BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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APRIL, 1943

A., II.—ORGANIC CHEMISTRY

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A., II.—Organic Chemistry

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I.—ALIPHATIC.

Semiquantitative extension of the electronic theory of the English school. A. E. Remick (*J. Org. Chem.*, 1942, **7**, 534—545).—The author advocates the summation of ΔH for all linkings made and broken in the rate-controlling step as the best method for judging the most probable reaction path. If this summation is made correctly taking into account the interaction between all the linkings involved the val. of ΔH finally obtained should be the heat of activation. Such calculations can be made with fair accuracy for simple compounds on the basis of the theory of abs. reaction rates. If these interactions are neglected and a simple summation is made of the ΔH vals. for the linkings made and broken, the results give a reasonably safe guide for comparing reactions involving unsubstituted, unconjugated compounds and hence form a semiquant. extension of the electronic theory of the English school. Since the method aims only at establishing a sequence of the relative probabilities of different conceivable rate-controlling steps, the calculations can be further simplified by omitting from consideration all of the ΔH terms for linkings which would occur in both or all of the reactions under consideration and which would accordingly cancel out in the final comparison. The resultant vals. of ΔH are designated "comparative heats of activation." Considerations are applied to (*a*) addition of halogens to C_2H_4 in which it is established that the most probable mechanism is $CH_2{:}CH_2 + Cl_2 \rightleftharpoons \overset{+}{C}H_2{:}\overset{-}{C}H_2 - - \overset{+}{Cl}{-}\overset{-}{Cl} \rightarrow CH_2Cl{\cdot}\overset{+}{C}H_2 + \overset{-}{Cl}$, that the reaction will lead to addition rather than to substitution, that C_2H_4 is the nucleophilic reagent in this reaction which may accordingly be placed in class *A* of the Ingold–Rothstein scheme, and that the velocity of halogen addition is $Cl_2 > Br_2 > I_2$; (*b*) addition of H halides to olefines in which the rate-controlling step is $CR_2{:}CH_2 + HX \rightarrow CR_2{:}CR_2{-}H{-}X$ and the predicted order of velocity (neglecting entropy factors) is HI > HBr > HCl; (*c*) hydrolysis of chlorides of N and P in which the relative probabilities of the mechanisms are $XCl_3 + H^+ \rightleftharpoons XCl_2 - - Cl{-}H \rightarrow ClX^+ + HCl > XCl_3 + H^+ \rightleftharpoons H - - XCl_2 - - Cl \rightarrow HXCl_2 + Cl^- > XCl_3 + OH^- \rightleftharpoons Cl_2X - - Cl - - OH \rightarrow Cl_2X + HOCl$. On the assumption that the 3 Cl atoms are removed by the same mechanism PCl_3 should yield HCl and $P(OH)_3$. For NCl_3 the comparative heats of activation for the three mechanisms are −58·6, −43·4, and +76·8 kg.-cal. Hence the second mechanism is the more probable and NCl_3 would be expected to yield HOCl and NH_3 on hydrolysis; (*d*) hydrolysis of alkyl halides which in acid solution is shown to follow the mechanism $MeX + AqH^+ \rightleftharpoons Me{-}X{-}H^+ + Aq \rightarrow Me^+ + HX + aq$; (*e*) cyanohydrin formation with aldehydes for which a more facile addition is predicted in a basic than in an acidic medium; (*f*) reactions of ethers with halogen hydrides etc. which probably follow the course, $MeOMe + HX \rightleftharpoons MeO(Me){\cdot}H{-}X \rightarrow MeOH + X' + Me^+$, and (*g*) reactions of alcohols with halogen hydrides in which the order of reactivity is calc. to be *tert.* > *sec.* > primary. H. W.

"Sliding" isomerism ("olisthomerism"). A. Balandin (*Acta Physicochim. U.R.S.S.*, 1942, **16**, 195—205).—Where it is possible by change of groups in different ways to arrive at the same compound from the same starting materials, the products are called "sliding" isomerides or olisthomerides. Thus, in the formation of MeOAc from AcOH and MeOH, the substances may combine as follows: $Me{:}OH + MeCO{:}OH$ and $Me{:}OH + MeCO{\cdot}O{:}H$. Conditions for the existence of this type of reaction are outlined. Reactions in which it may take place include esterification, formation of ethers from alcohols, formation of mixed acid anhydrides, mixed ketones, aldehydes from formic and another carboxylic acid, *sec.* amines from two primary amines, and the reaction between two different peroxides, etc. The investigation of the reactions provides an important method for comparing the strengths of linkings and the mobility of groups and atoms. Isotopes, artificial radioactivity, and optical activity can also be introduced into the study of the phenomenon. A. J. M.

Stereochemistry. III. Preparation of *d*-α-deutero-β-methylbutane. Its optical rotation. H. C. Brown and C. Groot (*J. Amer. Chem. Soc.*, 1942, **64**, 2563—2566).—*d*-CHMeEt·CH_2·OH (from fusel oil) and $SOCl_2$–C_5H_5N give *d*-CHMeEt·CH_2Cl, b.p. 99·5°/750 mm., α_D^{25} +1·33°, the Mg derivative of which with HCl gives EtPr$^\beta$ and with DCl gives *d*-CHMeEt·CH_2D, b.p. 27°/746 mm., α_{5461} <0·005°, probably <0·002°. R. S. C.

Isomerisation of *n*-pentane.—See B., 1943, II, 2.

Industrial synthesis of hexachloroethane. II. Chlorination of tetrachloroethane.—See B., 1942, II, 417.

Cyclic production of nitroparaffins.—See B., 1943, II, 38.

Synthesis of ethylenic and saturated hydrocarbons of *iso*-structure with a quaternary carbon atom. II. Reaction between β-bromo-βδ-dimethyl-Δ$^\gamma$-pentene and magnesium alkyl halides. R. J. Levina and J. B. Kagan (*J. Gen. Chem. Russ.*, 1941, **11**, 523—526).—$CMe_2{:}CH{\cdot}CMe_2Br$ and MgRX (X = Cl, Br) yield the hydrocarbons $CMe_2{:}CH{\cdot}CMe_2R$ (R = Me, *Et*, b.p. 132°, *Pr*$^\alpha$, b.p. 152—153·5°). These are hydrogenated to the hydrocarbons $CMe_2Bu^\beta R$ (R = Me, *Et*, b.p. 129—130°, *Pr*$^\alpha$, b.p. 151—152°). R. T.

Stability of butadiene in nitrogen mixtures at 250—500°.—See B., 1943, II, 1.

Photo-addition of hydrogen bromide to olefinic linkings. W. E. Vaughan, F. F. Rust and T. W. Evans (*J. Org. Chem.*, 1942, **7**, 477—489).—"Abnormal" addition of HBr to olefinic linkings ($CH_2{:}CHMe$, $CH_2{:}CHEt$, $CH_2{:}CH{\cdot}CH_2Br$, diallyl) has been effected photometrically in liquid and vapour phase without the intervention of O_2 or peroxides. In the liquid phase, quant. conversions can be obtained so rapidly that the method suggests itself for practical syntheses; irradiation with sufficiently short λ is the principal requirement. Some photo-dissociable materials (aldehydes, ketones, metal alkyls) are able to sensitise the "abnormal" addition even when the radiation used is not absorbed by HBr or the olefine. Certain materials (MeI, I) are powerful inhibitors of the gas-phase process. All the evidence substantiates previous conclusions that the mechanism of the "abnormal" addition is a chain reaction involving Br atoms and free radicals. H. W.

Olefine–oxygen-hydrogen bromide photo-reaction. F. F. Rust and W. E. Vaughan (*J. Org. Chem.*, 1942, **7**, 491—496).—The presence of large concns. of O_2 inhibits the photo-reaction of olefines (C_2H_4 and C_3H_6). The products of these retarded reactions include the *n*-monobromide, dibromide, bromohydrin, and H_2O. In the case of C_3H_6 CH_2AcBr is also formed. Peroxidic compounds are not found. CH_2AcBr (and, by analogy, any α-Br-ketone) acts as a powerful catalyst for the "abnormal" addition of HBr to olefines, even in the dark. H. W.

Cetene (Δ$^\alpha$-hexadecene). H. Suida and F. Drahowzal (*Ber.*, 1942, **75**, [*B*], 991—997).—Evidence is adduced in favour of the view that homogeneous Δ$^\alpha$-hydrocarbons are obtained from Mg alkyl chlorides and allyl halides. *n*-$C_{12}H_{25}Cl$ is converted by KCN into *n*-trideconitrile, b.p. 150·6°/10·5 mm., reduced by the rapid action of a slight excess of Na in boiling Bu$^\alpha$OH to *n*-$C_{13}H_{27}{\cdot}NH_2$, the hydrochloride of which is transformed by BzCl in C_6H_6 at 108—110° into *benztridecylamide*, m.p. 70·6°. This is converted by PCl_5 into *n*-$C_{13}H_{27}Cl$, b.p. 135·7—136°/9 mm. (corresponding bromide, b.p. 148—149°/9·5 mm., m.p. 6·0°), transformed by the successive action of Mg and $CH_2{:}CH{\cdot}CH_2Br$ into Δ$^\alpha$-hexadecene (cetene). H. W.

Addition of iodine trichloride to acetylene and the structure of β-chlorovinyliodochloride. R. C. Freidlina and A. N. Nesmejanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 892—894).—Addition of ICl_3 to C_2H_2 in either 3% or 15% HCl gives β-chlorovinyliodochloride (**I**), m.p. 74°, identical with the substance obtained by addition of Cl_2 to CHCl:CHI. C_2H_2 is eliminated from (**I**) by treatment with CsCl or C_5H_5N. A solution of (**I**) in $CHCl_3$ with C_5H_5N gives a ppt. of a double compound of (**I**) and C_5H_5N, reduced by $FeSO_4$ with evolution of I. F. R. S.

Purification of methanol.—See B., 1943, II, 39.

Constitution of pirylene: chemical evidence. H. Sargent, E. R. Buchman, and J. P. Farquhar (*J. Amer. Chem. Soc.*, 1942, **64**, 2692—2693; cf. A., 1943, I, 54).—Degradation of 1 : 1-dimethyl-2-bromomethylpyrrolidinium bromide gives mixed bases (*A*) (70%), b.p. ~56—70°/50 mm. (cf. lit.), from which 13% of a stable *base*, $C_7H_{13}N$, b.p. 65°/49 mm. (dilituarate, m.p. 161—162°; *picrate*, m.p. 100·5—101°), is obtained. The derived methiodide (**I**), m.p. 259° (decomp.) (lit. 257°) (corresponding methopicrate, m.p. 112·5—113°), is also

obtained from (*A*); it is stable to H_2O at 100° and resists hydrogenation, but gives the methochloride which with H_2–Pd–C in H_2O at 2 atm. yields n-C_5H_{11}·NMe_3X. Distilling (**I**) with conc. aq. KOH gives pirylene (**II**) (59—73%), b.p. 59·4°/744 mm., which is shown to be CMe:C·CH:CH_2 by physical properties, addition of 3 H_2 (Pd–C) to give n-C_5H_{12} and of HCl to give CHMe:CCl·CH:CH_2 [1 : 4-O:$C_{10}H_6$:O adduct, m.p. 180·7—181°; (**II**) does not react at 100°]. M.p. are corr. R. S. C.

Octadecyl alcohol (3 : 5-dinitrobenzoate, m.p. 77·5°) etc. in gorgonias.—See A., 1943, III, 181.

Silico-organic compounds. IV. Action of organic acid halides and of hydrohalogen acids on silico-orthoesters. H. W. Post and H. M. Norton (*J. Org. Chem.*, 1942, **7**, 528—533).—$Si(OEt)_4$ and AcCl (1 : 1) at 135° give $SiCl(OEt)_3$ in 90% yield. At 185° and with ratio 1 : 2 there is a fair yield of impure $SiCl_2(OEt)_2$ whilst with ratio 1 : 5 some $SiCl_3(OEt)$ is produced. At 200° in a steel bomb with ratios 1 : 2 and 1 : 1 only EtOAc could be identified, spongy siliceous polymerides being also produced. At 185° $Si(OBu^a)_4$ and AcCl (1 : 1) give $SiCl(OBu^a)_3$. A boiling equimol. mixture of $Si(OEt)_4$ and BzCl gives 70% of $SiCl(OEt)_3$ and 88% of EtOBz. With ratio 1 : 4 an identifiable product does not result. $Si(OEt)_3$·OAc and AcCl (1 : 2) do not react at 40°. At 185° and with ratio 1 : 1 there is no well-defined product; this is also the case with Si(OEt)·O·COEt. AcBr and $Si(OEt)_4$ (1 : 1) at 18·5° give 20% of EtBr, 80% of EtOAc, but no homogeneous compound of Si. Similarly BzBr gives 26% of EtBr and 68% of EtOBz. AcBr and $Si(OBu^a)_4$ give Bu^aBr, probably Bu^aOAc, and a little $SiBr(OBu^a)_3$. The possibility that Bu^a_2O is an intermediate is excluded experimentally. Passage of dry HCl through $Si(OEt)_4$ at room temp. gives a small amount of EtOH, mainly unchanged ester, and some polymerised compounds of Si. At 185° $Si(OEt)_4$ and HCl appear to afford EtCl. Reaction does not appear to occur between $Si(OBu^a)_4$ and HCl. HBr and $Si(OEt)_4$ appear to react more readily, giving EtBr and EtOH, whilst $Si(OBu^a)_4$ gives some Bu^aBr and very little Bu^aOH. $Si(OEt)_4$ and $Si(OBu^a)_4$ and HI yield the corresponding alcohol and iodide. H. W.

Mechanism of obtaining vinyl ethers. E. S. Vasserman and A. B. Bedrintzeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 34—36).—The kinetics of the reaction of vinylation of alcohols are studied. When C_2H_2 reacts with 96·5% EtOH in presence of KOH at 170—190°/~30 atm., the first stage is probably activation of C_2H_2, which then reacts with EtOH to give CH_2:CH·OEt. It is assumed that EtOH reacts only with dissolved C_2H_2, the concn. of which is approx. const. owing to large excess of it in the gaseous phase and the relatively high temp. A. T. P.

***aaa*-Trichloro-*γ*-nitro-*β*-hydroxyalkanes and their reduction products.** S. Malkiel and J. P. Mason (*J. Amer. Chem. Soc.*, 1942, **64**, 2515).—CCl_3·CH(OH)·CHR·NO_2 (from CCl_3·CHO, H_2O, CH_2R·NO_2, and aq. K_2CO_3 at 50—52°) with H_2–Raney Ni in EtOH at room temp./55 lb. give *aaa*-trichloro-*γ*-amino-*β*-hydroxy-propane (**I**), m.p. 44·7—45·7° (corr.) (lit. 42—43°), b.p. 138—146°/13 mm. (*Bz* derivative, m.p. 167·4°), -*n*-butane, b.p. 138—140°/9 mm. (*Bz* derivative, m.p. 182·5°), and -n-*pentane*, b.p. 136—142°/10 mm. (*Bz* derivative, m.p. 195·2°). Addition of $COMe_2$ to (**I**) in EtOH gives a *compound*, $C_3H_6ONCl_3$, m.p. 167·4—167·7° (corr.). R. S. C.

Purification of pentaerythritol.—See B., 1942, II, 419.

Preparation of divinyl ether.—See B., 1943, II, 3.

Ethyl peroxides. XIV. Oxidation of di*iso*propyl ether. A. Rieche and K. Koch (*Ber.*, 1942, **75**, [*B*], 1016—1028).—A sample of Pr^{β}_2O which had been kept in a metal container for 10 years contained trimeric (**I**), m.p. 98·5°, and dimeric (**II**), m.p. 131°, acetone peroxide, $COMe_2$, H_2O_2, and some $Pr^{\beta}OH$, AcOH, and HCO_2H. Oxidation appears to proceed thus: $Pr^{\beta}_2O + O_2 \rightarrow Pr^{\beta}O{\cdot}CMe_2{\cdot}O_2H$ (**III**); (**III**) + $H_2O \rightarrow OH{\cdot}CMe_2{\cdot}O_2H$ (**IV**) + $Pr^{\beta}OH$ and (**III**) $\rightarrow CMe_2{\cdot}O_2{\cdot}$ (becomes polymerised) + $Pr^{\beta}OH$; (**IV**) $\rightarrow COMe_2 + H_2O$. $Pr^{\beta}_2O + 2O_2 \rightarrow O(CMe_2{\cdot}O_2H)_2$ (**V**); (**V**) + $H_2O \rightarrow 2$(**IV**) (forms acetone peroxide); (**V**) $\rightarrow H_2O + 2CMe_2{\cdot}O_2{\cdot}$ (becomes polymerised); (**IV**) $\rightarrow COMe_2 + H_2O_2$. In boiling C_6H_6 or EtOH the mol. wt. of (**I**) agrees with the expected val. whereas that of (**II**) in boiling C_6H_6, EtOH, EtOAc, and $COMe_2$ is very variable. (**II**) is much more volatile, more sensitive to shock, and more explosive than (**I**). (**II**) is hydrolysed by acid considerably more rapidly than (**I**). The absorption spectra of (**I**) and (**II**) are recorded. H. W.

Keten acetals. XI. Pyrolysis of keten acetals and ortho-esters. S. M. McElvain, H. I. Anthes, and S. H. Shapiro (*J. Amer. Chem. Soc.*, 1942, **64**, 2525—2531; cf. A., 1943, II, 23).—The reaction, CHX:$C(OEt)_2$ (X = H, Cl, alkyl etc.) $\rightarrow CH_2X{\cdot}CO_2Et + C_2H_4$, occurs in glass at 200° (6 hr.; yield 20—100% dependent on the drying and usage of tubes), in *cyclo*hexane in steel at 200° (5—10% yield), or by rapid passage over glass chips, MnO_2, Al_2O_3, ZnO, or CrO_3 at 300—400° (60—80% yield). However, *keten Me*$_2$ *acetal* (**I**), b.p. 89—91°/740 mm., is 95% unchanged after heating for 24 hr. at 200°. $CMe(OMe)_3$ and Br give *Me*$_3$ *orthobromoacetate* (70%), b.p. 74—75°/17 mm., which with Na gives 70% of (**I**). CH_2:CH·OAc with Br and then CH_2:CH·CH_2·OH (**II**) or CH_2Ph·OH at 5° and later room temp. gives *diallyl* (45%), b.p. 101—102°/20 mm., and (*CH_2Ph*)$_2$ *bromoacetal* (75%), b.p. 190—195°/2 mm., respectively, which with $KOBu^{\gamma}$–$Bu^{\gamma}OH$ at the b.p. give, doubtless by way of the keten acetal, *allyl* Δ^{γ}-*pentenoate* (43%), b.p. 48—50°/8 mm., 160—162°/740 mm. [hydrolysed to (**II**) and CH_2:CH·$[CH_2]_2$·CO_2H], and *CH_2Ph* *o-tolylacetate* (46%), b.p. 158—162°/1·5 mm. (hydrolysed to CH_2Ph·OH and *o*-C_6H_4Me·CH_2·CO_2H), respectively. $CH_2X{\cdot}C(OEt)_3$ (X = H, Cl, or OEt) decomposes at 200° into $CH_2X{\cdot}CO_2Et$, EtOH, and C_2H_4; proof that the reaction occurs by way of CHX:$C(OEt)_2$ is provided by decomp. of $CMe(OEt)_3$ in presence of PhOH at 200° to EtOAc, EtOH, and PhOEt, and of OEt·CH_2·$C(OEt)_3$ similarly into OEt·CH_2·CO_2Et (47%) + OEt·CH_2·CO_2Ph (53%), EtOH, and C_2H_4. Similarly, $CMe(OR)_2$·OR′ [prep. from CH_2:$C(OR)_2$ and R′OH] gives (*a*) R′OH + CH_2:$C(OR)_2$ $\rightarrow$ (+PhOH) $CMe(OR)_2$·OPh $\rightarrow$ ROAc + PhOR and (*b*) ROH + CH_2:C(OR)·OR′ $\rightarrow$ (+PhOH) OR·CMe(OR′)·OPh $\rightarrow$ (*c*) R′OAc + PhOR, and (*d*) ROAc + PhOR′. The relative amounts in which these reactions occur are determined for R = Et, R′ = Bu^a, Bu^{β}, *sec.*-Bu, *iso*amyl, CH_2Bu^{γ}, and CH_2Ph, and for R = Bu^a, R′ = Et; they follow expectations. $CMe(OEt)_2$·O·CH_2Ph alone gives 84% of CH_2:C(OEt)·O·CH_2Ph and thence ~14% of *o*-C_6H_4Me·CO_2Et, b.p. 78—83°/3 mm. With $CH_2Br{\cdot}C(OEt)_3$ and $CHBr_2{\cdot}C(OEt)_3$ decomp. as above is complicated by loss of EtOBr ($\rightarrow$MeCHO + HBr) and by addition of HBr to the keten, leading to varied products. $CPh(OEt)_3$ at the b.p. gives EtOBz (60%) and Et_2O. The following are described. *Et_2 Bu^a*, b.p. 70—72°/15 mm., *Bu^{β}*, b.p. 64—66°/14 mm., sec.-*Bu*, b.p. 63—65°/15 mm., *isoamyl*, b.p. 80—82°/15 mm., *neopentyl*, b.p. 87—88°/28 mm., and *benzyl*, b.p. 121—122°/8 mm., *orthoacetate*; *Et Bu^a_2 orthoacetate*, b.p. 98—100°/13 mm.; *Ph* sec.-*Bu ether*, b.p. 184—185°. R. S. C.

Addition of sulphuric acid to olefines of high mol. wt. P. Baumgarten (*Ber.*, 1942, **75**, [*B*], 977—983).—Dodecene obtained by dehydrating dodecan-*a*-ol with hot, highly conc. H_3PO_4 or by the thermal decomp. of dodecyl palmitate is oxidised by BzO_2H to the corresponding oxide, which is hydrolysed by very dil. H_2SO_4 to the glycol and then quantitatively oxidised by $Pb(OAc)_4$. The substance obtained by the second reaction is thus shown to be Δ^a-dodecene (**I**) whereas the first method affords a mixture (**II**) of Δ^{β}- and Δ^{γ}-dodecene. Most complete action between (**I**) or (**II**) and H_2SO_4 is obtained by rapid use of a moderate excess of the monohydrate at ~0°, whereby 86% of alkyl sulphate can be produced. (**I**) gives a non-uniform product separable by $CHCl_3$, $COMe_2$, light petroleum, C_6H_6, etc. into the sparingly sol. *Na β-dodecyl sulphate* (**III**) and freely sol. Na *γ*-, *δ*-, and possibly *ε*-dodecyl sulphates (**IV**). The *a*-dodecyl compound (**V**) could not be detected. (**III**) is identified by hydrolysis to dodecan-*β*-ol, oxidised to dodecanone. Hydrolysis of (**IV**) gives a mixture of *sec.* alcohols oxidised to a mixture of ketones. Migration of SO_4 occurs during the action of H_2SO_4 on (**III**) whereby salts sol. in $CHCl_3$ are produced in considerable proportion whereas (**V**) is unchanged by this treatment. Similarly (**IV**) is partly converted into (**III**) by H_2SO_4. H. W.

Nature of the glycerophosphoric acid present in phosphatides. J. Folch (*J. Biol. Chem.*, 1943, **146**, 31—33).—Methods of isolation used to prepare glycerophosphoric acid (**I**) from phosphatides hydrolysed with acid or alkali yield optically active mixtures of *α*- + *β*-acids, and there is no evidence to show whether (**I**) in phosphatides is in *α*- or *β*-form. A. T. P.

Photo-addition of hydrogen sulphide to olefinic linkings. W. E. Vaughan and F. F. Rust (*J. Org. Chem.*, 1942, **7**, 472—476).—Ultraviolet radiation of short *λ* readily promotes the addition of H_2S to CH:CHEt, CH_2:CHMe, diallyl, CH_2:CHCl, diallyl ether, and CH_2:CH·CO_2Me with formation of mercaptans and sulphides. Light of *λ* transmissible by Pyrex is effective in initiating reaction if a small amount of photo-dissociable material such as $COMe_2$ is present. S of the ·SH or ·S· adds exclusively to C of the double linking which has the largest no. of H atoms. H_2S and olefine combine slowly in the gas phase under the influence of ultra-violet radiation. The mechanism is one of a free radical chain and is dependent on the preliminary dissociation of H_2S. H. W.

Solubilities of saturated fatty acids.—See A., 1943, I, 87.

Mechanism of oxidation of oleic and elaidic acids and their methyl esters by hydrogen peroxide in acetic acid. Configurations of *θ*$_1$-dihydroxystearic acids. G. King (*J.C.S.*, 1943, 37—38).—With H_2O_2 in AcOH at room temp., oleic acid yields mixed monoacetates (also obtained from oleic acid epoxide, m.p. 59·5°, and AcOH at room temp.) of dihydroxystearic acid, m.p. 95°, whilst elaidic acid gives some elaidic acid epoxide (**I**), m.p. 55·5°, and monoacetates [also obtained (with 50% of unchanged epoxide) from (**I**) and AcOH] of dihydroxystearic acid, m.p. 132°. Me oleate and elaidate behave similarly. Traces of peroxides are produced in all cases. It is concluded that in the oxidation in AcOH the epoxides are first formed, and by fission and inversion give the $(OH)_2$-acids. A. Lt.

Autoxidation of oxygen-active acids. V. Viscosimetric and volumetric analysis of the addition of oxygen to the triglycerides. W. Treibs (*Ber.*, 1942, **75**, [*B*], 953—957; cf. A., 1942, II, 392).—

Quant. viscosimetric and volumetric analysis of the addition of O_2 to glyceryl oleate dilinoleate from soya-bean oil and glyceryl linoleate dilinolenate from linseed oil shows that the autoxidative behaviour of the glycerides is an additive function of that of the individual active chains. As in the case of the corresponding Me ester, the glycerides form initially monomeric peroxides; these subsequently undergo condensation and dehydration. In the drying of the corresponding vegetable oils, the glyceryl residues are responsible for the film-building capacity and form the points of union of the macromol. film nets. H. W.

Preparation of tartaric acids.—See B., 1943, II, 41.

Preparation of crystalline anhydrous citric acid.—See B., 1943, II, 41.

Preparation of sodium pyruvate. W. v. B. Robertson (*Science*, 1942, **96**, 93—94).—Pptn. by approx. equiv. amount of NaOH–EtOH from $AcCO_2H$–EtOH gives an 80% yield after recrystallisation. E. R. R.

Preparation of calcium gluconate.—See B., 1943, II, 37.

Condensations. XVII. Acylation of the anions of alkyl esters by phenyl esters. Preparation of ethyl propionylacetate and related β-keto-esters. B. Abramovitch and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2271—2274; cf. A., 1942, II, 132).—Treating ROAc with $NaCPh_3$ and then with $EtCO_2R'$ gives $EtCO{\cdot}CH_2{\cdot}CO_2R$ and R'OH; R and R' must be chosen so as to allow ready separation of the products. Adding EtOAc and then p-*diphenylyl propionate* [prep. from p-$C_6H_4Ph{\cdot}OH$, NaOH, and $(EtCO)_2O$ at ~5°] to $NaCPh_3$ in Et_2O–N_2 at −5° and later keeping at 15° gives *Et propionylacetate* [*β-keto-n-valerate*] (**I**) (44%), b.p. 91—92°/17 mm.; use of EtCOCl gives 32% of $(EtCO)_2CH{\cdot}CO_2Et$ and thence 16% of (**I**). *n*-$C_5H_{11}{\cdot}OAc$ with $NaCPh_3$ and $EtCO_2Ph$ gives 30% of n-*amyl propionylacetate*, b.p. 113—115°/10 mm. $Bu^{\beta}CO_2Et$ with $NaCPh_3$ and $EtCO_2Ph$ gives 58% of $EtCO{\cdot}CHPr^{\beta}{\cdot}CO_2Et$, b.p. 107—109°/21 mm. *Bu*$^{\gamma}$ *cyanoacetate* (prep. from $CH_2Br{\cdot}CO_2Bu^{\gamma}$ and KCN–MeOH), b.p. 107—108°/23 mm., with $MgEtBr$–Et_2O gives a complex mixture. COMeEt with $NaCPh_3$ and Et_2CO_3 gives mainly products of ketonic self-condensation. R. S. C.

Synthetic differential growth inhibitor.—See A., 1943, III, 256.

Syntheses of ethylene αβ-disebacate and glyceryl αβγ-trisebacate. Metabolic experiments with ethylene αβ-disebacate and sebacic acid. B. Flaschentrager and R. Allemann (*Annalen*, 1942, **552**, 106—112).—Freshly distilled $(CH_2{\cdot}OH)_2$ and Δ$^{\omega}$-undecenoic acid at 150°/120 mm. and then at 155°/120 mm. give H_2O and C_2H_4 *diundecenoate*, (**I**), b.p. 200—219°/high vac. It is converted by ozonisation in EtOAc at −18° and hydrogenation (Pd sponge) followed by oxidation ($KMnO_4$ in $COMe_2$ at room temp.) of the ozonide into C_2H_4 H_2 *disebacate*, m.p. 92—94° [Na_2, $(NH_4)_2$, *Mg*, *Ca*, *Ba*, and Ag_2 salts]. Glyceryl triundecenoate is similarly transformed into *glyceryl* H_3 *αβγ-trisebacate*, m.p. 88—90° [$(NH_4)_3$, Na_3, $Mg_{1.5}$, $Ca_{1.5}$, $Ba_{1.5}$, and Ag_3 salts]. In the dog (**I**) behaves in the same manner as free sebacic acid. The ester union of (**I**) is rapidly hydrolysed in the tissue and esters can scarcely participate, even in chain reactions, in the degradation of fats. H. W.

Formaldehyde synthesis from methane and oxygen atoms. M. Kuschnerev and A. Schechter (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 560—562; cf. A., 1935, 1087).—Yields of CH_2O are recorded on CH_4 mixed with 10% O_2 + 90% A obtained by the action of the silent electric discharge. A. T. P.

Condensation products of acetaldehyde. E. E. Connolly (*J.C.S.*, 1943, 42).—Crude aldol contains 35% of recoverable MeCHO, of which 50% can be recovered at room temp., and the rest by distillation with C_6H_6 or passing through a tube at 100°, but when fractionated in a vac. yields mobile aldol, b.p. 75°/16 mm., which rapidly polymerises, especially in the presence of electrolytes. [*R*] of paraldol (supercooled liquid) shows that it is probably cyclic. Crude aldol with 2% of H_2SO_4 yields a viscid polymeride, b.p. 136°/17 mm., which with NH_2OH,HCl (slowly), or when distilled with dil. H_2SO_4, gives equimol. amounts of MeCHO and $CHMe{:}CH{\cdot}CHO$, and may be

$$CHMe{\cdot}O{\cdot}CHMe{\cdot}CH_2{\cdot}CH(OH){\cdot}O$$
$$O{\cdot}CH(OH){\cdot}CH_2{\cdot}CHMe{\cdot}O\text{——}CHMe.$$

A. Li.

Derivatives of aldol and of crotonaldehyde. IV. Relationships between the monomeric aldol and its dimeric forms. E. Späth, R. Lorenz, and E. Freund (*Ber.*, 1942, **75**, [*B*], 1029—1039).—Monomeric aldol (**I**), paraldol (**II**), and the "viscous dimeric aldol" (**III**) in H_2O or aq. MeOH give with NH_2OH, p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$, or p-$C_6H_4Br{\cdot}NH{\cdot}NH_2$ in approx. equal amount the corresponding derivatives of (**I**), b.p. 110—120° (bath)/1 Torr, m.p. 115·5—116°, and m.p. 126—127°, respectively. (**I**) appears to show a pronounced tendency to form non-cryst. derivatives or to lose H_2O; thus even in dil. solution at 20° (**I**) or (**II**) affords essentially the dimedon derivative of $CHMe{:}CH{\cdot}CHO$. In H_2O (**I**) and (**II**) ultimately give an equilibrium mixture containing 48% and 69% of (**II**) in 2·16 and 9·92% solution. At 10 Torr (**III**) can be depolymerised to (**I**). In H_2O (**III**) gives an immediate mol. wt. somewhat < is required by $C_8H_{18}O_4$ and this val. diminishes in time to that observed with (**II**). At 100° (**II**) and (**III**) are interconvertible. Probably (**II**) and (**III**) are structurally identical but differ sterically. H. W.

