W. Dilthey, W. Höschen, and O. Dornheim (J. pr. Chem., 1937, [ii], **148**, 210—216).—*p*-OMe·C_6H_4·CH:CHBz and β-$C_{10}H_7$·OH in EtOH–HCl give (with a *substance*, m.p. 307—308°) 2-*phenyl*-4-p-*anisyl*-5 : 6-*naphtha*-(1′ : 2′)-1 : 4-*pyran*, m.p. 205—206° (decomp.). This is converted by HCl–MnO_2 into the *chlorohydrochloride*, $C_{26}H_{19}O_2Cl$,HCl, which in $COMe_2$–MeOH–KOAc yields 2-*phenyl*-4-p-*anisyl*-5 : 6-*naphtha*-(1′ : 2′)-*pyranol*, m.p. 197—198° (decomp.) [picrate, new m.p. 210—212° (cf. A., 1935, 1130)]. The *perchlorate*, m.p. 250° (decomp.), of the last with AcOH–H_2O_2 gives 1-p-*anisoyl*-β-*naphthyl benzoate* (I), m.p. 178°. Attempted synthesis of 1-*p*-anisoyl-β-naphthol from β-$C_{10}H_7$·OH giving only β-*naphthyl anisate*, m.p. 113—114°, the hydrolysis product of (I) was reduced to *p-anisyl*-2-*hydroxy*-α-*naphthylcarbinol*, m.p. 107—108°, also obtained, m.p. 88—89°, from *p*-C_6H_4Br·OMe and 2-hydroxy-α-naphthaldehyde. *p*-Anisyl *p*′-methoxystyryl ketone and β-$C_{10}H_7$·OH yield 2 : 4-*di*-p-*anisyl*-5 : 6-*naphtha*-(1′ : 2′)-1 : 4-*pyran*, m.p. 193–194°, which with HCl–MnO_2 gives a *chloride* converted into 2 : 4-*di*-p-*anisyl*-*naphtha*-1′ : 2′-(5 : 6)-*pyranol*, decomp. 180° (*perchlorate*, m.p. 266—269°; *picrate*, m.p. 208—211°).

E. W. W.

Polymembered ring systems. VIII. New application of the dilution principle. A. Lüttringhaus and K. Ziegler (Annalen, 1937, **528**, 155—161).—Ethers OH·C_6H_4·O·$[CH_2]_n$·Br are readily obtained if alkylation is effected in presence of an excess of phenol and dihalide; in this case the alkali compound is present almost exclusively and two-sided reaction of the dihalide is prevented. Cyclisation of the compounds OR·C_6H_4·O·$[CH_2]_n$·Br (R = alkali) is effected by gradually adding equally conc. solutions of ether and dihalide at the same rate to a fixed vol. of the heated solvent, by adding a cold conc. solution of the pre-prepared K derivative to the heated solvent, or (best) by using an alkali the solubility of which is limited but sufficient to transform the ether as it is added into the reactive alkali compound (*e.g.*, use of K_2CO_3 and boiling amyl alcohol). *Resorcinyl* κ-*bromodecyl ether*, m.p. 56°, *resorcinol decamethylene ether*, $C_6H_4<^{O}_{O}>[CH_2]_{10}$, b.p. 135—138°/0·5 mm., m.p. 23° {converted by HI (*d* 1·7) in AcOH into *m*-$C_6H_4(OH)_2$ and $[CH_2]_{10}I_2$}, and its *dimeride*, $C_6H_4<^{O\cdot[CH_2]_{10}\cdot O}_{O\cdot[CH_2]_{10}\cdot O}>C_6H_4$, b.p. 200/0·2 mm., m.p. 105—106°, are described.

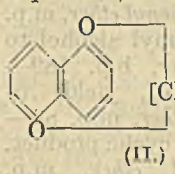
H. W.

Polymembered ring systems. IX. Pyrocatechol polymethylene ethers. K. Ziegler, A. Lüttringhaus, and K. Wohlgemuth (Annalen, 1937, **528**, 162—180).—Comparison of the yields of cyclic ethers obtained from the alkali salts of pyrocatechol ω-bromoalkyl ethers OH·C_6H_4·O·$[CH_2]_n$·Br (n = 2—10) is rendered somewhat uncertain by the difficulty of exact assessment, but is sufficiently accurate to show the absence of a well-marked min. such as is observed in the readiness of formation of cyclic ketones. Kinetic measurements of the rate of formation of NaBr from ONa·C_6H_4·O·$[CH_2]_n$·Br in EtOH afford an accurate measurement of the rate of cyclisation if the solutions are dil., and difficulties due to alcoholysis can be overcome by use of a large excess of NaOEt; the limit of applicability of the method appears to be reached when n = 10. The rate diminishes rapidly from the 6- through the 7- to the 8-ring, and then continuously but less rapidly as would be expected in a homologous series from which steric influences are absent. This absence is ascribed to the 2 O and possibly also to the 2 C of the C_6H_6 ring, to all of which H is not attached. The following *ethers* are obtained by the action of an excess of the alkylene dibromide on pyrocatechol and NaOEt (mol. ratio, 3 : 1): o-*hydroxyphenyl* γ-*bromopropyl*, b.p. 101°/0·25 mm., m.p. 59°, δ-*bromobutyl*, b.p. 117°/0·25 mm., ε-*bromoamyl*, b.p. 132°/0·25 mm., ζ-*bromohexyl*, b.p. 150°/0·17 mm., η-*bromoheptyl*, m.p. 32°, θ-*bromo-octyl*, ι-*bromononyl*, b.p. 165°/0·25 mm., m.p. 19°, κ-*bromodecyl*, b.p. 180°/0·24 mm. *o*-$C_6H_4(OH)_2$, $CH_2Cl·CH_2·OH$, and NaOEt afford o-*hydroxyphenyl* β-*hydroxyethyl ether*, b.p. 128°/0·7 mm., m.p. 100–101°, transformed by PBr_3 and C_5H_5N into o-*hydroxyphenyl* β-*bromoethyl ether*, b.p. 95°/0·25 mm. Gradual addition of these to a mixture of K_2CO_3

and boiling amyl alcohol affords the following *o-dioxybenzenes*: ethylene-; *trimethylene-*, b.p. 103°/10 mm.; *tetramethylene-*, b.p. 112°/10 mm.; *pentamethylene-*, b.p. 122°/10 mm.; *hexamethylene-*, b.p. 140°/10 mm., m.p. 38°; *heptamethylene-*, b.p. 156°/10 mm.; m.p. 17—18°; *octamethylene-*, b.p. 171°/10 mm., m.p. 46°; *nonamethylene-*, b.p. 185°/10 mm., m.p. 58°; *decamethylene-*, b.p. 197°/10 mm. H. W.

Polymembered ring systems. X. New dihydroxybenzene and dihydroxynaphthalene derivatives. A. LÜTTRINGHAUS (Annalen, 1937, **528**, 181—210).—*p*-$C_6H_4(OH)_2$ readily yields a polymethylene ether with 10, much less readily with 8, CH_2 groups whereas similar compounds with 7 or 6 CH_2 groups could not be obtained. From *m*-$C_6H_4(OH)_2$ an ether with 7 CH_2 groups is obtained with some difficulty, and the similar substance with 6 CH_2 is possibly formed in very small amount. 1 : 5- and 2 : 6-$C_{10}H_6(OH)_2$ afford ethers with 10 CH_2, but a compound with 8 CH_2 could not be derived from the latter. Consideration of at. distances in conjunction with readiness of ring formation appears to indicate a great stability of the plane or slightly bent form of the C_6H_6 nucleus, and to show that more energy is required for the deformation of a single mol. than can be derived from the kinetic mol. energy at 100—150°. Similarly, the energy required for alteration of the inclination of the 2 plane C_6H_6 nuclei in $C_{10}H_8$ towards one another is at any rate in excess of the mean energy of activation of processes occurring with reasonable rapidity between 100° and 150°. The very high mol. depression of the f.p. shown by various cyclic ketones is not shared with these complex ethers, but the introduction of a C_6H_6 nucleus into the ring system does not alter the general character of the odour in spite of the presence of a 2 ethereal O atoms.

Quinol is converted by Br·$[CH_2]_{10}$·Br and KOH in boiling EtOH into *quinol mono-κ-bromodecyl ether*, m.p. 76·77°, cyclised by K_2CO_3 in boiling amyl alcohol to *quinol decamethylene ether* (I), b.p. 120—125°/0·2 mm., m.p. 63°, in 79% yield. (I) does not react with MgMeI and is converted by 48% HBr in boiling Ac_2O into *p*-$C_6H_4(OH)_2$ and Br·$[CH_2]_{10}$·Br. *Quinol mono-ω-bromo-*n*-octyl ether*, m.p. 65°, is transformed into *quinol octamethylene ether*, b.p. 134°/0·8 mm., m.p. 65° (yield 18%), and the *dimeric octamethylene ether*, b.p. 235°/0·5 mm., m.p. 99°. Attempted cyclisation of *quinol mono-η-bromo-*n*-heptyl ether*, b.p. 164°/about 0·02 mm., m.p. 33°, gives small amounts of non-cryst. material volatile with steam, *quinol mono-η-amyloxy-*n*-heptyl ether*, b.p. 192—196°/0·8 mm., and the *dimeric heptamethylene ether*, $C_{26}H_{26}O_4$, m.p. 113°. *Quinol mono-ζ-bromo-*n*-hexyl ether* has m.p. 57°. *Resorcinol mono-η-bromo-*n*-heptyl ether*, b.p. 176°/0·04 mm., gives *resorcinol heptamethylene ether*, m.p. 109—109·5°, in 10% yield. Attempted cyclisation of *resorcinol mono-ζ-bromo-*n*-hexyl ether* gives a product which reacts with MgMeI, *dimeric resorcinol hexamethylene ether*, m.p. 114°, and *resorcinol mono-ζ-amyloxy-*n*-hexyl ether*, b.p. 173—176°/0·4 mm. *Resorcinol* β-β′*-bromoethoxyethyl ether*, b.p. 146°/0·06 mm., is transformed by K_2CO_3 in boiling amyl alcohol into the dimeric *ether*, $C_6H_4<O\cdot[CH_2]_2\cdot O\cdot[CH_2]_2\cdot O\atop O\cdot[CH_2]_2\cdot O\cdot[CH_2]_2\cdot O>C_6H_4$, m.p. 164°.


(II.)

*Quinol di-*n*-butyl*, m.p. 46°, and *di-*n*-amyl ether*, b.p. 192°/15 mm., m.p. 45°, are described. 1 : 5-$C_{10}H_6(OH)_2$ is transformed by Br·$[CH_2]_{10}$·Br and KOH in boiling EtOH into 1-*hydroxy-*5-*κ-bromo-*n*-decoxynaphthalene*, m.p. 70·5°, cyclised to 1 : 5-*dihydroxynaphthalene decamethylene ether* (II; $n = 10$), b.p. 160—164°/0·05 mm., m.p. 105°, in 61·5% yield. 1-*Hydroxy-*5-*ω-bromo-*n*-octoxynaphthalene* has m.p. 64°. 2-*Hydroxy-*6-*κ-bromo-*n*-decoxynaphthalene*, m.p. 96°, gives 1 : 6-*dihydroxynaphthalene decamethylene ether*, b.p. 130—135°/0·02 mm., m.p. 89—90°, in 22% yield. H. W.

Polymembered ring systems. XI. Form of the diphenyl and diphenylmethane molecules. A. LÜTTRINGHAUS (Annalen, 1937, **528**, 211—222).—Considerations of at. distances indicate that, provided distortion of the mol. does not occur, the conversion of *p*-OH·C_6H_4·C_6H_4·OH-*p*′ into an un- or do-decamethylene ether should occur. The failure to obtain a decamethylene ether is regarded as strong confirmation of the extended form and fixity of the Ph_2 system. Cyclisation of the somewhat similar $CH_2(C_6H_4\cdot OH\text{-}p)_2$ to a heptamethylene ether is possible. Gradual addition of KOH–EtOH to *p*-OH·C_6H_4·C_6H_4·OH-*p*′ and Br·$[CH_2]_{10}$·Br in boiling EtOH affords p-*hydroxy-*p′-*κ-bromo-*n*-decoxydiphenyl*, m.p. 127—128°, converted by K_2CO_3 in boiling amyl alcohol into p-*hydroxy-*p′-*κ-amyloxydecoxydiphenyl*, m.p. 111—113°. p-*Hydroxy-*p′-*κ-bromo-*n*-decoxydiphenylmethane*, m.p. 80—81°, is converted into pp′*-dihydroxydiphenylmethane decamethylene ether*, b.p. 206°/0·3 mm., m.p. 76° (yield 68%), which does not react with MgMeI, gives I·$[CH_2]_{10}$·I when treated with HI (*d* 1·7) in boiling Ac_2O, and affords $CH_2(C_6H_4\cdot OH\text{-}p)_2$ when heated with KOH–NaOH at 300° in absence of air. p-*Hydroxy-*p′-*ω-bromo-*n*-octoxydiphenylmethane*, m.p. 65—66°, yields pp′*-dihydroxydiphenylmethane octamethylene ether*, b.p. 168—170°/0·2 mm., m.p. 85—86°, in 29% yield whilst p-*hydroxy-*p′-*η-bromo-*n*-heptoxydiphenylmethane*, m.p. 78°, affords pp′*-dihydroxydiphenylmethane heptamethylene ether*, m.p. 120° (5%), and the dimeric *ether*, $CH_2<C_6H_4\cdot O\cdot[CH_2]_7\cdot O\cdot C_6H_4\atop C_6H_4\cdot O\cdot[CH_2]_7\cdot O\cdot C_6H_4>CH_2$, m.p. 136·5°. H. W.

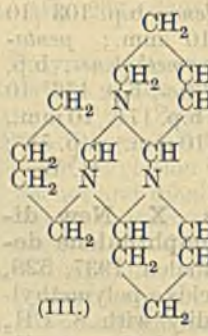
Polymembered ring systems. XII. Valency angle of the oxygen atom in derivatives of diphenyl ether. A. LÜTTRINGHAUS (Annalen, 1937, **528**, 223—233).—If the valency angle 110° is ascribed to O, close parallelism between ease of formation of cyclic ether with $O(C_6H_4\cdot OH\text{-}p)_2$ and $CH_2(C_6H_4\cdot OH\text{-}p)_2$ is to be expected. Since this is not observed, it appears that the angle of O is much more strongly affected by substituents than that of C^{IV} and cannot be regarded as const. The possibility that ·O· and ·CH_2· are so closely similar that corresponding compounds are isomorphous has been partly realised in the open systems OPh·CH_2Ph and (·CH_2Ph)$_2$ and is completely realised in the fixed systems fluorene and diphenylene oxide in which close similarity of valency angle is enforced. CH_2Ph_2 and Ph_2O, however, give a pronounced eutectic and there is evidence of

limited miscibility. Addition of KOH–EtOH to $O(C_6H_4{\cdot}OH\text{-}p)_2$ and $Br{\cdot}[CH_2]_2{\cdot}Br$ in boiling EtOH gives p-*hydroxy*-p-*κ*-*bromo*-n-*decoxydiphenyl ether*, m.p. 90·5°, cyclised by K_2CO_3 in boiling amyl alcohol to *pp'-diphenyl oxide decamethylene ether*, b.p. 189—195°/0·5 mm., m.p. 79—80°, in 36% yield. p-*Hydroxy*-p'-*ω*-*bromo*-n-*octoxydiphenyl ether*, m.p. 83—84°, gives at most, minimal amounts of cyclic product. p-*Hydroxy*-p'-*ζ*-*bromo*-n-*hexoxydiphenyl ether*, m.p. 78°, affords the dimeric *product*, $C_{36}H_{40}O_6$, m.p. 142°. H. W.