Preparation of higher fatty aldehydes.—See B., 1943, II, 4.

Preparation and polymerisation of methyl vinyl ketone. T. White and R. N. Haward (*J.C.S.*, 1943, 25—31; cf. B., 1938, 1326).—$COMe_2$ (4 mols.) with paraformaldehyde (1 mol.) at pH 8·3—8·5 (with MeOH–KOH) at the b.p. yields a product which on distillation with o-$C_6H_4(CO_2Bu)_2$ gives $CH_2Ac{\cdot}CMe_2{\cdot}OH$ (**I**) (4—5), $OH{\cdot}[CH_2]_2{\cdot}Ac$ (27—28), $OH{\cdot}CH_2{\cdot}CAc{:}CH_2$ (14—15), 1 : 3-*dioxanyl*-5 *isobutenyl ketone* (**II**), b.p. 90—92°/12 mm. (2 : 4-dinitrophenylhydrazone, but no oxime or $NaHSO_3$ derivative) (10—11), and 1 : 3-dioxanyl-5 Me ketone (3—4%). The "3-ketobutanol" of previous workers is a mixture of some of the above. (**II**) with cold alkaline $KMnO_4$ yields $COMe_2$, and with 2N-HCl, CH_2O. (**I**), or the crude condensation mixture, when distilled with 10% of H_3PO_4, and the product treated with Ac_2O and fractionated, yields $COMe{\cdot}CH{:}CH_2$ (**III**). The rate of polymerisation of (**III**) in various solvents has been studied. The rapid polymerisation in precipitants, and the discrepancies in the kinetics of polymerisation in C_6H_6, confirm that chain termination is retarded in liquids which do not dissolve the polymeride. A. Li.

Polymerisation of keto-alcohols. I. Preparation and mechanism of polymerisation of γ-ketobutyl alcohol. E. N. Rutovski, A. A. Berlin, and K. Zabirina (*J. Gen. Chem. Russ.*, 1941, **11**, 550—558).—Optimum conditions for prep. of $OH{\cdot}[CH_2]_2{\cdot}COMe$ (**I**) from $COMe_2$ and CH_2O are: pH 8·2—8·4, temp. 30—35°. The pH should be adjusted to 6·8 as soon as possible after completion of the reaction. Velocity of polymerisation rises with temp. from 50° to 150°. With the exception of Ac_2O neutral and acid catalysts (H_2O_2, $ZnCl_2$, P_2O_5, Bz_2O_2) have only a very small catalytic action. With 1% of Na_2O_2 the polymerisation reaction is completed after 2 hr., and with 1% of NaOH after 20 hr. Alkaline catalysts have no action in the polymerisation of $OH{\cdot}CH_2{\cdot}CHMe{\cdot}COMe$. Refractometric and surface tension studies suggest that at room temp. 83% of (**I**) is in the enolic form $OH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}OH$, and the catalytic action of alkalis is ascribed to their effect in shifting the equilibrium point towards this form. The polymeride obtained in presence of Bz_2O_2 (36 hr. at 80°) has a higher sintering point (240—243°) than when NaOH is used (160°); both polymerides are sol. in org. solvents, but not in H_2O, and are not affected by exposure to light. R. T.

Preparation of diacetyl.—See B., 1943, II, 4.

Manufacture of α-dimethylaminopropane-βγ-diol.—See B., 1943, II, 4.

Kinetics of amination of organic halogen compounds in liquid ammonia.—See A., 1943, I, 65.

Solubilities and compositions of the phospho-12-tungstates of di-amino-acids and of proline, glycine, and tryptophan. D. D. Van Slyke, A Hiller, and R. T. Dillon (*J. Biol. Chem.*, 1943, **146**, 137—157).—Solubilities of the phospho-12-tungstates of arginine (**I**) (A_3P_2,8H_2O: A = NH_2-acid, P = H_3PO_4,12WO_3), histidine (**II**) (A_3P_2,6 or 12H_2O), lysine (**III**) (A_3P_2,10H_2O), and cystine (AP,6H_2O) and of glycine (**IV**) (A_3P,5H_2O), proline (**V**) (A_3P,2·5H_2O), and tryptophan (A_3P,10H_2O), are measured under varying conditions of temp. and concn. of mineral acid, and approx. optimal conditions are recorded for the phosphotungstate separation of the $(NH_2)_2$-from the NH_2-acids in protein hydrolysates. The time required for complete pptn. of phosphotungstate varies inversely with the solubility; at room temp., (**I**) and (**III**), which form the least sol. phosphotungstates, reach max. pptn. in a few hr., (**II**) and *l*-cystine in 48 hr., and (**IV**) and (**V**) in 72—96 hr. (**II**) forms mixed phosphotungstates with (**I**) and (**II**), so that when the mol. sum of (**I**) + (**III**) is > that of (**II**), pptn. of (**II**) is more complete than is indicated by solubility of the isolated phosphotungstates. Solubility effect of derivatives of (**I**) and (**III**) on (**II**) is plotted as a function of the proportion of (**II**) in the mixture. (**II**) does not show a similar effect on the solubility of the phosphotungstates of (**I**) and (**III**). A. T. P.

Organic catalysts. XXIV. Aldol condensation in the presence of secondary amino-acids. W. Langenbeck and G. Borth (*Ber.*, 1942, **75**, [*B*], 951—953).—Sarcosine, *N*-ethylglycine, *N*-methylalanine, and $NHMe{\cdot}CHPh{\cdot}CO_2H$ are excellent accelerators of the transformation of MeCHO into aldol, crotonaldehyde, and a small proportion of products of higher b.p. *N*-Ethyl- and *N*-benzyl-alanine and α-methylamino*iso*butyric acid are completely inactive. The catalysts retain their activity over long periods. H. W.

***N*-Monochlorocarbamates.** P. Chabrier (*Compt. rend.*, 1942, **214**, 362—365; cf. *ibid.*, 1941, **213**, 310).—Interaction of $OR{\cdot}CO{\cdot}NCl_2$ and $OR{\cdot}CO{\cdot}NH_2$ affords $2OR{\cdot}CO{\cdot}NHCl$, which form salts. *Me* N-*chlorocarbamate*, m.p. 32° (NaOEt gives the *Na* salt, $OMe{\cdot}CO{\cdot}NNaCl$, decomp. 115°; *Ag* salt, decomp. 40°), $NHCl{\cdot}CO_2Et$ (*Na* salt, decomp. 140°), and *β-chloroethyl* N-*chlorocarbamate*, m.p. 42° (*Na* salt, decomp. 75°), are prepared. A. T. P.

New preparation and properties of carbamidoformic esters. P. Charrier (*Compt. rend.*, 1942, **214**, 495—497).—Alkali salts of

N-chlorocarbamates and amides give carbamidoformic esters: $NClNa{\cdot}CO_2R' + R{\cdot}CO{\cdot}NH_2 \rightarrow NH_2{\cdot}CO_2R'$ (**I**) + $NClNa{\cdot}COR$ (**II**); (**II**) → $RNCO + NaCl$; $RNCO + (I) \rightarrow NHR{\cdot}CO{\cdot}NH{\cdot}CO_2R'$. C_6H_6 is a particularly suitable medium but, in some cases, can be replaced by H_2O. EtOH is apt to lead to production of urethanes. Thus nicotinamide affords *Me nicotinylcarbamidoformate*, m.p. 218°, and Et nicotinoylcarbamate, m.p. 85°. The presence of halogen in amide or carbamate is no obstacle to the reaction. Thus NHClAc and $NClNa{\cdot}CO_2Me$ afford *Me chloromethylcarbamidoformate*, m.p. 168°, and NH_2Bz and $NClNa{\cdot}CO_2Et$ give *β-chloroethyl phenylcarbamidoformate*, m.p. 117·5°. Reaction appears general and the yields are good with simple aliphatic or aromatic amides but mediocre with $HCO{\cdot}NH_2$. Alkalis or alkali carbonates hydrolyse the esters and the products when acidified give CO_2 and monosubstituted carbamides in good yield: $NHR{\cdot}CO{\cdot}NH{\cdot}CO_2H \rightarrow NHR{\cdot}CO{\cdot}NH_2 + CO_2$. NH_3 transforms the esters into substituted biurets whilst N_2H_4 yields substituted semicarbazides $NHR{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$ which react readily with aldehydes and ketones. H. W.

Catalytic hydrogenation of cystine. K. E. Kavanagh (*J. Amer. Chem. Soc.*, 1942, **64**, 2721).—Cystine is readily hydrogenated to cysteine in 2N-HCl in presence of a little Pd deposited on a high-polymeric support (Pd–PVA). R. S. C.

Behaviour of cystine dimethyl ester dihydrochloride and of cysteine monomethyl ester monohydrochloride in the Sullivan reaction for cysteine and cystine. M. X. Sullivan, W. C. Hess, and H. W. Howard (*J. Washington Acad. Sci.*, 1942, **32**, 285—287).—The behaviour of cystine Me_2 ester dihydrochloride (**I**) and of cysteine Me ester monohydrochloride (**II**), m.p. 137—138·5°, softens at 110—130° (prep. from cysteine hydrochloride and HCl–MeOH at 45° for 10 min., followed by adding to excess of Et_2O at 0°), in the Sullivan reaction is compared with that of cystine (**III**) and cysteine (**IV**). (**I**) and (**II**) are hydrolysed by NaCN in aq. NaOH to (**III**) and (**IV**), respectively. (**I**) is hydrolysed by 0·1N-HCl at room temp. (22 hr.), whereas (**II**) is not. (**I**) and (**II**) are relatively stable in H_2O, and in solutions of low acidity at room temp., (**I**) is hydrolysed much more slowly than in 0·1N-HCl. (**I**) and (**II**) have a higher colorigenic val. than (**III**) and (**IV**), respectively, in the Sullivan reaction, when aq. NaCN is used to cleave the disulphide or to act as adjuvant in the cysteine reaction. If NaCN in N-NaOH is used, (**I**) gives approx. the same val. as (**III**). (**II**) treated with 0·1% NaCN in 0·8N-NaOH gives the same val. as (**IV**). A. T. P.

Taurine. A. A. Goldberg (*J.C.S.*, 1943, 4—5).—$NH_2{\cdot}[CH_2]_2{\cdot}SO_4H$ with aq. Na_2SO_3 at 140° (50 lb. pressure) for 20 hr. yields taurine (62%), which with the appropriate acid chloride (added gradually) in 5N-NaOH yields *Na phenylacetamido-*, *β-phenylpropionamido-*, and *acetylmandelamido-ethanesulphonate*. Median lethal dosages of these for mice are given. A. Li.

Manufacture of guanidine carbonate.—See B., 1942, II, 419.

Preparation of biuret.—See B., 1942, II, 421.

Reaction between thioamides and primary amines. M. J. Schlatter (*J. Amer. Chem. Soc.*, 1942, **64**, 2722).—$CS(NH_2)_2$ with NH_2Bu^a at the b.p. gives NH_3 and *N-n*-butyl-, b.p. 131·5°/5 mm., and with $CH_2Ph{\cdot}NH_2$ at 80° gives *N-n*-benzyl-thioacetamide, m.p. 65·1—65·3° (corr.), b.p. 158—162°/2 mm., but with $OH{\cdot}[CH_2]_2{\cdot}NH_2$ at 60—75° gives (?) *di-α-β'-hydroxyethyliminoethyl sulphide*, m.p. 101—101·5° (corr.) [picrate, m.p. 95—95·5° (corr.)]. H_2S and NH_3 may also be formed. R. S. C.

Acylation of acetonitrile by ethyl *n*-butyrate. Alcoholysis of the resulting keto-nitrile to ethyl *n*-butyrylacetate. B. Abramovitch and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2720—2721).—Adding MeCN and then Pr^aCO_2Et to $NaCPh_3$–Et_2O gives *β-keto-*n*-hexonitrile* (52%), b.p. 104—105°/11 mm., converted by HCl–EtOH into $COPr^a{\cdot}CH_2{\cdot}CO_2Et$. R. S. C.

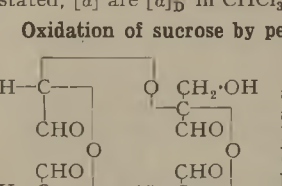
Preparation of adiponitrile.—See B., 1942, II, 417.

II.—SUGARS AND GLUCOSIDES.

Preparation of *d*-fructose 1 : 6-diphosphate by means of baker's yeasts. C. Neuberg and H. Lustig (*J. Amer. Chem. Soc.*, 1942, **64**, 2722—2723).—Fresh baker's yeast converts sucrose in aq. NaH_2PO_4–$NaHCO_3$–Et_2O into *d*-fructose 1 : 6-diphosphate, isolated as Ca salt. Dried, but not fresh, Fleischmann's yeast is also effective if CCl_4 is added. R. S. C.

***D*-Galactosan<1, 5>β<1, 6>.** R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 2435—2438).—The structure of *D*-galactosan<1, 5>β<1, 6> (**I**) is confirmed by oxidation by aq. HIO_4 at 20° to *L'*-oxy-*D*-methylenediglycollic dialdehyde and thence (Br–$SrCO_3$) Sr *L'*-oxy-*D*-methylenediglycollate, $+5H_2O$, and by consumption of 2 equivs. of $Na_2I_4O_7$ to give 0·98 HCO_2H. Pyrolysis of α-lactose and treating the product with $COMe_2$–$CuSO_4$ gives *L*-glucosan<1, 5>β<1, 6> (13%) and 3 : 4-*iso*propylidene-*D*-galactosan<1, 5>β<1, 6> (**II**) (18%), m.p. 151—152°, [α] −72·9°. In C_5H_5N, (**II**) gives 3 : 4-iso*propylidene*-D-*galactosan*<1, 5>β<1, 6> 2-*acetate*, m.p. 136—137°, [α] −51·4°, 2-*benzoate* (**III**), m.p. 119—120°, [α] +6·3°, and 2-p-*toluenesulphonate*, m.p. 118—119°, [α] −63·7°, and in 0·1N-HCl gives (**I**) (91%), m.p. 223—224°, [α] −22·0° in H_2O. In C_5H_5N, (**I**) gives the 2 : 3 : 4-*tribenzoate* (**IV**), m.p. 89—90°, [α] +84·8°, and *-tri*-p-*toluenesulphonate*, m.p. 103—104° (corr.), [α] −51·1°. Boiling 20% AcOH hydrolyses (**III**) to D-*galactosan*<1, 5>β<1, 6> 2-*benzoate*, m.p. 164—165°, [α] +47·2°, converted by BzCl–C_5H_5N into (**IV**), by $COMe_2$–$CuSO_4$ into (**III**), and by Ac_2O–C_5H_5N at room temp. into the 2-*benzoate* 3 : 4-*diacetate*, m.p. 103—104°, [α] +85·4°, or, similarly, 2-*benzoate* 3 : 4-*di*-p-*toluenesulphonate*, m.p. 119—120°, [α] +78·0°. Unless otherwise stated, [α] are $[\alpha]_D^{20}$ in $CHCl_3$. R. S. C.

Oxidation of sucrose by periodic acid. P. Fleury and J. Courtois (*Compt. rend.*, 1942, **214**, 366—368).—Sucrose (**I**) (1 mol.) and HIO_4 (3 mols.) at 14° (24 hr.) afford HCO_2H (1 mol.) and the *tetraldehyde* (**I**), oxidised by aq. Br to the corresponding *tetra-acid*, or by Br in $BaCO_3$ or $SrCO_3$, followed by pptn. with EtOH from aq. solution, the respective *Ba*$_2$ or *Sr*$_2$ salt. Acid hydrolysis at 100° of the salts affords glyceric, glyoxylic, and hydroxypyruvic acid, thus confirming the constitution assigned to (**I**). A. T. P.



(I.)

Stabilisation of the glycosidic linking by anhydride formation. B. Helferich and J. Werner (*Ber.*, 1942, **75**, 949—951).—Glycol iodohydrin *β-d*-glucoside (A., 1940, II, 40) is smoothly converted by boiling NaOH into *glycol β-*d*-glucoside anhydride* (**I**), m.p. 210—211°, $[\alpha]_D^{22}$ +56·0° in H_2O (*triacetate*, m.p. 125°, $[\alpha]_D^{18}$ +52·6° in $CHCl_3$), also obtained similarly from glycol chlorohydrin *β-d*-glucoside tetra-acetate. (**I**) is not hydrolysed by emulsin of sweet almonds nor appreciably by boiling with N-HCl or N-H_2SO_4 for 16 hr. H. W.

Synthesis of phenolic glucosides. T. H. Bembry and G. Powell (*J. Amer. Chem. Soc.*, 1942, **64**, 2419—2420).—The fully acetylated sugar, ArOH, and $POCl_3$ + 1% of H_2O in boiling C_6H_6 give *β*-phenyl-*d*-glucoside (44%), -galactoside (44%), and -fructoside tetra-acetate (33%; best prepared at room temp.), *β*-phenyl-*d*-xyloside triacetate (57%), *β*-1-naphthyl- (58%) and *β*-2-*diphenylyl*-d-*glucoside tetra-acetate* (35%), m.p. 155—156° (corr.), $[\alpha]_D^{22}$ −56° in $CHCl_3$, and thence *β*-2-*diphenylyl*-d-*glucoside* (90%), m.p. 76—77° (corr.), $[\alpha]_D^{25}$ −42° in EtOH. R. S. C.

Syntheses of natural phloridzin. G. Zemplén and R. Bognár (*Ber.*, 1942, **75**, [*B*], 1040—1043).—4-Benzoylphloracetophenone, KOH, and acetobromoglucose in aq. $COMe_2$ at room temp. yield 2-d-*glucosido*-4-*benzoylphloracetophenone tetra-acetate*, m.p. 176—177°, $[\alpha]_D^{23}$ −30·0° in C_5H_5N, condensed with *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ and conc. KOH to naringenin-2'-glucoside, m.p. 173—174°, softens at 149°, $[\alpha]_D^{26}$ −20·6° in 96% EtOH, −8·2° in C_5H_5N; this is hydrogenated (Pd–C in 96% EtOH) to phloridzin (+2H_2O), m.p. 108—110° (loss of H_2O), $[\alpha]_D^{25}$ −51·7° in 96% EtOH for the hydrated material. H. W.

Synthesis of glucohespertin, a hesperitin-7-glucoside. G. Zemplén and R. Bognár (*Ber.*, 1942, **75**, [*B*], 1043—1047; cf. Kolle *et al.*, A., 1936, 970).—4-*d*-Glucosidophloracetophenone tetra-acetate, KOH, and *iso*vanillin in aq. EtOH yield *hesperetin-4'-glucoside* (**I**) (chalkone form) (+3H_2O), m.p. ~110—115° (much evolution of H_2O), changes at 105°, $[\alpha]_D^{16}$ −32·6° in C_5H_5N, anhyd. m.p. ~200—204°, softens at 160° and becomes viscous at 165°, which gives an amorphous acetate. It is transformed by boiling 0·2% H_2SO_4 into *hesperetin-7-glucoside* (flavanone form) (+1H_2O), m.p. 206°, softens at 190°, $[\alpha]_D^{15}$ −53·9°, $[\alpha]_D^{25}$ −51·9° in C_5H_5N, but some difficultly removable hesperetin is simultaneously produced so that the homogeneous material is best obtained by hydrolysis of neohesperidin. It is converted by Ac_2O–C_5H_5N at room temp. into 7-*tetra-acetylglucosido-hesperetin diacetate*, m.p. 151—152°, $[\alpha]_D^{26}$ −23·7° in C_5H_5N. Hydrogenation (Pd–C in 96% EtOH) of (**I**) affords 3-*hydroxyphloretin-4'-glucoside* 4-*Me ether* (+2H_2O), m.p. indef. 88—92°, softens at 82°, $[\alpha]_D^{20}$ −59·7° in C_5H_5N, anhyd. m.p. 155—157° softens at 135°, which gives an amorphous acetate and is hydrolysed by boiling 3% HCl to 3-*hydroxyphloretin* 4-*Me ether*, m.p. 194—196°. H. W.

Vinyl ethers of cellulose. A. E. Favorski, V. I. Ivanov, and Z. I. Kuznetzova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 630—632).—Cellulose (**I**) and C_2H_2 in an autoclave at 120—150° in presence of a catalyst give mono- and di-vinyl ethers; under the conditions, cellulose is unchanged when C_2H_2 is replaced by N_2. The ethers are partly sol. or insol. in cuprammonium solution, and are hydrolysed to (**I**) and MeCHO. A. T. P.

III.—HOMOCYCLIC.

Conversion of *cyclo*pentane hydrocarbons of petroleum into *cyclo*hexane hydrocarbons. M. B. Turova-Poljak, N. D. Zelinski, and G. R. Hasan-Zade (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 551—554).—*cyclo*Pentane hydrocarbons are isomerised to *cyclo*hexane hydrocarbons by 10% of $AlCl_3$ at 35° for 15—18 hr.; dehydrogenation then yields the corresponding C_6H_6 derivative. Paraffin hydrocarbons in the petroleum are unaffected. The *cyclo*-

pentane content of petroleum can be determined by dehydrogenation (Pt–C) at 310° before and after treatment with $AlCl_3$. Methyl*cyclo*pentane affords *cyclo*hexane, and thence C_6H_6. A. T. P.

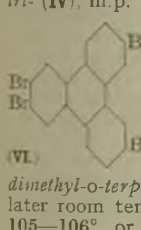
Reactions of neopentyl systems with electrophilic reagents. P. Skell and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2633—2635).—PhCHO and $MgBu^{\gamma}Cl$ give $CHPhBu^{\gamma}\cdot OH$ (**I**) with some $COPhBu^{\gamma}$. HBr in light petroleum at 0° gives $CHPhBu^{\gamma}Br$ (**II**), b.p. 103—104° (corr.)/7·5 mm., which is very slowly hydrolysed by H_2O, with MeOH–K_2CO_3 gives the Me ether, b.p. 94—95° (corr.)/20 mm., and with KOAc–AcOH gives the acetate, b.p. 123—124°/16 mm. With aq. $AgNO_3$ at room temp., (**I**) gives <70% of (**II**). $CPh_3\cdot CHPh\cdot OH$ with HBr–C_6H_6 or conc. H_2SO_4 at room temp. gives $(CPh_2{:})_2$. Differences from the CH_2Bu^{γ} series are as expected. R. S. C.

Rearrangement of 1 : 1 : 3 : 3 : 5 : 5-hexamethyl*cyclo*hexane-2 : 4 : 6-triol to hexamethylbenzene. E. B. Ayres and C. R. Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2461—2462).—Hexamethyl*cyclo*hexane-1 : 3 : 5-trione (A., 1940, II, 65) and H_2–Cu chromite at 200°/200 atm. give 1 : 1 : 3 : 3 : 5 : 5-*hexamethyl*cyclo*hexane*-2 : 4 : 6-*triol*, m.p. 251—251·5°, converted by conc. H_2SO_4 at 0° into C_6Me_6 (19·4%; very little by 85% H_3PO_4; none by $SOCl_2$). R. S. C.

Halogenation of *m*-diphenylbenzene. II. Monoiodo-derivative. W. A. Cook and K. H. Cook (*J. Amer. Chem. Soc.*, 1942, **64**, 2485—2486).—1 : 3 : 4-$C_6H_3Ph_2Cl$ with 28% aq. NH_3–CuCl–CaO–Cu ribbon at 190°/800—850 lb. gives 1 : 3 : 4-$C_6H_3Ph_2\cdot NH_2$, m.p. 74° (lit. 64°) (*phenylthiocarbamide* derivative, m.p. 135°), which by a diazo-reaction (KI) gives 4-*iodo*-1 : 3-*diphenylbenzene*, m.p. 67°, b.p. 235—240° (corr.)/1 mm. R. S. C.

Separation of anthracene from carbazole.—See B., 1943, II, 42.

***o*-Terphenyl. II. Derivatives prepared from the hydrocarbon.** C. F. H. Allen and F. P. Pingert (*J. Amer. Chem. Soc.*, 1942, **64**, 2639—2643; cf. A., 1942, II, 355).—*o*- (**I**) is less reactive than is *m*- or *p*-$C_6H_4Ph_2$, but reactions must not be forced to completion lest difficultly separable mixtures be formed. Traces of retained solvents affect the results; *e.g.*, traces of H_2O or EtOH favour polybromination and AcOH inhibits bromination or nitration. With anhyd. $AlCl_3$ and BzCl, (**I**) gives mixtures, but with the additive compound, $AlCl_3$,BzCl, in CS_2 gives a good yield of 4′-*benzoyl*-*o*-*terphenyl*, *p*-$C_6H_4Bz\cdot C_6H_4Ph$-*o*, m.p. 111°, also obtained from *o*-C_6H_4PhI by *p*-$C_6H_4Br\cdot COPh$ and Cu-bronze at 240° and converted by way of the *oxime*, *forms*, m.p. 68° and (stable) 138°, into the anilide and thence 4′-carboxy-*o*-terphenyl (**II**). With $AlCl_3$–Ac_2O–$PhNO_2$, (**I**) gives 4′-*acetyl*-*o*-*terphenyl* (~43%; less by AcCl or in CS_2), m.p. 94°, also obtained from *o*-C_6H_4PhI by *p*-$C_6H_4Br\cdot COMe$ and Cu-bronze at 220° and oxidised to (**II**) by NaOCl. According to the conditions, bromination gives 4′ : 4″-*di*- (**III**), m.p. 170°, 4 : 4′ : 4″-*tri*- (**IV**), m.p. 170°, or 4 : 5 : 4′ : 4″-*tetra-bromo*-*o*-*terphenyl* (**V**), m.p. 228° (or an isomeride, m.p. 120° after sintering), and finally 3 : 5 : 10 : 11-*tetrabromotriphenylene* (**VI**), m.p. >450° (block). Structures are proved by oxidation of (**III**), (**IV**), and (**V**) by CrO_3–AcOH to *p*-$C_6H_4Br\cdot CO_2H$, by bromination of (**IV**) to (**V**), and by prep. of triphenylene from (**VI**) by distilling with Zn dust.


(VI.)

1 : 2 : 3 : 6-$C_6H_3Ph_2Me_2$ gives 4 : 5 : 4′ : 5′-*tetrabromo*-3 : 6-*dimethyl*-*o*-*terphenyl*, m.p. 205°. Conc. HNO_3 in Ac_2O at 0—5° and later room temp. converts (**I**) into the 4′-NO_2- (**VII**) (78%), m.p. 105—106°, or with less cooling into the 4′ : 4″ (**VIII**), m.p. 218°, [also obtained from (**VII**) by fuming HNO_3 in Ac_2O at 10°—room temp.], and 2′ : 4′-$(NO_2)_2$-compound (**IX**), m.p. 169°. Oxidation (CrO_3–AcOH) of (**VIII**) gives *p*-$NO_2\cdot C_6H_4\cdot CO_2H$ and of (**IX**) gives 2 : 4 : 1-$(NO_2)_2C_6H_3\cdot CO_2H$. H_2–Raney Ni–EtOH yields 4′-*amino*-, m.p. 108° (less after keeping) (*Bz* derivative, m.p. 175°), and 4′ : 4″-*diamino*-*o*-*terphenyl*, m.p. 149°, unstable in air, converted by tetrazo-reactions into (**III**), (**I**), and a *bis*-β-*naphtholazo*-compound, m.p. 209° (decomp.). Br vapour and (**VIII**) give 4 : 5-*dibromo*-4′ : 4″-*dinitro*-*o*-*terphenyl*, m.p. 228°, and some (?) triphenylene derivative. R. S. C.

New type of condensation reaction under the influence of aluminium chloride. D. N. Kursanov and R. R. Zelvin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **36**, 17—21).—Contrary to Tzukervanik *et al.* (A., 1937, II, 331) the condensation product ($AlCl_3$) of EtOH with C_6H_6 has m.p. 179°. This and the product from HCO_2Et, EtOAc, or $CH_2Cl\cdot CO_2Et$ with C_6H_6 and $AlCl_3$ or PhEt with $AlCl_3$ is 9 : 10-dimethylanthracene, hydrogenated (Pd-black) to 9 : 10-*dimethyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydroanthracene*, m.p. 140—141·5°. F. R. G.

Synthesis of naphthalene-2 : 7-dialdehyde. Attempted synthesis of coronene. J. H. Wood and J. A. Stanfield (*J. Amer. Chem. Soc.*, 1942, **64**, 2343—2344).—2 : 7-$C_{10}H_6(CN)_2$ with $SnCl_2$–HCl–Et_2O and then boiling H_2O gives *naphthalene*-2 : 7-*dialdehyde* (24·3%), m.p. 142° (corr.) (*di*-2 : 4-*dinitrophenylhydrazone*, decomp. begins at 295°, complete at 312—313°), oxidised by $KMnO_4$ to 2 : 7-$C_{10}H_6(CO_2H)_2$. Attempts to obtain coronene from the derived dithioaldehyde (H_2S–HCl) by Cu and then heat alone or with Se failed. R. S. C.

Friedel–Crafts acylations of sterically hindered alkylbenzenes. G. F. Hennion and S. F. deC. McLeese (*J. Amer. Chem. Soc.*, 1942, **64**, 2421—2422).—*sec.*-Alkylbenzenes give ($AlCl_3$–CS_2; −10°) *p*-$C_6H_4Alk\cdot COMe$ (**I**) or *p*-$C_6H_4Alk\cdot COPh$ (**II**). *p*-Di-*sec.*-alkylbenzenes give similarly (at the b.p.) 2 : 5 : 1-$C_6H_3Alk_2\cdot COMe$ (**III**) and -$C_6H_3Alk_2\cdot COPh$ (**IV**). Yields are usually 60—88%. $Na_2Cr_2O_7$–H_2SO_4–AcOH at 65—75° converts (**I**) or (**III**) into *p*-$C_6H_4(CO_2H)_2$. With boiling HNO_3 (*d* 1·09), (**I**) gives *p*-$C_6H_4Alk\cdot CO_2H$, (**III**) gives 4 : 1 : 3-$C_6H_3Alk(CO_2H)_2$, (**II**) gives *p*-$C_6H_4Bz\cdot CO_2H$, and (**IV**) gives 2 : 1 : 4-$C_6H_3Bz(CO_2H)_2$. With CrO_3 and then HNO_3 (1 : 2; tube), (**III**; Alk = *sec.*-Bu) gives 1 : 2 : 4-$C_6H_3(CO_2H)_3$. The following are described. p-sec.-*Butyl*-, b.p. 134—135°/11 mm. (semicarbazone, m.p. 190—191°), p-sec.-*amyl*-, b.p. 144—145°/11 mm. (semicarbazone, m.p. 173—174°), p-sec.-*octyl*-, b.p. 134—135°/3 mm. (semicarbazone, m.p. 144—145°), 2-*methyl*-5-sec.-*butyl*-, b.p. 132—133°/11 mm. (semicarbazone, m.p. 114—115°), 2 : 5-*di*-sec.-*butyl*-, b.p. 148—149°/14 mm. (semicarbazone, m.p. 160—161°), and 2 : 5-*di*-sec.-*amyl*-, b.p. 126—127°/3 mm. (semicarbazone, m.p. 149—150°), -*acetophenone*; p-sec.-*butyl*-, b.p. 188°/9 mm., p-sec.-*amyl*-, b.p. 188—190°/5 mm., p-sec.-*octyl*-, b.p. 212—214°/5 mm., p-sec.-*dodecyl*-, b.p. 243—245°/4 mm., and 2 : 5-*di*-sec.-*butyl*-, b.p. 155°/3 mm., -*benzophenone*; p-sec.-*butyl*-, m.p. 91—92°, and -*amyl*-*benzoic acid*, m.p. 103—104°; 4-sec.-*butyl*-, m.p. 237—238°, and -*amyl*-*isophthalic acid*, m.p. 230—231°. *p*-$C_6H_4Bu^{\gamma}_2$ with AcCl–$AlCl_3$–CS_2 gives *p*-$C_6H_4Bu^{\gamma}\cdot COMe$. R. S. C.

Polymerisation of styrene catalysed by *p*-bromobenzenediazonium hydroxide. C. C. Price and D. A. Durham (*J. Amer. Chem. Soc.*, 1942, **64**, 2508—2509).—Adding NaOH to *p*-$C_6H_4Br\cdot N_2Cl$ and $CH_2{:}CHPh$ in H_2O at 0° yields a mixed *polymeride*, containing 4·2% of Br and (from η) 2 $CH_2{:}CHPh$ units; this is due to *p*-C_6H_4Br radicals. R. S. C.