Molecular compounds of pyrrole derivatives. M. Deželić (Bull. Soc. Chim. Yougoslav., 1936, 7, 91—113).—The fusion diagrams suggest 1 : 1 *compounds* in the systems Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate (I)–$CH_2Cl{\cdot}CO_2H$ (II), transition point (t.p.) 85·3°, –PhOH, t.p. 93°, –picric acid (III), –salicylic acid (IV), t.p. 107°, Et 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate (V)–(II), t.p. 74·5°, –(IV), m.p. 135°, –(III), t.p. 97°, –*o*- (VI), m.p. 114°, and –*m*-$C_6H_4(OH)_2$ (VII), m.p. 111°, Et 4-aldehydo-2 : 4-dimethylpyrrole-3-carboxylate (VIII)–(IV), m.p. 111·5°, –(VII), t.p. 98°, and –quinol (IX), m.p. 117·5°, and 2 : 1 *compounds* in the systems (I)–(IV), t.p. 113°, –(VI), t.p. 108·5°, –(VII), m.p. 139°, and –(IX), t.p. 108·5°, Et 2 : 5-dimethylpyrrole-5-carboxylate (X)–(III), t.p. 100°, (V)–(IX), m.p. 142°, and (VIII)–(IV), t.p. 111°. Compound formation is not observed in the systems (I), (V), (VIII), or (X)–AcOH, –($\cdot CH_2{\cdot}CO_2H)_2$, –BzOH, (X)–(II), –PhOH, –(IV), –(VI), –(VII), –(IX), and –benzoquinone, and (VIII)–(VI). R. T.

Some furan ketones with several double linkings (II) and some ethylenic ketones with a pyrrole nucleus. N. Maxim and I. Copuzeanu (Bull. Soc. chim., 1936, [v], **3**, 2251—2256).—Furfurylideneacetone with *p*-$C_6H_4Me{\cdot}CHO$ and EtOH–NaOH gives *furfurylidene*-(p-*methylbenzylidene*)*acetone*, m.p. 85°, b.p. 237°/18 mm. Similarly, *furfurylidene*-(o-*nitrobenzylidene*)*acetone*, m.p. 104° (corresponding m-, m.p. 125°, and p-, m.p. 159—160°, -NO_2- and o-*Cl*-, m.p. 80°, -compounds), has been prepared. The following have been prepared by treating pyrryl Me ketone with the appropriate aldehyde, EtOH, and NaOH: p-*methyl*-, m.p. 152—153°, o-*chloro*-, m.p. 124°, p-*methoxy*-, m.p. 137°, m-*nitro*-, m.p. 203—204°, p-*nitro*-, m.p. 204°, p-*dimethylamino*-, m.p. 199—200°, *-benzylidenemethyl pyrryl ketone*. H. G. M.

Diaminomethane and its derivatives. II. α-Aminopiperidine and the products of reduction of α-aminopyridine. III. Hydrolysis of diacetyl-α-aminopiperidine and the pseudodipiperideine of Ahrens. A. V. Kirsanov and J. N. Ivastchenko (Bull. Soc. chim., 1936, [v], **3**, 2279—2288, 2289—2295).—II. Contrary to the conclusions of previous workers (cf. Tschitschibabin *et al.*, A., 1930, 925), reduction of 2-aminopyridine (I) with Na–EtOH yields NH_3, $C_5H_{11}N$, and cadaverine, but no 2-aminopiperidine, considered to be too unstable for isolation. A mechanism for the formation of the foregoing products is given. Catalytic reduction (H_2–Pt) of the Ac derivative of (I), in presence of Ac_2O–AcOH, gives *NN'-diacetyl-2-aminopiperidine* (II), m.p. 122—123°, and similarly NN-diphenyl-2-aminopyridine in AcOH is hydrogenated to *NN-diphenyl-α-aminopiperidine*, m.p. 131—133°.



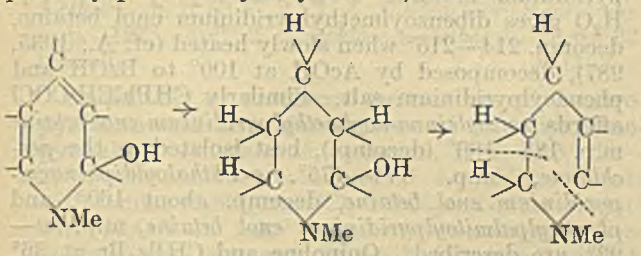
(III.)

III. Hydrolysis of (II) with NaOH gives *tripiperideine*, m.p. 94—95°, probably (III). This is the compound described by Ahrens (A., 1898, i, 686) as dipiperideine, and depolymerises when distilled to a product with a mol. wt. corresponding with a dipiperidine. The reduction of $KMnO_4$ by (III) is attributed to the possible presence of the monomeride in equilibrium with (III). H. G. M.

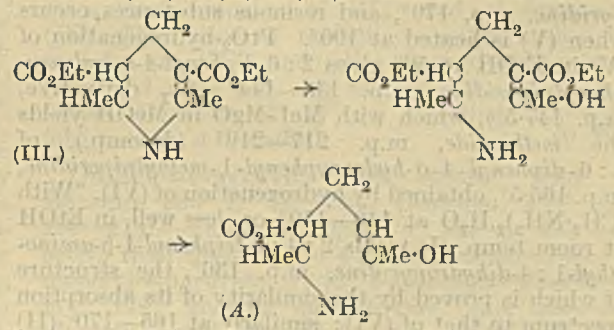
Aliphatic polyamines. V. J. van Alphen (Rec. trav. chim., 1937, **56**, 529—534).—αε-Dibromopentane and $(CH_2{\cdot}NH_2)_2$ in hot EtOH–KOH give 1-β-aminoethylpiperidine [picrate, m.p. 221° (Gabriel, A., 1921, i, 58, gives m.p. 214—215°); *Bz*, m.p. 59°, and *benzylidene* derivative, b.p. 205°/38 mm., reduced by Na–EtOH to the N-*benzyl* derivative, b.p. 178°/20 mm. (*hydrochloride*, $+2H_2O$, decomp. 210°; *picrate*, m.p. 60°; *phenylcarbamyl*, m.p. 156°, and *phenylthiocarbamyl* derivative, m.p. 148°)], which with PhNCO and PhNCS gives, respectively s-*phenyl*-β-1-*piperidinoethyl-carbamide*, m.p. 270°, and *-thiocarbamide*, m.p. 261°, and with CS_2–EtOH affords the internal *salt* $C_5H_{10}{>}^{+}NH{\cdot}[CH_2]_2{\cdot}NH{\cdot}CS{\cdot}S^-$, m.p. 126—128° (decomp.), converted at 140—170° into s-*di*-β-1-*piperindinoethylthiocarbamide*, m.p. 92°. J. W. B.

Derivatives of *p*-aminobenzenesulphonamide in the treatment of streptococcal infection in mice. W. H. Gray, G. A. H. Buttle, and D. Stephenson (Biochem. J., 1937, **31**, 724—730).—A no. of derivatives of *p*-aminobenzenesulphonamide (I) have been prepared and tested for toxicity and protective effect against infection with hæmolytic streptococci. A no. of the compounds tested are tolerated in larger doses than (I). The following are described: p-*acetamidobenzenesulphonylcyclohexylamide*, m.p. 224°; p-*aminobenzenesulphonylcyclohexylamide hydrochloride*, m.p. 227°; p-*acetamidobenzenesulphonyl*-p'-*sulphonamidophenylamide*, m.p. 280°; p-*aminobenzenesulphonyl*-p'-*sulphonamidophenylamide hydrochloride*, m.p. 224°; p-*aminobenzenesulphonpiperidide*, m.p. 164°; 2'-*pyrrolidone*-5'-*carboxy*-4-*aminobenzenesulphonamide*, m.p. 262°, optically inactive; 4 : 4'-*disulphonamidodiazoaminobenzene*, m.p. 172°; p-*cinnamylidene*-, m.p. 215°, p'-*methoxybenzylidene*-p-, m.p. 200°, 3' : 4'-*dimethoxybenzylidene*-4-, m.p. 196°, 3' : 4'-*diethoxybenzylidene*-4-, m.p. 216°, 3' : 4'-*methylenedioxybenzylidene*-4-, m.p. 219°, 3'-*nitrobenzylidene*-4-, m.p. 173°, 6'-*nitro*-3'-*hydroxybenzylidene*-4-, m.p. 197°, p'-*dimethylaminobenzylidene*-p-, m.p. 229°, and p-*furfurylidene*-, m.p. 196°, *-aminobenzenesulphonamides*; and p-*sulphonamidoglucoseanil*, m.p. 210°. *p*-Aminobenzenesulphonyldiethylamide and its Ac derivative previously mentioned but not described by Fourneau *et al.* (A., 1936, 1029) have m.p. 105° and 82°. A more convenient prep. of azobenzene-*p*-sulphonamide than that of Skandarow (1870) is described. E. A. H. R.

Tetrahydropyridine series. O. MUMM [with W. BUTTENSCHÖN, W. FRIEDRICHSEN, and W. GRASSMANN] (Annalen, 1937, **529**, 115—141).—Tetrahydropyridine derivatives are accessible by hydrogenation of C_5H_5N derivatives in which each atom in the ring bears a substituent; quaternary salts are the best starting materials and reaction probably proceeds by way of the ψ-base:



These highly substituted H_4-compounds are fairly stable; ring-opening occurs, though with less ease than in the H_2-series, and a remarkable thermal decomp., indicated by the dotted line, into CHR:NMe and a butadiene derivative is characteristic. Less fully substituted H_4-derivatives are obtained by disproportionation of H_2-compounds; they are less stable, particularly to O_2. Hydrogenation (colloidal Pt or PtO_2; 2 atm.) of Et_2 collidinedicarboxylate methosulphate in H_2O gives a 91% yield of *Et*$_2$ *N-methyltetrahydrocollidine-3 : 5-dicarboxylate*, b.p. 164°/12 mm. (blue fluorescence; *picrate*, m.p. 131°), hydrolysed by conc. HCl at 120° with loss of CO_2 and ring-fission to *β-methylamino-δ-methylheptan-ζ-one-γ-carboxylic acid* (*hydrochloride*, m.p. 148°; *picrate*, m.p. 187—188°; also obtained less well by hot 20% KOH–EtOH) and decomposing, when distilled at 760 mm., into CHMe:NMe (detected by hydrolysis to NH_2Me and MeCHO) and *Et γ-carbethoxy-β-methyl-*$\Delta^{\alpha\gamma}$*-hexadienoate* (I), b.p. about 142°/16 mm. Hydrolysis of (I) by hot 20% KOH–EtOH gives two (?) stereoisomeric *forms*, m.p. 156° (decomp.) (often 149° or oily) and 196° (decomp. about 270°), of the corresponding *dicarboxylic acid*; both forms absorb 2 H_2 (PtO_2; AcOH), but only the second gives smoothly *β-methyl-α-ethylglutaric acid*, m.p. 100—101°, which is also obtained by way of its *Et*$_2$ ester, b.p. 134°/18 mm., by hydrogenation of (I). Hydrogenation (PtO_2; EtOH) of Et_2 4-phenyllutidinedicarboxylate methosulphate leads to partial hydrogenation of the Ph and isolation of the impure 4-*phenyltetrahydro*-ester, b.p. about 205—220°/14 mm., which at about 300°/760 mm. gives *Et γ-carbethoxy-β-phenyl-*$\Delta^{\alpha\gamma}$*-hexadienoate*, b.p. 196—204°/14 mm., converted, by the methods used for (I), into the corresponding *dicarboxylic acid*, m.p. 157° (decomp.), and *β-phenyl-α-ethylglutaric acid*, m.p. 166° (*Et*$_2$ ester, b.p. 178—182°/11 mm.). Hydrogenation (colloidal Pt; 2 atm.) of Et_2 4-benzyl-lutidinedicarboxylate methosulphate gives *Et*$_2$ *4-benzyl-N-methyl-*Δ^2*-tetrahydrolutidinedicarboxylate*, m.p. 51° (*platinichloride*, m.p. 198—200°; *perchlorate*, m.p. 177°; yellowish-green fluorescence), and (?) the Δ^3*-ester*, an oil (only faintly fluorescent), converted into the solid isomeride by ultra-violet light; conc. HCl at 110° gives *4-benzyl-N-methyltetrahydrolutidine-3 : 5-dicarboxylic acid*, m.p. 176° (*hydrochloride*, m.p. 181°), and *β-methylamino-δ-benzylheptan-ζ-one-γ-carboxylic acid*, m.p. 206° (decomp.); distillation/vac. gives *Et γ-carbethoxy-β-benzyl-*$\Delta^{\alpha\gamma}$*-hexadienoate*, b.p. 198°/17 mm., and thence the corresponding *dicarboxylic acid*, m.p. 131°, and *Et*$_2$ *β-benzyl-α-ethylglutarate*, b.p. 190°/16 mm. Et_2 dihydrolutidinedicarboxylate (II) and HCl–AcOH give Et_2 lutidinedicarboxylate, *Et*$_2$ *tetrahydrolutidinedicarboxylate* (III), m.p. 89°, b.p. 161—165°/0·8 mm. [considered by Knoevenagel and Fuchs (A., 1902, i, 565) to be the H_6-ester; NO-derivative, m.p. 54°], and *Et* Δ^5*-tetrahydrolutidine-3-carboxylate* (IV), b.p. 108—110°/12 mm., 235°/760 mm. (*mercuri-* and *platini-chloride*, m.p. 138°; *picrate*, m.p. 120°); the amount of (IV) increases with time at the expense of (III) and it arises from (III) by the reactions (III) → (*A*) → (IV), which are also realised



from pure (III). The structure of (IV) is proved by hydrogenation (colloidal Pt; AcOH; 1 H_2 absorbed) to *Et hexahydrolutidine-3-carboxylate*, b.p. 102°/14 mm., 219°/760 mm. (*mercuri-* and *auri-chloride*, m.p. 147°; *perchlorate*, m.p. 163°). Hydrogenation (colloidal Pt) of (II) or (III) gives *Et*$_2$ *hexahydrolutidinedicarboxylate*, b.p. 154°/12·5 mm., 292°/770 mm., m.p. 58—59° [*platinichloride*, m.p. 208—210° (decomp.); *picrate*, m.p. 154°]. (III) is autoxidised in air; it absorbs 1 O_2 at room temp. to give *Et*$_2$ *2-hydroxymethylene-6-methylpiperidine-3 : 5-dicarboxylate*, b.p. 141—144°/0·7 mm., which absorbs 1 H_2 catalytically and at 100° absorbs a further 2 O_2 to give the oily *2-carboxylic acid*. R. S. C.

Formation of pyridines from 1 : 5-[αε-]diketones. K. W. MERZ and H. RICHTER (Arch. Pharm., 1937, **275**, 294—317).—Benzylidene- (I) and salicylidene-diacetophenone (II) [αγε-triphenyl- and αε-diphenyl-γ-*o*-hydroxyphenyl-penta-αε-dione] differ in their mode of condensation with NH_3 and primary bases. Dry NH_3–EtOH at room temp. converts (I) into 2 : 4 : 6-triphenylpyridine (III) [*dibromide hydrobromide*, m.p. 209—210° (decomp.), converted into (III) by C_5H_5N; *picrate*, m.p. 193·5°], *δ-imino-βδ-diphenylvalerophenone* (IV), m.p. 111—116°, and a N-free *substance*, m.p. 246—248°. (IV) is an intermediate product in this reaction and under other conditions forms the main product; it gives (III) when treated with acid or alkali, by spontaneous decomp., and when heated at 120°. Formation of (III) instead of the dihydropyridine is due to dehydrogenation, which leads also to some hydrogenation of (I) during the reaction; with NH_2Et (I) gives (III), evolution of C_2H_6 taking place instead of the dehydrogenation. With $C_6H_2(NO_2)_3$·OH in hot EtOH (IV) affords 2 : 4 : 6-*triphenyl-1 : 4-dihydropyridin*

picrate, m.p. 155°, without dehydrogenation. In AcOH at 100° (IV) affords by disproportionation (III) and 2 : 4 : 6-*triphenyltetrahydropyridine*, m.p. 125·5°. With H_2–Pt in EtOH at 45—50° (IV) yields ε-*amino*-αγε-*triphenylpentan*-α-*ol*, an oil [*hydrochloride*, m.p. 274—275° (decomp.); *H oxalate*, +*x*EtOH, m.p. 115·5°; *carbamide* derivative, m.p. 171—172°; with Ac_2O gives 1-*acetyl*-2 : 4 : 6-*triphenylpiperidine*, m.p. 161°]. Condensation of (II) with NH_3 and NH_2R occurs without dehydrogenation, giving 2 : 6-*diphenyl*-4-o-*hydroxyphenyl*-1 : 4-*dihydropyridine* (V), m.p. 145·5—146°, 1-*methyl*- (VI), m.p. 121°, and 1-*ethyl*-2 : 6-*diphenyl*-4-o-*hydroxyphenyl*-1 : 4-*dihydropyridine*, m.p. 128—129°, hydrolysed to the starting materials by hot AcOH or mineral acid. Disproportionation to 2 : 6-*diphenyl*-4-o-*hydroxyphenylpyridine*, m.p. 179°, and resinous substances occurs when (V) is heated at 190°. PtO_2-hydrogenation of (V) in EtOH at 50° gives 2 : 6-*diphenyl*-4-o-*hydroxyphenylpiperidine*, m.p. 143—144° (*Bz*$_2$ derivative, m.p. 147·5°), which with MeI–MgO in MeOH yields the *methiodide*, m.p. 217—219° (decomp.), of 2 : 6-*diphenyl*-4-o-*hydroxyphenyl*-1-*methylpiperidine*, m.p. 165·5°, obtained by hydrogenation of (VI). With $(CH_2{\cdot}NH_2)_2,H_2O$ at 140—150° or, less well, in EtOH at room temp. (I) yields 2 : 4 : 6-*triphenyl*-1-β-*aminoethyl*-1 : 4-*dihydropyridine*, m.p. 136°, the structure of which is proved by the similarity of its absorption spectrum to that of (VI); similarly at 165—170° (II) affords 2 : 4-*diphenyl*-4-o-*hydroxyphenyl*-1-β-*aminoethyl*-1 : 4-*dihydropyridine*, m.p. 150°. With N_2H_4,H_2O at 130° (I) gives 1-*amino*-2 : 4 : 6-*triphenyl*-1 : 4-*dihydropyridine*, m.p. 158·5—159°. R. S. C.

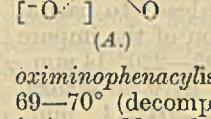
(A) **Hydrogenation of pyridine and pyridine bases under pressure in presence of nickel–silica gel catalysts.** M. I. Uschakov and A. I. Bronevski. (B) **Relative velocity of catalytic hydrogenation of pyridine and picolines in the hydrogenation of mixtures of pyridine bases.** M. I. Uschakov and E. V. Jakovleva (J. Gen. Chem. Russ., 1937, **7**, 750—752, 753—758).—(A) The velocity of hydrogenation (Ni–SiO_2 gel catalyst) at 150—200°/50—100 atm. falls in the series C_5H_5N > α- > β- > γ-picoline.

(B) C_5H_5N and α-picoline can be separated from their mixtures with β- and γ-picoline by fractional hydrogenation, as piperidine and α-pipecoline, as above, or by hydrogenation of the hydrochlorides, using a Pt catalyst. R. T.

Direct iodination of pyridine. Z. Rodewald and E. Plažek (Ber., 1937, **70**, [*B*], 1159—1162).—C_5H_5N and I do not react when heated in a sealed tube under varied conditions. Treatment of molten C_5H_5N,HCl with I gives pentaiodopyridine (I) in very small yields whilst most of the C_5H_5N remains unattacked. (I) and 3 : 5-*di-iodopyridine* (II), m.p. 173° (constitution established by conversion into 3 : 5-diaminopyridine), are formed when the vapours of C_5H_5N and I are heated. Replacement of I by ICl does not give appreciable improvement and considerable amounts of 2-chloropyridine result; addition of Hg or Fe salts is without influence. 2-Pyridyl-1-pyridinium iodide is obtained from C_5H_5N,HCl and I or ICl. The best yield results by the action of I in fuming H_2SO_4 (50% SO_3), whereby 3-iodopyridine (III) (yield 18%) and (II) are produced. 2- or 4-Iodopyridine could not be thus obtained and (III) could not be converted into (II). H. W.

Enol betaines. V. Reactions with acid chlorides. F. Kröhnke (Ber., 1937, **70**, [*B*], 1114—1117; cf. this vol., 208, 209).—Agitation of phenacylpyridinium bromide, BzCl, and K_2CO_3 in $CHCl_3$–H_2O gives dibenzoylmethylpyridinium enol betaine, decomp. 214—215° when slowly heated (cf. A., 1935, 987), decomposed by AcOH at 100° to BzOH and phenacylpyridinium salt. Similarly CHPh:CH·COCl affords *benzoylcinnamoylmethylpyridinium enol betaine* m.p. 185—186° (decomp.), best isolated as the *perchlorate*, m.p. 174—175°. o-*Phthaloyldiphenacylpyridinium enol betaine*, decomp. about 160°, and *phenacylpalmitoylpyridinium enol betaine*, m.p. 90—92°, are described. Quinoline and $CHBz_2Br$ at 36° slowly yield *dibenzoylmethylquinolinium enol betaine*, decomp. about 240°. *p*-Chloro- and *p*-bromo-phenacylpyridinium enol betaine yield additive *compounds*, m.p. 85° after slight decomp. and m.p. 80—90°, respectively, with BzCN. H. W.

Coloured oximinobetaines. F. Kröhnke and H. Kübler (Ber., 1937, **70**, [*B*], 1117—1120).—Treatment of phenacylpyridinium bromide (I) in 50% EtOH with an excess of amyl (II) or Et nitrite and *N*-NaOH at 0° gives the unstable basic *bromide* (III), m.p. about 55° (decomp.), transformed by *N*-HBr into *oximinophenacylpyridinium bromide* (IV), OH·N:CBz·N(C_5H_5)Br, m.p. 147° (decomp.) [corresponding *perchlorate*, m.p. 115° (decomp.)], also obtained directly from (I), $NaNO_2$, and *N*-HBr at 0°, or from (I) and (II) in EtOH at 0° or when heated. (III) is converted by 1·4*N*-K_2CO_3 at 35° into labile *oximinophenacylpyridinium enol betaine* (V), m.p. 46—48° (decomp.) varying with the mode of heating, which rapidly decomposes on contact with glass or earthenware but can be preserved on agate. It is transformed by the requisite amounts of HBr into (III) or (IV). When triturated with abs. EtOH (V) is transformed into red *needles*, m.p. about 42° (decomp.). When heated with 0·5—1*N*-NaOH (V) passes into a more stable, yellow *betaine*, decomp. about 61°. The constitution *A* for (V) is supported by the analogous formation of *oximinophenacylisoquinolinium bromide*, m.p. 161—162° (decomp.), and its conversion into the more stable *oximinophenacylisoquinolinium enol betaine*, m.p. 69—70° (decomp.). The betaine derived from *oximino*-p-*chlorophenacylpyridinium bromide*, m.p. 125° (decomp.), is more sensitive than the corresponding Cl-free derivative. *p*-Nitrobenzylisoquinolinium bromide appears to be transformed by NaOH (not Na_2CO_3) and $CHCl_3$ into the corresponding *aci*-nitrobetaine. H. W.



Synthesis of 2 : 4-dihydroxyquinoline derivatives from malonic esters and aromatic amines. A. Meyer and P. Heimann (Compt. rend., 1937, **204**, 1204—1206).—Arylamides of malonic esters, heated with paraffin oil to 250°, lose H_2O and give 2-hydroxy-4-alkoxyquinolines; under the same conditions, arylamides of *C*-substituted malonic esters lose EtOH

yielding 2 : 4-dihydroxy-3-alkylquinolines, whilst PCl_5 as condensing agent gives 2 : 3-dichloro-4-alkoxyquinolines. The following are prepared: 6-*chloro*-2-*hydroxy*-4-*ethoxy*-, m.p. 91°, 2-*hydroxy*-4-*ethoxy*-6-*methyl*-, m.p. 138°, 2-*hydroxy*-4-*ethoxy*-8-*methyl*-, m.p. 190°, 6-*chloro*-2 : 4-*dihydroxy*-3-*ethyl*-, m.p. 264°, 2 : 4-*dihydroxy*-8-*methyl*-3-*ethyl*-, m.p. 218°, 4 : 6-*dichloro*-2-*hydroxy*-, m.p. 138°, 2 : 3 : 8-*trichloro*-4-*ethoxy*-, m.p. 63·5°, 2 : 3 : 4 : 6-*tetrachloro*-8-*methoxy*-, m.p. 127°, and 2: 4-*dichloro*-8-*methoxy*-, m.p. 92° *quinoline*. J. D. R.

Reactivity of methoxy-derivatives of 3-nitropyridine and new derivatives of 3 : 4-pyridinopyrazine. O. Bremer (Annalen, 1937, **529**, 290—298).—Successive treatments of 4-pyridone nitrate with fuming H_2SO_4 and PCl_5–$POCl_3$ and of the product with MeOH at ≯20° give 3-*nitro*-4-*methoxypyridine hydrochloride*, converted by aq. K_2CO_3 into 3-nitro-4-methoxypyridine (I), m.p. 75°. $CHNa(CO_2Et)_2$ and (I) in boiling abs. EtOH give *Et*$_2$ 3-*nitro*-4-*methoxypyridylmalonate*, b.p. 157°/3 mm., hydrolysed by boiling 18% HCl to 3-*nitro*-4-*methylpyridine*, b.p. 85°/3 mm. [*hydrochloride*, m.p. 176° (decomp.)], transformed by PhCHO and piperidine at 160—170° into 3-*nitro*-4-*stilbazole*, m.p. 114—115°. Diazotisation of 3-amino-4-methoxypyridine followed by treatment with Cu powder–CuCl yields 3-*chloro*-4-*methoxypyridine*, b.p. 83—84°/3 mm. (*hydrochloride*). 5-Bromo-3-nitro-4-hydroxypyridine and PCl_5 containing a little $POCl_3$ at 160° give 4-*chloro*-5-*bromo*-3-*nitropyridine* (II), m.p. 49—50°, which with $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ at 100° gives 5-*bromo*-3-*nitro*-4-β-*hydroxyethylaminopyridine*, m.p. 120—121°. (II) and NaOMe in abs. MeOH afford 5-*bromo*-3-*nitro*-4-*methoxypyridine*, m.p. 39—40°; 5-*bromo*-3-*nitro*-6-*methoxypyridine* (III), m.p. 89°, is obtained similarly. At 170—180° (I) passes into 3-*nitro*-1-*methyl*-4-*pyridone*, m.p. 220°. $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ and (III) at 100° give 5-*bromo*-3-*nitro*-6-β-*hydroxyethylaminopyridine*, m.p. 136°. 3-Amino-4-butylaminopyridine and $Et_2C_2O_4$ at 170° give 2-*hydroxy*-3-*keto*-4-*butyl*-3 : 4-*dihydropyridino*-(3′ : 4′)-5 : 6-*pyrazine*, m.p. 256°; 2-*hydroxy*-3-*keto*-4-*phenyl*-3 : 4-*dihydropyridine*-(3′ : 4′)-5 : 6-*pyrazine*, m.p. >325°, is obtained similarly from 3-amino-4-anilinopyridine. H. W.

Esters of nicotinic acid. J. L. Goldfarb (J. Appl. Chem. Russ., 1937, **10**, 515—520).—The following esters have been prepared from nicotinyl chloride and the appropriate alcohol: *benzyl*, b.p. 179°/9 mm. (*methiodide*, m.p. 159—160°; *hydrochloride*, m.p. 72—74°; *picrate*, m.p. 156—157°), *furfuryl*, b.p. 152°/6 mm., m.p. 32—34° (*methiodide*, m.p. 137°; *hydrochloride*, m.p. 130°; *picrate*, m.p. 128°), β-*naphthyl*, b.p. 197—199°/1 mm., m.p. 160° (*methiodide*, m.p. 191—194°; *hydrochloride*, m.p. 191—194°; *picrate*, m.p. 177·5—178·5°), and cyclo*hexyl*, b.p. 150°/7 mm. (*methiodide*, m.p. 114·5—115·5°; *hydrochloride*, m.p. 120°; *picrate*, m.p. 116°), *nicotinate*. R. T.

Xanthurenic acid. I—III. Xanthurenic acid, kynurenic acid, and kynurenine. L. Musajo (Gazzetta, 1937, **67**, 165—171, 171—178, 179—188).—I. Urine of albino rats on a hyperprotein diet (almost entirely fibrin) contains the *Na* salt (+2H_2O) of *xanthurenic acid* (I), $C_{10}H_7O_4N$ [*Me* ester (II), m.p. 262°], which gives an intense green colour with aq. $FeSO_4$.

II. The *Ba*, *Cu*, and *Na*$_2$ salts of (I) are prepared. In C_5H_5N, (II) gives a *Bz*$_2$ derivative, m.p. 171°. When distilled with Zn in H_2, (I) yields quinoline. Heated at 300°, (I) loses CO_2; the HCl extract contains the *hydrochloride*, m.p. >300°, of a *dihydroxyquinoline*, m.p. >300° (*Bz*$_2$ derivative, m.p. 178°). With $POCl_3$–PCl_5, (I) gives a *Cl*-derivative, $C_{10}H_6O_3NCl$, m.p. 209—210° (decomp.); with Ac_2O, (I) gives the reddish-violet colour of a 2-hydroxyquinolinecarboxylic acid. Other colour reactions of (I), in comparison with kynurenic acid (III), are described.