Isomerisation of unsaturated hydrocarbons in presence of oxides of metals. V. Isomerisation of δ-phenyl-Δ$^{\alpha}$-butene and ε-phenyl-Δ$^{\alpha}$-pentene in presence of aluminium and chromium oxide. R. J. Levina and N. A. Schtscheglova. **VI. Isomerisation of δ-phenyl-Δ$^{\alpha}$-butinene in presence of chromic oxide.** R. J. Levina and E. M Panov (*J. Gen. Chem. Russ.*, 1941, **11**, 527—532, 533—536).—V. $Ph\cdot[CH_2]_2\cdot CH{:}CH_2$ passed over Al_2O_3 at 250° or over Cr_2O_3 at 225° yields $CHPh{:}CHEt$. $Ph\cdot[CH_2]_3\cdot CH{:}CH_2$ yields $CHPh{:}CHPr^{\alpha}$ when passed over Cr_2O_3 at 250°; with Br in Et_2O it yields *αβ-dibromo*-ε-*phenylpentane*, b.p. 172°/9 mm.

VI. $Ph\cdot[CH_2]_2\cdot C{:}CH$ passed over Cr_2O_3 at 250° yields $CPh{:}CEt$, with a mixture of polymerides. R. T.

Bromination of diphenylalkanes and preparation of stilbene derivatives. I. αβ-Diphenylethane.—See A., 1943, II, 92.

***s*-*p*-Dichlorotetraphenylethylene.** C. C. Price and P. E. Fanta (*J. Amer. Chem. Soc.*, 1942, **64**, 2726—2727).—*p*-$C_6H_4Cl\cdot COPh$ with PCl_5 at 150° gives *p*-$C_6H_4Cl\cdot CPhCl_2$ (90%), b.p. 189—194°/12 mm., which with NaI–$COMe_2$ gives a mixture [? $COPh\cdot CPh(C_6H_4Cl\text{-}p)_2$ + *p*-$C_6H_4Cl\cdot CO\cdot CPh_2\cdot C_6H_4Cl$-*p*), m.p. 126—145°, but with Zn in dry Et_2O gives *s*-*diphenyldi*-p-*chlorophenylethylene*, m.p. 202—203°, reduced by Na–EtOH to $(CHPh_2)_2$ and by H_2–Raney Ni in methyl*cyclo*hexane at 100°/110 atm. to a mixture including $CPh_2{:}CPh\cdot C_6H_4Cl$-*p*, m.p. 168° (lit. 165—166°, 162°). R. S. C.

Stereochemistry of diphenylpolyenes. L. Zechmeister and A. L. LeRosen (*Science*, 1942, **95**, 587—588).—Stereoisomerides of diphenyloctatetraene were prepared by several methods and separated by chromatographic analysis, developing the chromatogram with a C_6H_6–light petroleum on $Ca(OH)_2$. Preliminary details of the separation are given. E. R. R.

Isodimorphism of β-naphthol and naphthalene.—See A., 1943 I, 85.

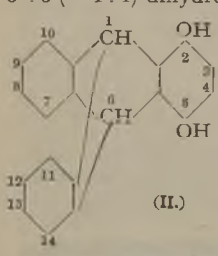
1 : 3 : 5 : 7-Tetranitronaphthalene and the isomeric tetranitro-derivatives obtained from 2 : 6-dinitronaphthalene by nitration. J. Chatt and W. P. Wynne (*J.C.S.*, 1943, 33—36).—Oxidation (HNO_3, *d* 1·16, at 200°) of 1 : 3-$C_{10}H_6(NO_2)_2$ yields only 3 : 5 : 1-$C_6H_3(NO_2)_2\cdot CO_2H$, whilst nitration (67% excess of $NO_2\cdot SO_3H$ in H_2SO_4) gives 1 : 3 : 8-$C_{10}H_5(NO_2)_3$. 2 : 6-$C_{10}H_6(NO_2)_2$ {from 2 : 6-$C_{10}H_6(OH)_2$ by amination [40% $(NH_4)_2SO_3$ in 20% aq. NH_3 at 140° under pressure], diazotisation, and treatment with $NaNO_2$ and cuprocupric sulphite} with HNO_3–H_2SO_4 yields 1 : 3 : 5 : 7- (**I**), m.p. 260°, decomp. 263—265° (43%), 1 : 2 : 6 : 8- (**II**), m.p. 138° (8·4%), and ?-*tetranitro*-*naphthalene*, m.p. 215° (1·3%). (**I**) yields with HNO_3 (*d* 1·16) at 200°, 3 : 5 : 1-$C_6H_3(NO_2)_2\cdot CO_2H$, with $POCl_3$–PCl_5 at 180—200°, a mixture of $C_{10}H_4Cl_4$ and $C_{10}H_3Cl_5$, and with $SnCl_2$ in EtOH–HCl, 1 : 3 : 5 : 7-$C_{10}H_4(NH_2)_4$, the *hydrochloride* of which when diazotised (in H_3PO_4–H_2SO_4) and treated with $CO(NH_2)_2$ followed by CuCl in conc. HCl yields a small amount of 1 : 3 : 5 : 7-$C_{10}H_4Cl_4$ (this could not be repeated). The constitution of (**I**) is confirmed by m.p. analogy and crystallographic examination. (**II**) yields with HNO_3 (*d* 1·16) at 190—200°, a mixture of 3 : 5 : 1 : 2-$(NO_2)_2C_6H_2(CO_2H)_2$ and 3 : 5 : 1-$C_6H_3(NO_2)_2\cdot CO_2H$, and with PCl_5–$POCl_3$ at 180°, a ?-*tetrachloronaphthalene*, m.p. 125—127°. A. I.I.

Action of aluminium chloride on tetrahydronaphthalene. A. Dansi and C. Ferri (*Gazzetta*, 1941, **71**, 648—651).—Tetrahydronaphthalene (**I**) and $AlCl_3$ at 35—80° give $C_{10}H_8$, an oily fraction [dehydrogenated (Se at 350°) to a *compound*, $C_{16}H_{10}$, m.p. 147—

152° (sublimes 180°/2·5 mm.)], and a *compound*, $C_{20}H_{30}$ (**II**), m.p. 150·5°, regarded as 1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-1 : 2 : 1′ : 2′-*bisnaphthalene*, different from the compound described by von Braun *et al.* (A., 1921, i, 405), and having a similar absorption spectrum to (**I**). With Br–$CHCl_3$, (**II**) gives a *compound*, $C_{20}H_{19}Br$, m.p. 152°, and with Se at 320—340°, a *compound*, $C_{20}H_{12}$, m.p. 165° (picrate, m.p. 195°), of characteristic absorption spectrum.

E. W. W.

Triptycene [9 : 10-*o*-phenyleneanthracene]. P. D. Bartlett, M. J. Ryan, and S. G. Cohen (*J. Amer. Chem. Soc.*, 1942, **64**, 2649—2653).—The adduct (**I**), obtained (83%) from anthracene and *p*-O:C_6H_4:O in boiling xylene, with 40% HBr (4 drops) in boiling AcOH gives 3′ : 6′(= 1 : 4)-dihydroxy-9 : 10-*o*-phenylene-9 : 10-dihydroanthracene



(II.)

[2 : 5-dihydroxytriptycene] (**II**) (90%), m.p. 338—340° (decomp.), converted by H_2–Raney Ni in dioxan at 200°/1140 lb. into a H_{12}-derivative, m.p. 220—224°, which is hydrogenated in the unsubstituted rings and is oxidised by air in aq. alkali. With H_2–Cu chromite in dioxan at 160°/2200 lb., (**I**) gives a *compound*, $C_{20}H_{20}O_2$, m.p. 226—228° (diacetate, m.p. 177—178°), stable in air and thus reduced in the quinol ring. Many attempts to remove the OH from (**II**) failed. $KBrO_3$–AcOH–H_2O oxidises (**II**) to the quinone (93%), m.p. 292—296°, the *dioxime*, m.p. 246° (decomp.), of which with $SnCl_2$–HCl–EtOH at ~60° gives 2 : 5-*diaminotriptycene* (**III**) (86%), m.p. 307° (decomp.) [hydrochloride (**IV**), decomp. >210°; Ac_2 derivative, decomp. 370°]. Attempts to remove the NH_2 directly from (**III**) failed. Treating (**IV**) in AcOH with, successively, H_2SO_4–AcOH–H_2O, $NaNO_2$, and $CO(NH_2)_2$ (all at 10°), addition to NaH_2PO_2–conc. HCl, keeping overnight, and sublimation of the product at 195°/2 mm., gives mono- + a little dichlorotriptycene, m.p. 222—223°, which with H_2–Pd–$CaCO_3$–N_2H_4–KOH–EtOH–H_2O gives *triptycene* [9 : 10-*o*-*phenylene*-9 : 10-*dihydroanthracene*] (**V**), m.p. 254·8—255·2°. Treating the tetrazonium solution from (**IV**) with NaH_2PO_2–HBr gives a very poor yield of 2 : 5-*dibromotriptycene*, m.p. 227—228°, debrominated to (**V**). Inability of (**V**) to become planar prevents resonance so that the central CH do not show the same properties as in $CHPh_3$. Thus, (**V**) is unaffected by $CKPhMe_2$–Et_2O–N_2, SO_2Cl_2–Bz_2O_2, and $(CH{\cdot}CO)_2O$ in boiling $PhNO_2$, and is barely affected by Cl_2–CCl_4; CrO_3–AcOH oxidises (**V**) to anthraquinone (76%) and ~6 CO_2; this is in accord with bond-fixation (Mills–Nixon effect) since the internal bond-angles are 109° 28′.

R. S. C.

***cyclo*Pentylamides of [aliphatic] carboxylic acids.**—See B., 1943, II, 74.

Nuclear alkylation of aromatic bases. V. Action of methyl alcohol on *m*-toluidine hydrochloride. R. W. Cripps and D. H. Hey (*J.C.S.*, 1943, 14—15; cf. A., 1931, 950).—*m*-$C_6H_4Me{\cdot}NH_2$,HCl (1 mol.) and MeOH (1 mol.) at 210—235° (8 hr.) give *o*-4-xylidine in ~35% yield, with some methylated acridines (**I**), but no phenols. With 2 or (better) 3 mols. of MeOH at 210—220° (5½ hr.), *ψ*-cumidine is formed in ~50% yield, with some (**I**); 4 mols. of MeOH at 260—280° (10 hr.) afford *iso*duridine, *iso*durenol, $C_6Me_5{\cdot}OH$, and (**I**). *m*-Methylation in the Hofmann–Martius reaction is established.

A. T. P.

Compounds of aromatic amines with lower fatty acids.—See A., 1943, I, 88.

Sulphonation of benzylethylaniline. L. Blangey, H. E. Fierz-David, and G. Stamm (*Helv. Chim. Acta*, 1942, **25**, 1162—1179).—NPhEt·CH_2Ph (**I**) with oleum at >60° gives (cf. Gnehm *et al.*, A., 1908, i, 112) mainly (~78%) m-*sulphobenzylethylaniline* (*K* and *Na* salts; corresponding *amide*, m.p. 98—99°), which is transformed by nascent Br and subsequent oxidation into *m*-$SO_3H{\cdot}C_6H_4{\cdot}CO_2H$. In addition ~16% of *p*- and <1% of *o*-$SO_3H{\cdot}C_6H_4{\cdot}CH_2{\cdot}$NPhEt (**II**) are formed with very little of a disulphonic acid. Excess of $ClSO_3H$ and (**I**) give mainly *m*-$SO_2Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}$NPhEt, whereas use of the calc. quantity of $ClSO_3H$ in $PhNO_2$ or application of the " baking " process affords *p*-$SO_3H{\cdot}C_6H_4{\cdot}$NEt·$CH_2$Ph. The synthesis of (**II**) from *o*-$CH_2Br{\cdot}C_6H_4{\cdot}SO_3H$ and NHPhEt is described.

H. W.

Mixed arylhydroxyalkylamines.—See B., 1943, II, 74.

Preparation of diphenylthiocarbazide and diphenylthiocarbazone (dithizone). O. Grummitt and R. Stickle (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 953—954).—Improved preps. of diphenylthio-carbazide and -carbazone are recorded.

J. D. R.

Vinylaryl esters.—See B., 1943, II, 73.

Condensation of methyldipropylcarbinols with phenol in presence of aluminium chloride. R. C. Huston and C. R. Meloy (*J. Amer. Chem. Soc.*, 1942, **64**, 2655—2657).—$CMePr^{\alpha}_2{\cdot}OH$, $^{s}CMePr^{\alpha}Pr^{\beta}{\cdot}OH$, and $CMePr^{\beta}_2{\cdot}OH$ with PhOH–$AlCl_3$ at 25—35° give δ-p-*hydroxyphenyl*-δ-*methyl*-n-*heptane* (65%), m.p. 63—63·5°, b.p. 282—284°/738 mm., 151—152°/6 mm. (3 : 5-*dinitrobenzoate*, m.p. 124·5—126°; *α*-*naphthylurethane*, m.p. 105—106°), γ-p-*hydroxyphenyl*-βγ-*dimethyl*-n-*hexane* (47%), m.p. 72—73°, b.p. 279—281°/738 mm., 122—124°/2 mm. (3 : 5-*dinitrobenzoate*, m.p. 97—98°; *α*-*naphthylurethane*, m.p. 127·5—128·5°), and γ-p-*hydroxyphenyl*-βγδ-*trimethyl*-n-*pentane* (60%), m.p. 57—58·5°, b.p. 275—277°/738 mm., 116—117°/2 mm. (3 : 5-*dinitrobenzoate*, m.p. 103—103·5°; *α*-*naphthylurethane*, m.p. 106—107°), respectively. The same compounds are obtained by condensing the carbinols with C_6H_6 and nitrating, reducing, diazotising, and hydrolysing the products (no details).

R. S. C.

Compound formation between the isomeric hydroxydiphenyls and pyridine. S. E. Hazlet and R. W. Morrow (*J. Amer. Chem. Soc.*, 1942, **64**, 2625—2628).—F.p. diagrams show that C_5H_5N with *o*- or *m*-$C_6H_4Ph{\cdot}OH$ gives stable 1 : 1 additive compounds, f.p. 38·2° (corr.) or 35·5° (corr.), respectively, but with *p*-$C_6H_4Ph{\cdot}OH$ gives unstable 1 : 1 and 1 : 2 additive compounds.

R. S. C.

Halogenation of esters in the diphenyl series. II. Chlorination of *p*-diphenylyl benzoate and benzenesulphonate. (Miss) C. M. S. Savoy and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1942, **64**, 2719—2720; cf. A., 1943, II, 28).—*p*-$C_6H_4Ph{\cdot}OBz$ with Cl_2 and a trace of I in CCl_4 gives 4′-*chloro*-4-*diphenylyl benzoate* (55%), m.p. 182°, also obtained by benzoylation of *p*-$C_6H_4Cl{\cdot}C_6H_4{\cdot}OH$-*p* (**I**) and hydrolysed to (**I**) by KOH–EtOH. *p*-$C_6H_4Ph{\cdot}O{\cdot}SO_2Ph$ gives similarly 4′-*chloro*-4-*diphenylyl benzenesulphonate* (21%), m.p. 74—75°, similarly obtained from, and hydrolysed to, (**I**). 2-*Chloro*-, m.p. 59—60°, 2 : 6-*di*-, m.p. 128—129°, and 2 : 6 : 4′-*tri*-*chloro*-4-*diphenylyl benzenesulphonate*, m.p. 125—126°, are also prepared.

R. S. C.

Isomorphism of β-naphthol and naphthalene.—See A., 1943, I, 85.

Isomerides of stilbœstrol. II. W. H. Linnell and H. S. Shaikmahamud (*Quart. J. Pharm.*, 1942, **15**, 384—388; cf. A., 1942, II, 9). —*m*-$C_6H_4Et{\cdot}OH$ and cold AcOH–Br give 3 : 4 : 1-$C_6H_3EtBr{\cdot}OH$, b.p. 145—148°/10 mm. (3 : 5-*dinitrobenzoate*, m.p. 105—105·5°), methylated (Me_2SO_4–40% NaOH) to 3 : 4 : 1-$C_6H_3EtBr{\cdot}OMe$, b.p. 130—132°/15 mm., which did not form a Grignard reagent or Li derivative, and did not give a tolane with Ag_2C_2. *m*-$C_6H_4Et{\cdot}OMe$ is converted (method : Adams *et al.*, A., 1924, i, 860) into 4 : 2 : 1-$OMe{\cdot}C_6H_3Et{\cdot}CHO$ (**I**), b.p. 120—135°/6 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 193—194°; *azine*, m.p. 110—111°, not convertible into a stilbene by heat), which could not be induced to undergo the benzoin condensation. 4-*Methoxy*-2-*ethylthiobenzaldehyde*, m.p. 95—100° (red at 180°) [from (**I**)–HCl–H_2S–EtOH or (**I**)–H_2S–EtOH–piperidine], with Cu-bronze at 250° in N_2 gives 4 : 4′-*dimethoxy*-2 : 2′-*diethylstilbene* (**II**), m.p. 96—97°, demethylated (MgMeI at 160—170°; poor yield) to the $(OH)_2$-derivative (**III**), m.p. 150°. The œstrogenic activity of (**II**) and (**III**) is small (doses of 5 and 1 mg., respectively).

H. B.

Action of diazo-compounds on quinones. Preparation of diphenyl derivatives. G. B. Marini-Bettolo (*Gazzetta*, 1941, **71**, 627—635).—2-*p*-Nitrophenyl-1 : 4-benzoquinone (**I**) (cf. Kvalnes, A., 1935, 86) is reduced (SO_2–H_2O) to 4′-*nitro*-2 : 5-*dihydroxydiphenyl*, m.p. 195° [*Me*$_2$ *ether* (**II**), m.p. 104°; *diacetate*, m.p. 115°]. Sn–HCl reduction of (**II**) gives 4′-*amino*-2 : 5-*dimethoxydiphenyl*, m.p. 145° (hydrochloride, m.p. 225°; picrate, m.p. 184°; 2 : 5-*dimethoxydiphenyl*-4′′-*azoresorcinol*, m.p. 105°), converted (diazo-method) into 4′-*hydroxy*-2 : 5-*dimethoxydiphenyl*, m.p. 158°. With Ac_2O–H_2SO_4, (**I**) gives 4′-*nitro*-2 : 4 : 5-*triacetoxydiphenyl*, m.p. 130°. 2-*m*-Nitrophenyl-1 : 4-benzoquinone (*loc. cit.*) similarly gives 3′-*nitro*-2 : 5-*dihydroxy*-, m.p. 83°, -*dimethoxy*-, m.p. 84°, and -*diacetoxy*-, m.p. 100°, 3′-amino-2 : 5-dimethoxy- (*hydrochloride*, m.p. 190°; azoresorcinol derivative, m.p. 96°), and 3′-nitro-2 : 4 : 5-triacetoxy-diphenyl, m.p. ~60°. *p*-$NH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}N_2Cl$ in aq. NaOAc and benzoquinone in EtOH give 2-*phenyl*-1 : 4-*benzoquinone*-4′-*sulphonamide*, m.p. 204°.

E. W. W.

Water-soluble compounds with antihæmorrhagic activity. B. R. Baker and G. H. Carlson (*J. Amer. Chem. Soc.*, 1942, **64**, 2657—2664).—Data *A* below are doses in μg. necessary for vitamin-*K* activity. 1 : 2 : 4-OAc·$C_{10}H_5Me{\cdot}OH$ (**I**) (*A* 2), prepared by partial deacetylation of 2 : 1 : 4-$C_{10}H_5Me(OAc)_2$ (A., 1942, II, 285), with Me_2SO_4–K_2CO_3–$COMe_2$ gives 1-*acetoxy*-4-*methoxy*-2-*methylnaphthalene*, m.p. 67—68°, hydrolysed by NaOMe or, better, NaOH–$Na_2S_2O_4$ in aq. MeOH to 4-*methoxy*-2-*methyl*-1-*naphthol*, m.p. 101—103°, which with $(NH_4)_2SO_3$–NH_3–H_2O at 175—180° and then Ac_2O–C_6H_6 gives 1-*acetamido*-4-*methoxy*-2-*methylnaphthalene* (**II**), m.p. 197—199°. 3 : 1-$C_{10}H_5Me{\cdot}OH$ (**III**) (*A* 5) with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ and then $Na_2S_2O_4$ gives 4-*amino*-3-*methyl*-1-*naphthol hydrochloride*, chars at 270°, converted by $K_2Cr_2O_7$ into 1 : 2 : 4-O:$C_{10}H_5Me$:O (*A* 1) and by Ac_2O–NaOAc–H_2O at 75° into the *Ac* derivative, m.p. 206—208°. With Me_2SO_4–K_2CO_3–$COMe_2$ this gives (**II**), thus proving the orientation of (**I**) etc. The appropriate naphthol with succinic or glutaric anhydride (**IV**) in C_5H_5N at room temp. gives 4-*acetoxy*-3-*methyl*-1-*naphthyl H succinate* (*A* 3), m.p. 136—138°, and *glutarate* (*A* 4), m.p. 109—110° (with some *di*-4-*acetoxy*-3-*methyl*-1-*naphthyl glutarate*, m.p. 164—166°), and 3-*methyl*-1-*naphthyl H succinate* (*A* 10), m.p. 109—111°. 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ (**V**) (*A* 1), (**IV**), and $NPhMe_2$ in boiling $CHCl_3$ give 2-*methyl*-1 : 4-*naphthaquinol di*-(*H glutarate*) (*A* 10), m.p. 156—158°. 4-*Acetoxy*-3-*methyl*-1-*naphthyl chloroacetate* (prep. by $CH_2Cl{\cdot}COCl$–$NPhMe_2$–$CHCl_3$ at 25° and later the b.p.), m.p. 103·5—104°, is converted by NMe_3–$COMe_2$ at room temp. into the N-*trimethylglycinate chloride* (*A* 4), m.p. 217°. 2-

Methyl-1 : 4-*naphthaquinol bischloroacetate* (prep. in $NPhMe_2$–$CHCl_3$), m.p. 109—110°, gives similarly the *di*-N-*trimethylglycinate dichloride* (*A* 12), $+2H_2O$, m.p. 204°. Hydrogenation of 4-*acetoxy*-3-*methyl*-1-*naphthyl carbobenzyloxy*-β-*alanate* [prep. from (**I**), $COCl·[CH_2]_2·NH·CO_2·CH_2Ph$, and $NPhMe_2$ in boiling $CHCl_3$], m.p. 106·5—108°, gives the β-*alanate hydrochloride* (*A* 4), $+H_2O$, m.p. 164—167°. $ClSO_3H$, $POCl_3$, or $PSCl_3$ with (**I**) and C_5H_5N in CCl_4 etc. gives *Na* 4-*acetoxy*-3-*methyl*-1-*naphthyl sulphate* (*A* 6), the *Na*$_2$ *phosphate* (*A* 4), $+H_2O$, or *Na*$_2$ *thiophosphate* (*A* 10), $+H_2O$, respectively. Acetobromoglucose with (**I**)– or (**III**)–K_2CO_3–$COMe_2$–$CHCl_3$ gives 4-*acetoxy*-3-*methyl*-1-, m.p. 180—181°, or 3-*methyl*-1-*naphthylglucoside tetra-acetate*, m.p. 135—137°, respectively, and thence (hot NaOMe–MeOH) 4-*hydroxy*-3-*methyl*-, m.p. 206—208° (*A* 3), or 3-*methyl*-1-*naphthylglucoside*, m.p. 223—225° (*A* 10), respectively. Acetobromomaltose with (**I**) or (**III**) etc. gives 4-*acetoxy*-3-*methyl*-, m.p. 183—184°, or 3-*methyl*-1-*naphthylmaltoside hepta-acetate*, m.p. 152·5—154°, and 4-*hydroxy*-3-*methyl*-, m.p. ($+H_2O$) 145—150° (*A* 5), or 3-*methyl*-1-*naphthylmaltoside*, m.p. 175—178° (*A* 20), respectively. $CO_2Et·CH_2·CHMe·CHPh·CO_2Et$ in 5 : 1 (vol.) H_2SO_4–H_2O at 100° gives 4-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthoic acid* (**VI**), m.p. 107—110°, decarboxylated by CuO in quinoline at 200—215° to 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**VII**), b.p. 142—143°/16 mm. (oxime, m.p. 121—122·5°). Heating (**VI**) with S at 255—265° and then distilling with CuO at 1 mm. gives (**III**), m.p. 88—90°, resolidifies, remelts at 92·5—93°, also obtained from (**VII**) by Br and then boiling $NPhMe_2$. 2 : 1-$C_{10}H_6Me·NO_2$ with H_2–Raney Ni in MeOH at 1—3 atm. gives 2 : 1-$C_{10}H_6Me·NH_2$ [hydrochloride (*A* 50), new m.p. 228—231° (decomp.); Ac derivative (*A* >50), new m.p. 191—192°], which with δ-gluconolactone in 2 : 1 H_2O–AcOH–N_2 at 100° gives *glucono*-2-*methyl*-1-*naphthalide* (*A* >50), m.p. 212—214°. 1 : 2-$NO_2·C_{10}H_5·CH_2·CO_2H$ with H_2–Raney Ni–NaOH–H_2O–MeOH at room temp. gives 1-*amino*-2-*naphthylacetic acid* (*A* >200), m.p. 238—240° (decomp.). $(NH_4)_2SO_3$–NH_3–H_2O with (**III**) or (**V**) at 165° gives 3 : 1-$C_{10}H_6Me·NH_2$ [*hydrochloride* (*A* >25), m.p. 265—267°] or 2 : 1 : 4-$C_{10}H_5Me(NH_2)_2$ (**VIII**) [*dihydrochloride* (*A* 3), m.p. 299—301°; *Ac*$_2$ derivative (**IX**), m.p. 308—309°], respectively. $Na_2S_2O_4$–NaOH–H_2O at 70° or $SnCl_2$–HCl–H_2O reduces 1 : 2 : 4-$NH_2·C_{10}H_5Me·N_2·C_6H_4·SO_3H$-*p*, leading to (**IX**), which is also obtained from 2 : 1-$C_{10}H_6Me·NH_2$ by *p*-$CO_2H·C_6H_4·N_2·HSO_4$ in H_2SO_4–H_2O and then H_2–Pd–C etc. Boiling 1 : 1 (vol.) conc. HCl–EtOH hydrolyses (**IX**) to 4-*acetamido*-3-*methyl*-1-*naphthylamine*, m.p. 190—191° (hydrochloride), also obtained from 4 : 2 : 1-$NO_2·C_{10}H_5Me·NHAc$ by H_2–Raney Ni in EtOH at room temp., and converted by $(CH_2·CO)_2O$ in hot $CHCl_3$ into N-4-*acetamido*-3-*methyl*-1-*naphthylsuccinamic acid*, +AcOH and anhyd., m.p. 250° (decomp. if preheated to 240°), resolidifies, remelts at 269—271°. This is also obtained from (**VIII**) and $(CH_2·CO)_2O$ by way of N-4-*amino*-3-*methyl*-1-*naphthylsuccinamic acid* (*A* >50), m.p. 192° (decomp.). 1 : 4-*Dimethoxy*-2-*chloromethylnaphthalene* (**X**) [from 1 : 4-$C_{10}H_6(OMe)_2$ (modified prep.; new m.p. 86—87·5°) and $CH_2Cl·OMe$–AcOH at 25°], m.p. 62—63°, with NH_3–SO_2–H_2O at 135° gives impure 1 : 4 : 2-$C_{10}H_5(OMe)_2·CH_2·SO_3K$, oxidised by $K_2Cr_2O_7$–H_2SO_4–H_2O at 90—100° to *K* 2-*sulphomethyl*-1 : 4-*naphthaquinone* (*A* >50) [S-*benzylthiuronium* salt, m.p. 182—183° (decomp.)]. With boiling EtOH–KOH–H_2S (excess), (**X**) gives *di*-1 : 4-*dimethoxy*-2-*naphthylmethyl disulphide*, m.p. 116—117°, also obtained by, successively, $CS(NH_2)_2$–EtOH, NaOH–aq. EtOH, and I–NaOH–H_2O, and converted by H_2O_2–AcOH etc. into *K* and S-*benzylthiuronium* 3-*hydroxy*-2-*sulphomethyl*-1 : 4-*naphthaquinone* (*A* >50), m.p. 200—201° (decomp.). Potencies, *A*, are also recorded as follows: 2 : 1-$C_{10}H_6Me·OH$ 5; 2-piperidinomethyl-1-naphthol and 1 : 4-$NH_2·C_{10}H_6·NHAc$ >50. The esters of org. acids are too easily hydrolysed to be of use, but those of the inorg. acids are stable even to sterilisation. The glucosides are stable in H_2O, even when sterilised, if air is excluded or reducing agents are present.

R. S. C.

Acetylenic ethers. III. Halogen derivatives of phenoxyacetylene. T. L. Jacobs and W. J. Whitcher (*J. Amer. Chem. Soc.*, 1942, **64**, 2635—2638; cf. A., 1942, II, 214).—*Ph tri-iodovinyl ether*, m.p. 129—129·5°, is obtained from OPh·C:C·MgBr by I–Et_2O or from OPh·C:CH (**I**) by I–KI–KOH, but only in traces from OPh·C:CNa by I; very unstable liquids (? OPh·C:CI) are also obtained in all cases. Slimmer's Br_2-compound, m.p. 29—29·5°, b.p. 117—118°/6 mm. (A., 1903, i, 249), was *Ph ββ-dibromovinyl ether* (**II**), since with boiling conc. HCl–EtOH–2 : 4 : 1-$(NO_2)_2C_6H_3·NH·NH_2$ it gives $[CH:N·NH·C_6H_3(NO_2)_2$-2 : 4$]_2$, m.p. 311—312° (lit. 326—328°), with O_2–C_6H_6 gives OPh·CHBr·COBr and thence (KOPh) $(OPh)_2CH·CO_2Ph$, and with fuming HNO_3 at −10° gives 2 : 4 : 1-$(NO_2)_2C_6H_3·OH$ and 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2·OH$ [OPh·CBr:CHBr (**III**) gives smoothly $CHBr_2·CO_2·C_6H_3(NO_2)_2$]. In ultra-violet light (**III**) gives an oil (? an isomeride), but (**II**) is unchanged. KOBr–KOH–(**I**) at −5° to −8° gives OPh·C:CBr, a very unstable oil, distillable only at very low pressure and converted by Br–CCl_4 into OPh·CBr:CBr_2 and by $Hg(OAc)_2$–HCl–H_2O–Et_2O at 10° into $CH_2Br·CO_2Ph$.

R. S. C.

β-3 : 4-Methylenedioxyphenyl*iso*propylamine. J. Elks and D. H. Hey (*J.C.S.*, 1943, 15—16).—Piperonal and $CHBrMe·CO_2Et$–NaOEt at room temp., then at 100° (bath), give Et αβ-oxido-β-3 : 4-methylenedioxyphenyl-α-methylpropionate, b.p. 184—186°/14 mm.; hydrolysis (NaOH–90% aq. EtOH) and subsequent decarboxylation give 3 : 4-methylenedioxybenzyl Me ketone, b.p. 154—156°/11 mm. This with $HCO·NH_2$ at 160—165°, followed by hydrolysis (dil. HCl), affords β-3 : 4-methylenedioxyphenyl*iso*propylamine, b.p. 138—140°/12 mm. (*Ac* derivative, m.p. 93°).

A. T. P.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1943, III, 63.

Diaminobenzyl alcohols.—See B., 1943, II, 74.

Crystalline vitamin-*A*. J. G. Baxter and C. D. Robeson (*J. Amer. Chem. Soc.*, 1942, **64**, 2411—2416).—By suitable crystallisation at low temp. vitamin-*A* forms solvent-free crystals (photomicrograph), m.p. 63—64°, and solvated crystals (*A*) containing ~1 MeOH (photomicrograph), m.p. 7—10°, or ~1 HCO_2Me, m.p. −4° to 2° or 7—10°, the solvents being retained at <0°/high vac. (cf. A., 1938, III, 53; 1939, III, 601; 1940, III, 371). It is uncertain whether (*A*) are definite compounds. The absorption max. at 328 (? 324) mμ. has extinction coeff. 1780. The $SbCl_3$ colour has an absorption max. at 622 mμ., having $E^{1\%}_{1cm.}$ 4800; results by the Evelyn photoelectric colorimeter are discussed. The biological potency is 4·3 × 10^6 U.S.P. XI units per g. The mol. wt., elimination max., *n*, Ac and I vals. confirm the accepted structure.