III. The urine from which (I) is extracted contains small amounts of (III) and of kynurenine (IV). The urine of rabbits on a fibrin diet also contains (I), (III), and (IV); that of dogs contains (III) and (IV) only. A method for obtaining increased amounts of (IV) by injecting tryptophan into rabbits is described. E. W. W.

Quinolyl-4-pyruvic and -acetic acid. W. Borsche and L. Bütschli (Annalen, 1937, **529**, 266—273).—The side chains of the 2- are more active than those of the 4-quinolyl compounds. Et quinolyl-4-pyruvate (I) [2 : 4-*dinitrophenylhydrazone*, m.p. 179°, and its *hydrochloride*, m.p. 239—240° (decomp.)] and PhCHO in presence of piperidine at 140° afford α-*keto*-γ-*hydroxy*-γ-*phenyl*-β-4-*quinolylbutyrolactone*, m.p. 227° (decomp.), whilst with β-$C_{10}H_7{\cdot}NH_2$ in AcOH at 100° they give 4 : 5-*diketo*-2-*phenyl*-1-2′-*naphthyl*-3-4″-*quinolylpyrrolidine*, m.p. 180° (with a *substance*, decomp. 277°). (I) with the requisite diazo-compound in AcOH containing NaOAc yields the β-*phenylhydrazone*, m.p. 174° (decomp.), and β-p-*tolylhydrazone*, m.p. 172° (decomp.), of αβ-*diketo*-β-4-*quinolylpropionic acid*. *Et* αβ-*diketo*-β-4-*quinolylpropionate* β-p-*tolylhydrazone* has m.p. 147°. *Et* α-*oximino*-β-4-*quinolylpropionate*, m.p. 183—184°, is hydrolysed by alkali to the corresponding *acid*, m.p. 198° (decomp.), which passes at 200° into *quinolyl*-4-*acetonitrile* (II), m.p. 144—145°. With the requisite diazo-compound this gives the *phenylhydrazone*, m.p. 168°, and p-*anisylhydrazone*, m.p. 188°, of *quinolyl*-4-*glyoxylonitrile* and with *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ in MeOH it affords the corresponding p-*dimethylaminoanil*, m.p. 133—135°. With PhCHO, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, and *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ (II) in presence of piperidine gives α-4-*quinolylcinnamonitrile*, m.p. 139—140°, p-*methoxy*-α-4′-*quinolylcinnamonitrile*, m.p. 143—144°, and 3-4′-*quinolylcoumarin*, m.p. 194°, whilst with isatin it affords 2-*keto*-3-4′-*quinolylcyanomethene*-2 : 3-*dihydroindole*, m.p. 278°. With EtOH–HCl at 100° (II) gives *Et* 4-*quinolylacetate*, m.p. 64° (*picrate*, m.p. 157°, after softening), which affords *Et* 4-*quinolylglyoxylate phenylhydrazone*, m.p. 196°, and is hydrolysed by 2*N*-NaOH to 4-*quinolylacetic acid*, m.p. 90° (much decomp.). H. W.

Reactivity of benzylacetone in Pfitzinger's reaction. G. B. Crippa and E. Scevola (Gazzetta, 1937, **67**, 119—122).—Isatin in 50% KOH with $COMe{\cdot}CH_2{\cdot}CH_2Ph$ gives 2-β-phenylethylquinoline-4-carboxylic acid (A., 1927, 1200). E. W. W.

Synthesis of 1-benzyltetrahydro*iso*quinoline bases. E. Späth, F. Kuffner, and F. Kesztler (Ber., 1937, **70**, [*B*], 1017—1019).—Homopiperonal and homopiperonylamine are kept in Et_2O at 15—20° for 30 min. The solution is evaporated and the residue is shaken violently with HCl (1 : 1) at 100° for 1 hr., whereby 6 : 7-3′ : 4′-dimethylenedioxy-1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m.p. 84—85°, is obtained in 2·33% yield. It is further identified by conversion into 2 : 3-12 : 13-dimethylenedioxyberbine, m.p. 213—214°. The observations of Hahn and Schales (A., 1936, 618) could not be confirmed. H. W.

Imidochlorides. V. Synthesis of hydroxycarbethoxyphenyl-α- and -β-naphthaquinolines. V. R. Heeramaneck and R. C. Shah (J.C.S., 1937, 867).—Et α- and β-naphthyliminobenzylmalonate are cyclised by heating to *Et* 4-*hydroxy*-2-*phenyl*-α-*naphthaquinoline*-3-*carboxylate*, m.p. 228—230°, and *Et* 1-*hydroxy*-3-*phenyl*-β-*naphthaquinoline*-2-*carboxylate*, m.p. 280—282° (*acid*, m.p. 248—250°; *picrate*, m.p. 179—181°). F. R. S.

Medicinal products from acridine compounds. III. Tetrahydro-derivatives. O. J. Magidson and A. I. Travin (J. Gen. Chem. Russ., 1937, **7**, 842—852).—5-Chloroanthranilic acid and *cyclo*hexanone (I) (150°; 90 min.) yield 7-*chloro*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 385°, which with $POCl_3$ (120°; 3 hr.) gives 5 : 7-*dichloro*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 84—85°, and this with PhOH (120°; 3 hr.) gives 7-*chloro*-5-*phenoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 127—128°, and with PhOH and NH_2·CHMe·$[CH_2]_4$·NEt_2 (180°; 5 hr.) yields 7-*chloro*-5-(δ-N-*diethylamino*-α-*methylbutyl*)*amino*-1 : 2 : 3 : 4-*tetrahydroacridine*, b.p. 230—240°/1 mm. (*meconate*, decomp. at 85—90°). 4-Chloroanthranilic acid and (I) yield 8-*chloro*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 380°, from which 5 : 8-*dichloro*-, m.p. 87—89°, 8-*chloro*-5-*iodo*-, m.p. 115—116°, and 8-*chloro*-5-(δ-N-*diethylamino*-α-*methylbutyl*)*amino*-1 : 2 : 3 : 4-*tetrahydroacridine* are prepared as above. 5-Nitroanthranilic acid and (I) at 220° yield 7-*nitro*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 324—325°, identical with that obtained by nitration of 1 : 2 : 3 : 4-tetrahydroacridone at −15°, and from which 5-*chloro*-7-*nitro*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 148—149°, is obtained with $POCl_3$ at 125° (3 hr.). 5-*Chloro*-8-*nitro*-, m.p. 149—150°, and 8-*nitro*-5-(δ-N-*diethylamino*-α-*methylbutyl*)*amino*-1 : 2 : 3 : 4-*tetrahydroacridine* (*meconate*, decomp. at 110—115°) are prepared analogously. 1 : 2 : 3 : 4-Tetrahydroacridine-5-carboxylic acid and $POCl_3$ (100°; 1 hr.) yield the acid *chloride*, m.p. 198—200° (decomp.), from which the *diethylamide*, m.p. 102—103° (*hydrochloride*, m.p. 245—246°), and β-N-*diethylaminoethylamide dihydrochloride*, m.p. 246—248°, and the β-N-*diethylaminoethyl ester* (*dihydrochloride*, m.p. 188—189°) are prepared. R. T.

Acridones. X. *p*-Chlorophenylanthranil and 3-chloroacridone. I. Tanasescu and A. Silberg (Bull. Soc. chim., 1936, [v], **3**, 2383—2385; cf. A., 1936, 1509).—*p*-Aminophenylanthranil (I) (A., 1933, 275) is converted (Sandmeyer) into p-*chlorophenylanthranil*, m.p. 152°, which with boiling H_2O, EtOH, Zn, and $CaCl_2$ gives 4-*chloro*-2′-*aminobenzophenone*, m.p. 120° (*Bz* derivative, m.p. 136°), and with $NaNO_2$ and conc. H_2SO_4 gives 3-chloroacridone. Attempts to convert (I) into 3-aminoacridone by this method failed. H. G. M.

Photoluminescence spectrum of glycerol solution of trypaflavine.—See A., I, 346.

Syntheses of isomeric ethylphenanthridines. H. Kondo and S. Uyeo (Ber., 1937, **70**, [*B*], 1094—1097).—Treatment of *o*-C_6H_4Br·CHO and 1 : 3 : 2-C_6H_3EtBr·NH_2 with Cu powder at 230—240° gives 1-*ethylphenanthridine*, b.p. 110—140° (bath)/0·03 mm. [*picrate*, m.p. 231°; *styphnate*, m.p. 226° (decomp.); double *compound* with $HgCl_2$, m.p. 212—219°]. 3 : 1 : 4-NO_2·C_6H_3Et·NH_2 is transformed into 4-*bromo*-3-*nitroethylbenzene*, b.p. 127°/4 mm., reduced to 4-*bromo*-3-*aminoethylbenzene*, b.p. 113—115°/4·5 mm. (*Ac* derivative, m.p. 108—109°), which with *o*-C_6H_4Br·CHO and Cu powder at 240—250° gives 2-*ethylphenanthridine*, b.p. 110—140°/0·04 mm. (*picrate*, m.p. 216°; *styphnate*, decomp. 236°). *p*-C_6H_4Et·NHAc and Br in AcOH afford 3-*bromo*-4-*acetamidoethylbenzene*, m.p. 92°, hydrolysed to 3-*bromo*-4-*aminoethylbenzene*, b.p. 100—101°/3 mm., m.p. about 9°, which with *o*-C_6H_4Br·CHO gives 3-*ethylphenanthridine*, b.p. 120—130° (bath)/0·05 mm., m.p. 62—63·5° [*styphnate*, m.p. 252° (decomp.); *picrate*, m.p. 230°]. *o*-C_6H_4Et·NHAc is converted by conc. HNO_3 in Ac_2O–AcOH at 0° into the 3-NO_2-derivative, hydrolysed to 3-*nitro*-2-*aminoethylbenzene*, b.p. 146—149°/5 mm., m.p. 29—30·5° (*hydrochloride*). The base is transformed into 2-bromo-3-nitroethylbenzene and thence into 2-*bromo*-3-*aminoethylbenzene* (*Ac* derivative, m.p. 112°), which affords 4-*ethylphenanthridine* [*picrate*, m.p. 223° (decomp.); *styphnate*, m.p. 216° (decomp.)]. H. W.

New ring systems. III. Phenyl-1 : 2-methoxynaphthylamine *o*-8-ketone. W. Knapp (Monatsh., 1937, **70**, 251—258).—1-$C_{10}H_7Br$ and *o*-NH_2·C_6H_4·CO_2H are converted by Cu powder and anhyd. K_2CO_3 in boiling $PhNO_2$ into o-1′-*naphthylaminobenzoic acid* (I), m.p. 207°, and o-*di*-1′-*naphthylaminobenzoic acid*, m.p. 272—274° (decomp.). (I) and P_2O_5 in boiling PhMe afford 3 : 4-benzacridone, m.p. 365—366° (incipient decomp.). 1 : 2-$C_{10}H_6Br$·OMe (improved prep. from β-$C_{10}H_7$·OMe and Br in AcOH) similarly yields o-2′-*methoxy*-1′-*naphthylaminobenzoic acid* (II), m.p. 208—209° (sparingly sol. *alkali* salts), more advantageously obtained from 1 : 2-NH_2·$C_{10}H_6$·OMe and *o*-C_6H_4Cl·CO_2H, and o-*di*-2′-*methoxy*-1′-*naphthylaminobenzoic acid*, m.p. 250—251° (cryst. *alkali* salts). *Phenyl*-1-2-*methoxynaphthylamine* o-8-*ketone* (III), $C_6H_4<^{NH}_{CO}>C_{10}H_5$·OMe, m.p. 190—192°, is obtained from (II) and P_2O_5 in boiling PhMe. Treatment of (II) with PCl_5 gives a reddish-brown mixture, apparently unchanged by $AlCl_3$ and giving a product not identical with (III). When heated above its m.p. (I) gives NHPh·$C_{10}H_7$-α; similarly (II) affords *phenyl*-2-*methoxy*-α-*naphthylamine*, m.p. 82—83°. H. W.

Identification of phenylhydrazones and isomeric pyrazolines obtained from chalkones. L. C. Raiford and W. J. Peterson (J. Org. Chem., 1937, **1**, 544—552).—Chalkonephenylhydrazones on filter-paper with Br vapour give a yellow colour, changing to orange or brick-red; the isomeric pyrazolines give an immediate green colour. Differentiation is also possible by reduction and by crystal form. Hydrogenation (PtO_2) of COPh·CH:CHPh and *p*-C_6H_4Cl·CO·CH:CHPh gives COPh·C_2H_4Ph (*phenylhydrazone*, an oil) and p-*chloro*-β-*phenylpropiophenone*, m.p. 73° (*oxime*, m.p. 91—92°). Na–Hg–CO_2 reduces chalkones and their phenylhydrazones to β-phenylpropiophenones and their phenylhydrazones, respectively, but does not affect 1 : 3 : 5-triphenylpyrazolines; Na–EtOH reduces the phenylhydrazones to NH_2Ph. The following are described: *phenylhydrazones*, m.p. 116—118°, 101—102°, and 106—107°, of *p*-bromo-, -methyl- (forms, m.p. 77°, 55—56°, and 44°), and -methoxy-β-phenylpropiophenone, respectively; 1 : 5-*diphenyl*-3-p-*chloro*-, m.p. 150—150·5°, -*bromo*-, m.p. 156—157°, -*hydroxy*-, m.p. 116—118°, -*methoxy*-, m.p. 141—141·5°, -*acetoxy*-, m.p. 165—166°, -m-*nitro-phenyl*-, m.p. 131°, and -3-p-*tolyl-pyrazoline*, m.p. 152—153°. R. S. C.

Action of ethyl oxalate on pyrazolones. G. Perroncito (Gazzetta, 1937, **67**, 158—164).—1-Phenyl-3-methylpyrazol-5-one (I) and $Et_2C_2O_4$ at 180° give *bis*-(1-*phenyl*-3-*methyl*-5-*keto*-4-*pyrazolylene*)-*glycol Et*$_2$ *ether* (II), m.p. 163° (*Br*$_4$ additive compound, m.p. 80°). $Me_2C_2O_4$ gives the *Me*$_2$ *ether* (III), m.p. 193°. $H_2C_2O_4$ gives methenyldi-(1-phenyl-3-methylpyrazol-5-one) (A., 1930, 1182). With boiling 20% KOH, (II) or (III) gives *bis*-(1-*phenyl*-3-*methyl*-5-*keto*-4-*pyrazolyl*) *diketone*, m.p. 137° (corresponding *quinoxaline*, m.p. >300°; *monophenylhydrazone*). With Zn–AcOH, (II) yields *bis*-(1-*phenyl*-3-*methyl*-5-*keto*-4-*pyrazolyl*)*glycol Et*$_2$ *ether*, m.p. 208°.