R. S. C.

Crystalline aliphatic esters of vitamin-*A*. J. G. Baxter and C. D. Robeson (*J. Amer. Chem. Soc.*, 1942, **64**, 2407—2410).—Vitamin-*A* and RCOCl in C_5H_5N–$(CH_2Cl)_2$ give the *acetate* (**I**), m.p. 57—58°, *palmitate*, m.p. 27—28°, and β-naphthoate, m.p. 74—75° (cf. lit.), and *divitamin*-A *succinate*, m.p. 76—77°. Extinction coeffs. at 328 mμ. and of the $SbCl_3$ colours at 620 mμ. are given. The biological potency of all the esters is that calc. (**I**) is most stable. Photomicrographs are given.

R. S. C.

Reaction of Grignard reagents with ketone acetals. R. J. Levina, S. G. Kulikov, and P. G. Parschikov (*J. Gen. Chem. Russ.*, 1941, **11**, 567—572).—$CMe_2(OEt)_2$ with MgPhBr yields α-*phenyliso*propyl *Et ether*, b.p. 68°/4 mm., and with Mg *cyclo*hexyl bromide gives α-*cyclohexyliso*propyl *Et ether*, b.p. 74—75°/18 mm.; these ethers do not react further with the reagents. trans-, b.p. 134—136°/29 mm., and cis-β-*ketodecahydronaphthalene* Et_2 *acetal*, b.p. 132—133°/12 mm., are prepared. *cyclo*Hexanone Et_2 acetal with Grignard reagents affords *cyclo*hexanol and unidentified products.

R. T.

Malonic ester synthesis and Walden inversion. W. E. Grigsby, J. Hind, J. Chanley, and F. H. Westheimer (*J. Amer. Chem. Soc.*, 1942, **64**, 2606—2610).—Epoxy*cyclo*pentane (1 mol.) and $CH_2(CO_2Et)_2$ (2 mols.), in boiling EtOH–NaOEt (1 mol.) give, with inversion, *Et*$_2$ trans-2-*hydroxy*cyclo*pentyl-malonate* (**I**) (70—75%; none isolated if 1 mol. of ester is used; 27% in C_6H_6), b.p. 75°/10^{-4} mm., hydrolysed by boiling N-aq. NaOH (more slowly by more conc. alkali) to the *-malonic acid* (**II**), m.p. 118·4—118·7° (decomp.; corr.). In boiling C_5H_5N, (**II**) gives *trans*-2-hydroxy*cyclo*pentylacetic acid, m.p. 53·3—54·3° (corr.), slowly converted at 160°, as also is (**II**), into the lactone of *cis*-2-hydroxy*cyclo*pentylacetic acid (unaffected by boiling C_5H_5N). (**I**) is slowly decomposed by NaOEt–EtOH. Its formation is discussed.

R. S. C.

Constitution of *o*-carboxylic acids in solution.—See A., 1943, I, 80.

Complex formation of boric acid with salicylic acid in aqueous solution. Salts of monosalicylboric acid.—See A., 1943, I, 92, 95.

Salicylamide. Ammonolysis of methyl salicylate. E. R. Kline (*J. Chem. Educ.*, 1942, **19**, 332).—Details for the ammonolysis on a laboratory scale are given.

L. S. T.

Hydroxylamine derivatives of anthranilic acid. A. W. Scott and B. L. Wood, jun. (*J. Org. Chem.*, 1942, **7**, 508—516).—The compound obtained from isatoic anhydride by Meyer *et al.* (A., 1886, 358) is not *o*-aminobenzhydroxamic acid (**I**) but *O*-*o*-aminobenzoylhydroxylamine (**II**) (cf. Pope, *Diss., Univ. of Georgia*, 1941). It is converted by Bz_2O at ~70° into the Bz derivative, m.p. 157°, which, like (**II**), does not give the $FeCl_3$ test until it has been warmed with NaOH. This with KOBu^α in Bu^{α}OH affords a K salt which rearranges in hot H_2O to 2 : 4-diketo-3-phenyltetrahydroquinazoline, m.p. 280°, and *o*-$CO_2H·C_6H_4·NH·CO·NHPh$, m.p. 182°. (**I**), m.p. 149°, obtained from *o*-$NH_2·C_6H_4·CO_2Me$ and NH_2OH, is fairly stable up to 140° and gives a marked test for hydroxamic acid with $FeCl_3$; the dry Na salt passes when heated into 2-hydroxybenziminazole (**III**), m.p. 302—303°. (**I**) (as Na salt) is converted by BzCl in dioxan into the *Bz*$_2$ derivative, m.p. 169°, the K salt of which rearranges to (**III**) in boiling H_2O.

H. W.

***α*-Arylphthalides.**—See B., 1943, II, 75.

Carvacrolphthalein. M. H. Hubacher (*J. Amer. Chem. Soc.*, 1942, **64**, 2538—2539).—Carvacrol (**I**), *o*-$C_6H_4(CO)_2O$, and $SnCl_4$ at 100° give *carvacrolphthalein* (**II**) (8%; traces by $ZnCl_2$), m.p. 293·5—294·7° [*diacetate*, m.p. 217·8—219·7°; *Me*$_2$ *ether*, m.p. (partial) 202°, resolidifies, remelts at 211·5—212·2°]. Ehrlich's compound (G.P. 225,983; B., 1910, 1474) was thymolphthalein (**III**) (similarly pre-

pared in 62—70% yield), new m.p. 252·4—253·1° (*diacetate*, m.p. 153·0—153·6°; Me_2 ether, m.p. 175·9—176·7°), since this is obtained from impure (**I**). M.p. are corr. (**II**) and (**III**) are not laxative to *Rhesus* monkeys. R. S. C.

Synthesis of 4-hydroxy-2-naphthoic acids. R. D. Haworth, B. Jones, and Y. M. Way (*J.C.S.*, 1943, 10—13).—Et_2 α-aceto-α-benzylsuccinate [from CH_2PhCl and $CO_2Et{\cdot}CH_2{\cdot}CNaAc{\cdot}CO_2Et$ in PhMe at 120—130° (bath)] is hydrolysed (2N-NaOH) to benzylsuccinic acid, the anhydride (prep. by cold AcCl), m.p. 95—97° (lit. 102°), of which with $AlCl_3$–$PhNO_2$ gives 4-keto-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid, m.p. 145—147°, converted by Br–$CHCl_3$ into its 3-*Br*-derivative, m.p. 177—180°, and thence [$NPhEt_2$ at 100° (bath)] into 4 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ (**I**), m.p. 220—222°. Similarly prepared are p-*methylbenzylsuccinic acid*, m.p. 112—115° (*anhydride*, m.p. 88·5°), 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, m.p. 205—207° (3-*Br*-derivative, m.p. 167—168°), and 4-*hydroxy*-6-*methyl*-2-*naphthoic acid* (11% yield), m.p. 240—241°; p-*methoxybenzylsuccinic acid*, m.p. 100—101° (*anhydride*, m.p. 92—93°), 4-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, m.p. 151° (3-*Br*-derivative, m.p. 171°), and 4-*hydroxy*-6-*methoxy*-2-*naphthoic acid*, m.p. 238—239°; m-*chlorobenzylsuccinic acid*, m.p. 125—127° (*anhydride*, m.p. 75·5°), 7-*chloro*-4-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, m.p. 190—191° (3-*Br*-derivative, m.p. 180—184°), and 7-*chloro*-4-*hydroxy*-2-*naphthoic acid*, m.p. 285—287° (some 6 : 1-$C_{10}H_6Cl{\cdot}OH$ is formed also) (Me ester, m.p. 218—220°; Me ether, m.p. 251—258°), oxidised by $KMnO_4$–aq. $NaHCO_3$ to 4 : 1 : 2-$C_6H_3Cl(CO_2H)_2$. 3-*Bromo*-4-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, m.p. 199—202°, affords 4 : 1 : 2-$OH{\cdot}C_{10}H_5Ph{\cdot}CO_2H$ (+ some 4 : 1-$C_{10}H_5Ph{\cdot}OH$). Phenylmethylitaconic acid, m.p. 125—140° [probably a mixture of isomerides from COPhMe, $(CH_2{\cdot}CO_2Et)_2$, and NaOEt], is converted by boiling AcCl, followed by $AlCl_3$–$PhNO_2$ at 0°, into (probably) 3-methylindenone-2-acetic acid, m.p. 125—145°, and 4-*hydroxy*-1-*methyl*-2-*naphthoic acid* (15—20%), m.p. 203—207° [*Me*, m.p. 171—174°, and *Et* ester, m.p. 127—129°; *Me ether*, m.p. 158—160° (*Me* ester, m.p. 99·5°)]. *o*-$C_6H_4Me{\cdot}COMe$, $Et_2C_2O_4$, and cold EtOH–NaOEt give (after hydrolysis) *o-toluoylpyruvic acid*, m.p. 118°, but conditions for conversion into (**I**) are not established. Colours of azo-dyes derived from RN_2Cl and the above acids are given. PhN_2Cl and (**I**) in aq. NaOH afford an azo-dye (mixture), hydrogenation (Pd–C, EtOH) and subsequent oxidation ($FeCl_3$–aq. HCl) of which yields naphthaquinonecarboxylic acids, m.p. 153—160° (decomp.), decarboxylated to 1 : 4-naphthaquinone (proving initial coupling at C_1) and a product, m.p. 130—150°. A. T. P.

Reaction of furoic acid with tetrahydronapthalene. C. C. Price and N. C. Deno (*J. Amer. Chem. Soc.*, 1942, **64**, 2601—2602).—Tetrahydronaphthalene, furoic acid (**I**), and $AlCl_3$ give s-*octahydro*-1-*anthroic* (**II**) (6·3%), m.p. 153—153·5° [(? 9 : 10-)$(NO_2)_2$-derivative, m.p. 230—235°], and -1-*phenanthroic acid* (0·25%), m.p. 143—143·5°. With Cu chromite in quinoline at 235°, (**II**) gives 1 : 2 : 3 : 4-tetrahydroanthracene and anthracene, but with S at 180—190° gives a substance, m.p. 216—226°. $C_{10}H_8$, (**I**), and $AlCl_3$ give neutral, amorphous products. R. S. C.

Syntheses in the hydroaromatic series. VII. Preparation of partly hydrogenated derivatives of 7-methoxyphenanthrene-2-carboxylic acid and of 7-methoxy-2-acetophenanthrene. E. Dane and O. Hoss (*Annalen*, 1942, **552**, 113—125; cf. A., 1939, II, 429).—7-Methoxy-9 : 10-dihydrophenanthrene-2-carboxyl chloride (**I**), b.p. 208—210°/0·025 mm., is transformed successively into 2-diazoaceto-, m.p. 149° (decomp.), 2-chloroaceto- (**II**), m.p. 117°, and 2-*aceto*-7-*methoxy*-9 : 10-*dihydrophenanthrene* (**III**), m.p. 133°. (**III**) is hydrolysed by HBr (*d* 1·48) in boiling AcOH to 7-*hydroxy*-2-*aceto*- (**IV**), m.p. 188—189°, and (**II**) is transformed by prolonged hydrogenation (Pd–$BaSO_4$) into 7-*methoxy*-2-α-*hydroxyethyl*- (**V**), m.p. 116—117°, -9 : 10-*dihydrophenanthrene*. Alternatively (**I**) is converted by $ZnMe_2$ in PhMe and CO_2 at room temp. into (**III**), which with NaOEt and HCO_2Et in Et_2O–dioxan gives the corresponding *CH(OH)*: derivative, m.p. 136—137°. (**III**), (**IV**), and (**V**) are physiologically inactive. 6-Methoxy-1-acetylenyl-3 : 4-dihydronaphthalene (**VI**) and $CH_2{:}CH{\cdot}CO_2H$ in HBr–Et_2O at room temp. yield 7-methoxytetrahydrophenanthrene-2-carboxylic acid (**VII**), m.p. 210—216° (slight decomp.); the *Me* ester, m.p. 92°, is dehydrogenated by *p*-O:C_6H_4:O in PhOMe at 152° to Me 7-methoxydihydrophenanthrene-2-carboxylate, m.p. 85°, and in absence of solvent at 200—220° into Me 7-methoxyphenanthrene-2-carboxylate (**VIII**), m.p. 134°. (**VII**) is transformed by $SOCl_2$ and C_5H_5N in PhMe into the chloride, which with CH_2N_2 in Et_2O affords 7-*methoxy*-2-*diazoacetotetrahydrophenanthrene* (**IX**), m.p. 148° (decomp.), with a 1 : 1 *adduct*, m.p. 159° (decomp.), of (**IX**) and CH_2N_2. (**IX**) gives the corresponding CH_2Cl ketone, m.p. 132°, attempted hydrogenation (Pd–$BaSO_4$ in MeOH containing $CaCO_3$) of which gave (**III**) and (**V**). (**VII**) is hydrogenated (Pd–C in PhOMe) to 7-methoxyoctahydrophenanthrene-2-carboxylic acid converted by the usual sequence of reactions into 7-*methoxy*-2-*chloroaceto*-*octahydrophenanthrene*, m.p. 99°, reduced to the corresponding, non-cryst., Cl-free ketone which is hydrolysed to 7-*hydroxy*-2-*aceto*-*octahydrophenanthrene*, m.p. 158—159°. Regulated hydrogenation (Pd–$CaCO_3$ in stable *cyclo*hexane) of (**VI**) and treatment of the vinyl derivative produced with $CH_2{:}CH{\cdot}CO_2H$ at 100° gives 7-*methoxyhexahydrophenanthrene*-2-*carboxylic acid*, m.p. 185°, which appears to yield 7-methoxyphenanthrene, m.p. 99°, when heated with Se at 300—320°. The non-cryst. Me ester is dehydrogenated by *p*-O:C_6H_4:O in PhOMe to a *Me methoxytetrahydrophenanthrenecarboxylate*, m.p. 107°, and further by Pd at 250—260° and then at 300° to (**VIII**). H. W.

α-Hydroxy-α′-*p*-bromophenylmaleimide. G. S. Skinner, C. A. Coghlan, and A. S. Berlin (*J. Amer. Chem. Soc.*, 1942, **64**, 2600—2601).—Adding Br and H_2O to $CN{\cdot}CHPh{\cdot}CO{\cdot}CO_2R$ [reacting as $CN{\cdot}CPh{:}C(OH){\cdot}CO_2R$] (R = Et, Me, or Bu$^\alpha$) in $CHCl_3$ at 45—50° gives an additive compound, which at ~50° loses HBr, rearranges, and cyclises to α-*hydroxy*-α′-p-*bromophenylmaleimide* (**I**), m.p. 239—240°, which in hot aq. Na_2CO_3 gives a *Na* salt (**II**), decomp. 321°. Omission of the H_2O leads to less (**I**) and some ? $C_6H_4Br{\cdot}CH_2{\cdot}CN$. With CH_2PhCl, (**II**) gives the N-*CH_2Ph* derivative, m.p. 169—170°, or with AgX gives the unstable Ag salt, converted by EtI–Et_2O into the *N*-Et derivative, m.p. 191—192°. Boiling HNO_3–H_2O or $KMnO_4$–$NaHCO_3$–H_2O oxidises (**I**) to *p*-$C_6H_4Br{\cdot}CO_2H$. Aq. NaOH at room temp. slowly hydrolyses (**I**) to *p*-$C_6H_4Br{\cdot}CH_2{\cdot}CO_2H$, NH_3, and $Na_2C_2O_4$. (**I**) is also obtained from α-hydroxy-α′-phenylmaleimide by Br in $PhNO_2$ at room temp. R. S. C.

***dl*- and *meso*-γγ′-Diphenyl-γγ′-suberodilactone.** C. C. Price and A. J. Tomisek (*J. Amer. Chem.* Soc., 1942, **64**, 2727).—$COPh{\cdot}[CH_2]_2{\cdot}CO_2H$ and Zn dust in boiling 80—90% AcOH give γ-phenyl-γ-butyrolactone (30—40%) and γγ′-diphenyl-γγ′-suberodilactones, m.p. 267° (9%) and 165° (clear at 175·5°) (6%). R. S. C.

Bromination of diphenylalkanes and preparation of stilbene derivatives. I. αβ-Diphenylethane. S. Bance, H. J. Barber, and A. M. Woolman (*J.C.S.*, 1943, 1—4).—$(CH_2Ph)_2$ and Br (excess) in boiling CCl_4 give $(CHPhBr)_2$, which could not be further brominated; in boiling H_2O–AcOH, a mixture of 2 : 4′ : αβ-*tetrabromo*-αβ-*diphenylethane* (**I**), m.p. 170—175°, and the 4 : 4′ : αβ-isomeride (**II**) [also obtained from $(p\text{-}C_6H_4Br{\cdot}CH_2)_2$ and Br in boiling $CHCl_3$ or AcOH] results, but gradual addition of the Br gives a product containing <4 Br per mol. (**II**) with CuCl or CuCN (2 mols.) in boiling C_5H_5N yields 4 : 4′-dibromo-, converted by CuCN in C_5H_5N at 220° (bath) into 4 : 4′-dicyano-stilbene (**III**), also obtained from (**II**) and CuCN (4 mols.) in C_5H_5N at 200—210°. (**II**) in EtOH with MeOH–KOH affords 4 : 4′ : α-*tribromostilbene*, m.p. 82—83°. (**III**) with Br in $PhNO_2$ at 200° in bright light yields αβ-*dibromo*-4 : 4′-*dicyano*-αβ-*diphenylethane* (**IV**), m.p. 269° (decomp.), which with MeOH–KOH gives α-*bromo*-4 : 4′-*dicyanostilbene*, m.p. 144—145° (130—132° after melting, supercooling, and remelting). This or (better) (**IV**) with EtOH–MeOH–KOH yields 4 : 4′-*dicyanotolane* (**V**), m.p. 252—255°, reduced (H_2, Raney Ni in dioxan) to cis-4 : 4′-*dicyano*-, m.p. 152—154° [gives the *trans*-compound in boiling $PhNO_2$–I (trace)], converted via the imino-ether into cis-4 : 4′-*diamidino-stilbene* (+H_2O), m.p. 204—206° (decomp.). 4 : 4′-*Diamidinotolane dihydrochloride* (+0·5 H_2O) is prepared from (**V**). Residues from crystallisation of (**III**) when sublimed at 250°/1 mm. yield 4-*bromo*-4′-*cyanostilbene*, m.p. 187—188°. (**I**) with CuCl in C_5H_5N yields 2 : 4′-*dibromostilbene*, m.p. 84—85°, oxidised ($KMnO_4$ in 80% $COMe_2$) to *o*- and *p*-$C_6H_4Br{\cdot}CO_2H$. (**I**) with CuCN (4 mols.) in C_5H_5N yields 2 : 4′-*dicyanostilbene*, m.p. 136—137°. 2-*Cyano*-4′-*amidinostilbene* has m.p. 200—205° (decomp.); the diamidine could not be obtained by the $NaNH_2$ method. A. Li.

Formation of diethyl *cyclo*butane-1 : 1-dicarboxylate by the Kishner process. V. P. Golmov and B. A. Kazanski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 37—40).—$Cl{\cdot}[CH_2]_3{\cdot}Br$ (**I**) and $CHNa(CO_2Et)_2$ in boiling EtOH, or (**I**)–$CH_2(CO_2Et)_2$–Et_2O–NaOEt–EtOH at room temp., give $Cl{\cdot}[CH_2]_3{\cdot}CH(CO_2Et)_2$ (**II**) (52%), some $(Cl{\cdot}[CH_2]_3)_2C(CO_2Et)_2$ and $[CH_2]_3[CH(CO_2Et)_2]_2$. (**II**) is the intermediate in the Kishner reaction, and is convertible by boiling EtOH–NaOEt into Et_2 *cyclo*butane-1 : 1-dicarboxylate. A. T. P.

***cyclo*Butane derivatives. III. *cis*-*cyclo*Butane-1 : 3-dicarboxylic acid.** E. R. Buchman, A. O. Reims, and M. J. Schlatter (*J. Amer. Chem. Soc.*, 1942, **64**, 2703—2705).—Distillation at 2 mm. of the mixed anhydride from *trans*-*cyclo*butane-1 : 3-dicarboxylic acid (**I**) or its Ag salt and boiling AcCl gives the anhydride, m.p. 47·5—48°, of, and thence (evaporation with 6N-HCl), *cis*-*cyclo*butane-1 : 3-dicarboxylic acid (**II**), m.p. 143—143·5° (cf. *J.C.S.*, 1898, **73**, 330). With MeOH–H_2SO_4, (**II**) gives the Me_2 ester (**III**), b.p. 110—111°/20 mm., and thence the *dihydrazide*, m.p. 172—174°. The *di*-p-*bromophenacyl* ester (prep. from the Na_2 salt) has m.p. 121·2—121·7°. (**II**) is largely carbonised by conc. HCl at 180° and at 200° alone gives only its anhydride. (**I**) is obtained from (**III**) by boiling MeOH–NaOMe, followed by hydrolysis (evaporation with 6N-HCl). $CH_2(CO_2Et)_2$ and 40% CH_2O, best with a little piperidine at 0° (later room temp.), give, after hydrolysis (NaOH–MeOH at 0° and later room temp.) and boiling with HCl, $CO_2H{\cdot}C(:CH_2){\cdot}[CH_2]_2{\cdot}CO_2H$ (**IV**) (20%), m.p. 131—132°, b.p. 175°/3·5 mm., a *substance*, $C_8H_{10}O_2NCl$, m.p. 220—220·5°, $CO_2H{\cdot}[CH_2]_3{\cdot}CO_2H$, pentane-αγε-tricarboxylic acid, and αα′-*dimethyleneglutaric acid*, m.p. 152—153° (cf. *J.C.S.*, 1900, **77**, 294; 1908, **93**, 1777; 1909, **95**, 1166). (**II**)

and (**IV**) are distinguishable by resistance of (**II**) to, and oxidation of (**IV**) by, $KMnO_4$ and by ready addition of HBr or CH_2N_2 to (**IV**) (CH_2N_2–Et_2O and then NH_3–EtOH at 100° give the *pyrazoline-diamide*, $C_7H_{12}O_2N_4$, m.p. 145—145·5°). HCl–EtOH largely polymerises (**IV**) but gives also 43% of Et_2 ester, b.p. 132—133°/23 mm., which yields no cryst. dihydrazide; the *anhydride* has m.p. 51—51·5°, b.p. 112—115°/2 mm.; the dichloride ($SOCl_2$), b.p. 82—83°/5 mm., gives the *diamide*, m.p. 164—165°; the *di*-p-*bromophenacyl* ester has m.p. 121·6—121·7°. M.p. are corr. R. S. C.

Chemical components of the roots of *Decalepis hamiltonii*. V. 4-Methylresorcylaldehyde as preservative.—See A., 1943, III, 294.

Gossypol. II. Anilino-derivatives. III. Methylation. K. S. Murty and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **A**, **16**, 141—145, 146—150).—II. With excess of NH_2Ph, gossypol (**I**) forms "*tetra-anilinogossypol*" (**II**), m.p. 303° (decomp.) [probably results from the change 2CHO → 2CH(NHPh)$_2$], which decomposes on heating for a long time at 110° or for a short period at 180° into NH_2Ph and gossypoldianil (**III**), m.p. 303° (decomp.). (**I**) and NH_2Ph (2 mols.) in Et_2O give the impure additive *compound*, [2CHO → 2CH(OH)·NHPh], m.p. 303° (decomp.). Acetylation and methylation of (**II**) or (**III**) yield only derivatives of (**I**), NH_2Ph being removed.

III. Adams' method (A., 1938, II, 452) of methylating (**I**) does not appear to give a homogeneous Me_6 ether (**II**), m.p. 130°, which is obtained from gossypol hexa-acetate with Me_2SO_4 and alkali in $COMe_2$, from (**I**) and CH_2N_2 in MeOH, or MeI and K_2CO_3 in $COMe_2$, or Me_2SO_4 and alkali. The methods which do not employ alkali hydroxide give less coloured products. (**II**) is unaffected by hot dil. H_2SO_4 and hence does not appear to have the constitution corresponding with the structure of the glycosides. H. W.

Reductions with nickel–aluminium alloy and aqueous alkali. I. Carbonyl group. D. Papa, E. Schwenk, and B. Whitman (*J. Org. Chem.*, 1942, **7**, 587—590).—The reduction of alkali-sol. CO compounds proceeds smoothly and with good yields with Ni–Al (Raney alloy) whereas alkali-insol. compounds require a solvent, *e.g.*, EtOH, PhMe. Compounds COPhR, where R = H, aryl, or alkyl, give the corresponding hydrocarbon, whereas Ph·[CH_2]$_x$·COR or CHPh:CH·[CH_2]$_x$·COR, where R is H or alkyl, give generally the corresponding alcohol. p-*γ-Phenylpropylphenoxyacetic acid* has m.p. 92—93°. H. W.

Acyloins, di- and poly-ketones. I. Syntheses in the αδ-diphenylbutane series. I. P. Ruggli and B. Hegedüs (*Helv. Chim. Acta*, 1942, **25**, 1285—1296).—CH_2Ph·CHO (prep. from CHPh:CH·CO_2H described) is converted through the H sulphite into CH_2Ph·CH(OH)·CN and thence by CH_2Ph·MgCl into *αδ-diphenylbutan-β-ol-γ-one* (**I**), m.p. 52° (*p-nitrobenzoate*, m.p. 83—84°; *semicarbazone*, m.p. 167—169°, softens at 164°). (**I**) and $NHPh·NH_2$ in boiling 70% AcOH give the corresponding *osazone*, m.p. 172—174°, and *phenylhydrazone*, m.p. 111—113°. (**I**) is reduced by Na in boiling EtOH to [CH_2Ph·CH(OH)·]$_2$, m.p. 129—131°. (**I**) is also obtained in small yield by the action of Na powder on CH_2Ph·CO_2Et. Reduction of CH_2Ph·COCl by Mg–MgI_2 gives a liquid with odour of CPh:CH [hydrogenated (Raney Ni) to a compound $C_6H_{10}O$ which could not be caused to react with reagents for ·OH or :CO], a mixture of compounds, and CH_2Ph·CO_2[CH_2]$_2$·Ph, converted by CH_2Ph·MgCl into $(CH_2Ph)_3C$·OH, m.p. 113—114°. H. W.

Effect of solvents on the acylation of phenol with acid chlorides of high mol. wt. A. W. Ralston, A. Ingle, and M. R. McCorkle (*J. Org. Chem.*, 1942, **7**, 457—461; cf. A., 1941, II, 66).—$PhNO_2$ has a much greater *para*-directing influence than CS_2 on the Friedel–Crafts acylation of PhOH with C_nH_{2n+1}·COCl (n = 7, 9, 11, 13, 15, and 17) in presence of an excess of $AlCl_3$. In $C_2H_2Cl_4$ only resinous products are obtained with chlorides more complex than C_7H_{15}·COCl. The length of the alkyl chain has little influence on the *o*/*p* ratio for a given solvent. o-, m.p. 35·0—35·5°, and p-, m.p. 63·5—64·0°, *-hydroxydecophenone* are new. H. W.

Rearrangement of phenyl octoate with ferric chloride, titanium tetrachloride, stannic chloride, and zinc chloride. A. W. Ralston, E. W. Segebrecht, and M. R. McCorkle (*J. Org. Chem.*, 1942, **7**, 522—527).—$FeCl_3$ is comparable to $AlCl_3$ as catalyst in the rearrangement of Ph octoate but gives a greater ratio of *p*- (**I**) to *o*- (**II**) -hydroxyoctophenone for the same % of ester conversion. When $FeCl_3$ is used the (**I**)/(**II**) ratio is less as the mol. amount of catalyst increases whereas with $AlCl_3$ the reverse is true; (**I**) and (**II**) appear unchanged when heated for 6 hr. at 70° with a mol. ratio of $FeCl_3$. $TiCl_4$ is less effective than $FeCl_3$ and the (**I**)/(**II**) ratio is less. Substantial amounts of octoic acid and *p*-octoylphenyl octoate (**III**) are also produced. With $TiCl_4$ and $PhNO_2$ as solvent the (**I**)/(**II**) ratio exceeds that in $C_2H_2Cl_4$; in CS_2 the change proceeds less rapidly than in $C_2H_2Cl_4$ or $PhNO_2$. Rearrangement of (**I**) or (**II**) is not caused by $TiCl_4$. $SnCl_4$ is a much weaker catalyst than either $FeCl_3$ or $TiCl_4$; even at 150° the yields of (**I**) and (**II**) are quite small and a large proportion of ester is recovered unchanged. (**III**) is produced in notable amount. $ZnCl_2$ has only very slight catalytic activity in $PhNO_2$ or $C_2H_2Cl_4$ under conditions varying from 6 hr. at 100° to 24 hr. at 160°. H. W.

Derivatives of 2-propionyl-1-naphthol. C. M. Brewster and G. G. Watters (*J. Amer. Chem. Soc.*, 1942, **64**, 2578—2580).—1 : 2-OH·$C_{10}H_6$·COEt (**I**) is best obtained from α-$C_{10}H_7$·OH, $EtCO_2H$, and $ZnCl_2$ at 145—150° or, less well, by displacement of Ac from 1 : 2-OH·$C_{10}H_6$·COMe (**II**). With BzOH–$ZnCl_2$, (**II**) gives a little 1 : 2-OH·$C_{10}H_6$·COPh. (**I**) is triboluminescent, gives an *Et ether*, b.p. 175—180°/15 mm., *phenylhydrazone*, m.p. 136°, 4-*Br*-, m.p. 98—99° (with RBr–NaOH–H_2O–COMeEt gives an *Et*, m.p. 68—69°, and *Pr^a ether*, b.p. 298—303°/690 mm., and with *o*-C_6H_4Cl·CHO–KOH–H_2O–EtOH at 0° gives a o-C_6H_4Cl-CH: derivative, m.p. 129°), an o-C_6H_4Cl-CH:, m.p. 93—94°, and (by HNO_3–AcOH) 4-NO_2-derivative, m.p. 162—163° (*phenylhydrazone*, m.p. 199—200°). Clemmensen reduction of (**I**) gives 2 : 1-$C_{10}H_6Pr^a$·OH, m.p. 48—50° (*Et*, b.p. 294—296°/690 mm., and *Bu^a ether*, b.p. 304—306°/692 mm.). R. S. C.

Study of the mechanism of the Beckmann rearrangement by the isotopic method. A. E. Brodski and G. P. Mikluchin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 558—559).—Beckmann rearrangement of CPh_2:N·OH by PCl_5–Et_2O at −15°, with subsequent addition of H_2O enriched in ^{18}O, gives NHBzPh, which is hydrogenated (MoS_3) at 90 atm. The *d* of the H_2O obtained after hydrogenation is in accordance with that of the H_2O applied to hydrolysis. Results suggest that the Beckmann change cannot be explained by direct intermol. rearrangement, but that there is an intermediate elimination of O (*e.g.*, as H_2O), and subsequent rearrangement, possibly within the substituted ammonium ion. A. T. P.

Study of mechanisms of chemical reactions with oxygen isotopes. II. Beckmann rearrangement.—See A., 1943, I, 64.

***p*-Acylation of polyalkylbenzophenones by aryl 2 : 4 : 6-trialkylbenzoates.** R. C. Fuson, E. M. Bottorff, R. E. Foster, and S. B. Speck (*J. Amer. Chem. Soc.*, 1942, **64**, 2573—2756).—COPhM (M = mesityl or other highly hindered Ph) and MCO_2Ar in presence of bases, *e.g.*, Na, MgEtBr, MgMBr, Mg + MgI_2, give *p*-$C_6H_4(COM)_2$ and ArOH (cf. A., 1942, II, 311). *p*-Tolyl mesitoate (**I**) and MgPhBr in Bu$^a_2$O–N_2 at 100° give p-*dimesitoylbenzene* (**II**) (34%), m.p. 244—246° [and *p*-cresol (74%); cf. *loc. cit.*], also obtained (44%) by Friedel–Crafts reaction (*A*) [*p*-$C_6H_4(COCl)_2$, *s*-$C_6H_3Me_3$, and $AlCl_3$ in boiling CS_2]. Similarly m-*tolyl mesitoate*, m.p. 38—39°, and MgPhBr give a little (**II**), *o*-C_6H_4Ph·CO·$C_6H_2Me_3$-1 : 2 : 4 : 6, and *m*-cresol (80%); (**I**) with *o*- or *m*-C_6H_4Me·MgBr gives 2 : 5-*dimesitoyltoluene* (**III**) (29 and 11%, respectively), m.p. 189° [(*A*) gives 29%], and with *m*-OMe·C_6H_4·MgBr gives 2 : 5-*dimesitoylanisole* (**IV**) (3·5%), m.p. 210° [(*A*) gives 35%]; *p*-tolyl 2 : 4 : 6-tri*iso*propyl- and *-triethyl-benzoate*, b.p. 170—171°/3 mm., with MgPhBr give p-*di*-2 : 4 : 6-*tri*iso*propyl*- (**V**), m.p. 223—225° [(*A*) gives 50%], and *-triethyl-benzoylbenzene* (**VI**), m.p. 119—120° [(*A*) gives 67%]. 2 : 4 : 6 : 1-$C_6H_2Me_3$·COPh (**VII**) and (**I**) with Mg + MgI_2 in PhMe–Bu$^a_2$O–Et_2O–N_2 at 115° give 40% and at 60° give 36% of (**II**), with a small amount of a compound, m.p. 189°; use of MgEtBr or MgPhBr at 115° gives 13—14%, of 2 : 4 : 6 : 1-$C_6H_2Me_3$·MgBr at 115° gives 17%, of Na at 100° gives 8%, but of $ZnCl_2$ gives none. *Ph dibromomesityl ketone* [prep. by bromination of (**VII**); 23%], m.p. 113°, with (**I**)–Mg–MgI_2 at 60° gives 27% of 1-*mesitoyl*-4-*dibromomesitoylbenzene* (27%), m.p. 274—277°. m-*Tolyl mesityl ketone* [prep. by (*A*); 91%], m.p. 67°, with (**I**)–Mg–MgI_2 at 115° gives (**III**) (32%). *m*-OMe·C_6H_4·CO·$C_6H_2Me_3$-1 : 2 : 4 : 6 with (**I**)–Mg–MgI_2 at 70° gives (**IV**) (35%). m-*Dimesitoylbenzene* [prep. by (*A*); 94%], m.p. 149—151°, with (**I**)–Mg–MgI_2 at 115° gives 13% of 1 : 2 : 4-C_6H_3(CO·$C_6H_2Me_3$-1 : 2 : 4 : 6)$_3$. With 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO_2Me–Mg–MgI_2 at 115°, (**VII**) gives only $C_6H_2Me_3$·CO_2H, but with 2 : 4 : 6-*tribromophenyl mesitoate*, m.p. 86°, at 100° gives (**II**) and 2 : 4 : 6 : 1-$C_6H_2Br_3$·OH. *Mesityl α-$C_{10}H_7$ ketone* [prep. by (*A*); 60%], m.p. 159°, with (**I**)–Mg–MgI_2 at 115° gives 1 : 4-*dimesitoylnaphthalene* (**VIII**) (30%), *forms*, m.p. 171° and 193·5° (softens at 171°). p-*Tolyl* 2 : 3 : 5 : 6-*tetramethylbenzoate*, m.p. 138°, and 2 : 3 : 5 : 6 : 1-C_6HMe_4·COPh [prep. by (*A*); 40%], m.p. 119°, with Mg–MeI_2 at 60° give p-*di*-2 : 3 : 5 : 6-*tetramethylbenzoylbenzene* (54%), m.p. 246° [(*A*) gives 67%]. 2 : 4 : 6 : 1-$C_6H_2Pr^{\beta}_3$·CO_2·C_6H_4Me-*p* and 2 : 4 : 6-tri*iso*propylbenzophenone [prep. by (*A*); 81%], m.p. 97—99°, with MgEtBr at 140° give a trace of (**V**). 2 : 4 : 6 : 1-$C_6H_2Et_3$·CO_2·C_6H_4Me-*p* and 2 : 4 : 6-*triethylbenzophenone* [prep. by (*A*); 81%], b.p. 144—145°/3 mm., with Mg–MgI_2 at 115° give 16% of (**VI**). Impure 1 : 4-$C_{10}H_6$(COCl)$_2$ and *s*-$C_6H_3Me_3$ give (by *A*) (**VIII**) (45%) and some (probably) *mesityl* 4-*cyano*-1-*naphthyl ketone*, m.p. 134° (corr.) (arising from the intermediate 4 : 1-CN·$C_{10}H_6$·CO_2H). R. S. C.

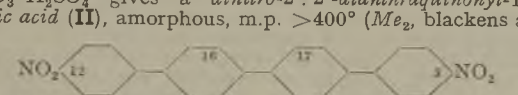
Addition of magnesium methyl iodide to mesityl *tert.*-butyl diketone. R. C. Fuson and J. A. Robertson [and, in part, J. W. Corse] (*J. Org. Chem.*, 1942, **7**, 466—471; cf., A., 1939, II, 508).—Each of the CO groups of mesityl Bu$^{\gamma}$ diketone (**I**) reacts with MgMeI in the αβ-manner forming the corresponding ketol. If the condensation of Bu$^{\gamma}$CO·CHO with *s*-$C_6H_3Me_3$ in presence of $AlCl_3$ is carried out at a low temp. over a long period of time the main product is *mesitoyltert.-butylcarbinol* (**II**), m.p. 44°, instead of pivalylmesitylcarbinol (**III**), m.p. 117—118°. (**II**) affords an *acetate*, m.p. 68°, and is converted by NaOEt–EtOH at 75° under N_2 into (**III**), which itself is unchanged under these conditions. (**II**) or (**III**) is oxidised

by $CuSO_4$ in aq. C_5H_5N at 100° to (**I**), b.p. 115—118°/2 mm. (*oxime*, m.p. 139°), in 83% yield. (**I**) is hydrogenated (PtO_2 in EtOH) to (**III**). (**II**) is reduced (Cu chromite–EtOH–H_2 at 175°/1500 lb.) to *α-mesityl-β-*tert.*-butylethylene glycol*, m.p. 84—85° (*diacetate*, m.p. 73—74°), which is dehydrated by boiling, dil. H_2SO_4 to 2 : 4 : 6-*trimethylbenzyl Bu$^\gamma$ ketone*, m.p. 80—81° (*oxime*, m.p. 147°), which does not contain active H. (**I**) and MgMeI in Et_2O afford *mesitoylmethyl*-tert.*-butylcarbinol* (**IV**), m.p. 81—82° (*acetate*, m.p. 77°), which contains 1 active H (Zerevitinov), and *pivalylmesitylmethylcarbinol* (**V**), m.p. 104—105°, which contains 1 active H but also does not give an acetate. AcOH–60% H_2SO_4 at 100° converts (**IV**) into $COMeBu^\gamma$ and *s*-$C_6H_3Me_3$ whilst 50% H_2SO_4 at 100° transforms (**V**) into *α-mesitylvinyl Bu$^\gamma$ ketone* (**VI**), b.p. 112°/3 mm., reduced (PtO_2 in EtOH) to *α-mesitylethyl Bu$^\gamma$ ketone* (**VII**), m.p. 86°, which does not react with Ac_2O–C_5H_5N. Similar reduction of (**VI**) followed immediately by aeration of the solution gives the *enol peroxide*, $CMe(C_6H_4Me_3)\cdot O$ $CBu^\gamma(OH)$——O, m.p. 106°. Mesityl Bu$^\gamma$ ketone does not appear to react with MgMeI in boiling Bu^α_2O. H. W.

Mechanism for the formation of anthraquinone from *o*-benzoylbenzoic acid. M. S. Newman (*J. Amer. Chem. Soc.*, 1942, **64**, 2324—2325).—Addition of *o*-$C_6H_4Bz\cdot CO_2H$ (**I**) in 98—99% H_2SO_4 to cold MeOH gives 60% of a 40 : 56 mixture of *ψ*- and normal esters with 30% of unchanged (**I**). The *ψ*-ester is the primary product, being shown to be partly isomerised under the experimental conditions. Formation of anthraquinone (**II**) from (**I**) proceeds by the reactions: (**I**) + $2H_2SO_4 \rightarrow 2HSO_4' + H_3O^+ +$ *o*-$C_6H_4\langle^{CO—}_{C^+Ph}\rangle O$ $\rightleftharpoons$ *o*-$C_6H_4Bz\cdot C^+O \rightarrow$ (**II**) + H^+. R. S. C.

Structure of 2-nitroindane-1 : 3-dione. G. Wanag and J. Bungs (*Ber.*, 1942, **75**, [*B*], 987—990).—Comparative titrations of 2-nitroindane-1 : 3-dione (**I**) and Et indane-1 : 3-dione-2-carboxylate (**II**) in C_6H_6, Et_2O, AcOH, EtOH, and H_2O with Br in the same solvents show that (**I**) is strongly isomerised in H_2O and EtOH but much less markedly in Et_2O and C_6H_6 whereas (**II**) is more uniformly isomerised (66—90%) in different solvents. Isomerisation of (**II**) occurs very rapidly in H_2O, EtOH, and AcOH but slowly in Et_2O and C_6H_6. In any given solvent the behaviour of (**I**) differs from that of (**II**) and hence from that of a true keto-enol. Hence (**I**) isomerises to the ketonitronic acid, $C_6H_4\langle^{CO}_{CO}\rangle C{:}N(:O)\cdot OH$. H. W.

Dinitrodibenzanthrone. D. J. Bennett, R. R. Pritchard, and J. L. Simonsen (*J.C.S.*, 1943, 31—33).—The dinitrobenzanthrone (*Bz*-2-*Bz*-2′-dinitroviolanthrone) (**I**) (prep. described) of Maki *et al.* (A., 1936, 338) cannot be the 16 : 17-derivative since oxidation with aq. CrO_3–H_2SO_4 gives a *dinitro*-2 : 2′-*dianthraquinonyl*-1 : 1′-*dicarboxylic acid* (**II**), amorphous, m.p. >400° (*Me*$_2$, blackens at 218°,



(*A*.)

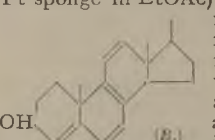
gradual decomp. >218°, and *Et*$_2$ ester, sinters at 169—173°, m.p. 179—189°, decomp. >190°). (**I**) may be (*A*). (**II**) and aq. $Fe(OH)_2$–NaOH give the $(NH_2)_2$-acid; the tetrazonium sulphate and Zn dust in boiling $C_5H_{11}\cdot OH$ afford 2 : 2′-dianthraquinonyl-1 : 1′-dicarboxylic acid (*Me*$_2$ ester, decomp. ~374°), also obtained by oxidising dibenzanthrone (**III**). The magnetic susceptibilities of (**III**) and 3 : 3′-dibenzanthronyl are $-0{\cdot}32 \times 10^{-6}$ and $-0{\cdot}54 \times 10^{-6}$, respectively. A. T. P.

Substituted anthraquinones.—See B., 1943, II, 75.

IV.—STEROLS AND STEROID SAPOGENINS.

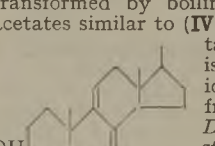
Catalytic reduction of cholesterol α-oxide. H. E. Stavely (*J. Amer. Chem. Soc.*, 1942, **64**, 2723—2724).—Cholesterol α-oxide (**I**) and H_2–Pd–AcOH give slowly a mixture, which after acetylation (Ac_2O–C_5H_5N) and chromatography gives cholestanyl acetate, cholestane-3 : 5-diol monoacetate, m.p. 181° (lit. 177°) [free diol, m.p. 216—217° (lit. 201°)], and α-cholestane-3 : 5 : 6-triol diacetate [also obtained from the acetate of (**I**) and hot AcOH]. R. S. C.

(A) Action of mercuric acetate on Δ$^{6:8}$-cholestadien-3-ol (*iso*dehydrocholesterol). (B) Action of lead tetra-acetate on *iso*dehydrocholesterol. A. Windaus, U. Riemann, H. H. Rüggeberg, and G. Zühlsdorff (*Annalen*, 1942, **552**, 135—142, 142—152; cf. A., 1938, II, 185).—(A) *iso*Dehydrocholesteryl *p*-nitrobenzoate (**I**) in $CHCl_3$ and $Hg(OAc)_2$ in AcOH rapidly yield HgOAc and the p-*nitrobenzoate* (*A*), m.p. 210—211°, $[\alpha]_D^{18}$ −116·2° in $CHCl_3$, of an unidentified alcohol, $C_{27}H_{40}O_2$, which does not react with NH_2OH, is probably dihydric, contains 4 double linkings, and arises from *iso*dehydrocholesterol (**II**) by reaction with 3 O. *iso*Dehydrocholesteryl 3 : 5-dinitrobenzoate yields a similar *ester*, $C_{34}H_{42}O_7N_2$, m.p. 223—224°. After removal of (*A*) an amorphous material remains which is hydrolysed to a doubly unsaturated, dihydric *alcohol* (**III**), $C_{27}H_{44}O_2$, m.p. 228°, $[\alpha]_D^2$ −51·4° in C_5H_5N (*di*-3 : 5-*dinitrobenzoate*, m.p. 172°). It is converted by boiling Ac_2O into a *cholestatrienyl acetate* (**IV**), m.p. 102—103° (absorption max. at 285 mμ.), hydrolysed to an alcohol, m.p. 99—100°, which becomes yellow on exposure to air and is hydrogenated (Pt sponge in EtOAc) to α-cholesteryl acetate, m.p. 76—77°. The mother-liquors from (**III**) yield a very characteristic 3 : 5-*dinitrobenzoate*, $C_{34}H_{42}O_6N$, m.p. 219°, $[\alpha]_D^{20}$ −146° in $CHCl_3$, hydrolysed to a monohydric alcohol (*B*), m.p. 115°, softens at 108°, $[\alpha]_D$ −311° in $CHCl_3$, shown by its absorption spectrum to have 4 double linkings in unbroken conjugation. It is formed from (**I**) by absorption of 2 O. It and its acetate, m.p. 114—119°, $[\alpha]_D^{19}$ −225·5° in $CHCl_3$, are very sensitive to air.



(*B*.)

(B) (**I**) in $CHCl_3$ is converted by $Pb(OAc)_4$ in AcOH at 0° and subsequently at room temp. into a *cholestatrienyl* p-*nitrobenzoate* (**V**), m.p. 167—168° (turbid), hydrolysed by alkali to a cholestatrienol, m.p. ~100°, $[\alpha]_D^{17}$ −81·2° in $CHCl_3$ [*acetate* (**VI**), m.p. 103—104°, $[\alpha]_D^{17}$ −77·6° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 198°, $[\alpha]_D^{17}$ −65·0° in $CHCl_3$], which becomes yellow in air. The mother-liquors from (**V**) yield an amorphous residue hydrolysed to a mixture of cholestadienediols the composition of which varies greatly with slight differences in experimental technique. The ethereal solution deposits (**III**), better obtained by use of $Hg(OAc)_2$. The more freely sol. material is purified through its additive products with digitonin and then yields a *di*-3 : 5-*dinitrobenzoate*, m.p. 176°, hydrolysed to a *cholestadienediol*, m.p. 196°, which may not be quite homogeneous. It and the non-cryst. residues obtained from it are transformed by boiling Ac_2O into a mixture of cholestatrienyl acetates similar to (**IV**). The chief portion has $[\alpha]_D$ −77° but contains 10—20% of a strongly dextrorotatory isomeride the parent alcohol of which appears identical with $\Delta^{5:7:9(11)}$-cholestatrienol derived from 7-dehydrocholesterol or *iso*pyrovitamin-D_3 by oxidation with $Hg(OAc)_2$. The constitution (*C*) is ascribed to (**III**). Re-examination of the action of BzO_2H on (**II**) shows that the acetate, m.p. 148°, of cholestatrienol can be directly isolated by crystallisation from $COMe_2$–MeOH; the mother-liquors therefrom contain (**VI**). H. W.



(*C*.)

Isolation of androsterone sulphate. E. H. Venning, M. M. Hoffman, and J. S. L. Browne (*J. Biol. Chem.*, 1943, **146**, 369—379).—A cryst. conjugated androgen *Na androsterone sulphate* (**I**), $C_{19}H_{29}O_2\cdot SO_3Na$, m.p. 144° or $+H_2O$, m.p. ~190° (decomp.) (semicarbazone, m.p. 245°), is isolated (details given, including a final chromatographic separation) from the urine of a man with an interstitial cell tumour of the testis. Acid hydrolysis of (**I**) affords (chromatographic analysis) variable amounts of androsten-17-one and androsterone. Synthetic dehydro*iso*androsterone sulphate is hydrolysed by HCl to dehydro*iso*androsterone and 3-chloro-Δ^5-androsten-17-one. A. T. P.

Steroids and sex hormones. LXXVIII. Oxidation of Δ$^{4\ 17}$-pregnadien-3-one by monoperphthalic acid. L. Ruzicka, M. W. Goldberg, and E. Hardegger (*Helv. Chim. Acta*, 1942, **50**, 1297—1305).—Δ$^{4:17}$-Pregnadien-3-one (**I**) [*semicarbazone*, m.p. 224—226° (decomp.)] is converted by OsO_4 followed by Na_2SO_3 into Δ^4-17 : 20-*dihydroxypregnen*-3-*one*, m.p. 204—205°, oxidised by $Pb(OAc)_4$ in AcOH at room temp. to Δ^4-androstene-3 : 17-dione, m.p. 169—170°. (**I**) is oxidised by *o*-$CO_2H\cdot C_6H_4\cdot CO_3H$ at room temp. to a mixture of *isomerides*, $C_{21}H_{30}O_2$, A, m.p. 174·5—175·5°, $[\alpha]_D$ +82° in $CHCl_3$ [*semicarbazone*, m.p. 227—228° (decomp.); no colour with $C(NO_2)_4$], B (main product), m.p. 188·5—190°, $[\alpha]_D$ +106° in $CHCl_3$ [*semicarbazone*, m.p. 217—218° (decomp.); no colour with $C(NO_2)_4$], and C, m.p. 189—190°, $[\alpha]_D$ +111° in $CHCl_3$ [*semicarbazone*, decomp. 200°, m.p. 207°; yellow colour with $C(NO_2)_4$]. *C* gives an *acetate*, m.p. 152·5—153·5°, with Ac_2O–C_5H_5N, which do not affect *A* or *B*. The absorption spectra of *A*, *B*, and *C* are almost identical and characteristic of αβ-unsaturated ketones. *A* and *B* are possibly oxido-compounds and *C* a doubly unsaturated, CO-alcohol. M.p. are corr. (vac.). H. W.

5-Methyl-2-ethylpyridine, a dehydrogenation product of solanidine.—See A., 1943, II, 103.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Essential oil of *Cupressus macrocarpa*.—See B., 1943, III, 62.

Vetiverone. S. Sabetay and L. Trabaud (*Helv. Chim. Acta*, 1942, **25**, 1187).—A claim for priority against Naves (A., 1942, II, 371). H. W.

Isolation of lupeol from the osage orange (*Maclura pomifera*, Raf.). L. J. Swift and E. D. Walter (*J. Amer. Chem. Soc.*, 1942, **64**, 2539—2540).—Dry osage oranges (1 kg.) yield to light petroleum a mixture, whence chromatography (Al silicate) and alkaline hydrolysis afford lupeol (**I**) (2·3 g.), for which crystallo-optical properties and a

photomicrograph are given. With conc. H_2SO_4–Ac_2O–$CHCl_3$, (**I**) gives a red colour, also given by the dried latex of the fruit.
R. S. C.

Phenolic behaviour of buchu-camphor and its derivatives. II. Comparison with phenols and keto-enols [in pH of dilute aqueous solutions]. (Signa.) C. Straneo (*Gazzetta*, 1941, **71**, 646—647; cf. A., 1940, II, 136).—The pH (quinhydrone electrode) of 0·001N-aq. buchu-camphor (**I**), 6·65, is comparable with that of diphenols; in the OMe ether of (**I**) and in its 1- and 8- (alcoholic) -OH-derivatives the pH in 0·01N- and 0·001N-aq. solutions is comparable with that of monophenols (**II**). The pH of methyl*cyclo*hexane-1 : 2-diones (**III**) is slightly > that of (**II**), suggesting that in (**III**) both CO groups can enolise.
E. W. W.

Sesquiterpenes. LV. Stepwise degradation of norcedrenedicarboxylic acid. P. A. Plattner, G. W. Kusserow, and H. Klaut (*Helv. Chim. Acta*, 1942, **25**, 1345—1364).—In the prep. of norcedrenedicarboxylic acid (**I**) according to Ruzicka *et al.* (A., 1929, 932), *dihydroxycedranone*, (?) $C_{15}H_{24}O_3$, m.p. 126—127° (*semicarbazone*, m.p. 181—182°; *p-nitrobenzoate*, m.p. 175°), is obtained as by-product; it does not give a yellow colour with $C(NO_2)_4$ or react with $FeCl_3$. (**I**), has m.p. 209°, $[\alpha]_D^{14}$ −39·4° in $CHCl_3$, and is best obtained (with $CO_2H{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$ and neutral compounds) by the oxidation of cedrenol in $COMe_2$ by $KMnO_4$ and of the acidic product by HNO_3 (*d* 1·4). (**I**) is transformed by H_2SO_4–MeOH into the *Me H* ester, m.p. 98·5—99·5°, and by CH_2N_2 into the Me_2 ester (**II**), $[\alpha]_D^{23}$ −43·5° in MeOH, partly hydrolysed by alkali to the Me H ester, m.p. 130—131°. Isomerisation is not observed when (**I**) or cedrenedicarboxylic acid is heated with conc. HCl at 180°, when the anhydride of (**I**) is heated at 210—220°, or when (**II**) is boiled with NaOMe–MeOH. The monocarboxylic acid, $C_{12}H_{18}O_2$, m.p. 90—90·5°, obtained by bromination of (**I**) followed by decarboxylation and removal of HBr does not show the absorption typical of αβ-unsaturation. Its *Me* ester is oxidised by BzO_2H in $CHCl_3$ to the *oxido*-ester, $C_{13}H_{20}O_3$, b.p. 132—133°/12 mm., $[\alpha]_D$ −42·3° in MeOH, transformed by boiling aq. dioxan into the *(OH)$_2$-ester*, $C_{13}H_{22}O_4$, m.p. 105°, $[\alpha]_D$ −36° in MeOH, with smaller amounts of two *isomerides*, m.p. 134°, $[\alpha]_D$ −63° in MeOH, and m.p. 120—120·5°, $[\alpha]_D$ −8° in MeOH, respectively. With an excess of Br followed by CH_2N_2, (**I**) yields *Me$_2$ bromonorcedrenedicarboxylate* (**III**), m.p. 61—62°, $[\alpha]_D$ −26·8° in MeOH, with some *Me H* ester, m.p. 195—196°. (**III**) retains Br somewhat firmly but when treated with KOH in boiling aq. dioxan, followed by CH_2N_2, fractional distillation, and eventual hydrolysis, gives the monocarboxylic acid, $C_{12}H_{18}O_2$, m.p. 90—91° (*loc. cit.*), *Me$_2$ dihydronorcedrenedicarboxylate* (**IV**), $[\alpha]_D^{17}$ −70° in CHCl, and *Me$_2$ hydroxynorcedrenedicarboxylate*, m.p. 105°. With KOAc in $COMe_2$ at 150° (or 180° with large charges) (**III**) gives (**IV**), hydrolysed with difficulty to the *acid* (**V**), m.p. 212—213°, $[\alpha]_D$ −91° or −87° (*c* = 2·7 or 1·2) in MeOH, hydrogenated to (**I**) and apparently transformed by boiling Ac_2O into a polymeric anhydride. (**V**) is oxidised by $KMnO_4$ in alkaline solution to the *ketodicarboxylic acid*, $C_{12}H_{28}O_6,H_2O$ (also anhyd.), m.p. 142·5—143°, $[\alpha]_D$ −35° in MeOH [*p-nitrophenylhydrazone*, $C_{18}H_{23}O_6N_3$, m.p. 182—183°; *Me$_2$* ester, b.p. ~110°/1 mm., $[\alpha]_D$ +21° in MeOH (*p-nitrophenylhydrazone*, m.p. 106°)]. This is oxidised [$Pb(OAc)_4$ in AcOH at room temp. and then at 70—80°] to the *anhydride* (**VI**), $C_{11}H_{16}O_3$, b.p. 125°/high vac., $[\alpha]_D^{23}$ −22·9° in MeOH, hydrolysed to the dicarboxylic *acid*, m.p. 88·5—89°, $[\alpha]_D^{15}$ +13°, +17·9° (*c* = 0·6, 1·15) in MeOH, $[\alpha]_D^{15}$ −4·9° in $CHCl_3$ (*Me$_2$* ester, b.p. ~80°/high vac., $[\alpha]_D^{23}$ +26·3° in MeOH). The acid is obtained in less pure form and poorer yield by oxidation with H_2O_2. Attempts to cyclise it by CaO at 260—320° give (**VI**). (**VI**) is converted by PBr_3 followed by Br, esterification with MeOH, fractional distillation, and hydrolysis into the lactonecarboxylic *acid*, $C_{11}H_{16}O_4$, m.p. 187°. M.p. are corr.
H. W.

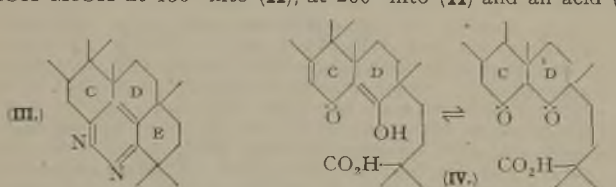
Sesquiterpenes. LVI. Degradation of dihydroeudesmol by chromic acid. L. Ruzicka, P. A. Plattner, and A. Fürst [and, in part, A. Ahl] (*Helv. Chim. Acta*, 1942, **25**, 1364—1374).—Eudesmol is reduced (Raney Ni–EtOH–H_2 at 100°/100 atm.) to dihydroeudesmol (**I**), m.p. 86—87°, $[\alpha]_D$ +16·8° in $CHCl_3$, which is dehydrated with about equal readiness when it is treated with $KHSO_4$ or when converted into the hydrochloride and then treated with KOH–EtOH. The products obtained by decomp. of the ozonide of the resulting dihydroeudesmene by H_2O give indefinite semicarbazones; reductive fission leads to more tractable products, but the yields are unsatisfactory. (**I**) is oxidised by CrO_3 in AcOH at 75—80° to 3-keto-5 : 9-dimethyldecahydronaphthalene (**II**) (semicarbazone, m.p. 222°, $[\alpha]_D$ +26° in AcOH) and an *acid*, probably 1 : 3-*dimethyl*cyclo*hexane*-1 : 2-*diacetic acid*, m.p. 141—143° [*Me$_2$* ester, $[\alpha]_D$ +5·5°, +4·6° (*c* = 1·61; 1·30) in $COMe_2$]. (**II**) is converted by PhCHO and KOH in aq. EtOH into the *mono-*, m.p. 141—143°, $[\alpha]_D$ +20·63° in EtOH, and by PhCHO and HCl in Et_2O and treatment of the product with NaOAc in AcOH into the *di-*, m.p. 198—200°, $[\alpha]_D^{17}$ −14·6° in $CHCl_3$, *-benzylidene* derivative. Ozonisation of the last named compound leads to (?) 1 : 3-*dimethyl*cyclo*hexane*-2-*carboxylic*-1-*acetic acid*, m.p. 132—134°, $[\alpha]_D$ +47·1° in $COMe_2$ (*Me$_3$* ester, $[\alpha]_D$ +45·3° in COMe; *Me ester anilide*, m.p. 100—102°, $[\alpha]_D$ +78° in $COMe_2$). M.p. are corr.
H. W.

Triterpenes. LXVIII. α-Elemolic acid. L. Ruzicka, E. Rey, and M. Spillmann (*Helv. Chim. Acta*, 1942, **25**, 1375—1402).—Since identical CO-acids are not obtained from α- (**I**) and β- (**II**) -elemolic acids, these triterpene acids cannot be epimerides with respect to the *sec.*-OH. (**I**) and (**II**) lose 3 C as $COMe_2$ when ozonised or oxidised by CrO_3 or $KMnO_4$ with production of a new CO_2H; hence the readily hydrogenated double linking in (**I**) and (**II**) must be present in a side-chain with terminal $\cdot CH{:}CMe_2$. The difficultly reactive double linking of (**I**) is oxidised by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ to an oxido-compound whereas the latent, not yet hydrogenated double linking of (**II**) is not affected by the oxidant and in this respect resembles the double linking of α-amyrin. A partial, mutual transformation in the two series is observed during many oxidations and hydrogenations which possibly depend on a displacement of the difficultly reactive double linking. Since the active double linking is in the same position in the two elemic acids it is highly probable that they differ from one another solely in the position of the difficultly reactive linking and have an otherwise similar structure. Since the relationship between (**I**) and (**II**) is very similar to that between lanosterol and cryptosterol in respect of oxidation with CrO_3, ozonisation, hydrogenation, and dehydrogenation by Se it is probable that there is a close analogy between these groups of tetracyclic triterpene derivatives. (**I**), m.p. 224—225°, $[\alpha]_D$ −24·0°, isolated from Manila elemi resin (A., 1942, II, 266) is shown to be homogeneous by further treatment with Girard reagent *T* and by chromatography of its Me ester, m.p. 143—144°, $[\alpha]_D$ −17·6°, in light petroleum over Al_2O_3. The following new or revised data are recorded: acetyl-α-elemolic acid (**III**), m.p. 241—242°, $[\alpha]_D$ −36·1°; α-elemonic acid (**IV**), m.p. 286—287°, $[\alpha]_D$ −76·0° (Me ester, m.p. 161—162°, $[\alpha]_D$ −90·2°; oxime, m.p. 227—228°, $[\alpha]_D$ −84·4°); dihydro-α-elemonic acid, m.p. 309—310°, $[\alpha]_D$ −97·0° (oxime, m.p. 233—234°, $[\alpha]_D$ −117·2°); dihydro-α-elemolic acid, m.p. 237—238°, $[\alpha]_D$ −22·6° [acetate (**VI**), m.p. 250—251°, $[\alpha]_D$ −33·1°]; acetyl-α-elemolyl chloride, m.p. 209—210°, $[\alpha]_D$ −120°; β-elemonic acid, m.p. 224—225°, $[\alpha]_D$ +43·2°. Catalytic hydrogenation (PtO_2 in AcOH) of (**I**) gives (**V**) and (after methylation) *Me acetyldihydro-α-elemolate* (**VII**), m.p. 130·5—131°, $[\alpha]_D$ −40·7°, and Me dihydro-α-elemolate. (**VI**) is obtained by catalytic hydrogenation (PtO_2 in AcOH) of (**III**); under similar conditions Me α-elemolate is reduced to (**VII**). (**III**) in EtOH containing Raney Ni at 60° is hydrogenated to (**VI**), whereas (**I**) gives (**V**) when reduced in EtOH containing Raney Ni at 200°/160 atm. (**I**) is reduced (H_2 at 180°/60 atm., PtO_2–AcOH) to a *dihydrodeoxo-α-elemolic acid*, m.p. 247—248°, $[\alpha]_D$ +3·6°. (**IV**) is transformed by N_2H_4,H_2O followed by NaOEt–EtOH at 190° into deoxy-α-elemonic acid, m.p. 263—263·5°, $[\alpha]_D$ −20·8°, hydrogenated (PtO_2 in AcOH) to dihydrodeoxo-α-elemonic acid, m.p. 284—285°, $[\alpha]_D$ −51·7° (Me ester, m.p. 118·5—119·5°, $[\alpha]_D$ −56·0°). Me α-elemolate is converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in $CHCl_3$ into its *dioxide*, m.p. 203—204°, $[\alpha]_D$ −6·0°, which does not give a yellow colour with $C(NO_2)_4$ and could not be satisfactorily hydrolysed in acid, alkaline, or neutral solution; large amounts of non-cryst. material are simultaneously formed. (**VII**) is oxidised by SeO_2 in aq. dioxan at 230° to an isomeric *Me acetyl-α-elemolate* (**VIII**), m.p. 126—127°, $[\alpha]_D$ −89·0°, which could not be hydrogenated (PtO_2 in AcOH); it is oxidised by CrO_3 in AcOH at 100° to *Me diketoacetyldihydro-α-elemolate*, m.p. 144·5—145·5°, $[\alpha]_D$ −26·9°, also obtained apparently by oxidising the known Me acetyldihydro-α-elemolate with CrO_3. (**I**) is oxidised by CrO_3 in AcOH to (**IV**) and β-elemonic acid, m.p. 225°, $[\alpha]_D$ +43·2° (Me ester, m.p. 103—104°, $[\alpha]_D$ +34·5°). (**IV**) is converted by Na and EtOH followed by CH_2N_2 into *Me* epi-α-*elemolate* (**IX**), m.p. 141·5°, $[\alpha]_D$ −49·2°, which does not give a cryst. acetate and is hydrogenated (PtO_2 in AcOH at room temp.) to *Me* epi*dihydro-α-elemolate*, m.p. ~100° and 151—152° after resolidification at 130—140°, $[\alpha]_D$ −50·3°. (**IX**) is oxidised by CrO_3 in AcOH to Me α-elemonate, m.p. 161—162°, $[\alpha]_D$ −89·0°. (**IV**) is hydrogenated (PtO_2 in AcOH at 100°) to the H_2-compound and epi*dihydro-α-elemolic acid*, m.p. 265—265·5°, $[\alpha]_D$ −60·0°; the latter substance is produced under the same conditions but at room temp. CrO_3 and (**VIII**) in AcOH at 50° afford (after esterification) Me_2 trisnoracetyl-α-tritelemenoldicarboxylate, m.p. 133—135°. Ozonisation of Me α-elemonate and decomp. of the ozonide by boiling H_2O gives Me_2 trisnor-α-tritelemenonedicarboxylate, m.p. 161—161·5°, $[\alpha]_D$ −146·0°. Dehydrogenation of (**I**) by Se at 350° affords a hydrocarbon mixture which gives additive *products*, $C_{22}H_{17}O_6N_3$, m.p. 145—146°, and $C_{22}H_{17}O_5N_3$ or $C_{23}H_{19}O_6N_3$, m.p. 159—160°, with $C_6H_3(NO_2)_3$, 1 : 7 : 8-trimethylphenanthrene, m.p. 146—147° [additive product, m.p. 192—192·5°, with $C_6H_3(NO_2)_3$], 1 : 7-dimethylphenanthrene [isolated as the additive compound, m.p. 159—160°, with $C_6H_3(NO_2)_3$ and as the picrate, m.p. 130—131°], and a *homologue*, $C_{24}H_{18}$, of picene, m.p. 345—346°. M.p. are corr. (vac.). $[\alpha]_D$ are determined in $CHCl_3$.
H. W.