E. W. W.

Derivatives of *cyclo*tetramethylenepyrazole and their molecular compounds with substituted barbituric acids. H. Ruhkopf (Ber., 1937, **70**, [*B*], 939—942).—Et *cyclo*hexan-2-onecarboxylate and NHPh·NH_2 afford the corresponding *phenylhydrazone*, m.p. 98°, which passes when heated into 1-*phenyl*-3 : 4-*cyclotetramethylenepyrazol*-5-*one*, b.p. ~200°/12 mm., m.p. 180°, whence the 2-*methyl* (I), b.p. 220°/12 mm., m.p. 106·5°, 2-*ethyl*, b.p. ~250°/12 mm., m.p. 106°, 2-*benzyl*, b.p. 294°/40 mm., m.p. 82°, and 2-*acetyl*, b.p. 225°/40 mm., m.p. 131°, derivatives. *cyclo*Tetramethylenepyrazolones, unsubstituted at 2, do not give mol. compounds with barbituric acids. Such *compounds* (1 : 1), m.p. 108°, 161°, and 120·5°, respectively, are given by (I) with diethyl-, dipropyl-, (II), and allyl*iso*propyl- (III) -barbituric acid. Similar *compounds* (1 : 1), m.p. 146·5° and 140°, respectively, are obtained from 1-phenyl-2-methyl-3 : 4-*cyclo*trimethylenepyrazol-5-one and (II) or (III). H. W.

Action of hydroxylamine and hydrazine on acetylenic thioamides. D. E. Worrall (J. Amer. Chem. Soc., 1937, **59**, 933—934).—CPh:CNa and PhNCO in Et_2O give *phenylpropiolthioanilide*, decomp. 113—114°, sol. in NaOH, decomposed by heat at 100°, by acid in EtOH, Hg salts, or Br; in hot EtOH it gives the *dimeride*, CPh:C·C(NPh)·S·CPh:CH·CS·NHPh, sinters at about 250°, sol. in NaOH, and yields with Br a *dibromide*, decomp. 226—227°, and decomp. products; with NH_2OH it gives 3-*anilino*-5-*phenyl*isooxazole, m.p. 142—143° [yields 3-p-*bromo*-, m.p. 158° (gives BzOH, when oxidised), and 3-2′ : 4′-*dinitro-anilino*-5-*phenyl*-isooxazole, m.p. 245—246°], and some 1-*phenacyl*-*benzthiazole*, m.p. 190—191°; with NHPh·NH_2 it gives 3-*anilino*-1 : 5-*diphenylpyrazole*, m.p. 153—154° [*Br*$_2$-, m.p. 181°, and (*NO*$_2$)$_3$-derivative, m.p. 197—198°], and with N_2H_4 yields 3-*anilino*-5-*phenyl*-*pyrazole*, m.p. 166—167°, which affords 3-2′ : 4′ : 6′-*tri-bromo*-, decomp. 206—207°, and -*nitro-anilino*-5-*phenylpyrazole*, decomp. 266°. R. S. C.

Lactim–lactam tautomerism. I. Oxidation by perbenzoic acid of the double linking between carbon and nitrogen. M. M. Botvinnik and N. L. Gavrilov. **II. Oxidation of glyoxaline and its derivatives by perbenzoic acid.** M. M. Botvinnik and M. A. Prokofiev (J. pr. Chem., 1937, [ii], **148**, 170—190, 191—204).—I. BzO_2H (I) in $CHCl_3$ is a quant. reagent for the (fixed) C:N linking; the amount used is determined iodometrically. It oxidises (CHPh:N·CH_2·CO_2)$_2$Ba to NH_3, $H_2C_2O_4$, and BzOH. Histidine dihydrochloride (II), NH:C(NH_2)$_2$, and trimethyloxazole are all oxidised, with decomp. NH_2Me, NH_2·CH_2·CO_2H (III), NH_2·CHMe·CO_2H, CO(NH_2)$_2$, (CO·NH_2)$_2$, and NHBz·CH_2·CO_2H are not oxidised, nor are Abderhalden's enolised NH_2-acid anhydrides, nor uric acid (IV), or *iso*leucylhydantoin (V). The K salt of (IV) and *OO*′-dibenzylglycine anhydride are, however, oxidised. Thus (I) does not oxidise a lactim unless displacement of equilibrium to the lactam is excluded. In presence of MgO, however, (III), (IV), and (V) are oxidised by (I). The action of (I) on CH_2Ac·CO_2Et and on CH_2Bz·COMe (A., 1930, 1579) is confirmed.

II. Oxidation of glyoxaline by (I) is dependent on time and on concn. of (I); the intermediate *glyoxaline dioxide*, $C_3H_4O_2N_2$, decomp. 135°, is isolated; CO(NH_2)$_2$, but no $H_2C_2O_4$, is formed. Glyoxaline-4 : 5-dicarboxylic acid is not oxidised: it even stabilises (I). The oxidation of (II) and of 2-methyl-4 : 5-dihydroglyoxaline by (I) is studied. E. W. W.

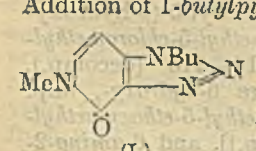
Synthesis of aneurin. T. Hoshino and M. Ohta (Proc. Imp. Acad. Tokyo, 1937, **13**, 101—102).—Aneurin is synthesised from 4-methyl-5-(β-hydroxyethyl)thiazole and 6-*amino*-2-*methyl*-5-*chloromethyl*-*pyrimidine hydrochloride*, m.p. 214—215° (decomp.). Other compounds mentioned are 6-*hydroxy*-, m.p. 183—184°, and 6-*amino*-2-*methyl*-5-*ethoxymethyl*-[*hydrochloride*, m.p. 212° (decomp.)], and 6-*amino*-2-*methyl*-5-*hydroxymethyl*-*pyrimidine*, m.p. 195—196° [*hydrochloride*, m.p. 218—219° (decomp.)]. A. Li.

Degradation of histidine and other glyoxaline derivatives by ascorbic acid. S. Edlbacher and A. von Segesser (Biochem. Z., 1937, **290**, 370—377).—A measurable but small amount of deamination occurs when a mixture of histidine (I) and ascorbic acid is oxygenated at 38°, but when to the mixture in PO_4''' buffer at p_H 7 traces of $Fe_2(SO_4)_3$

or hæmin are added and O_2 is bubbled through, 80% of (I) is decomposed and subsequent alkalisation to the phenolphthalein red colour gives one, and more strongly with excess of NaOH gives two, equivs. of N as NH_3. Oxidative disruption of the glyoxaline ring must therefore have occurred. The reaction does not occur when N_2 replaces O_2. When subjected to the same treatment, (I) Me ester, glyoxalinyl-lactic acid, methylhistidine, histamine, hydroxymethylglyoxaline, and glyoxaline behave similarly, whilst glycine, alanine, phenylalanine, dihydroxyphenylalanine, tyrosine, valine, leucine, arginine, ornithine, aspartic and glutamic acids, proline, creatine, uric acid, allantoin, thymine, guanine, dialuric acid, and sturine give only traces of NH_3 and hypoxanthine, adenine, and carnosine give 30% and cystine and serine 25% of NH_3. P. W. C.

Condensations of aromatic amines with formaldehyde in media containing acid. V. Substituted dihydroquinazolines from *p*-chloroaniline and *p*-bromoaniline. E. C. WAGNER and A. EISNER (J. Amer. Chem. Soc., 1937, 59, 879—883).—*p*-$C_6H_4Br{\cdot}NH_2$ and CH_2O in dil. HCl at room temp. give 6-*bromo*-3-p-*bromophenyl*-3 : 4-*dihydroquinazoline* (I), m.p. 205·8° (25·9%; *picrate*, m.p. 242°) [obtained, but not identified, by Cairncross *et al.* (A., 1936, 487)], a *base*, b.p. 134—135°, and small amounts of methylated products (cf. *loc. cit.*). *p*-$C_6H_4Cl{\cdot}NH_2$ yields similarly 6-*chloro*-3-p-*chlorophenyl*-3 : 4-*dihydroquinazoline* (II), m.p. 192° (*picrate*, m.p. 239°), and a *base*, m.p. 135°. (*p*-$C_6H_4Cl{\cdot}N{\cdot}CH_2{\cdot})_3$, m.p. 151°, *p*-$C_6H_4Cl{\cdot}NH_2$, and *p*-$C_6H_4Cl{\cdot}NH_2$,HCl in $PhNO_2$ at 80—90° give 4-*chloro*-N-5′-*chloro*-2′-*aminobenzylaniline*, m.p. 93° (*benzylidene* derivative, m.p. 139°), converted by CH_2O in KOH–EtOH into 6-*chloro*-3-p-*chlorophenyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, m.p. 158°, and by 90% HCO_2H at 100° into (II). Similarly the *trimeride*, m.p. 168·8°, of p-*bromo*-N-*methyleneaniline* gives p-*bromo*-N-5′-*bromo*-2′-*aminobenzylaniline*, m.p. 117·6° (*benzylidene* derivative, m.p. 144·6°) [with a little (I)], 6-*bromo*-3-p-*bromophenyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline* (III), m.p. 173°, and (I). Reduction of (I) and (II) could not be effected without dehalogenation. With Na–EtOH (I), (II), and (III) give 3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline. M.p. are corr. R. S. C.

Pyridino-3 : 4-triazoles. II. O. BREMER (Annalen, 1937, **529**, 288—290; cf. A., 1935, 993).—Addition of 1-*butylpyridino*-(3′ : 4′)-4 : 5-*triazole methosulphate* and KOH to aq. $K_3Fe(CN)_6$ at 0° gives 2′-*keto*-1′-*methyl*-1-*butyl*-1 : 2-*dihydropyridino*-(3′ : 4′)-4 : 5-*triazole* (I), m.p. 112°, converted by HNO_3 (*d* 1·4) in conc. H_2SO_4 at >5° into the 5′-*nitro*-, m.p. 103°, by Br in AcOH–KOAc into the 5′-*bromo*-, m.p. 138°, and by PCl_5 and $POCl_3$ into the 5′-*chloro*-, m.p. 136°, -derivative.



(I.)

H. W.

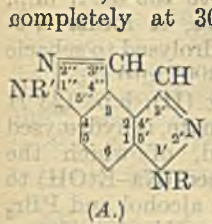
Hydrazine derivatives analogous to barbituric and uric acid. B. HEPNER and S. FAJERSZTEJN (Bull. Soc. chim., 1937, [v], 4, 854—862).—Cyanoacethydrazide is converted by 40% NaOH at room temp. into 3-*imino*-5-*ketopyrazolidine* (I), decomp. 204° after darkening at 175°, which with a large excess of boiling Ac_2O gives 3-*imino*-5-*keto*-1 : 4 : 4-*triacetyl*-, m.p. 190—192°, and 3-*imino*-5-*keto*-2 : 4 : 4-*triacetyl*-, m.p. 130°, -*pyrazolidine*. 3-*Imino*-5-*keto*-1 : 4 : 4-*tribenzoylpyrazolidine* has m.p. 185°. (I) and PhCHO in boiling EtOH afford 3-*imino*-5-*keto*-4-*benzylidenepyrazolidine* (+2H_2O), m.p. 244°, which does not react with HNO_2. 3-*Imino*-5-*keto*-4-*oximinopyrazolidine*, m.p. >300° after changing colour at 100° and darkening at 200°, is reduced by $Na_2S_2O_4$ to (impure) 3 : 4-*diamino*-5-*hydroxypyrazole* (II) [*sulphate* (III); *hydrochloride*; *oxalate*; *acetate*; *picrate*], which strongly reduces $KMnO_4$ and NH_3–Ag_2O. (III) and CH_2O give 3-*imino*-4-*methyleneamino*-5-*ketopyrazolidine* (+2CH_2O,H_2O). (II) and PhNCS in EtOH afford 3 : 4-*diphenylthiocarbamido*-5-*hydroxypyrazole* (+1·5H_2O); attempts to prepare an analogous compound from PhNCO were unsuccessful owing to instability of the product. (II) is transformed by KCNO into 3-*imino*-4-*carbamido*-5-*ketopyrazolidine* (+H_2O), converted by heating its *Na* or *Ba* salt into 5 : 7-*dihydroxyglyoxalinopyrazole*, NH$<$CO·C·NH / NH·C·NH$>$CO. H. W.

Alloxantin series. (MISS) D. NIGHTINGALE (J. Amer. Chem. Soc., 1937, **59**, 806—808).—1-Methylalloxantin, +3H_2O, m.p. 226° (decomp.), is obtained from methylalloxan and dialuric acid or uramil. The 1′-Me isomeride, +3H_2O, m.p. 226° (decomp.), is obtained from methyluramil and alloxan. Separate identity is believed to be established by rapid pptn. of K dialurate from the 1-Me compound and slow pptn. from its isomeride by hot KOAc; the reaction of the 1′-Me compound is considered as due to gradual oxidation of the alloxan by 1-methyldialuric acid (I), which is shown to occur in a separate experiment. Similar results are obtained with 1 : 3- and 1′ : 3′-dimethylalloxantin and support the semiacetal structure of alloxantin. Benzoyldialuric acid and the substituted alloxans give *benzoyl*-1-*methyl*-, m.p. 233° (decomp.), and -1 : 3-*dimethyl*-*alloxantin*, decomp. 237°. *Benzoylmethyldialuric acid*, m.p. 185—187° (*K* salt, +H_2O), from (I) and BzCl at 120°, does not react with alloxan. R. S. C.

Action of acetaldehyde and benzaldehyde on 5-aminotetrazole. R. STOLLÉ and K. HEINTZ (J. pr. Chem., 1937, [ii], **148**, 217—220).—The reported prep. of 4-amino-1-methylmethenyl-[1 : 2 : 3 : 5]-tetrazole (cf. A., 1935, 1509) from 4-amino-[1 : 2 : 3 : 5]-tetrazole [*i.e.*, 5-amino-1 : 2 : 3 : 4-tetrazole (I)] and MeCHO is not confirmed. The actual product is an aldol derivative, 4-*γ*-*hydroxybutylideneamino*-1 : 2 : 3 : 4-*tetrazole*, m.p. 170° (*Ag* salt); (I) does not condense with BzCHO at 100°, or at 150°, at which temp. it yields guanylaminotetrazole. E. W. W.

Dipyrazolobenzenes. V. VESELÝ and A. MEDVEDEVA (Coll. Czech. Chem. Comm., 1937, **9**, 176—184).—6 : 1 : 2 : 3-$NO_2{\cdot}C_6H_2Me_2{\cdot}NHAc$ with N_2O_3 in Ac_2O gives its *NO*-derivative, m.p. 85° (decomp.), converted in boiling C_6H_6 into 5-nitro-4-methylindazole (Noelting, A., 1904, i, 690) (*Ac* derivative, m.p. 127—127·5°), reduced (Fe–AcOH) to the 5-NH_2-compound, m.p. 197°, the Ac_2 derivative of which affords its 5-*NO*-derivative, m.p. 94° (decomp.), con-

verted by boiling C_6H_6 into the 1′-*Ac* derivative (*A*; R = Ac, R′ = H), sinters 205—208°, not melting completely at 305°, of 4′ : 5′ : 2 ; 1 : 4″ : 5″ : 3 : 4-*dipyrazolobenzene* (*A*; R = R′ = H), m.p. >320° (1′ : 1″-Ac_2 derivative, m.p. 215°; *Ag* salt), obtained by hydrolysis with KOH–EtOH and also by direct decomp. of the $(NO)_2$-derivative of 1 : 2 : 3 : 6-$C_6H_2Me_2(NHAc)_2$. Similarly 5 : 1 : 4 : 2-$NO_3{\cdot}C_6H_2Me_2{\cdot}NHAc$ (improved prep.) gives a *NO*-derivative, m.p. 92—93° (decomp.), converted into 5-nitro-6-methylindazole (*loc. cit.*), reduced to the 5-NH_2-compound, m.p. 223—224°, the Ac_2 derivative, m.p. 233—234°, of which affords a *NO*-derivative, converted into the 1′-*Ac* derivative, m.p. 275—278° (decomp.), of 5′ : 4′ : 1 : 2 : 5″ : 4″ : 4 : 5-*dipyrazolobenzene*, m.p. >330° (1′ : 1″-Ac_2 derivative, m.p. 303—305°; *Ag* salt).