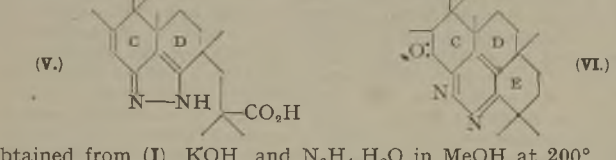
Triterpenes. XLIX. β-Elemonic acid. L. Ruzicka, H. Häusermann, and E. Rey (*Helv. Chim. Acta*, 1942, **25**, 1403—1409).—Oxidation (CrO_3 in AcOH) of acetyldihydro-β-elemolic acid at room temp. gives *diketoacetyldihydro-β-elemolic acid*, m.p. 269—270°, $[\alpha]_D$ +23·6° in $CHCl_3$ (*Me* ester, m.p. 176·5—177·5°, $[\alpha]_D$ +35·6° in $CHCl_3$), which is shown by its absorption spectrum to contain

the group CO·C:C·CO. It is hydrogenated (PtO_2 in AcOH) to (?) *ketoacetyltetrahydro-β-elemolic acid*, m.p. 273—275°, which does not give a yellow colour with $C(NO_2)_4$. Treatment of β-elemonic acid (**I**) in CCl_4 with O_3 until the product fails to decolorise Br–H_2O and decomp. of the product with hot H_2O yields $COMe_2$ in considerable amount but a cryst. material could not be obtained from the acidic products. Similar treatment of Me β-elemonate (**II**) affords $COMe_2$, an *acid* (**III**), $C_{28}H_{42}O_5$, m.p. 210—211°, $[\alpha]_D$ +37·5° in $CHCl_3$ (*Me* ester), which gives a marked yellow colour with $C(NO_2)_4$, and a non-cryst. neutral material, oxidised (CrO_3 in AcOH) to (**III**). (**III**) is also obtained by oxidation of (**III**) with $KMnO_4$ in boiling $COMe_2$ in addition to 80% of a neutral, amorphous substance. Hydrogenation (PtO_2 in EtOH–AcOH at room temp.) of deoxo-β-elemonic acid affords *dihydrodeoxo-β-elemonic acid*, m.p. 259—260°, $[\alpha]_D$ +9·35° in $CHCl_3$ (*Me* ester, m.p. 100—100·5°, $[\alpha]_D$ +4·8° in $CHCl_3$), which gives a distinct yellow colour with $C(NO_2)_4$. (**I**) and anhyd. HCO_2H in $CHCl_3$ at room temp. yield the *substance*, $C_{31}H_{48}O_5$, m.p. 240—242°; at higher temp. a cryst. material does not result. M.p. are corr. H. W.

Triterpenes. LXX. Further transformations of β-amyradienedionol. L. Ruzicka and O. Jeger (*Helv. Chim. Acta*, 1942, **25**, 1409—1419).—β-Amyradienedionol acetate is oxidised by CrO_3 (cf. Simpson, A., 1938, II, 448) to its oxide (**I**), m.p. 290—291°, and a *compound*, $C_{32}H_{42(44)}O_6$, m.p. 288—290° (decomp.). (**I**) is hydrolysed by boiling KOH–MeOH or by 10% HCl–MeOH at ~200° to β-amyradienedionol oxide (**II**), m.p. 310—312° (vac.; decomp.). (**I**) and N_2H_4,H_2O in EtOH at 200° give the pyridazine derivative (**III**), m.p. 292—293° (*Ac* derivative, m.p. 261°). (**I**) is converted by KOH–MeOH at 130° into (**II**), at 200° into (**II**) and an acid (**III**),



and at 210° into (**IV**) and an unidentified, non-cryst. product. (**IV**), m.p. 239—240° (*Me* ester, m.p. 114—115°; *acetate*, m.p. 157—158°), gives a dark yellow colour with $C(NO_2)_4$, a grey-green to black-green colour with $FeCl_3$, and is not lactonised at 230°/vac. It does not react with NH_2OH in EtOH at 80—200° but with N_2H_4,H_2O at 200° yields the *compound* (**V**), m.p. 264—265°, also



obtained from (**I**), KOH, and N_2H_4,H_2O in MeOH at 200°. (**III**) is oxidised by H_2O_2 in AcOH to a non-cryst. product acetylated to (**VI**), m.p. 253° (decomp.), which is reduced (Wolff–Kishner) to (**III**). M.p. are corr. H. W.

Saponin of fenugreek seeds. G. Soliman and Z. Mustafa (*Nature*, 1943, **151**, 195—196).—The pure saponin (separation described), m.p. 190—200°, afforded in hydrolysis a cryst. mixture, m.p. 184°, of sapogenins from which a *compound*, $C_{27}H_{42}O_3$, m.p. 198° (free OH; 2 inactive O), was isolated. It appears to belong to the sarsasapogenin group. A. A. E.

Saponins and sapogenins. XX. Bethogenin and trillogenin, new sapogenins from *Trillium erectum*. S. Lieberman, F. C. Chang, M. R. Barusch, and C. R. Noller (*J. Amer. Chem. Soc.*, 1942, **64**, 2581—2583).—Hydrolysis of the extract of the root of *T. erectum* yields diosgenin, trillin (anhyd.), m.p. 269·5—271° (preheated bath), $[\alpha]_D^{26}$ −103·4°, $[\alpha]_{Hg}^{26}$ −127·2° in dioxan (acetate, m.p. 204—205°, $[\alpha]_D^{30}$ −71·4°, $[\alpha]_{Hg}^{30}$ −80·2° in dioxan), chlorogenin, *bethogenin* (**I**), $C_{27}H_{40}O_4$, m.p. 193—194°, $[\alpha]_D^{24}$ −98·4° in dioxan, and *trillogenin* (**II**), $C_{27}H_{48}O_4$, m.p. 206—210°, $[\alpha]_D^{24}$ −41·6°, $[\alpha]_{Hg}^{24}$ −54·3° in dioxan. (**I**) is unstable when kept or recrystallised, is unsaturated [$C(NO_2)_4$], gives an *acetate*, m.p. 230—232°, $[\alpha]_D^{24}$ −94·4° in dioxan, and *benzoate*, m.p. 212—215°, $[\alpha]_D^{24}$ −65·1° in dioxan, shows 1 active H, with H_2–PdO–EtOAc at 30 lb. and then Ac_2O–C_5H_5N gives *tetrahydrobethogenin diacetate*, m.p. 141—144°, $[\alpha]_D^{24}$ −156° in dioxan, and gives an *oxime*, m.p. 241—243°, but with Ac_2O does not isomerise. The side-chain of (**II**) may be open, since a *tetra-acetate*, m.p. 102—103°, $[\alpha]_D^{24}$ 0, $[\alpha]_{Hg}^{24}$ −3·5° in dioxan, is obtained by Ac_2O–NaOAc. R. S. C.

VI.—HETEROCYCLIC.

Reaction of furoic acid with tetrahydronaphthalene.—See A., 1943, II, 91.

Preparation of β-2-furylacrylic acid. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1942, **A**, **16**, 163—166).—β-2-Furylacrylic acid, m.p. 141°, is obtained in 66—67% yield by heating an equimol. mixture of furfuraldehyde, $CH_2(CO_2H)_2$, and C_5H_5N at 100° for 2 hr. H. W.

Condensation of succinic acid with acetylacetone. Z. F. Stefanovskaja, V. V. Dorofeev, and I. A. Trefiliev (*J. Gen. Chem. Russ.*, 1941, **11**, 518—522).—$(CH_2{\cdot}CO_2Na)_2$ and CH_2Ac_2 in Ac_2O are heated for 20 hr. at 100°, and the product is treated with dil. HCl and extracted with Et_2O. The Et_2O-sol. fraction consists chiefly of a resinous acid, and this, heated with H_2O at 100° (12 hr.), yields 1-*acetonyl-4-methylfuran-2-carboxylic acid*, m.p. 121—122°. R. T.

Halogen compounds derived from 2 : 5-diphenyl-3-methylfuran. R. E. Lutz and C. E. McGinn (*J. Amer. Chem. Soc.*, 1942, **64**, 2583—2585).—2 : 5-Diphenyl-3-methylfuran in $CHCl_3$ gives, successively, the 4-Br-derivative (**I**), 4-*bromo*-2 : 5-*di*-p-*bromophenyl*-3-*methyl*- (**II**), m.p. 168—169°, and -3-*bromomethyl-furan* (**III**) (75%), m.p. 212—213°. Structures are proved by indifference of the products to Zn dust–AcOH, except that (**III**) gives (**II**). With HNO_3–AcOH, (**I**) gives *cis*-COPh·CMe:CBr·COPh, reduced by Zn dust–AcOH to COPh·CHMe·CH_2·COPh. (**II**) and (**III**) give similarly cis-*β-bromo-αδ-di*-p-*bromophenyl-γ-methyl*- (**IV**) (91%), m.p. 119·5—120°, and *-γ-bromomethyl-Δβ-butene-αδ-dione* (**V**) (90%), m.p. 117—117·5°, both reduced by $SnCl_2$–AcOH–conc. HCl to 2 : 5-*di*-p-*bromophenyl*-3-*methylfuran* (**VI**), m.p. 158—159°. (**VI**) and cis-*αδ-di*-p-*bromophenyl-β-methyl-Δβ-butene-αδ-dione* (**VII**), m.p. 115—116° (unaffected by I–$CHCl_3$–light), are interconvertible by HNO_3 and $SnCl_2$. Zn dust–AcOH reduces (**IV**), (**V**), and (**VII**) to *αδ-di*-p-*bromophenyl-β-methylbutane-αδ-dione*, m.p. 120—120·5°. R. S. C.

Conversion of unsaturated 1 : 4-diketones into furans and hydroxyfuranones. R. E. Lutz and C. E. McGinn (*J. Amer. Chem. Soc.*, 1942, **64**, 2585—2588).—Further examples are provided of the greater ease of dehydration of *cis*- compared with *trans*-COPh·CR:CR′·COPh. Spatial as well as energy relations may be the cause, in accord with formation of some hydroxyfuranones from *cis*-diketones. *trans*- (**I**) (modified prep.) and *cis*-COPh·CH:CMe·COPh (**II**) [prep. from 2 : 5-diphenyl-3-methylfuran (**III**) by HNO_3–AcOH at 10°; 81% yield] with HBr–AcOH give 4-bromo-2 : 5-diphenyl-3-methylfuran (**IV**) [also obtained from (**III**) by Br–$CHCl_3$], with Zn dust in AcOH give CHMeBz·CH_2Bz (**V**), and with $SnCl_2$–conc. HCl–AcOH give (**III**) (96%) [also obtained from (**V**)], but with Ac_2O–H_2SO_4 at room temp. (**II**) gives 4-*acetoxy*-2 : 5-*diphenyl*-3-*methylfuran* (**VI**) (50—68%), m.p. 94—95°, and with Bz_2O–H_2SO_4 gives an oily Bz-compound, whereas (**I**) does not react; with $ZnCl_2$–Ac_2O–AcOH *trans*- but not *cis*-(2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CH:)$_2$ gives the saturated diketone. (**VI**) could not be converted into the 4-Cl-compound. With Br–CCl_4, (**VI**) gives 2-*bromo*-2 : 5-*diphenyl*-4-*methyl*-2 : 3-*dihydrofuran*-3-*one*, m.p. 88—89° (with boiling EtOH gives the 2-OEt-compound), *cis*-COPh·CMe:CBr·COPh [prep. from (**IV**) by conc. HNO_3–AcOH at 80°] with H_2SO_4 (2 drops) in AcOH at 0° gives 2-acetoxy-, with H_2SO_4 in AcCl at 0° gives 2-chloro-, and with HCl–MeOH gives 2-methoxy-2 : 5-diphenyl-4-methyl-1 : 2-dihydrofuran-2-one. 3-Bromo-2 : 4 : 5-triphenylfuran (prep. from COPh·CPh:CH·COPh by 30% HBr–AcOH at room temp.) gives similarly 2-acetoxy-, 2-chloro-, and 2-methoxy-2 : 4 : 5-triphenyl-1 : 2-dihydrofuran-3-one. R. S. C.

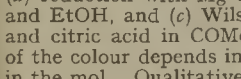
Constitution of the photodimerisates of the coumarins and furocoumarins. F. von Wessely and I. Plaichinger (*Ber.*, 1942, **75**, [*B*], 971—976).—Evidence is adduced in favour of the view that the photodimerides of coumarins and furocoumarins are *cyclo*butane derivatives. α-Dicoumarin (Ström, A., 1904, i, 505) could not be hydrogenated in cold or hot AcOH containing Pd. Me_2 dicoumarate Me_2 ether, m.p. 133·5—135° (corr.), softens at 130°, obtained from it by Me_2SO_4 and NaOH, is similarly resistant. Analogously diherniarin (**II**) could not be hydrogenated. On the other hand the compound $\left[\begin{matrix}O\text{—}CO\\ C_6H_4{\cdot}CH\end{matrix}\!\!>\!C\cdot\right]_2$ obtained by Dyson (*J.C.S.*, 1887, **51**, 68) by condensing *o*-OH·C_6H_4·CHO with $(CH_2{\cdot}CO_2H)_2$ readily absorbs 2 H_2 in presence of Pd–C or under the action of Na–Hg. The product obtained by the action of Br on (**I**) is a substitution compound, the constitution of which has not been determined. H. W.

Synthetic experiments in the benzopyrone series. VI. Action of aluminium chloride on angelicin, psoralen, and related compounds. B. Krishnaswamy and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **A**, **16**, 151—156).—Angelicin is converted by C_6H_6 and $AlCl_3$ at room temp. into 8-*αβ-diphenylethylumbelliferone*, m.p. 205—206°, which gives a blue fluorescence in dil. alkali and a bright violet fluorescence in conc. H_2SO_4. Similarly, psoralen affords 6-*αβ-diphenylethylumbelliferone*, m.p. 259—260°, transformed by MeI and K_2CO_3 in anhyd. $COMe_2$ into the Me ether, m.p. 172—173°. The following observations show that the coumarin ring is not involved and that the furan ring is the active centre: (*a*) coumarin (**I**) and 6-nitrocoumarin are unaffected; (*b*) umbelliferone and 4-methylumbelliferone Me ether undergo simple demethylation; (*c*) coumarone is polymerised too readily to allow condensation with C_6H_6; (*d*) coumarilic acid (**II**) undergoes smooth addition to 3-*phenyldihydro-*

coumarilic acid, m.p. 143—144°. Coumaric acid resembles (**II**) in this reaction and differs from (**I**). H. W.

Useful colour reactions of anthoxanthins and related compounds. S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **A**, **16**, 129—134).—The scope of the following colour reactions has been investigated using a large no. of natural and synthetic flavones (**I**), flavonols (**II**), flavonones (**III**), and certain related compounds: (*a*) reduction with Mg and HCl–EtOH, (*b*) reduction with Na–Hg and EtOH, and (*c*) Wilson's H_3BO_3 test using a mixture of H_3BO_3 and citric acid in $COMe_2$. For the first two reactions the nature of the colour depends in general on the no. of OH and OMe groups in the mol. Qualitatively it is not easy to effect minor distinctions between (**I**), (**II**), and (**III**). Wilson's test is very sp. for 5-hydroxy- and 5-methoxy-flavones and (**II**) and *o*-hydroxy- and methoxy-chalkones. It is not given by (**III**) and simple aromatic ketones which do not satisfy the sp. conditions. A combination of the three reactions gives much useful information. H. W.

Preparation of substances resembling tocopherol and flavonols from benzopyrylium salts. P. Karrer and W. Fatzer (*Helv. Chim. Acta*, 1942, **25**, 1129—1138).—Passage of dry HCl into a solution of 2 : 5 : 4 : 6 : 1-$(OH)_2C_6HMe_2$·CHO and COPh·CH_2·OMe in anhyd. HCO_2H at 0° and then at 20° leads to 6-hydroxy-3-methoxy-2-phenyl-5 : 7-dimethylbenzopyrylium chloride (**I**), hydrogenated (Pt in AcOH) to 6-*hydroxy*-2-*phenyl*-5 : 6-*dimethylchroman*-3-*one*, m.p. 141° (*oxime*, m.p. 216°), which does not contain OMe. (**I**) is transformed by NaOAc in MeOH into the *Me ether* (**II**), m.p. 179° (vac.) [analogously the *Et ether*, m.p. 163—164°, or 172° (vac.)], of the



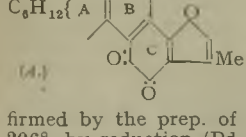
(III.)

6-hydroxy-3-methoxy-2-phenyl-5 : 7-dimethylbenzopyrylium base. (**II**) is oxidised by $FeCl_3$ to the *quinone* (**III**), m.p. 116°, which gives an absorption spectrum very similar to that of tocopherolquinone, and 6-*hydroxy*-2 : 3-*dimethoxy*-5 : 7-*dimethylflavanone*, m.p. 141° (*Me ether*, m.p. 117° after softening). H. W.

Oxidation of benzopyrylium salts to flavonols. P. Karrer and W. Fatzer (*Helv. Chim. Acta*, 1942, **25**, 1138—1140).—The double salt of $FeCl_3$ and 3-methoxy-2-phenylbenzopyrylium chloride passes in MeOH into the *Me ether* of the carbinol base, which is oxidised by *o*-$C_6H_4(CO_3H)_2$ to 2 : 3-*dimethoxyflavanone*, m.p. 177°, hydrolysed by acid to the corresponding flavonol, m.p. 169°. H. W.

Tetrahydrocannabinol analogues with marihuana activity. XV. R. Adams, S. Loewe, C. W. Theobald, and C. M. Smith (*J. Amer. Chem. Soc.*, 1942, **64**, 2653—2655; cf. A., 1943, II, 69).—*m*-C_6H_4Et·OH with H_2–Raney Ni in EtOH at 200°/136 atm. gives 3-*ethyl*cyclo*hexanol* (89%), b.p. 96°/20 mm., 192·5—193°/748 mm. (3 : 5-*dinitrobenzoate*, m.p. 133—134°), oxidised by $Na_2Cr_2O_7$–H_2SO_4 to 3-ethyl*cyclo*hexanone (72%), b.p. 81°/12 mm. (semicarbazone, m.p. 166—167°; *p*-nitrophenylhydrazone, m.p. 128—129°), which with $Et_2C_2O_4$–NaOEt etc. gives *Et* 5-*ethyl*cyclo*hexanone*-2-*carboxylate* (54%), b.p. 96—98°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 122—122·5°). *Et* 5 : 5-, b.p. 125—128°/14 mm., 4 : 5-, b.p. 116°/10 mm., and 3 : 5-*dimethyl*cyclo*hexanone*-2-*carboxylate*, b.p. 103°/4 mm. (2 : 4-*dinitrophenylhydrazones*, m.p. 89°, 146—147°, and 175°, respectively), and *cyclo*heptanone-2-carboxylate (14%), b.p. 77—79°/0·4 mm. [Cu salt, m.p. 193—194°; gives 1-phenyl-3 : 4-pentamethylene-5-pyrazolone, m.p. 207—210° (decomp.)], are similarly prepared. Standard methods lead to 3″-*hydroxy*-4′-*ethyl*-, m.p. 167—169°, -4′ : 4′-, m.p. 190—190·5°, -4′ : 5′-, m.p. 174·5—175·5°, and -4′ : 6′-*dimethyl*-, m.p. 151·5—152·5°, -5″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenz*-2-*pyrone* and 5-*hydroxy*-7-n-*amyl*-3 : 4-*pentamethylenecoumarin*, m.p. 178·5—179°, which yield 3″-*hydroxy*-2 : 2-*dimethyl*-4′-*ethyl*- (**I**), b.p. 172°/0·1 mm., -2 : 2 : 4′ : 4′- (**II**), m.p. 89—89·5°, -2 : 2 : 4′ : 5′- (**III**), b.p. 181—182°/0·05 mm., and -2 : 2 : 4′ : 6′-*tetramethyl*- (**IV**), b.p. 186°/0·05 mm., -4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenz*-2-*pyran* and 5-*hydroxy*-2 : 2-*dimethyl*-7-n-*amyl*-3 : 4-*pentamethylene*-1 : 2-*benzpyran* (**V**), b.p. 180—182°/0·05 mm. Potencies relative to the 2 : 2 : 4′-Me_3 compound as unity are (**I**) 0·22, (**II**) 0·10, (**III**) 0·11, (**IV**) 0·75 (convulsant), and (**V**) 0·21, showing the depressing effect of variations in structure. M.p. are corr. R. S. C.

Quinone dyes of the phenanthrofuran series. III. Constitution of tanshinone II. F. von Wessely and T. Lauterbach (*Ber.*, 1942, **75**, [*B*], 958—970).—Tanshinone II (**I**) is probably *A*. Extraction of the roots of *Salvia miltiorrhizae* with Et_2O affords (**I**), $C_{19}H_{18}O_3$, m.p. 216°, which is separated from tanshinone I (**II**) partly by crystallisation and partly by chromatography in C_6H_6 over Al_2O_3. It does not contain OAlk. The presence of the *o*-quinonoid group is confirmed by the prep. of a *quinoxaline* derivative, $C_{25}H_{22}ON_2$, m.p. 206°, by reduction (Pd sponge in EtOH) and subsequent methylation to *leucotanshinone Me*$_2$ *ether* (**III**), m.p. 92°, softens at 90°, $[\alpha]_D^{17}$ ±0° (*picrate*, m.p. 105—107°), and by reductive acetylation to the corresponding *diacetate*, m.p. 176°, softens at 172°. The third O of (**I**) is probably contained in a hetero-ring since (**I**) does



(I.)

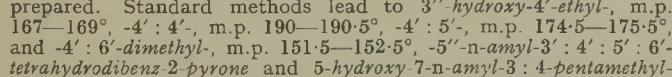
not react with Zerevitinov's or carbonyl reagents. Hydrogenation of (**I**) with a little Pd sponge in EtOH ceases with the absorption of 1 H_2 but with much Pd sponge in AcOH (**I**) and (**III**) fairly rapidly absorb 5 H_2 with partial loss of OMe in the case of (**II**). It is concluded that an aliphatic double linking is absent. Drastic oxidation of (**I**) by HNO_3 at 150° affords 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$ in excellent yield whereas the action of $KMnO_4$ in $COMe_2$ leads to a difficultly separable mixture of acids. With CrO_3 according to Kuhn–Roth (**I**) gives 1 mol. of AcOH whereas under less drastic conditions the product is an *anhydride* (**III**), $C_{14}H_{14}O_3$, of an *o*-dicarboxylic acid, m.p. 136°, softens at 134°, $[\alpha]_D^{17}$ ±0° [corresponding *acid*, m.p. 196—198° (decomp.)]. Oxidation of (**I**) and (**II**) is similar in causing loss of 5 C and 4 H. The probable assumption that (**I**) contains a substituted furan ring is strengthened by the formation of (**IV**) by the ozonisation of (**III**). The same difference (CH_6) is observed between the mol. formula of (**I**) and (**II**) and those of their products of oxidation by CrO_3. (**IV**) and CrO_3 (Kuhn–Roth) give 1/3 mol. of AcOH. 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$ is obtained in excellent yield by oxidation of (**IV**) with HNO_3. Hydrogenation (Pd sponge in AcOH) of (**IV**) causes absorption of 3 H_2 and production of a non-homogeneous product from which a monocarboxylic *acid*, $C_{14}H_{18}O_2$, m.p. 235°, is obtained; all the absorbed H appears to be required to convert 1 CO of (**IV**) into Me and since only 3 H_2 are similarly absorbed in presence of PtO_2 and AcOH it appears that an aliphatic double linking is not present in (**IV**). (**IV**) is therefore very probably the dicarboxylic anhydride of an alkylated tetrahydronaphthalene or indane. Thermal decomp. of the acid corresponding to (**IV**) gives a hydrocarbon resembling $C_{10}H_7Me$ and yielding a picrate which could not be completely purified. (1 : 2 : 3 : 4-Tetrahydronaphthalene and its 1 : 1-Me_2 derivative are partly dehydrogenated when passed over heated Na_2CO_3.) Dehydrogenation of (**IV**) does not occur readily with $K_3Fe(CN)_6$ in alkaline solution, with Pd sponge at 230°, or with heated Se. $KMnO_4$ in hot alkaline solution followed by treatment of the product (**V**) with CH_2N_2 converts (**IV**) the Me_3 ester, $C_{14}H_{16}O_7$ (**VI**), m.p. 148—151°, which does not give AcOH (Kuhn–Roth), cannot be acetylated, does not react with carbonyl reagents, and does not yield CH_4 (Zerevitinov); the function of the seventh O is not determined. It is oxidised by HNO_3 to 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$. (**VI**) is also obtained by esterification of (**V**) with HCl–MeOH but one CO_2H reacts only with difficulty. H. W.

Dioxanate of iodine pentafluoride. A. F. Scott and J. F. Bunnett (*J. Amer. Chem. Soc.*, 1942, **64**, 2727).—IF_5 and dioxan give a 1 : 1 additive *compound*, m.p. 112° (decomp.; instantaneous), hydrolysed in air to HIO_3. R. S. C.

Diphenospiran derivative with constitutional relationships to the tocopherols. P. Karrer and W. Fatzer (*Helv. Chim. Acta*, 1942, **25**, 1140—1143).—Passage of HCl into a solution of 3 : 6 : 2 : 4 : 1-$(OH)_2C_6HMe_2$·CHO and Me $\beta\zeta\kappa$-trimethyltridecyl ketone gives a blue *pyrylium* salt, $C_{36}H_{51}O_4Cl$, (**I**) converted by NaOAc or $NaHCO_3$ in EtOH into 6 : 6′-*dihydroxy*-5 : 7 : 5′ : 7′-*tetramethyl*-3′-$\gamma\eta\lambda$-*trimethyldodecyldipheno*-2 : 2′-spiro*pyran*, re-converted by HCl into (**I**). Catalytic reduction of (**I**) gives a liquid. H. W.

Structure of indigoids.—See A., 1943, I, 49.

Basicity studies of *tert.* vinylamines. R. Adams and J. E. Mahan (*J. Amer. Chem. Soc.*, 1942, **64**, 2588—2593).—Heterocyclic compounds containing endo- or exo-cyclic N·C:C are stronger bases than their saturated analogues, probably owing to equilibration of the former with the quaternary compounds, *e.g.*,



The following p$K'H$ (= pK_{H_2O} − pK_{ion}) in H_2O at 25° are recorded. 1 : 2-Dimethyl- 11·94, 1-methyl-2-*n*-butyl-, {b.p. 88·5°/30 mm.; 54% obtained from 1-methyl-2-pyrrolidone by $MgBu^aBr$ in Et_2O–N_2 at room temp., with 14% of 1-*methyl*-2 : 2-*di*-n-*butylpyrrolidine*, b.p. 122°/18 mm. [*methiodide*, m.p. 211° (corr.)]} 11·90, 2-*methyl*-1-*ethyl*- [b.p. 73·5—74·5°/55 mm.; prep. from Br·$[CH_2]_3$·COMe (**I**) by NH_2Et–EtOH; 52%; unstable in air] 11·92, and 2-*methyl*-1-n-*butyl*-Δ^2-*pyrroline* [b.p. 82—83·5°/16 mm.; 39% from (**I**) by NH_2Bu^a–EtOH] 11·90 in 25% MeOH at 26°; 1 : 2-dimethyl- 10·26, 1-methyl-2-*n*-butyl- 10·24, 2-methyl-1-ethyl- 10·64, 2-methyl-1-*n*-butyl- 10·69, and 1-methyl-pyrrolidine 10·36; 1-methyl-Δ^3-pyrroline 9·92; 1 : 2-dimethyl- 10·26, 2-methyl-1-ethyl- 10·70, 1-propenyl- (b.p. 51—53°/10 mm.) 10·66 in 25% MeOH at 28°, 1-propyl- 10·48, 1-allyl- 9·69, 2-methyl- 10·99, and 1-*n*-butyl-piperidine 10·49; piperidine 11·12; NMe_2·$[CH_2]_4$·COMe 9·67; *n*-C_5H_{11}·CH:CH·NEt_2 10·38 in 50% MeOH at 28°; *n*-C_7H_{15}·NMe_2 9·94 in 50% MeOH at 26°; 1 : 1 piperidine–EtCHO in 25% MeOH 10·77 at 27°; 1 : 1 $NHEt_2$–*n*-C_6H_{13}·CHO in 50% MeOH 10·50 at 27°. Butyrolactone and NH_2Bu^a at 280° give 95% of 1-n-*butyl*-n-*pyrrolidone*, b.p. 121°/16 mm. The formula of lysergic acid (A., 1938, II, 463) needs revision. R. S. C.

Anhydrides of basic amino-acids. D. W. Adamson (*J.C.S.*, 1943, 39—40).—"*dl*-Lysine anhydride," obtained by heating *dl*-lysine Me ester dihydrochloride with NaOMe, contains 40% of dl-3-*amino-homopiperidone* (**I**), b.p. 167°/12 mm., m.p. 68—71° [*hydrochloride*, m.p. 294—296° (decomp.); *picrate*, darkens 215°, m.p. 233° (de-

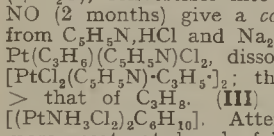
comp.); cf. Fischer *et al.*, A., 1905, i, 121]. *p*-NHAc·C_6H_4·SO_2Cl and (**I**) give 3-(p-*acetamidobenzenesulphonamido*)*homopiperidone*, m.p. 286—288° (decomp.), hydrolysed (HCl) to ε-*amino*-α-(p-*aminobenzenesulphonamido*)-n-*hexoic acid*, m.p. 286° (decomp.). *d*-NH_2·$[CH_2]_2$·$CH(NH_2)$·CO_2H,2HCl in MeOH with HCl affords l-3-*aminopyrrolidone*, b.p. 175°/20 mm., m.p. 106—108°, $[\alpha]_D^{18}$ −31·7° in H_2O (*hydrochloride*, m.p. 198—200°; *picrate*, m.p. 185—187°; 3-*Ac* derivative, m.p. 176°), which similarly forms 3-(p-*acetamidobenzenesulphonamido*)*pyrrolidone*, m.p. 222—224° (decomp.), and γ-*amino*-α-(p-*aminobenzenesulphonamido*)-n-*butyric acid*, m.p. 259—260° (decomp.). F. R. S.