(*A*.)

J. W. B.

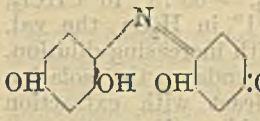
Pyrrole-blacks. I, II. P. Pratesi (Gazzetta, 1937, **67**, 188—199, 199—206; cf. this vol., 123).—I. β-3-Methyl-4-pyrrylpropionic acid (I) after some months in air and light gives a black *substance*, oxidised (CrO_3) to methylmaleimidepropionic acid (II). With $FeCl_3$–Et_2O, (I) gives a black *substance*, oxidised to (II); with H_2O_2 in presence of $Fe^{\cdots}$, (I) forms a similar *substance*. 3-Methyl-4-ethylpyrrole (III) with $FeCl_3$ gives a *substance*, oxidised (CrO_3) to methylethylmaleimide. 1-Methyl-2 : 5-diethylpyrrole does not yield pigments.

II. With H_2O_2–$Fe^{\cdots}$, (III) gives a *substance*, which with CH_2N_2 yields a methylated *product*. The behaviour of other pyrrole derivatives towards oxidation, and towards I, is studied, and the structure of pyrrole-blacks is discussed. E. W. W.

Accelerating action of metallic salts and organic compounds in the aniline-black condensation. E. Justin-Mueller (Bull. Soc. chim., 1936, [v], **3**, 2257—2266).—The effects of $CuSO_4$, NH_4VO_3, HVO_3, $VOCl_2$, $FeSO_4$, $FeCl_3$, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$ on the oxidation (*a*) of guaiacum resin with H_2O_2 and with $NaClO_3$, and of leuco-phenolphthalein (cf. A., 1917, ii, 432) with H_2O_2 are recorded and compared with their effects in the aniline-black condensation (*b*) (cf. lit.). Cu and V salts promote the liberation of active O from H_2O_2 and $NaClO_3$ and hence accelerate the reactions (*a*) and (*b*). V salts, especially $VOCl_2$, also accelerate these reactions by transference of O through an intermediate oxidation product ($H_4V_2O_7$). *p*-$C_6H_4(NH_2)_2$ and aminoazobenzene act only by means of a similar transference of O through an oxidation product. H. G. M.

Application of the cyanohydrin method to the synthesis of alkylamino-acids (hydroxyalkylamino-acids). A. I. Kiprianov and B. A. Raschkovan (J. Gen. Chem. Russ., 1937, **7**, 1026—1032).—NHMe·CH_2·CH_2·OH, HCl, KCN, and various aldehydes or ketones, in aq. EtOH, yield 2-phenyl-3-methyl-, 2 : 3-dimethyl-, and 2 : 2 : 3-*trimethyl-tetrahydro-oxazole*, b.p. 75—76°, with PhCHO, MeCHO, and $COMe_2$, respectively. $NH_2{\cdot}[CH_2]_3{\cdot}OH$,HCl similarly gives 2-*phenyltetrahydro-oxazine*, b.p. 175—176°/25 mm. (*benzoate*, m.p. 127°; *picrate*, m.p. 131°), with PhCHO, and $NH_2{\cdot}[CH_2]_2{\cdot}OH$, KCN, and MeCHO yield α-(β′-*hydroxyethyl*)*aminopropionic acid*, m.p. 193°, originating from hydrolysis of the corresponding α-nitrile; it is supposed that the above oxazoles and oxazines are produced from analogous nitriles by elimination of HCN. R. T.

Catalytic formation of resazurin. H. Eichler (Monatsh., 1937, **70**, 73—78).—Addition of aq. Na(K)NO_2 at 17—32° to *m*-$C_6H_4(OH)_2$–H_2O–H_2SO_4 containing MnO_2 (but not with H_2O_2, PbO_2, etc.) affords resazurin (I) (A., 1934, 1234), also formed in MeOH or EtOH solution. (I) is reduced in alkaline solution at room temp. by $FeSO_4$ or $Na_2S_2O_4$ to hydroresorufin, converted in air into resorufin (II), also obtained by reduction of (I) with $NaHSO_3$ or Na_2SO_3 at the b.p. Slow addition of *m*-$C_6H_4(OH)_2$ to $NaNO_2$–H_2SO_4 at <50° gives the *indophenol* of resorcinol (annexed formula), the postulated intermediate (Nietzki *et al.*, A., 1890, 156) in the formation of (II). Conclusions regarding the relationship between colour, fluorescence, and constitution in this group of compounds are summarised.



J. W. B.

Hydroxydiphenyl–isatin condensation products.—See B., 1937, 530.

Manufacture of compounds of the azaphenanthrene series.—See B., 1937, 530.

Preparation of carboxylic acid amides derived from aza-compounds [-phenanthrenes].—See B., 1937, 530.

Thiazane [tetrahydrothiazine] synthesis. R. D. Cogill (J. Amer. Chem. Soc., 1937, **69**, 801—802).—Di-β-diethoxyethyl sulphide, $S[CH_2{\cdot}CH(OEt)_2]_2$, prepared from $CH_2Br{\cdot}CH(OEt)_2$ and K_2S or KHS, with 0·5% HCl at 40—50° gives 3 : 5-*dihydroxythioxan*, m.p. 73°, converted into the Et_2 *ether* by HCl–EtOH, and by HCN–NH_3 into *tetrahydrothiazine-3-nitrile-5-carboxylamide*, m.p. 192° (decomp.), which with hot conc. HCl gives *tetrahydrothiazine-3 : 5-dicarboxylic acid*, m.p. 253—254° (decomp.). R. S. C.

Production of alkylaminoalkoxybenzthiazoles.—See B., 1937, 530.

Preparation of 1-thiol-5-*tert.*-butylbenzthiazole.—See B., 1937, 530.

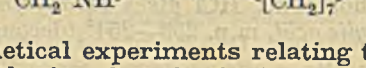
Oxidation of leuco-methylene-blue by nitrates and nitrites. E. Aubel, O. Schwarzkopf, and Glaser (Compt. rend. Soc. Biol., 1937, **125**, 12—13).—Leuco-methylene-blue is oxidised by NO_3' in the light, and is not affected by heavy metals, whereas oxidation by NO_2' is catalysed by light and by heavy metals. H. G. R.

Quinoline derivatives. I. T. N. Ghosh (J. Indian Chem. Soc., 1937, **14**, 113—115).—*p*-Tolylthiocarbamidoacetic acid, m.p. 147—148° (decomp.), obtained from the corresponding thiohydantoin, with Ac_2O gives 2-*keto*-5-p-*tolylaminodihydro*-1 : 4-*thiazole*, m.p. 157—158°, which with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ yields 2-*keto*-3-*o*-*nitrobenzylidene*-5-p-*tolylaminodihydro*-1 : 4-*thiazole*, m.p. 200—201°, reduced to 5-p-*tolylaminothiazole*-2 : 3(2′ : 3′)-*quinoline*, m.p. 191—192°. A

similar series of reactions with p-*phenetylthiocarbamidoacetic acid*, m.p. 134—135° (decomp.), affords 2-*keto*-5-p-*phenetylaminodihydro*-1 : 4-*thiazole*, m.p. 193—194°, 2-*keto*-3-o-*nitrobenzylidene*-5-p-*phenetylaminodihydro*-1 : 4-*thiazole*, m.p. 177—178°, and 5-p-*phenetylaminothiazole*-2 : 3(2′ : 3′)-*quinoline*, m.p. 175°. F. R. S.

Accelerators for vulcanisation of rubber.—See B., 1937, 592.

Alkaloids of *Anabasis aphylla*. XII. Specific rotation of anabasine, in relation to the method of extraction from the plant, the nature of the solvent, and the concentration. S. S. Norkina, T. Narkuziev, and A. P. Orekhov (J. Gen. Chem. Russ., 1937, 7, 951—955).—Anabasine has $[\alpha]_D$ −81° with no solvent, −75·25° in $COMe_2$, −71·24° in C_6H_6, −71·06° in $C_2H_4Cl_2$, −68·78° in $CHCl_3$, −45·85° in EtOH, and −39·1° in H_2O; the val. of $[\alpha]_D$ in H_2O or C_6H_6 falls with increasing dilution. The val. of $[\alpha]_D$ found also depends on the isolation procedure; racemisation is least with extraction with $C_2H_4Cl_2$, *via* the silicofluoride or benzoate. R. T.

Constitution of carpaine. III. G. Barger, R. Robinson, and T. S. Work (J.C.S., 1937, 711—713).—Carpamic acid, obtained by hydrolysis of carpaine (I) (cf. Barger, J.C.S., 1910, **97**, 466), is not readily affected by $K_2Cr_2O_7$–H_2SO_4, giving no ketone. With P–HI, it affords a *hydrocarbon*, $C_{14}H_{28}$ (?), b.p. about 90°/high vac., similar to a *hydrocarbon* obtained from myristic acid. Exhaustive methylation of (I), followed by catalytic reduction, yields a lactone, hydrolysed to an *acid*, $C_{14}H_{28}O_3$, m.p. 20—25°, with one *C*-Me. Successive treatment of carpamic acid hydrochloride with PCl_5 and KOH leads to anhydrocarpamic acid, reduced (PtO_2–H_2) to *deoxycarpamic acid*, m.p. 181°, and oxidised with O_2 to a monobasic acid ($COMe\cdot[CH_2]_7\cdot CO_2H$?), and with $KMnO_4$ to agelaic and other acids. (I) is probably  . F. R. S.

Synthetical experiments relating to carpaine. I. Synthesis of a basic long-chain lactone. G. Barger, R. Robinson, and Y. Urushibara. **II.** G. Barger, R. Robinson, and W. F. Short. **III. Derivatives of tetrahydrofuran and intermediates of the aliphatic series.** G. Barger, R. Robinson, and L. H. Smith (J.C.S., 1937, 714—715, 715—718, 718—725).—I. γ-Keto-Δ$^{\mu}$-tetradecenoic acid and HBr give μ-*bromo*-γ-*ketotetradecoic acid*, m.p. 56°, debrominated to the corresponding OH-*acid*, m.p. 63—64°, which is oxidised (AcOH–CrO_3) to γν-*diketotetradecoic acid*, m.p. 95·5°. The Br-acid and NH_2Me afford ν-*methylamino*-γ-*ketotetradecoic acid hydrochloride*, reduced (Na–Hg) to the -γ-*hydroxytetradecoic acid*, m.p. 153° (*hydrobromide*), which is tasteless in solution, but forms a bitter-tasting lactone, analogous to carpamic acid and carpaine, respectively.

II. N-*Bromo*-κ-*methylaminoundecoic acid*, obtained from κ-methylaminoundecoic acid (*hydrochloride*, m.p. 105—105·5°) and NaOBr, does not react with H_2SO_4 to form a pyrrolidine. $C_4H_4N\cdot MgBr$ with θ-carbethoxynonoyl chloride gives Et sebacate, αθ-*di*-2′-*pyrryloctane*, m.p. 138°, and *Et* θ-2′-*pyrroylnonoate* (I), m.p. 28°, hydrolysed to the *acid*, m.p. 85—85·5°, whilst with Et sebacate, it forms N-θ-*carbethoxynonylpyrrole*, m.p. 43°, hydrolysed to sebacic acid and C_4H_4N, and converted at 300° into (I).

III. *Et tetrahydrofurfurylmalonate* (II), b.p. 123°/1 mm., from the bromide and Et malonate, is hydrolysed to β-tetrahydrofurylpropionic acid, of which the *Et* ester, b.p. 105°/11 mm., is reduced (Na–EtOH) to γ-tetrahydrofurylpropan-α-ol. The alcohol and PBr_3 give *γ-tetrahydrofurylpropyl bromide* (III), b.p. 100—101°/16 mm., which with (II) affords *Et bistetrahydrofurfurylmalonate*, b.p. 165°/0·5 mm., hydrolysed to ββ′-*bistetrahydrofurylisobutyric acid*, b.p. 173°/0·35 mm., a compound structurally related to cuskhygrine. Tetrahydrofurfuryl *p*-toluenesulphonate has m.p. 38·7—39·1°. (III), KCN, and NaI give *tetrahydrofurylacetonitrile*, b.p. 92·4°/13 mm., hydrolysed to the *acid*, b.p. 144—146°/16 mm. (II) and λ-bromoundecanyl acetate afford μμ-*dicarboxy*-ν-*tetrahydrofuryltridecan*-α-*ol*, m.p. 108—109°. An improved method of prep. of Et 2-furoylacetate is described. Et ε-hydroxyhexoate is converted by $SOCl_2$ into the -*chloro*-, b.p. 106°/14 mm., and by PBr_3 or HBr–H_2SO_4 into the -*bromo*-ester, b.p. 122—125°/12 mm., which with $CH_2Ac\cdot CO_2Et$ forms *Et* α-*acetylsuberate*, b.p. 154—158°/0·28 mm., hydrolysed to η-*ketononoic acid*, m.p. 40—41° (2 : 4-*dinitrophenylhydrazone*, m.p. 88—89°; *semicarbazone*, m.p. 136°; *Et* ester, b.p. 141—142°/11 mm., and its *semicarbazone*, m.p. 108°; p-*phenylphenacyl* ester, m.p. 93·5—95°) (cf. Godchot *et al.*, A., 1931, 731). *Et* ζ-*bromoheptoate*, b.p. 135°/17 mm., and $CH_2Ac\cdot CO_2Et$ similarly give θ-ketodecoic acid, m.p. 47·5—48·5° [*semicarbazone*, m.p. 115—116° (+2H_2O, m.p. 127°); p-*phenylphenacyl* ester, m.p. 68—70°] (cf. van Romburgh, A., 1912, i, 38). Et η-ketononoate and Mg *n*-amyl bromide yield a OH-ester, converted into p-*phenylphenacyl* η-*hydroxy*-η-*methyltridecoate*, m.p. 68—71°. $CH_2Ac\cdot CO_2Et$ and $OPh\cdot CH_2\cdot CH_2\cdot CH_2Br$ give *Et di*(*phenoxypropyl*)*acetoacetate*, m.p. 61—62°, and *Et* γ-*phenoxypropylacetoacetate*, b.p. 164°/1 mm., which with carbomethoxypropionyl chloride forms a substance, hydrolysed by KOH to *Me* δ-*phenoxybutyl ketone*, b.p. 136—137°/1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 97—98°), and an acid reduced (Clemmensen) and esterified to *Et* δ-*phenoxyvalerate*, b.p. 115—117°/0·42 mm., and Et η-phenoxyoctoate, b.p. 135—140°/0·42 mm. (*acid*, m.p. 68—70°). δ-Phenoxyvaleric acid forms a chloride, b.p. 142—144°/8 mm., characterised as the *anilide*, m.p. 84·5—85·5°. F. R. S.

Alkaloids of ergot.—See A., III, 267.

Preparation of lysergic acid hydrazide.—See B., 1937, 621.

Cotarnine series. VIII. Derivatives of 1-aminomethylhydrocotarnine. B. B. Dey and (Miss) P. L. Kantam (J. Indian Chem. Soc., 1937, **14**, 91—94).—Anhydrocotarninomethylamine (*picrate*, m.p. 200°; *sulphate*, m.p. 220°) is obtained, by reduction of the nitromethane, as an oil and not a solid (cf. Magidson *et al.*, A., 1935, 767), and from it are obtained *benzoyl*-, m.p. 125° (*hydrochloride*, m.p. 238—240°; *picrate*, m.p. 175—177°), *acetyl*-, m.p. 141°, p-*nitrobenzoyl*-, m.p. 138° [*hydrochloride* (+H_2O),

m.p. 234°, *nitrate*, m.p. 190°, *picrate*, m.p. 138°], p-*aminobenzoyl*-, m.p. 185° (*Ac* derivative, m.p. 135°; *picrate*, m.p. 167°), m-*nitrobenzoyl*-, m.p. 95° (*hydrochloride*, m.p. 185°; *picrate*, m.p. 196—198°), m-*aminobenzoyl*-, m.p. 80°, o-*nitrobenzoyl*-, m.p. 143—145° [*hydrochloride*, m.p. 240° (decomp.); *picrate*, m.p. 165°], and o-*aminobenzoyl-aminomethylhydrocotarnine* (*picrate*, m.p. 175°), and a *product* $C_{17}H_{28}O_3N_2I_2,2H_2O$, m.p. 135° (decomp.), by the action of MeI.

F. R. S.

Alkaloids of: (A) ***Convolvulus pseudocantabricus***. A. P. Orekhov and R. A. Konovalova. (B) ***Arundo donax***. (C) ***Cytisus caucasicus***. A. P. Orekhov and S. S. Norkina. (D) ***Cytisus ratisbonensis***. S. S. Norkina and A. P. Orekhov. (E) ***Genista tinctoria***. S. S. Norkina, T. Narkuziev, and A. P. Orekhov (J. Gen. Chem. Russ., 1937, **7**, 646—653, 673—675, 743—746, 853—856, 906—910).—(A) Four new alkaloids, *convolvine* (I), $C_{16}H_{21}O_4N$, m.p. 115° (*nitrate*, m.p. 212—214°), *convolamine* (II), $C_{17}H_{23}O_4N$, m.p. 114—115° [*hydrochloride*, m.p. 237—239°; *picrate*, m.p. 263—264° (decomp.); *platinochloride*, m.p. 216—217°; *aurichloride*, m.p. 202—203°; *methiodide*, m.p. 273—275°], *convolvidine* (III), $C_{33}H_{42}O_8N_2$ or $C_{33}H_{44}O_8N_2$, m.p. 192—193°, and *convolvicine* (IV), $C_{10}H_{16}N_2$, b.p. 250—260° (*picrate*, m.p. 260—262°), have been isolated from Central Asiatic specimens of the plant. When hydrolysed with 10% KOH in MeOH (I) yields nortropine and veratric acid (V), and is identical with veratroylnortropine. (II) is the *N*-Me derivative of (I), and is synthesised from tropine and veratroyl chloride in PhMe (at the b.p.). (II) gives (V) and an unidentified NH_2-alcohol, m.p. 272—273°, when hydrolysed. (IV) is present in traces only, and no information as to its structure was obtained.

(B) Donaxine (A., 1935, 634, identical with von Euler's gramine, A., 1936, 741) [*picrate*, m.p. 144—145°; *perchlorate*, m.p. 181°; *platinochloride*, m.p. 180—181° (decomp.); *methiodide*, m.p. 176—177°] yields skatole when distilled from Zn; von Euler's results are thus confirmed.

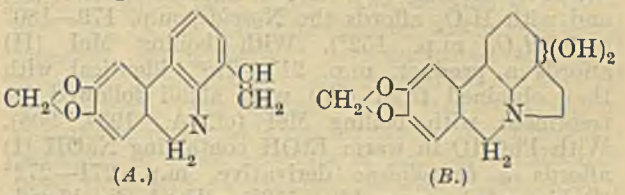
(C) *d*-Lupanine (VI), pachycarpine, and an alkaloid, m.p. 120—121°, not identical with cytisine (VII) or methylcytisine (VIII) have been found in extracts of the plant.

(D) The plant contains 0·16% of alkaloids, consisting of (VI), with traces of *l*-sparteine (IX) when the material is collected in May, and of (VI) 70%, and (IX) 30% in October.

(E) The plant contains 0·33% (dry wt.) of alkaloids, of which anagyrine, (VII), (VIII), and an unknown *alkaloid*, m.p. 95—96° (*picrate*, m.p. 244—246°), were isolated.

R. T.

***Lycoris* alkaloids. X. Constitution of lycorine.** H. Kondo and S. Uyeo (Ber., 1937, **70**, [*B*], 1087—1093).—2 : 3-NH_2·C_6H_3Br·CO_2Me and 6-bromopiperonal (I) are converted by Cu powder at 200° into *Me* 6 : 7-*methylenedioxyphenanthridine*-1-*carboxylate*, m.p. 149—151°, which could not be caused to react with MeI or Me_2SO_4 and therefore could not be transformed into the corresponding *N*-methylphenanthridone (A., 1935, 1387). Lycorine-anhydromethine (II) (*loc. cit.*) is hydrogenated to *dihydrolycorineanhydromethene*, m.p. 87·5° [*picrate*, m.p. 174° (decomp.); *methiodide*, m.p. 236° (decomp.) after softening at about 225°], which when distilled with Zn dust gives 1-methylphenanthridine, phenanthridine, and 6 : 7-*methylenedioxy*-1-*ethylphenanthridine* (III), m.p. 142° [*picrate*, m.p. 257° (decomp.)]. The constitutions *A* and *B* are therefore assigned to (II) and lycorine, respectively. 2 : 3-$(NO_2)_2C_6H_3Et$ with $SnCl_2$–HCl–EtOH at 0—2° gives 2-*nitro*-3-*aminoethylbenzene*, m.p. 32—33° (*Ac* derivative, m.p. 114—115°), which is converted into



3-*bromo*-2-*nitroethylbenzene*, b.p. 113°/3 mm., whence 3-*bromo*-2-*aminoethylbenzene* (IV), b.p. 115°/7 mm. (*Ac* derivative, m.p. 122°, oxidised to 3-bromo-2-acetamidobenzoic acid, m.p. 212°). Treatment of (IV) with (I) and Cu powder at 210—220° affords (III).

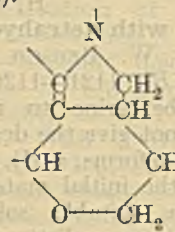
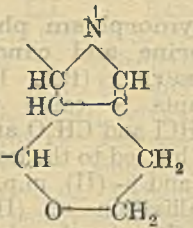
H. W.

Polymorphism phenomena with tetrahydroberberine and canadine. H. W. Bersch and W. Seufert (Ber., 1937, **70**, [*B*], 1121—1126).—Attempts to cause tetrahydroberberine to react with HCl and CH_2O at 100° did not give the desired result but led to the isolation of two forms, α- (I), m.p. 167°, and β- (II), m.p. 171°, of the initial material. Crystallisation of (II) from a suitable solvent gives (I), whereby, however, mixtures distinguishable under a lens are frequently observed. When melted and allowed to re-solidify, preferably in a high vac., (I) passes into (II). Failure in the catalytic reduction of berberine salts by previous authors is attributed largely to the use of sparingly sol. materials. This difficulty is overcome by conversion of these salts through the :CMe_2 derivatives into the freely sol. acetates which are readily hydrogenated (PtO_2); the differing methods of reduction do not appear to affect the relative proportions of (I) and (II) formed. The possibility of a diastereoisomeric relationship between (I) and (II) is not supported by their similar behaviour towards bromocamphorsulphonic acid, but the evidence is not conclusive by reason of the ready isomerisation of (I) and (II). Also the *methobromide*, m.p. 250—252°, from liquid MeBr and (I) is identical with that derived from (II). α-*l*-Canadine, m.p. 133°, $[\alpha]_D^{20}$ −297·1° in $CHCl_3$, passes when melted and allowed to cool in a high vac. into β-l-*canadine*, m.p. 142°, $[\alpha]_D^{20}$ −298·2° in $CHCl_3$, which is too unstable to permit recrystallisation. α- and β-l-*Canadine methobromide* have $[\alpha]_{5461}$ +145·6° and +145·1° in $CHCl_3$, respectively. The evidence in favour of isomerism due to asymmetric N is therefore negative and the forms are hence regarded provisionally as polymorphous.

H. W.

Constitution of strychnine. V. Neostrychnine. M. Kotake and M. Yokoyama (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, **31**, 321—332).—Strychnine or methylstrychnine with Se at 250—260° affords neostrychnine (I), m.p. 226—228° (hydro-

chloride), identical with the product obtained by Robinson *et al.* (A., 1932, 527). Tafel's base (II) gives no (I) under the same conditions. With Me_2SO_4 in warm MeOH (I) affords the *methosulphate* (III), m.p. 242—243°, converted by aq. NaI into the *methiodide* (IV), decomp. 315° [also obtained from (I) or (II) with boiling MeI–MeOH], which with AgCl–H_2O gives the *methochloride*, m.p. 267—268°; (III) with hot aq. NaBr similarly affords the *methobromide*, m.p. 312°. With hot CH_2PhCl (I) affords the *benzylochloride* [+0·5*EtOH*, m.p. 235° (decomp.)] and with H_2O_2 affords the N-*oxide*, m.p. 179—180° (+3·5H_2O, m.p. 152°). With boiling MeI (II) affords a product, m.p. 217—218°, identical with that obtained from (IV) with alkali followed by treatment with boiling MeI (cf. A., 1934, 908). With PhCHO in warm EtOH containing NaOH (I) affords a *benzylidene* derivative, m.p. 271—272° (Robinson's has m.p. 158—159°). The hydrochloride of (I) loses its HCl in vac. [strychnine (V) hydrochloride does not], which indicates that (IV) is less basic than (V). It is suggested that the double linking in (V) has shifted into either of the positions shown in (VI) or (VII).

(VI.)  (VII.) 

With $KMnO_4$ in $COMe_2$ at 10° (I) affords *diketoneostrychnine*, m.p. 234—235° [*mono*-p-*nitrophenylhydrazone*, m.p. 269—270° (decomp.); *monoxime* + 1·5H_2O, m.p. 317—318° (decomp.); *monobenzylidene* derivative +1H_2O (VIII), m.p. 307—308° (decomp.)], which with conc. HCl affords a *hydrochloride*, decomp. 315°, converted by $AuCl_3$–EtOH into an *aurichloride*, m.p. 201—203°. 6*N*-HCl dissolves (I), and an oil, sol. in hot H_2O, is pptd. by NaOH, which indicates that (I) is probably altered by acid. With $KMnO_4$ in $COMe_2$ at 29° (VIII) affords *dihydroxybenzylideneneostrychnine*, m.p. 229°; the benzylidene derivative of (V) under similar conditions affords a (*OH*)$_4$-compound, decomp. 231°. With Ag_2O in warm MeOH (IV) gives *de*-N-*methylneostrychnine*, m.p. 227—229°. J. L. D.

Constitution of strychnine. VII. Absorption spectra of strychnine and its derivatives. M. Kotake, K. Mori, and T. Mitsuwa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, **31**, 333—334).—Indole, indolylethylamine, and yohimbine have analogous absorption spectra, but different from that of strychnine (I). (I), dihydro- and neo-strychnine, strychninonic acid, Tafel's base, β- and ε-strychninolone, and α-dihydrostrychninolone have the same absorption spectra as acylcarbazolines and probably contain the same skeleton. J. L. D.

Synthesis of domesticin ethyl ethers. H. Shishido (Bull. Chem. Soc. Japan, 1937, **12**, 150—154).—3 : 4-Methylenedioxyphenylacetic acid with 3-methoxy-4-ethoxy-β-phenylethylamine at 180—190° affords 3 : 4-*methylenedioxyphenylacet*-β-(3′-*methoxy*-4′-*ethoxyphenyl*)*ethylamide*, m.p. 114—115°, which with $POCl_3$ in PhMe at 130—140° followed by treatment with MeI gives 6-*methoxy*-7-*ethoxy*-1-*piperonyl*-N-*methyldihydroisoquinoline*, m.p. 145°, reduced (Zn–H_2SO_4) to the corresponding H_4-compound (I), m.p. 105—106°. (I) with conc. HNO_3–AcOH below 5° affords 6′-*nitro*-6-*methoxy*-7-*ethoxy*-1-*piperonyl*-N-*methyltetrahydroisoquinoline*, m.p. 178—179°, reduced ($SnCl_2$–HCl) to the 6′-NH_2-compound, m.p. 96—98° [*monohydrochloride*, m.p. 228° (decomp.)], the diazonium derivative of which when boiled with Cu affords a product, reduced (Zn–HCl) to dl-2 : 3-*methylenedioxy*-6-*methoxy*-5-*ethoxy*-N-*methylaporphin*, m.p. 132° [*hydrochloride*, m.p. 275—277° (decomp.)], resolved with *d*-tartaric acid into the l-*base*, m.p. 129—131°, $[\alpha]_D^{15}$ −110·9° in MeOH [d-*tartrate*, m.p. 237° (decomp.); *hydrochloride*, m.p. 257° (decomp.)], and with *l*-tartaric acid into the *d*-base, m.p. 131°, $[\alpha]_D^{15}$ +110·8° in MeOH [l-*tartrate*, m.p. 237° (decomp.); *hydrochloride*, m.p. 257° (decomp.)], identical with domesticin Et ether. J. L. D.

Diarsyls. IX. Tetra-3-amino-4-hydroxyphenyldiarsyl. F. F. Blicke, J. F. Oneto, and G. L. Webster (J. Amer. Chem. Soc., 1937, **59**, 925—927; cf. this vol., 267).—Di-*p*-hydroxyphenylarsinic acid, m.p. 246—247° (decomp.), with Br–AcOH gives $C_6H_2Br_3$·OH and with HI–AcOH gives quantitatively AsI_3. Di-3-nitro-4-hydroxyphenylarsinic acid yields, by standard methods, *di*-3-*nitro*-4-*hydroxyphenyl*-*chloro*-, m.p. 142—143°, and -*bromoarsine*, m.p. 131—132°, by $Fe(OH)_2$ di-3-amino-4-hydroxyphenyl-arsinic acid, decomp. 218° (darkens at 210°), and -chloroarsine dihydrochloride, *tetra*-3-*amino*-4-*hydroxyphenyldiarsyl oxide*, m.p. 152—155° (decomp.), and thence (H_3PO_2) *tetra*-3-*amino*-4-*hydroxyphenyldiarsyl*, m.p. 193—194°, stable when solid, unstable in alkaline solution [*tetrahypophosphite*, m.p. 202° (decomp. from 200°); *dihydrochloride* (I), m.p. 170—172°]. Di-*p*-anisylbromoarsine yields *tetra*-p-*anisyldiarsyl oxide*, m.p. 132—134°, and with $KMnO_4$ or H_2O_2 gives *di*-p-*anisylarsinic acid*, m.p. 190—191°, converted into the 3 : 3′-(NO_2)$_2$-, m.p. 231° (decomp.; softens at 220°), and -(NH_2)$_2$-*acid*, m.p. 183—184° (decomp.). Of these and other diphenylarsine derivatives only (I) is curative against *T. equiperdum* in white rats. R. S. C.