Dihydropyridones.—See B., 1943, II, 74.

Compound formation between the isomeric hydroxydiphenyls and pyridine.—See A., 1943, II, 88.

Co-ordination tenacity of unsaturated molecules. A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 347—350).—The co-ordination tenacity of unsaturated mols. under normal conditions (not to be confused with the relative stability of the derived complexes) decreases in the order: NO > CO > CHPh:CH_2 > C_4H_6 and C_2H_4 > C_3H_6 and C_4H_8. In 3 days, CO displaces C_3H_6 from C_5H_5N·H[$PtCl_3$·C_3H_6] in H_2O, to give C_5H_5N·H[$PtCOCl_3$] (**I**), which with C_5H_5N affords Pt carbonylpyridinedichloride, [$PtCO(C_5H_5N)Cl_2$] (**II**); substitution occurs similarly in the case of ethylene Zeise's salt, and this method is the best for preparing CO compounds of Pt. Neither C_3H_8 nor C_2H_4 displaces CO from (**II**). NO reacts slowly with the C_2H_4 salt, and after 20 days, 50% of *Pt nitrosylpyridine dichloride*, [$PtNO(C_5H_5N)Cl_2$], is formed, which is unchanged with an EtOH solution of CHPh:CH_2. A slightly acid solution of C_5H_5N·H[$PtCl_3$(CHPh:CH_2)] with CO gives (**I**) (+H_2O), convertible into (**II**). An acidified solution of (**I**) and NO (2 months) give a *complex*, $(C_5H_5N$·$H)_2PtCl_6$, also obtained from C_5H_5N,HCl and Na_2PtCl_6. Pt propylenepyridine dichloride, $Pt(C_3H_6)(C_5H_5N)Cl_2$, dissolved in diallyl (**III**) affords a *complex*, $[PtCl_2(C_5H_5N)$·$C_3H_5]_2$; thus the co-ordination stability of (**III**) is > that of C_3H_8. (**III**) and $[Pt(C_2H_4)NH_3Cl_2]$ give a *complex*, $[(PtNH_3Cl_2)_2C_6H_{10}]$. Attempts to make compounds with two or more unsaturated mols. failed. A. T. P.

Steroids and sex hormones. LXXIX. 5-Methyl-2-ethylpyridine, a dehydrogenation product of solanidine. V. Prelog and S. Szpilfogel [with E. Stahlberger] (*Helv. Chim. Acta*, 1942, **25**, 1306—1313).—Dehydrogenation of solanine or solanidine (**I**) by Se in a sealed tube at 300—320° gives *5-methyl-2-ethylpyridine* (**II**), characterised as the picrate, m.p. 143·5—144·5° or (indef.) 150—150·5°, and *styphnate*, m.p. 170° (decomp.). (**I**) is probably *A. Et* β-*amino*-Δ$^{\alpha}$-*pentenoate*, b.p. 105°/13 mm., obtained by passing NH_3 into a mixture of NH_4NO_3 and COEt·CH_2·CO_2Et in Et_2O, is converted by $CMeNa(CO_2Et)_2$ followed by HCl into 4 : 6-*dihydroxy*-5-*methyl*-2-*ethylpyridine*, m.p. 238°, transformed by $POCl_3$ at 210° into the 4 : 6-Cl_2-compound, b.p. 125—130°/12 mm., which is reduced (Raney Ni in MeOH containing NaOMe) to (**II**), b.p. 73—76° (bath)/12 mm. Analogously NH_2·CMe:CH·CO_2Et and $CHMe(CO_2Et)_2$ afford 4 : 6-*dihydroxy*-, m.p. 276·5°, whence successively 4 : 6-*dichloro*-2 : 5-*dimethylpyridine*, b.p. 120° (bath)/12 mm., and 2 : 5-lutidine (picrate, m.p. 170·5°) result. M.p. are corr. H. W.



Synthetic production of growth substances. S. S. Nametkin and N. A. Dzbanovski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 330—332).—Syntheses of 3-indolyl-acetic (heteroauxin) and -butyric acid, and of α-$C_{10}H_7$·CH_2·CO_2H, are discussed. A. T. P.

Synthesis of γ-3-indolylbutyric acid by a new procedure. S. S. Nametkin, N. A. Dzbanovski, and A. G. Rudnev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 333—335).—Indole and MgEtI in PhOMe (not in Et_2O) at 65—70° give C_8H_6N·MgI, converted by Cl·$[CH_2]_3$·CN in PhOMe, first cold and then at 120° for 1 hr. (mixture becomes red), into a complex, decomposed by cold aq. AcOH–C_6H_6 to γ-3-indolyl-butyronitrile, which is hydrolysed by boiling 20% aq. KOH (8 hr.; yield 83·5%) to the -butyric acid (cf. Jackson *et al.*, A., 1931, 363). A. T. P.

Solubilities and compositions of the phospho-12-tungstates of diamino-acids and of proline, glycine, and tryptophan.—See A., 1943, II, 82.

Nitration of lepidine and 2-chlorolepidine. S. E. Krahler and A. Burger (*J. Amer. Chem. Soc.*, 1942, **64**, 2417—2419).—8-Nitrolepidine (**I**) and Br give 8-nitro-4-dibromomethylquinoline (89%), m.p. 111·5—112·5°, hydrolysed by $AgNO_3$ in 60% AcOH at 100° to 8-nitroquinoline-4-aldehyde (**II**) (97%), m.p. 163—173°, which is obtained less well from (**I**) by SeO_2. $KMnO_4$–$COMe_2$–H_2O at 40° converts (**II**) into 8-*nitrocinchonic acid* (71%), m.p. 253—254° (decomp.), which, when heated with Cu-bronze at 100 mm., gives 8-nitroquinoline. 2-Chlorolepidine (**III**) and Br in NaOAc–AcOH give 2-*hydroxy*-4-*dibromomethylquinoline* (12%), m.p. 307—308° (decomp.), whence the aldehyde could not be obtained. Condensation of *o*-C_6H_4Cl·NO_2, CH_2Ac·CO_2Et, and a trace of HCl over H_2SO_4 in vac. and then heating in paraffin at 240° gives 8-*chloro*-4-*hydroxyquinaldine* (**IV**) (29%), m.p. 229—230°, converted by $POCl_3$ at 100° into 4 : 8-*dichloroquinaldine* (**V**) (85%), m.p. 87—88° (with Zn dust gives quinaldine). With boiling piperidine, (**V**) gives 8-*chloro*-4-*piperidino*- (**VI**), m.p. 124—125° (picrate, m.p. 161—163°), and with boiling NaOMe–MeOH gives 8-*chloro*-4-*methoxy-quinaldine* (**VII**), m.p. 122—124°. The product previously (A., 1942, II, 36) believed to be 2-chloro-5-nitrolepidine is the 8-NO_2-compound (cf. A., 1942, II, 150). The 8-chlorolepidine compounds of Kermack *et al.* (A., 1933, 513) are the quinaldine derivatives (**IV**)—(**VII**). With $CH_2(CO_2Et)_2$–NaOEt–EtOH and then KOH–EtOH, (**III**) gives only 2-ethoxylepidine. The prep. of 2-keto-4-methyl-1 : 2-dihydroquinoline-1 : 8-diazoimide, m.p. 236—237·5°, is improved; in boiling EtOH it gives 2-hydroxylepidine and MeCHO. R. S. C.

Reaction between halogen derivatives of 6-methoxyquinoline and alkoxides. A. M. Berkenheim and L. V. Antik (*J. Gen. Chem. Russ.*, 1941, **11**, 537—540).—7-Bromo-6-methoxyquinoline (**I**), m.p. 110—111° (prepared by Skraup's reaction from 4 : 2 : 1-NH_2·C_6H_3Br·OMe), when heated with ONa·$[CH_2]_2$·NEt_2 (**II**) for 5·5 hr. at 120—180°, gives 6-methoxyquinoline, instead of the expected 6-methoxy-7-β-diethylaminoethoxyquinoline. 7-*Bromo*-6-*ethoxyquinoline*, m.p. 89—90° (Skraup synthesis), 8-*bromo*-6-*methoxyquinoline*, m.p. 65—66° (Sandmeyer reaction, from 8-amino-6-methoxyquinoline), and 8-iodo-6-ethoxyquinoline react in the same way as (**I**) with (**II**) or NaOEt. R. T.

Condensation of 8-hydroxy-6-methoxyquinoline with γ-halogeno-α-diethylaminopropane. A. M. Berkenheim and N. S. Spasokukotski (*J. Gen. Chem. Russ.*, 1941, **11**, 541—544).—6 : 8-Dihydroxyquinoline and NaOEt in EtOH with *p*-C_6H_4Me·SO_3Me yield 8-hydroxy-6-methoxyquinoline, the Na salt of which condenses with NEt_2·$[CH_2]_3$·Cl in EtOH (5 hr. at 50°) to 6-*methoxy*-8-γ-*diethylaminopropoxyquinoline*, b.p. 198—200°/1—1·25 mm. This does not exhibit any anti-malarial properties. R. T.

Condensation reactions of *iso*quinoline-1-aldehyde. R. S. Barrows and H. G. Lindwall (*J. Amer. Chem. Soc.*, 1942, **64**, 2430—2432).—1-Methyl*iso*quinoline (prep. from the 3 : 4-H_2-derivative by boiling with Raney Ni; 70—75% yield) with SeO_2 in warm dioxan (later at 100°) gives *isoquinoline*-1-*aldehyde* (42%), m.p. 55—55·5° (reduces Tollens' reagent; adds $NaHSO_3$; *semicarbazone*, m.p. 195—197°; *oxime*, m.p. 171—172°; *phenylhydrazone*, m.p. 174—175°). With $MeNO_2$ and $NHEt_2$ (2 drops) this gives 1-β-*nitro*-α-*hydroxyethyl*isoquinoline (71%), m.p. ~106—107°; with COPhMe–alkali gives, according to the conditions, β-*hydroxy*-β-1-*isoquinolylpropiophenone* (85%), m.p. 114·5—115°, β-1-*isoquinolylacrylophenone* (60—77%), m.p. 145·5—146°, or αε-*diphenyl*-γ-1-*isoquinolyl*-n-*pentane*-αε-*dione* (42%), m.p. 133—133·5°; with CH_2Ph·CN–NaOEt–EtOH gives α-*phenyl*-β-1-*isoquinolylacrylonitrile* (92%), m.p. 96·5—97°, and with CH_2Ph·CO_2Et–NaOEt–EtOH gives *Et* β-*hydroxy*-α-*phenyl*-β-1-*isoquinolylpropionate* (45%), m.p. 134·5—135·5°; Perkin condensation with CH_2Ph·CO_2H does not occur. 1 : 3-Dimethyl-6 : 7-methylenedioxy*iso*quinoline and SeO_2 in dioxan give (?) 3-*methyl*-6 : 7-*methylenedioxy*isoquinoline-1-*aldehyde* (34%), m.p. 186·5—188·5° (*oxime*, m.p. 215—216°). R. S. C.

Deamination of 8-nitro-5-amino*iso*quinoline. B. Keilin and W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 2442—2444).—5-Acetamido*iso*quinoline with KNO_3–H_2SO_4 at 15—20° gives the 8-NO_2-derivative (71%), m.p. 226—228°, hydrolysed by conc. HCl to 8-*nitro*-5-*amino*isoquinoline (97%), m.p. 268—270° (decomp.) [*hydrochloride*, +H_2O and anhyd., m.p. 289—291° (decomp.)], which with $NaNO_2$–HCl at −10° to 0° and then H_3PO_2 gives 8-chloro*iso*quinoline (**I**) (70%), new m.p. 55·5—56·5° (*picrate*, m.p. 189·5—191·5°). *Et*$_2$ o-*chlorobenzylideneaminoacetal*, b.p. 114—117°/2 mm., with P_2O_5–H_2SO_4 gives 9% of (**I**). M.p. are corr. R. S. C.

Reaction of carbazole with malonic esters to 1 : 9-malonylcarbazoles. P. Baumgarten and M. Riedel (*Ber.*, 1942, **75**, [*B*], 984—986).—Thermal condensation of NH_2Ph with $CH_2(CO_2Et)_2$ under different conditions, alone or in the presence of $PhNO_2$, paraffin, or *n*-$C_{12}H_{25}$·OH or under the influence of NaOEt, or decomp. by heat of $CH_2(CO$·$NHPh)_2$ does not give substituted quinolines, which are readily derived from NH_2Ph and $CHR(CO_2Et)_2$ (R = aryl or Et). Analogously $NHPh_2$ and $CH_2(CO_2Et)_2$ at ~240° give 2 : 4-diketo-1-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline, m.p. ~300° (decomp.), in ~80% yield. Indole is not reactive. Carbazole does not react with $CH_2(CO_2Et)_2$, $CH_2(CO$·$NH_2)_2$, or $CH_2(COCl)_2$, but is transformed by $CHEt(CO_2Et)_2$ at 270—280° into 1 : 9-*ethylmalonylcarbazole* (**I**), m.p. 257—258°. 1 : 9-*Phenylmalonylcarbazole*, m.p. 207—208°, is obtained similarly. (**I**) is oxidised by $KMnO_4$ to carbazole-1-carboxylic acid, m.p. 270—271°. Reduction (Clemmensen) of (**I**) affords 1(β) : 9-α-*ethylacryloylenecarbazone*, m.p. 128—129°, oxidised ($KMnO_4$ in $COMe_2$ at room temp.) to (**I**). H. W.

Chemotherapeutic search for antimalarials. I. Synthesis of 1-amino-3-methoxy- and 8-chloro-1-amino-3-methoxy-acridine. B. V. Samant (*Ber.*, 1942, **75**, [*B*], 1008—1015).—*m*-Nitro-*p*-anisidine is converted by diazotisation and subsequent boiling with H_2O containing $CuSO_4$, NaBr, and Cu wool into 4-*bromo*-3-*nitroanisole*, b.p. 153—154°/13 mm., m.p. 32°, which condenses with

o-NH_2·C_6H_4·CO_2H, Na_2CO_3, and reduced Cu in boiling 4-methylcyclohexanol to *2'-nitro-4'-methoxydiphenylamine-2-carboxylic acid* (**I**), m.p. 228—230° (decomp.), and with 4-chloroanthranilic acid, m.p. 231° (obtained from 2 : 4 : 1-$C_6H_3Cl_2$·CO_2H, 37% NH_3, and freshly reduced Cu at 120°), to *5-chloro-2'-nitro-4-methoxydiphenylamine-2-carboxylic acid* (**II**), m.p. 268—271° (decomp.). When boiled with $POCl_3$ (**I**) gives *5-chloro-1-nitro-3-methoxyacridine*, m.p. 205—206° (decomp.), whilst (**II**) yields 5 : 8-*dichloro-1-nitro-3-methoxyacridine*, m.p. 270—271° (decomp.). When treated successively with $POCl_3$ and 25% aq. NH_3 (**I**) affords *1-nitro-3-methoxyacridone*, m.p. 236°, and (**II**) gives *8-chloro-1-nitro-3-methoxyacridone*, m.p. 277—278° (decomp.). These are reduced ($SnCl_2$) to *1-amino-3-methoxyacridone*, m.p. 254—256° (decomp.), and *8-chloro-1-amino-3-methoxyacridone*, decomp. 287—293°, respectively, which are converted (Na–Hg) into *1-amino-3-methoxyacridine*, m.p. 135—136° [*monohydrochloride*, m.p. 254—256° (decomp.); *monopicrate*, m.p. 201—203° (decomp.); *monomethiodide*, m.p. 211—212° (decomp.)], and *8-chloro-1-amino-3-methoxyacridine*, m.p. 191° [*monohydrochloride*, m.p. 237—238° (decomp.)]. *Me* 2 : 4-*dichlorobenzoate*, b.p. 132°/15 mm., is incidentally described. H. W.

Preparation and therapeutic properties of certain acridine derivatives. III. 5-Styrylacridines and their quaternary salts. W. Sharp, (Miss) M. M. J. Sutherland, and F. J. Wilson (*J.C.S.*, 1943, 5—7).—5-Methylacridine (**I**) (*metho*-p-*toluenesulphonate*, m.p. 204°) and *o*-NO_2·C_6H_4·CHO give *α*-(*o-nitrophenyl*)-*β*-(*5-acridyl*)*ethanol*, m.p. 177°. *m*-NO_2·C_6H_4·CHO and (**I**) with $ZnCl_2$ afford 5-*m-nitrostyrylacridine* (**II**), m.p. 210°, and without $ZnCl_2$, *α*-(*m-nitrophenyl*)-*β*-(*5-acridyl*)*ethanol*, m.p. 145°, and an *isomeride* (*cis–trans* ?) of (**II**), m.p. 207°, are obtained. Reduction of (**II**) yields 5-*m*-aminostyrylacridine, m.p. 234° (lit. 232—234°); the *Ac* derivative, m.p. 252°, can be converted into the *methochloride*, decomp. >200°. Similarly, with $ZnCl_2$ (**I**) and *p*-NO_2·C_6H_4·CHO give 5-*nitrostyrylacridine*, m.p. 293° (Br-substitution *product*, m.p. >360°), and without $ZnCl_2$, *α*-(*p-nitrophenyl*)-*β*-(*5-acridyl*)*ethanol*, m.p. 174°, is formed in addition. 5-p-*Aminostyrylacridine*, m.p. 242° (lit. 209°), yields an *Ac* derivative, m.p. 263°, whence the *methochloride hydrochloride*, decomp. ~250°. 5-p-*Dimethylaminostyrylacridine methochloride*, decomp. >200°, is also described. These results do not agree entirely with those obtained by Porai-Koschitz *et al.* (A., 1907, i, 974). F. R. S.

Complex formation between iodine and μ-thiodihydroglyoxalines. T. B. Johnson and C. O. Edens (*J. Amer. Chem. Soc.*, 1942, **64**, 2706—2708).—2-Thiol-4 : 5-dihydroglyoxaline (**I**) [prep. from $(CH_2$·$NH_2)_2$ with CS_2 and then conc. HCl at 100°] absorbs 6 I in aq. KI at room temp. to give bis-4 : 5-dihydro-2-glyoxalinyl disulphide and therefrom the additive *compound* (**II**), $C_6H_{10}N_4S_2$,HI,$2I_2$, m.p. 119°. The *periodide* (**III**), $C_6H_{14}N_4S_2$,HI,$2I_2$, m.p. 67°, of di-4-methyl-4 : 5-dihydro-2-glyoxalinyl disulphide is similarly obtained from 2-*thio*-4-*methyl*-4 : 5-*dihydroglyoxaline* [prep. as (**I**)], m.p. 100°. In boiling H_2O, (**II**) gives di-4 : 5-dihydro-2-glyoxalinyl sulphide hydriodide (**IV**), I, and H_2SO_4; by this method (**III**) gives only an oil. With aq. NH_3, (**II**) gives exothermally, *inter alia*, (**I**) and NH_4I. CH_2Cl·CO_2H and (**I**) in boiling H_2O give 4 : 5-*dihydro-2-glyoxalinylthiolacetic acid*, m.p. 223° (decomp.). With I–KI–H_2O, (**IV**) gives a *periodide*, $C_6H_{10}N_4S$,HI,I_3, m.p. 170—175°, converted at 125° into (**IV**) and I. 5-*Methyl*-4 : 5-*dihydro-2-glyoxalinylthiolacetic acid*, m.p. 215°, is prepared as above, but (**IV**) gives only its *hydrochloride*. 2-Thiol-5-methylglyoxaline with I–KI–H_2O gives *di-5-methyl-2-glyoxalinyl disulphide periodide*, $C_8H_{10}N_4S_2$,HI,I_2, cryst., decomp. when heated. R. S. C.

Ultra-violet absorption spectra and structure of *N*-phenylpyrazolone derivatives. IV. General survey of spectra and structure in relation to pharmacodynamic action. N. A. Valjaschko and V. I. Blizniukov (*J. Gen. Chem. Russ.*, 1941, **11**, 559—566).—Antipyrine (**I**) and pyramidone (**II**) are complex mesomeric systems, of which those having the hydrazo- and diazo-structures of NHPh·NH_2 (**III**) predominate; the pharmacodynamic action of (**I**) and (**II**) is connected with these structures. The lower toxicity of (**I**) and (**II**) as compared with (**III**) is ascribed to resonance in the pyrazolone ring, which causes reduced lability of the electrons of the N atoms. The effect of substituting a 2-Me or a 4-NMe_2-group into the pyrazolone ring is still further to favour the above structures as compared with (**III**). R. T.

Iminazolines.—See B., 1943, II, 76.

1-Carbamyl-5-methylpyrazole-3-carboxylic acid. A. L. Lehninger (*J. Amer. Chem. Soc.*, 1942, **64**, 2507—2508).—CH_2Ac·CO·CO_2H and NH_2·CO·NH·NH_2,HCl in warm H_2O give *1-carbamyl-5-methylpyrazole-3-carboxylic acid* (80—85%), decomp. from 155°, m.p. 232—234° (corr.) (cf. von Auwers *et al.*, A., 1930, 789), from which the CO·NH_2 is removed by boiling with H_2O. R. S. C.

Hydrolysis of acetylsulphanilic acid derivatives. III. S. I. Lurie, O. I. Starobogatov, and E. S. Nikitskaja (*J. Gen. Chem. Russ.*, 1941, **11**, 545—549).—The Ag salt of 2-methylglyoxaline (**I**) and *p*-$NHAc$·C_6H_4·SO_2Cl (**II**) in EtOH (1·5 hr. at the b.p.) yield 1-p-*acetamidobenzenesulphonyl*-2-*methylglyoxaline*, m.p. 93—94·5°, readily hydrolysed with production of *p*-NH_2·C_6H_4·SO_3H by HCl in aq. EtOH (30 min. at the b.p.). *β*-Bromoethylphthalimide and (**I**) in xylene (6 hr. at the b.p.) yield *β*-(*2'-methyl-1'-glyoxalinyl*)*ethylphthalimide*, m.p. 161—162°. This is heated with N_2H_4 in EtOH (30 min. at the b.p.), 10% HCl is added, and boiling is continued for a further 90 min., affording *β*-(*2'-methyl-1'-glyoxalinyl*)*ethylamine dihydrochloride*, m.p. 196—198°, which, condensed with (**II**) in aq. $COMe_2$ gives the corresponding N-*acetylsulphanilamide*, m.p. 212—214°, hydrolysed by HCl in aq. EtOH to the *β*-(*2'-methyl-1'-glyoxalinyl*)-*ethylamide* of *sulphanilic acid*. 4-Amino-2-phenylquinoline (**III**) and (**II**) in C_5H_5N (15 min. at the b.p.) yield the *2'-phenyl-4'-quinolylamide* of N-*acetylsulphanilic acid*, m.p. 269—270°, hydrolysed as above to *p*-NH_2·C_6H_4·SO_3H and (**III**). R. T.

Ultra-violet absorption spectra of barbituric acid derivatives. III. Ionisation and 5-monosubstituted barbituric acid derivatives. IV. 5 : 5-Disubstituted barbituric acid derivatives. R. E. Stuckey (*Quart. J. Pharm.*, 1942, **15**, 370—376, 377—383).—III. The increase in the absorption (A., 1941, II, 148) of barbituric acid (**I**) on dilution follows the increase in the degree of ionisation. The spectra of 5-methyl- (**II**), m.p. 205—207°, and 1 : 5-*dimethyl-barbituric acid* (**III**), m.p. 171—172° [from $CHMe(CO_2Et)_2$, NH_2·CO·$NHMe$, and EtOH–NaOEt], in aq. acid and alkali are similar to those of (**I**). Oxidation (H_2O_2) or evaporation of aq. solutions of (**II**) and (**III**) gives 5-hydroxy-5-methyl-, m.p. 225—227°, and 5-*hydroxy*-1 : 5-*dimethyl-barbituric*, m.p. 166—167°, respectively. 1 : 3 : 5-Trimethylbarbituric acid could not be prepared from $CHMe(CO_2Et)_2$ and $CO(NHMe)_2$.

IV. 5 : 5-Disubstituted barbituric acids in general show a peak in alkaline solution at ~2500 A. and thereby allow the determination of small amounts (if known) in extracts etc. 5 : 5-Dimethylbarbituric acid is anomalous and presumably forms a stable keto ion; differences in other properties are noted. 1 : 5 : 5-*Trimethylbarbituric acid* (from Ag 1-methylbarbiturate and MeOH–MeI) also shows only end absorption in both acid and alkali. The 1 : 3 : 5 : 5-Me_4 compound resembles other derivatives methylated in the 1- and 3-positions. H. B.

***N*-Aralkylbarbituric acids.** A. Ardis, J. S. Buck, and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, **64**, 2514).—1-*Benzyl*-, m.p. 64°, and 1-*β-phenylethyl*-, m.p. 74°, -5-*ethyl*-5-n-*butylbarbituric acid* and 1-*benzyl*-, m.p. 87—88°, and 1-*β-phenylethyl*-, m.p. 106—107°, -5-*ethyl*-5-iso*amylbarbituric acid* are prepared. R. S. C.

Chemotherapy of bacterial infections. VII. Synthesis of sulphanilamide derivatives of the pyrimidine group. K. Ganapathi, C. V. Deliwala, and M. V. Shirsat (*Proc. Indian Acad. Sci.*, 1942, **A, 16**, 115—125; cf. A., 1941, II, 338).—Addition of a mixture of HCO_2Et and EtOAc to powdered Na in dry Et_2O at 0° and treatment of the product after remaining overnight at room temp. with sulphanilylguanidine (**I**) and NaOEt in EtOH gives *2-sulphanilamidopyrimidone* (**II**), m.p. 268—269°, in 50—60% yield. Successive additions of (**I**) and CH_2Ac·CO_2Et or its *α*-alkyl derivatives to NaOEt in EtOH and boiling of the mixture lead to the following *2-sulphanilamido-4-methyl-5-alkylpyrimidones* in which the alkyl is represented by H, m.p. 253—254°, *Me*, m.p. 238—239°, *Et*, m.p. 208—209°, *Bu*$^{\alpha}$, m.p. 121—122°, iso*amyl*, m.p. 190—193°, and n-C_6H_{13}, m.p. 108—110°. 2-Acetsulphanilamido-4-methyl- (**III**), m.p. 273°, and -iso*amyl*, m.p. 228—229°, *-pyrimidone* are obtained similarly. 2-Sulphanilamido-4-methylpyrimidone (**IV**) is considerably resistant to boiling 3N-HCl but suffers some hydrolysis when boiled for ~6 hr. with 37% HCl; 2-amino-4-methylpyrimidone results but NH_2·C_6H_4·SO_2·NH_2 could not be isolated. (**IV**) appears indifferent towards 30% NaOH. (**IV**), Me_2SO_4, and aq. NaOH in boiling $COMe_2$ yield *2-sulphanilylmethylamido*-1 : 4-*dimethylpyrimidone*, m.p. 160—165° after shrinking. (**III**) and boiling $POCl_3$ yield the *compound*, $C_{13}H_{13}O_3N_4ClS$, m.p. >280°, which does not give a halogen-free compound when boiled with Zn dust and H_2O. 2-Amino-4-methylpyrimidone is transformed by NaOH and Me_2SO_4 into 2-*amino*-1 : 4-*dimethylpyrimidone*, m.p. >280°, which when dissolved in NaOH and treated with $NaHCO_3$, *p*-NH_2·C_6H_4·SO_2Cl, and $COMe_2$ affords *2'-amino-4'-methyl-6'-pyrimidonyl* p-*acetamidobenzenesulphonate*, m.p. 193—194°. Acetsulphanilylguanidine and mesityl oxide (**V**) in boiling abs. EtOH containing NaOEt give 2-sulphanilylimido-4 : 4 : 6-*trimethyl*-2 : 3 : 4 : 5-*tetrahydropyrimidine* (**VI**), m.p. 190—193° (*Ac* derivative, m.p. 241—242°), and *2-sulphanilamido*-4 : 4 : 6-*trimethyl*-4 : 5-*dihydropyrimidine*, m.p. 228—230° (*Ac* derivative, m.p. 217—218°). In different experiments *compounds*, $C_{13}H_{16}O_2N_4S$, m.p. 130—135° and 190—193°, respectively, were obtained from (**I**) and (**V**). (**II**), (**V**), and (**VI**) are devoid of therapeutic activity. H. W.

***N*^{1}-Sulphanilamidoalkylpyrimidines.** G. W. Raiziss and M. Freifelder (*J. Amer. Chem. Soc.*, 1942, **64**, 2340—2342).—*p*-$NHAc$·C_6H_4·SO_2Cl and the appropriate aminopyrimidine in C_5H_5N at 60° give 55—95% of 2-*N*^{4}-acetylsulphanilamido-4-methyl-, m.p. 244°, -4-*ethyl*-, m.p. 274°, -4-n-*propyl*-, m.p. 258°, -4-iso*butyl*-, m.p. 233°, -4-n-*amyl*-, m.p. 222—223°, -4-hexyl-, m.p. 216°, -4 : 5-dimethyl-, m.p. 272—273°, -5-*methyl*-4-*ethyl*-, m.p. 286°, and -4-*phenyl*-, m.p. 287°, *-pyrimidine*, 2-*N*^{4}-acetylsulphanilamido-5 : 6 : 7 : 8-tetrahydroquinazoline, m.p. 259°, and 2 : 5-di-*N*^{4}-acetylsulphanilamidopyrimidine, m.p. 295° (decomp.), hydrolysed by boiling 5%

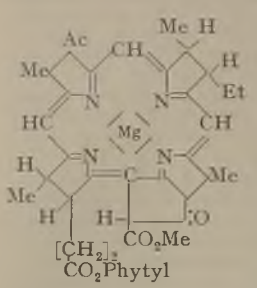
NaOH to the corresponding *p*-NH_2·C_6H_4·SO_2·NH-compounds (40—60% yield), m.p. 235—236°, 242°, 212—214°, 232°, 226°, 204°, 222°, 215°, 264°, 247°, and 241—242°, respectively. The 4 : 5-Me_2 and 4-Me compounds have good antipneumococcal (type II) activity (mice), the Et derivative slight activity, but the others none. $NH{:}C(NH_2)_2,H_2CO_3$ with ONa·CH:CH·COR in MeOH gives 2-*amino*-4-*isobutyl*-, m.p. 119°, -4-n-*amyl*-, m.p. 90°, and -5-*methyl*-4-*ethyl*-, m.p. 157°, -*pyrimidine*. 2-Amino-4-hexylpyrimidine, obtained from COMe·C_6H_{13}-*n*, has m.p. 92—93° (cf. A., 1941, II, 377; 1942, II, 151) and is oxidised by HNO_3 to 2-amino-5-*n*-amylpyrimidine-4-carboxylic acid. (**I**) does not condense with *iso*cytosine, divicine, or purines such as adenine or guanine.