Preparation of arylmercuric nitrates.—See B., 1937, 520.

Reversible splitting of organomercuric cyanides with hydrogen chloride. E. Carr (Iowa State Coll. J. Sci., 1935, **10**, 61—63).—Mainly theoretical. The stability of the C·Hg linking in a series of compounds is estimated by thermal decomp. and by irreversible fission with HCl. Ch. Abs. (*r*)

Structure of organo-magnesium complexes. V. V. Tschelincev (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 337—340).—The structure RMg···Et_2O···I (heat of formation 6·6 kg.-cal. when R = Et) rather than R···Et_2O···MgI is preferred for Grignard etherates for the following reasons: (1) complete analogy with the complexes of MgI_2, (2) Et_2O remains in the complex when it is converted into OR·Mg···Et_2O···I, (3) Et_2O

and ROH are incorporated only between Mg and I and not between Mg and OR; thus MgI_2 forms complexes with 6, 4, and 2 EtOH, whereas OR·MgI forms complexes with 3, 2, and 1 EtOH, *e.g.*, OR·MgI,3EtOH (−29·7 kg.-cal.), OR·MgI,2β-$C_{10}H_7$·OH (−12·1), and OR·MgI,*o*-C_6H_4Me·OH (−4·7). Structural formulæ are suggested. J. W. B.

Acylseleno-ureas [-carbamides]. I. B. Douglass (J. Amer. Chem. Soc., 1937, **59**, 740—742).—Acyl chlorides and KSeCN in $COMe_2$ give solutions which are shown to contain much *acyliso**selenocarbimide*** by reaction with amines to give selenocarbamides. The following are described: *benzoyl-*, m.p. 194—195°, N-*benzoyl*-N′-*phenyl-* (I), m.p. 144—145°, -N′-*o-*, m.p. 124—125°, and -*p-tolyl-*, m.p. 154—155°, -N′-β-*naphthyl-*, m.p. 171—172°, -N′-*benzyl-*, m.p. 115—116°, and -N′N′-*diethyl-*, m.p. 110°, N-*acetyl*-N′-*phenyl-*, m.p. 184—185°, and N-*pyromucyl*-N′-*phenyl-selenocarbamide*, m.p. 106—107°. M.p. are corr. Yields are variable. $AgNO_2$ in EtOH converts (I) into NHPh·CO·NHBz. R. S. C.

Selenium derivatives of salicylic acid. R. E. Nelson and G. S. Boase (Proc. Indiana Acad. Sci., 1934, **44**, 135—137).—Bromination of 5 : 5′-selenodisalicylic acid (I) yields 3 : 5-dibromosalicylic acid, m.p. 223°. Me_2 5 : 5′-selenodisalicylate selenodichloride (II) with Me salicylate and $AlCl_3$ affords *Me_2 5 : 5′-selenodisalicylate* (III), m.p. 158°, converted into the *selenodibromide*, m.p. 143°, by Br; with Me_2SO_4 (III) gives (I). With aq. NaCN (II) affords *5 : 5′-selenodisalicylate selenodihydroxide*, m.p. 137°. Ch. Abs. (*r*)

Physicochemical studies of organometallic and furan compounds. W. E. Catlin (Iowa State Coll. J. Sci., 1935, **10**, 65—67).—Vals. are given for the relative reactivities of various halogenated furyl derivatives. Halogens attached to the furan ring are inert. The parachors of certain furan derivatives were measured. Data are given for the ionisation consts. of furan acids. The relative reactivities of organometallic compounds were measured by adding them in excess to an acid, and following the reaction by extracting the unchanged acid with H_2O. Using CCl_3·CO_2H at 25°, relative reactivities were: $PbEt_4$ 6, $PbPh_4$ 56, $HgPh_2$ 57, $BiPh_3$ 40, $PbPh_3Et$ 2000. With HCl (25°) vals. were $SnEt_4$ 6·9 and (at 10°) $PbEt_4$ 410, $SnPh_4$ 75, $HgEt_2$ 30. Diatomaceous earth and O_2 (or oxidation products) catalysed the reactions. Ch. Abs. (*e*)

Preparation of proteins by ultracentrifuging.—See A., III, 253.

Use of refractometry in organic analysis. M. M. Samigin (J. Phys. Chem. Russ., 1936, **8**, 839—844).—Knowledge of *d* and *n* of a compound is sometimes sufficient for determining its type. J. J. B.

Quantitative macro- and micro-determination of sulphur in organic compounds. A. Schöberl (Angew. Chem., 1937, **50**, 334—337).—The material is burnt in air or O_2 in a SiO_2 tube, the combustion being localised and prevented from striking back by the insertion of fritted quartz discs. SO_3 + any SO_2 is adsorbed in H_2O_2. SO_4'' is determined by pptn. with benzidine. J. S. A.

Determination of sulphur and chlorine in combustible materials. H. Krekeler (Angew. Chem., 1937, **50**, 337; cf. preceding abstract).—The method is applicable to the determination of halogens, alkaline $Na_2S_2O_3$ being used as absorbent. 0·01% of Cl in combustible gases may be so determined. J. S. A.

Determination of arsenic and antimony in organic compounds and mixtures. E Schulek and R. Wolstadt (Z. anal. Chem., 1937, **108**, 400—406).—Org. material is destroyed by heating with conc. H_2SO_4 + 30% H_2O_2. The solution is treated with 20% HCl + KBr, and distilled, the process being repeated. As is distilled over quantitatively, Sb^{III} remaining in the flask. Both As and Sb are titrated with $KBrO_3$. For titration with 0·01*N*-$KBrO_3$, α-naphthoflavone is added as indicator. For the determination of small amounts of As, the distillate is freed from HCl by evaporation with H_2SO_4 + 30% H_2O_2. As is then reduced with N_2H_4,H_2SO_4 before titration with $KBrO_3$. J. S. A.

Destruction of organic mercury compounds for the determination of this element. C. V. Bordeianu (Ann. Sci. Univ. Jassy, 1935, **20**, 129—131).—The organo-Hg compound (0·3—0·5 g.) mixed with finely powdered $KMnO_4$ (1—1·5 g.) is treated dropwise with cold fuming HNO_3 (10 c.c.), then with conc. H_2SO_4 (1—2 c.c.), and the mixture is heated at 100°. After dilution (50 c.c.) the excess of $KMnO_4$ is destroyed by 3% H_2O_2 and the Hg is determined by thiocyanate. The error is very small. J. W. B.

Determination of chromium in organic compounds. C. F. Miller (Chem. Analyst, 1936, **25**, No. 1, 5—6).—Wet digestion of a 10-g. sample with conc. H_2SO_4 and HNO_3 is recommended. The solution is made alkaline and oxidised with Na_2O_2. The Cr is determined iodometrically or colorimetrically with diphenylsemicarbazide. Ch. Abs. (*e*)

Micro-determination of hydroxyl and amino-groups. F. H. Stodola (Mikrochem., 1937, 180—183).—The material is acetylated at 95—100° with a weighed quantity of a standard Ac_2O–C_5H_5N mixture. The excess of Ac_2O is then titrated back with CO_2-free NaOH–EtOH. J. S. A.

Determination of fumaric acid in protein solutions containing succinic acid. E. Stotz (J. Biol. Chem., 1937, **118**, 471—477).—Fumaric acid (I) is pptd. as Hg^I salt in presence of 5% HNO_3 and the Hg^I oxidised to Hg^{II} which is then titrated with standard KCNS. 2—12 mg. of (I) can be determined in presence of proteins and succinic and malic acids. J. N. A.

Spectrophotometric studies of colour development in the analysis of sugar by the Benedict method and of cholesterol by the Liebermann–Burchard reaction. F. W. Sunderman and J. Razek (J. Biol. Chem., 1937, **118**, 397—404).—The development of colour in the two above reactions is studied by means of a photo-electric spectrophotometer which recorded within 10 sec. the transmission at each λ throughout the visible range, the first curve being obtained 2 min. after prep. of the solution and

subsequent curves at intervals up to 1 hr. The optimal spectral zone is selected. P. W. C.

Microscopic tests for amino-acids. J. D. Surmatis and M. L. Willard (Mikrochem., 1937, **21**, 167—170).—The reactions of the usual alkaloid reagents and of heavy-metal salts with glycine (I), cystine (II), tyrosine (III), alanine, leucine, glutamic acid, aspartic acid, phenylalanine, and proline are described. For (I), (II), and (III) the crystal habits of the ppts. obtained serve as sp. tests. J. S. A.

Microscopy of amino-acids and their compounds. III. Copper salts. B. Cunningham, M. Macintyre, and P. L. Kirk (Mikrochem., 1937, **21**, 245—249).—Characteristic crystal habits and optical data are described for the Cu salts of alanine, aspartic acid, cystine, glycine, *iso*leucine, leucine, lysine, methionine, norleucine, norvaline, phenylalanine, serine, and α-amino-*n*-valeric acid. J. S. A.

Inhibitors of colour development in the Sullivan method for cystine.—See A., III, 288.

***p*-Aminobenzenesulphonamide and its determination.** E. Schulek and I. Boldizsar (Z. anal. Chem., 1937, **108**, 396—400).—*p*-Aminobenzenesulphonamide (I), m.p. 165° (corr.), may be determined bromatometrically by addition of a 10—30% excess of 0·1*N*-$KBrO_3$ to a solution of the material in HCl. KBr + HCl are added, using a stoppered reaction vessel. KI is then added, and the I liberated is titrated with $Na_2S_2O_3$. Alternatively, (I) is hydrolysed by refluxing with 70% H_2SO_4, whereby NH_3 is split off quantitatively. The liquid is then made alkaline, and NH_3 is distilled into 0·1*N*-acid. J. S. A.

Colorimetric determination of the components of 3 : 4-dihydroxyphenylalanine–tyrosine mixtures. L. E. Arnow (J. Biol. Chem., 1937, **118**, 531—537).—3 : 4-Dihydroxyphenylalanine (I) is determined colorimetrically against a standard of (I), or, using a green Wratten 61 filter, of pyrocatechol, by the colour produced on adding HCl, $NaNO_2$–Na_2MoO_4 (giving yellow), followed by NaOH (giving red). Tyrosine is determined by adding $HgSO_4$–H_2SO_4, heating at 100°, adding $NaNO_2$, centrifuging if (I) is present, and comparing the yellow colour against a standard. E. W. W.

Microchemical detection of di- and tri-hydric phenols by drop reactions. J. Kisser and Y. Kondo (Mikrochem., Molisch Festschr., 1936, 259—270).—Characteristic sensitive colour reactions of *o*-, *m*-, and *p*-$C_6H_4(OH)_2$, 1 : 3 : 5- and 1 : 2 : 3-$C_6H_3(OH)_3$ with $FeCl_3$, $Ti_2(SO_4)_3$, $(NH_4)_2Ce(NO_3)_6$, *p*-$Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$, fast red salt *B*, and $AgNO_3$ + NH_3 are described. J. S. A.

Identification of isomeric piperic acids by microchemical methods. H. Lohaus and M. Steiner (Mikrochem., 1937, **21**, 159—166).—The characteristic crystal habits and optical characteristics of piperic, *iso*piperic, *iso*chavicic, and γ-bromo*iso*chavicic acids, and of Me γ-bromo*iso*chavicate are described. J. S. A.

Bromatometric determination of 8-hydroxyquinoline. Determination of 8-hydroxyquinoline in pharmaceutical preparations. E. Schulek and O. Clauder (Z. anal. Chem., 1937, **108**, 385—396).—Sufficient material to contain 20—40 mg. of 8-hydroxyquinoline (I) is dissolved in HCl, and the solution is made just alkaline. KBr, a 10—30% excess of 0·1*N*-$KBrO_3$, and HCl are added, a stoppered reaction vessel being used. After keeping for 5 min. in the dark, KI is added, and the I liberated is titrated with $Na_2S_2O_3$. (I) may be isolated from pharmaceutical preps. by distillation in steam from a solution of p_H 8. Alternatively, (I) may be extracted with CS_2, $CHCl_3$, etc. from neutral solutions, or accompanying org. materials may be extracted by utilising the amphoteric properties of (I). J. S. A.

Microchemistry of methylxanthides. (Caffeine, theobromine, theophylline.) G. Denigès (Mikrochem., Molisch Festschr., 1936, 52—58).—Caffeine (I), theobromine (II), and theophylline (III) give ppts. of characteristic habit with NaOBr + HCl. Characteristic crystals are also obtained by evaporating solutions of (I) in HCl, (II) in $CHCl_3$, and (III) in $COMe_2$. J. S. A.

Micro-analysis of nitrogen in certain pyrimidines by the Dumas method. D. F. Hayman and S. Adler (Ind. Eng. Chem. [Anal.], 1937, **9**, 197).—The low vals. of N given for certain pyrimidines by the Pregl micro-Dumas method are corr. by mixing the substance with Cu acetate and CuO and heating to a high temp. A. Li.

Microchemical differentiation of alkaloids on basis of the m.p. of their picrates, picrolonates, and styphnates. L. Kofler and F. A. Müller (Mikrochem., 1937, **22**, 43—77).—Data are given as to the appearance, solubility, and m.p. of the ppts. obtained with aconitine, *apo*morphine, arecoline, atropine, berberine, brucine, quinine, quinidine, cinchonine, cinchonidine, cocaine, codeine, cotarnine, coniine, duboisine, emetine, ephedrine, ephetonine, heroine, homatropine, hydrastine, hydrastinine, hyoscyamine, lobeline, lupinine, mescaline, morphine, narceine, narcotine, nicotine, papaverine, paracodeine, pelletierine, physostigmine, pilocarpine, scopolamine, sparteine, strychnine, thebaine, theobromine, tropacocaine, veratrine, and yohimbine. Colchicine, caffeine, and theophylline give no ppts. with the reagents. J. S. A.

Reaction for distinguishing between anabasine sulphate and nicotine sulphate. S. A. Katz (Z. anal. Chem., 1937, **108**, 408).—The Roussin Et_2O–I reagent deposits a periodide from solutions of nicotine only. J. S. A.

Comparative microscopic tests of anabasine and related compounds; its purification and some physical constants. M. E. Zerbey, M. T. Orinick, and M. L. Willard (Mikrochem., 1937, **21**, 171—179).—Reactions of non-homogeneous distillation samples of anabasine with alkaloid reagents are described. *n*, *d*, and $[\alpha]^{25}$ for the impure material are recorded. J. S. A.