R. S. C.

Synthesis of aminobenzoylenecarbamides and of dihydroxyquinoxalines isomeric with "luminol." E. H. Huntress and (Miss) J. V. K. Gladding (*J. Amer. Chem. Soc.*, 1942, **64**, 2644—2649).—Analogues of luminol differing therefrom in arrangement of the CO and NH in the heterocyclic ring are not chemiluminescent when oxidised [H_2O_2–$K_3Fe(CN)_6$]. 6 : 2 : 1-NO_2·$C_6H_3(NH_2)$·CO_2H (**I**) with KCNO–AcOH in H_2O and then NaOH at 40° gives 5-*nitro*-2 : 4-*dihydroxyquinazoline* (67%), m.p. 357—358° (sealed tube), sol. in alkali, and converted by Me_2SO_4–5% KOH into the 1 : 3-Me_2 *ether* (77%), m.p. 275—277°. 2 : 4-Dihydroxyquinazoline with fuming HNO_3–H_2SO_4 gives the 6-NO_2-derivative (86%), m.p. 331—332° (*Me_2 ether*, m.p. 213—214°). 4 : 2 : 1-NO_2·$C_6H_3(NH_2)$·CO_2H with $CO(NH_2)_2$ at 200° gives 7-*nitro*-2 : 4-*dihydroxyquinazoline* (76%), m.p. 337° (decomp.) [K salt; Me_2 ether, m.p. 229—230° (uncorr.)], and some amide. 3 : 2 : 1-NO_2·$C_5H_3(NH_2)$·CO_2H (**II**) and $CO(NH_2)_2$ at 180—190° give 8-*nitro*-2 : 4-*dihydroxyquinazoline* (**III**) (68%), m.p. 272—273° (sealed tube) [with conc. HNO_3–H_2SO_4 at 100° gives the 6 : 8-$(NO_2)_2$-compound, m.p. 263—265° (uncorr.); *Me_2 ether*, m.p. 217—218°], and some 3-*nitro*-2-*aminobenzamide*, m.p. 234—235° [hydrolysed to (**II**), m.p. 267—268° (decomp.); with $CO(NH_2)_2$ at 200° gives (**III**)]. (**II**) is obtained by the reactions, (*a*) 3 : 1 : 2-NO_2·C_6H_3Me·NHAc → (neutral $KMnO_4$) 3 : 2 : 1-NO_2·C_6H_3(NHAc)·CO_2H (74%) → (**II**) (87%), and (*b*) 3 : 2 : 1-NO_2·$C_6H_3(CO)_2O$ → (aq. NH_3) 3 : 1 : 2-NO_2·$C_6H_3(CO_2H)$·CO·NH_2 (70%) → (Hofmann) (**II**) (90%). (**I**) is prepared thus: 3 : 2 : 1-NO_2·$C_6H_3(CO_2NH_4)_2$ → (at 235—250°) 3 : 2 : 1-NO_2·$C_6H_3(CO)_2NH$ (94%) → (0·5N-NaOH) 6 : 1 : 2-NO_2·$C_6H_3(CO_2H)$·$CONH_2$ (76%) → (Hofmann) (**I**) (90%). 5-, m.p. 295° (decomp.; sealed tube), 6-, decomp. >330°, 7-, m.p. >350°, and 8-*amino*-2 : 4-*dihydroxyquinazoline*, m.p. 279—281° (decomp.), are prepared from the NO_2-compounds by $SnCl_2$–HCl. 3 : 1 : 2-NO_2·$C_6H_3(NH_2)_2$ and $Et_2C_2O_4$ at the b.p. give 5-*nitro*- (60%), m.p. 295° (decomp.; sealed tube), and thence (aq. Na_2S) 5-*amino*-2 : 3-*dihydroxyquinoxaline* (44%), m.p. 344° (uncorr.; sealed tube). 4 : 1 : 2-NO_2·$C_6H_3(NH_2)_2$ and $H_2C_2O_4$ at 150°, later 180—200°, give 6-*nitro*- (73%), m.p. 343—344° (decomp.; sealed tube), and thence 6-*amino*-2 : 3-*dihydroxyquinoxaline* (75%), decomp. ~330°, m.p. >350°. Unless otherwise stated, m.p. are corr. (block).

R. S. C.

Bacteriochlorophyll. III. H. Mittenzwei (*Z. physiol. Chem.*, 1942, **275**, 93—121; cf. Fischer *et al.*, A., 1938, II, 297).—Further confirmation of the fine structure of dehydrobacteriophæophorbide and chlorophyll *a* is found in the identity of the phytol from bacteriophæophytin with that of stinging nettles now established by means of the Ag salt of the corresponding phthalate. Also the oxime of "natural" 2-acetylchlorin e_6 is identical with that from the synthetic material. Natural 2-acetylmethylphæophorbide is smoothly converted by methanolysis into 2-acetylchlorin e_6 Me_3 ester. Ring-closure of bacteriochlorin e_6 Me_3 ester (**I**) to bacteriomethylphæophorbide (**II**), m.p. 260°, is effected with some difficulty by KOMe–MeOH in boiling C_5H_5N or by NaOMe–MeOH in $COMe_2$. Optical activity of the bacterio-substances can be observed by use of white light but the vals. are influenced to an unusual extent by the presence of small amounts of impurity. (**II**) is not satisfactorily hydrogenated directly, with Pd–tetrahydronaphthalene or Pd–HCO_2H, but is transformed by $Al(OPr^{\beta})_3$ into *bacterio*-2-*deacetyl*-2-*α-hydroxymesomethylphæophorbide*, which could not be caused to crystallise but passes in a high vac. into *bacterio*-2-*deacetyl*-2-*vinylmethylphæophorbide*. Similar reduction of (**I**) to non-cryst. *bacterio*-2-*deacetyl*-2-*α-hydroxymesochlorin* e_6 *Me_3 ester*, softens at 128°, proceeds more readily and does not cause loss of the "bacterio" type of spectrum. It loses H_2O at ~200°. A cryst. Ac derivative could not be prepared but the structure of the compound is established by its re-oxidation by $KMnO_4$ in C_5H_5N to (**I**). In a high vac. it passes into *bacterio*-2-*deacetyl*-2-*vinylchlorin* e_6 *Me_3 ester* (**III**), m.p. 240—241°, with only small amounts of chlorin e_6 and 2-α-hydroxychlorin e_6. (**III**) can be catalytically hydrogenated to the 2-Et compound (**IV**), which adds CHN_2·CO_2Et, but the change is not quant. and the ultimate evidence of the presence of CH_2:CH· is afforded by dehydrogenation with *p*-O:C_6H_4:O. Oxidation of (**I**) or (**II**) by CrO_3–H_2SO_4 gives no methylethylmaleimide (**V**) but only small amounts of a colourless liquid. The same result is obtained by the oxidation of (**III**), whereas 2-acetylchlorin e_6 Me_3 ester affords (**V**). These observations can only be explained by the assumption that the "superfluous" H atoms of the bacterio-series are attached to nucleus II particularly since (**IV**) gives (**V**) which can only proceed from nucleus I. Products of the oxidative fission of nucleus III have never been unquestionably isolated. The most important evidence in favour of the position of the "superfluous" H atoms in nucleus II is obtained by the optical examination of the basic products of fission of the bacterio-derivatives. The oil is strongly dextrorotatory and most probably consists of *d*-α-methyl-α′-ethylsuccinic anhydride, so that the H atoms in the *αα′* positions are already present in the initial material. The acid fractions of the oxidation of the chlorophyll *a*, 2-acetyl-, and bacterio-series invariably give a colourless, lævorotatory liquid which appears to be a hæmotricarboxylimide; nucleus IV is therefore similar in all derivatives of the chlorophyll and bacteriochlorophyll (**VI**) series. The annexed structure is proposed for (**VI**).



H. W.

Reactions of morpholine. A. R. Ingram and W. F. Luder (*J. Amer. Chem. Soc.*, 1942, **64**, 2506—2507).—Morpholine and $SnCl_4$ give a 2 : 1 additive *compound*, m.p. 215—235° (decomp.). In hot CCl_4 or $CHCl_3$ rapidly, or slowly in the cold, it gives the hydrochloride and (?) 1-tri- or 1-di-chloromethylmorpholine, respectively.

R. S. C.

Amino-ketones. I. Synthesis of amino-alcohols and αγ-diamino-compounds from β-amino-ketones. N. H. Cromwell, Q. T. Wiles, and O. C. Schroeder (*J. Amer. Chem. Soc.*, 1942, **64**, 2432—2435).—CHPh:CH·COMe with morpholine or piperidine in light petroleum (b.p. 88—100°) at the b.p. and then 0° and finally with HCl gives δ-*morpholino*- (**I**), m.p. 152°, and δ-*piperidino*-δ-*phenylbutan*-β-*one hydrochloride* (**II**), m.p. 158°, converted by KOH–NH_2OH,HCl–MeOH–H_2O at room temp. into α-*morpholino*-, m.p. 107°, and α-*piperidino*-γ-*oximino*-α-*phenylbutane*, m.p. 105°, respectively, which with H_2–Raney Ni–EtOH give the base and Ph·$[CH_2]_2$·CHMe·NH_2 but with Na–EtOH give γ-*amino*-α-*morpholino*-, b.p. 130°/1 mm. (*Bz* derivative, m.p. 158°), and -α-*piperidino*-α-*phenylbutane*, b.p. 112°/1 mm. (*Bz* derivative, m.p. 144°), respectively. Catalytic hydrogenation of (**I**) or (**II**) causes fission, but 3% Na–Hg in H_2O, kept just acid by HCl, at −3° yields δ-*morpholino*- (*hydrochloride*, m.p. 156°; *benzoate hydrochloride*, m.p. 236°) and δ-*piperidino*-δ-*phenylbutan*-β-*ol*, b.p. 137°/1 mm. (hygroscopic hydrochloride; *benzoate hydrochloride*, m.p. 217°). *Ph* β-*morpholino*-, m.p. 178° (unchanged by Na–EtOH), and β-*anilino*-β-*phenylethyl ketoxime*, m.p. 131°, are also prepared.

R. S. C.

Benzylideneaminomorpholine compounds. L. Dugan, jun., and H. M. Haendler (*J. Amer. Chem. Soc.*, 1942, **64**, 2502).—4-o-, m.p. 75—76·5°, -m-, m.p. 145—147·5°, and -p-*hydroxybenzylidene*-, m.p. 167—168°, 4-o-, m.p. 99—101°, and 4-m-*nitrobenzylidene*-, m.p. 114—114·5°, 4-*vanillylidene*-, m.p. 153—154·5°, and 4-*piperonylideneaminomorpholine*, m.p. 76—77°, 4-p-*salicylidene*-, m.p. 161—162°, -*piperonylidene*-, m.p. 167·5—169°, -*vanillylidene*-, m.p. 205—207°, -*furfurylidene*-, m.p. 208—209°, and 4-p-α-o′-*hydroxyphenylethylideneaminophenylmorpholine*, m.p. 206—207°, are described.

R. S. C.

2-Phenyloxazole. *p*-Substituted derivatives. J. J. Rosenbaum and W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 2444—2445).—Et_2 p-*nitrobenzylideaminoacetal*, m.p. 56—57°, b.p. 165—168°/2 mm., or *p*-NO_2·C_6H_4·CO·NH·CH_2·$CH(OEt)_2$ with P_2O_5–H_2SO_4 gives 2-p-*nitrophenyloxazole* (**I**) (40% and 45%, respectively), m.p. 163·5—164·5°, oxidised by $KMnO_4$ or aq. Br to *p*-NO_2·C_6H_4·$CONH_2$ and reduced by H_2–Raney Ni–EtOH or $SnCl_2$–conc. HCl to 2-p-*aminophenyloxazole*, m.p. 121—123° [*picrate*, m.p. 182·5—184° (decomp.); *Ac*, m.p. 191·5—192·5°, *Bz*, m.p. 163·5—164·5°, p-*NHAc*·C_6H_4·SO_2, m.p. 226·5—228°, and p-NH_2·C_6H_4·SO_2 (**II**) derivative, m.p. 191·5—192·5°]. Deamination yields 2-phenyloxazole, whence (**I**) is regenerated by KNO_3–H_2SO_4 at room temp. and later 70°. M.p. are corr. (**II**) is less effective than sulphathiazole in staphylococcal, or than sulphanilamide in streptococcal, infections in mice.

R. S. C.

Taste differences in compounds having :N·C(:S)· linking. C. Y. Hopkins (*Canad. J. Res.*, 1942, **20**, **B**, 268—273).—OH·CHMe·CH_2·NH_2 (25 g.) and CS_2 (38 g.), refluxed with EtOH–KOH, yields 2-*thion*-5-*methyloxazolidine*, m.p. 72—73°; with 50 g. of CS_2, the corresponding thiazolidine, m.p. 93—94°, is obtained in poor yield (cf. Gabriel and Ohle, A., 1917, i, 563). COMe·CHMeCl with KCNS in aq. $NaHCO_3$ at room temp. affords 2-*keto*-4 : 5-*dimethylthiazoline*, m.p. 149—150°, and with NH_2·CS_2NH_4 in EtOH at room temp. 2-*thion*-4 : 5-*dimethylthiazoline*, m.p. 166—168°. Tcherniac's method (*J.C.S.*, 1919, **115**, 1071) applied to COMe·CH_2Cl gives 2-keto-4-methylthiazoline, m.p. 193°. 5-Bromo-2-keto-4-methylthiazoline, m.p. 150°, was prepared by the method of Ochiai and Nagasawa (A., 1939, II, 455). OH·CMe_2·CH_2·NH_2 with CS_2, refluxed in KOH–EtOH, yields 2-*thion*-4 : 4-*dimethyloxazolidine*, m.p. 123—125°. All m.p. corr. For taste differencs in above and other compounds, see A., 1943, III, 236.

F. O. H.

Reactions of retene- and phenanthra-quinoneimine with aldehydes. New example of an aldol-type condensation. C. W. C. Stein and A. R.

Day (*J. Amer. Chem. Soc.*, 1942, **64**, 2567—2569).—Retenequinoneimine (**I**) with Pr$^{\alpha}$CHO in presence of NH_2Bu^{α} or NEt_3 in boiling abs. EtOH gives 84—92% of 2-n-*propylreteneoxazole*, m.p. 100·5—101·3°. Similarly, (**I**) and PhCHO in EtOH + NH_2Bu^{α} (68%), NEt_3 (84%), or piperidine (92%) gives 2-*phenylreteneoxazole* (**II**), m.p. 174·5—176° (occasionally 178—180°), but use of NH_2Ph gives only 9·7% and of C_5H_5N or NaOEt gives none; use of KOH–EtOH gives ~25% of (**II**), much side-reaction occurring. *o*-OH·C_6H_4·CHO–(**I**)–NH_2Bu^{α} in EtOH give 2-o-*hydroxyphenylreteneoxazole* (51%), m.p. 245·5—247°. Phenanthraquinoneimine with PhCHO and piperidine (97%), NEt_3 (77%), or NH_2Ph (17·5%) in EtOH gives 2-*phenylphenanthroxazole*, m.p. 205—206°, or with Pr$^{\alpha}$CHO–NEt_3–EtOH gives 2-n-*propylphenanthroxazole* (50%), m.p. 84—86°, neither condensation occurring in absence of base. The primary reaction is an aldol-type condensation thus (*B* = base): ·$C_{(9)}O·C_{(10)}$(:NH)· + $B \rightleftharpoons BH^+ + [·CO·\dot{C}{:}N]^- \rightleftharpoons$ (+ RCHO) [·CO·$\dot{C}$:N·CHR·O·]$^-$ $\rightleftharpoons$ (+ RCHO) ·CO·$\dot{C}$:N·CHR·OH $\rightleftharpoons$ ·C(OH):C·N:CR·OH → (**II**) etc. M.p. are corr. R. S. C.

Reactions of retene- and phenanthra-quinoneimine with Schiff bases. New example of an aldol-type condensation. C. W. C. Stein and A. R. Day (*J. Amer. Chem. Soc.*, 1942, **64**, 2569—2573).—Retenequinoneimine (**I**) with *benzylidene*-n-*butylamine* (**II**), b.p. 112—113°/4 mm., in boiling, dry EtOH gives 78% [93·5% if 2 mols. of (**II**) are used] of 2-phenylreteneoxazole (**III**). The reaction occurs also in PhMe and 1 mol. of NH_2Bu^{α} is evolved; (**II**) is not hydrolysed to PhCHO; a reaction mechanism is discussed similar to that for the reaction with RCHO–base (preceding abstract) with NR replacing the second O, but it is uncertain whether loss of NH_2R occurs at or after ring-closure. The basicity of the Schiff's base or presence of a stronger base affects the yield: *e.g.*, CHPh:NPh and (**I**) give 21%, but in presence of piperidine (**IV**) (1 equiv.) give 90% of (**III**); with CHPr$^{\alpha}$:NBu$^{\alpha}$, (**I**) gives 7% of 2-*n*-propylreteneoxazole, but if (**IV**) is also added gives 23%; CHPr$^{\alpha}$:NPh with or without (**IV**) gives no oxazole. CHPr$^{\alpha}$:NBu$^{\alpha}$ is dimeric (Rast), CHPh:NPh and CHPh:NBu$^{\alpha}$ are mainly monomeric, but CHPr$^{\alpha}$:NBu$^{\alpha}$ is trimeric; probably only the monomeric compound reacts. Phenanthraquinoneimine with (**II**) (79%), CHPh:NPh alone (21·7%) or with (**IV**) (85%) gives 2-phenylphenanthroxazole and with CHPr$^{\alpha}$:NBu$^{\alpha}$ alone (0·8%) or with (**IV**) (30%) gives 2-*n*-propylphenanthroxazole but does not react with CHPr$^{\alpha}$:NPh. R. S. C.

Riboflavin monoborate, m.p. 290—292°, and tetrabenzoylriboflavin, m.p. 131—136°.—See A., 1943, III, 189.

Phenylthiolthiazolines. J. B. Niederl and W. F. Hart (*J. Amer. Chem. Soc.*, 1942, **64**, 2487—2488).—Contrary to expectation (A., 1941, II, 206), CH_2:CH·CH_2·NCS with PhSH, *o*- and *m*-C_6H_4Me·SH (**I**), etc. gives 2-*phenyl*-, m.p. 171°, 2-o-*tolyl*-, m.p. 164°, and 2-m-*tolyl*- (**II**), m.p. 139°, *-thiol*-5-*methylthiazoline*, which are stable to acid and yield the corresponding *picrates*, m.p. 141°, 133°, and 118°, respectively. With aq. $NaHCO_3$, (**II**) gives (**I**) and 5-*methylthiazolid*-2-*one*, *keto*-, m.p. 39°, and enol (*hydrochloride*, m.p. 204°) form. R. S. C.

Properties of the nitrogen–carbon–nitrogen system in N^1-heterocyclic sulphanilamides. R. G. Shepherd, A. C. Bratton, and K. C. Blanchard (*J. Amer. Chem. Soc.*, 1942, **64**, 2532—2537).—Contrary to statements in the literature, notably Ewins *et al.* (B.P. 512,145, 517,272; B., 1940, 94, 326), sulphapyridine (**I**) and CH_2N_2–Et_2O give 50—80% of a 7 : 3 mixture of 2-*sulphanilyl*-N-*methylaminopyridine*, 2-X·SO_2·NMe·C_5H_4N (**II**), m.p. 86·5—87°, and 2-*sulphanilylimido*-1-*methyl*-1 : 2-*dihydropyridine*, 2-X·SO_2·N:C_5H_4NMe (**III**), m.p. 232—233°. N^4-Acetylsulphapyridine and CH_2N_2–Et_2O give more slowly a 6 : 4 mixture of 2-N^4-*acetylsulphanilyl*-N-*methylaminopyridine* (**IV**), m.p. 119·5—120°, and 2-N^4-*acetylsulphanilylimido*-1-*methyl*-1 : 2-*dihydropyridine* (**V**), m.p. 239—240°. The Na salt of (**I**) with Me_2SO_4 or CH_2PhCl gives, as main products, (**III**) and 2-*sulphanilylimido*-1-*benzyl*-1 : 2-*dihydropyridine* (**VI**), m.p. 235°, respectively. The appropriate Na salt and halogen derivative yield similarly (**V**), 2-N^4-*acetylsulphanilamido*-1-*carbethoxymethyl*-, m.p. 212—213°, and -1-*benzyl*-1 : 2-*dihydropyridine* (**VII**), m.p. 213—214°, 2-*sulphanilylimido*-1-*carbethoxymethyl*-, m.p. 200·5—201° [and thence, by KOH–MeOH, the 1-$CO_2H·CH_2$ derivative (**VIII**), + H_2O, m.p. 97—98°], and -1-*carbamylmethyl*-1 : 2-*dihydropyridine* (**IX**), m.p. 230° (decomp.) [with alkali gives (**VIII**)], 2-*sulphanilylimido*- (**X**), m.p. 250—251°, and 2-N^4-*acetylsulphanilylimido*-3-*methyl*-2 : 3-*dihydrothiazole* (**XI**), m.p. 272—273°. OH·$[CH_2]_2$·Cl and the appropriate Na salt at 130° give 2-N^4-*acetylsulphanilylimido*-1-*β-hydroxyethyl*-1 : 2-*dihydropyridine*, m.p. 217—218°, and -3-*β-hydroxyethyl*-2 : 3-*dihydrothiazole*, m.p. 231—232° (decomp.), hydrolysed by NaOH–EtOH to 2-*sulphanilylimido*-1-*β-hydroxyethyl*-1 : 2-*dihydropyridine* (**XII**), m.p. 184—185°, and -3-*β-hydroxyethyl*-2 : 3-*dihydrothiazole* (**XIII**), m.p. 159—160°, respectively. Structures are proved by (i) alkaline hydrolysis of (**IV**) to (**II**), of (**V**) to (**III**), of (**VII**) to (**VI**), and of (**XI**) to (**X**), (ii) hydrolysis of (**II**)—(**XIII**) by 12N-HCl at 100° to *p*-$NH_2·C_6H_4·SO_3H$ and the appropriate base, (iii) synthesis of (**IV**) from *p*-NHAc·$C_6H_4·SO_2$·NHMe and 2-bromopyridine and of (**V**), (**VII**), and (**XI**) from *p*-NHAc·$C_6H_4·SO_2Cl$ and the appropriate *N*-substituted 1 : 2-dihydro-base, (iv) by conversion of the $CO_2Me·CH_2$ compound by CH_2N_2 into an alkali-labile substance, and (v) spectroscopic evidence. In abs. EtOH 2-imino-1 : 2-dihydropyridines and -2 : 3-dihydrothiazoles show absorption max. at 3215 and 2600 A., respectively. Absorption spectra show that (**I**), its Ac derivative and sulphathiazole contain large amounts of the imino-form in EtOH. 2-Aminothiazole and $CH_2I·CO_2Et$ at 130—180° give 2-*imino*-3-*acetoxyethyl*-, m.p. 153·5—154·5°, and thence 2-imino-3-hydroxyethyl-2 : 3-dihydrothiazole (*picrate*, m.p. 159·5—161°). The ring-Me and -OH·$[CH_2]_2$ compounds are approx. as active biologically as the parent compounds *in vivo* (less *in vitro*), but the 2-XSO_2·NMe-compounds are almost inactive. M.p. are corr. R. S. C.

Sulphanilamides of thiazoles etc.—See B., 1943, III, 63.

Chemotherapy of bacterial infections. VIII. Synthesis of carboxylic acid derivatives of 2-sulphanilamidothiazole. K. Ganapathi, C. V. Deliwala, and M. V. Shirsat (*Proc. Indian Acad. Sci.*, 1942, **A**, **16**, 126—128).—Addition of $CH_2Cl·CO_2Et$ and HCO_2Et to Na in dry Et_2O and, after neutralisation, treatment of the product with $CS(NH_2)_2$, yields *Et* 2-*aminothiazole*-5-*carboxylate*, m.p. 160—161°. 2-Sulphanilamidothiazole derivatives are obtained by condensing the appropriate aminothiazole with *p*-NHAc·$C_6H_4·SO_2Cl$ in presence of C_5H_5N, hydrolysing the product with 5N-HCl–EtOH (1 : 1) which may remove only Ac, and removal of the ester group by alkali. Protracted hydrolysis may cause decarboxylation. The following are described: *Et* 2-*sulphanilamidothiazole*-5-*carboxylate*, m.p. 227—228° (*Ac* derivative, m.p. 228—229°); 2-sulphanilamido-4-methylthiazole-5-carboxylic acid, m.p. 195°; Et 2-acetsulphanilamido-4-methylthiazole-5-carboxylate, m.p. 154° and 248° after resolidification; 2-sulphanilamidothiazole-4-acetic acid, m.p. 182° (Et ester, m.p. 170—171°); *Et* 2-*sulphanilamido*-4-*methylthiazole*-5-*acetate*, m.p. 183—184° (*Ac* derivative, m.p. 203—204°); *α*-2-*sulphanilamido*-4-*thiazolyl*-*hexoic acid*, m.p. 157—158°, and "-tert.-" *butyric acid*, m.p. 174° (*Et* ester, m.p. 169—170°); 2-*sulphanilamido*-4-*methyl*-, m.p. 236—237°, and -4 : 5-*dimethyl*-, m.p. 243—244°, *-thiazole*. H. W.

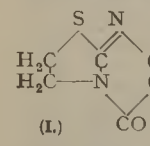
Thiazoles. XXVI. Acyl derivatives of 2-aminothiazoles. E. J. Masters and M. T. Bogert (*J. Amer. Chem. Soc.*, 1942, **64**, 2712—2713; see below).—2-Aminothiazole (**I**) with $CH_2(CO_2Et)_2$ and NaOEt–EtOH gives approx. equal amounts of *Et* N-2-*thiazolylmalonamate* (**II**), m.p. 149—149·5°, and *malondi*-2-*thiazolylamide*, darkens at ~258°, decomp. 271° [also obtained from (**II**) at > the m.p. or in boiling NaOEt–EtOH]. $CO_2K·CH_2·CO_2Et$ gives similarly N-2-*thiazolylmalonamic acid* (54%), which at the m.p., 185·8—186·6°, gives CO_2 and 2-acetamidothiazole, m.p. 206·5—207° (lit., 203°), also obtained from (**I**) by Ac_2O. $CHEt(CO_2Et)_2$ gives only (46%) *Et* N-2-*thiazolylethylmalonamate* [*α-carbethoxy*-n-*butyr*-2-*thiazolylamide*], m.p. 117·8—118·8°. Cyclisation does not occur (cf. *loc. cit.*) as (**I**) cannot react as a 2-NH: compound. M.p. are corr. R. S. C.

Reactions and derivatives of 2-aminobenzthiazole. T. Wagner-Jauregg and E. Helmert (*Ber.*, 1942, **75**, [*B*], 935—949).—*o*-$NO_2·C_6H_4·NH_2$ is converted by diazotisation and treatment with with $CoCl_2$–KCNS at 0—10° into *o-nitrothiocyanobenzene*, m.p. 136° (corr.), transformed by aq. $FeSO_4$–NH_3 at 100° into 2-*aminobenzthiazole* (**I**), m.p. 130—131° [*hydrochloride*, m.p. 238—240°; *Et H sulphate*, m.p. 130—132°, obtained from (**I**) and Et_2SO_4–H_2O at room temp. and reconverted into (**I**) by dil. alkali hydroxide; *Ac* derivative (**II**), m.p. 189—192°]. 2-*Hydnocarpamidobenzthiazole*, m.p. 87—89°, obtained by use of the acid chloride in C_6H_6–C_5H_5N, is physiologically inactive. EtI and (**I**) give 2-amino-3-ethylbenzthiazoline, m.p. 83—87°. (**II**), EtI, and NaOEt in abs. EtOH at 100° followed by alkaline hydrolysis yield 2-*ethyliminobenzthiazoline*, b.p. 142°/0·14 mm., m.p. 88—89°. 2-*Ethylimino*-3-*ethylbenzthiazoline* has b.p. 125°/0·15 mm. (**I**) and $NEt_2·[CH_2]_2$·Cl,HCl under N_2 at 130—140° afford 2-*imino*-3-*β-diethylaminoethylbenzthiazoline*, b.p. 165—175°/0·2 mm. [*dihydrochloride*, m.p. 263—265° (decomp.)]. Similarly, 2-amino-6-ethoxybenzthiazole (**II**) gives 2-*imino*-6-*ethoxy*-3-*β-diethylaminoethylbenzthiazoline*, b.p. 190—205°/0·4 mm. [*dihydrochloride*, m.p. 241—242° (decomp.)]. When heated with $NEt_2·[CH_2]_2$·OH, quartz sand, and P_2O_5 at 200° (**I**) yields a fraction, b.p. 160—180°/0·2 mm., and a *compound*, $C_{20}H_{22}N_4S_2$, possibly $S<\begin{matrix}C_6H_4\\C(:NEt)\end{matrix}>N·[CH_2]_2·NEt·C<\begin{matrix}N\\S\end{matrix}>C_6H_4$, m.p. 88—89° (*sulphate*, m.p. 230—233°, softens at 205° and shrinks together at 210° when slowly heated; *ethiodide*, m.p. 224°). Freshly distilled MeCHO and (**I**) in C_6H_6 yield 2-*imino*-3-*α-hydroxyethylbenzthiazoline*, m.p. 120—122° when rapidly heated, which with P_2O_5 and (**I**) in C_6H_6 at room temp. gives *di-αα*-2-*imino*-3-*benzthiazolinylethane*, m.p. 165—167°. (**I**) when heated at 230° under N_2, preferably in presence of Pd–C or with quartz–P_2O_5–H_2O at 200°, affords 2-*imino*-3-*benzthiazolyl*-2′-*benzthiazoline*, m.p. 257—258° (*Ag* and *Na*, m.p. >360°, salts). (**II**) is transformed by NH_4Cl at 230—250° into 2-*imino*-6-*ethoxy*-3-6′-*ethoxy*-2-*benzthiazolylbenzthiazoline*, m.p. 217—219°. 2-Acetamidobenzthiazole is oxidised by H_2O_2 in AcOH at 100° to 1-*keto*-2-*acetamidobenzthiazole*, m.p. 196°, hydrolysed by HCl (*d* 1·19)–aq. Pr$^{\alpha}$OH at 100° to 1-*keto*-2-*aminobenzthiazole hydrochloride*, decomp. 225°, darkens at 220°. 1-*Keto*-2-*imino*-3-*ethylbenzthiazoline*,

m.p. 211—213°, is obtained similarly. Diazotised arsanilic acid and (I) yield the *compound*, $C_{13}H_{11}O_3N_4SAs$, m.p. 176—178° (C_5H_5N salt). H. W.

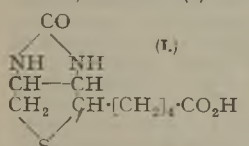
Benzthiazoles.—See B., 1943, II, 75.

Thiazoles. XXV. Thiazolidinopyrimidines of barbituric acid type. E. J. Masters and M. T. Bogert (*J. Amer. Chem. Soc.*, 1942, **64**, 2709—2712; cf. A., 1942, II, 153).—Adding $(CH_2)_2NH$ to 48% HBr at 0—5° (not the reverse addition) gives $Br\cdot[CH_2]_2\cdot NH_2,HBr$ (80%), new m.p. 172·3—174·3°, and thence (KCNO) $Br\cdot[CH_2]_2\cdot NH\cdot CS\cdot NH_2$ (60%), new m.p. 173·6—174·2°, and (aq NaOH) 2-aminothiazoline (86%), m.p. 84—85°, which, reacting as the 2-NH: compound, with $CH_2(CO_2Et)_2$ in boiling NaOEt–EtOH (not alone at 195°) gives 4 : 6-*diketo*-1 : 4 : 5 : 6-*tetrahydrothiazolidino*-3′ : 2′-1 : 2-*pyrimidine* [" 5 : 7-*dioxo*-2 : 3 : 6 : 7-*tetrahydro*-5-*thiazolo*[3 : 2a]*pyrimidine* "] [(I), R = H] (88%), m.p. 244·5—245·5°. Use of $CHR(CO_2Et)_2$ gives


(I.)

4 : 6-*diketo*-5-*methyl*- (72%), m.p. 272—276°, -*ethyl*- (70%), m.p. 224·4—224·7°, -iso*propyl*- (76%), m.p. 262·3—262·8°, -*phenyl*- (45%), m.p. 247·2—247·7°, and -*benzyl*-1 : 4 : 5 : 6-*tetrahydrothiazolidino*-3′ : 2′-1 : 2-*pyrimidine* [(I), R = Alk etc.] (82%), m.p. 241·9—242·3°. NaOEt–AlkI–EtOH converts the substituted (I) into 4 : 6-*diketo*-5 : 5-*diethyl*- (29%), m.p. 138·2—138·7°, -5-*ethyl*-5-iso*propyl*- (33%), m.p. 92·6—93·1°, -5-*ethyl*-5-n-*butyl*- (31%), m.p. 89·7—90·3°, -5-*phenyl*-5-*ethyl*- (36%), m.p. 120·3—121·3°, and -5-*benzyl*-5-*ethyl*-1 : 4 : 5 : 6-*tetrahydrothiazolidino*-3′ : 2′-1 : 2-*pyrimidine* (30%), m.p. 136—136·4°. With *iso*-$C_5H_{11}\cdot O\cdot NO$ in 30% EtOH at room temp. —50°, [(I), R = H] gives the 6-N·OH-compound (61%), m.p. 175—178°, converted by $Na_2S_2O_4$–NH_3–H_2O into the 6-NH_2-compound (54%). $+H_2O$, red at 174°, decomp. 194°. KCNO in hot H_2O then gives the 6-*carbamido*-derivative (80%), m.p. 261—263°, which with $H_2C_2O_4$ at 185° gives *thiazolidino*-2′ : 3′-2 : 3- or -3′ : 2′-1 : 2-*uric acid* (36%), m.p. >300°. M.p. are corr. R. S. C.

Structure of biotin : dethiobiotin. V. du Vigneaud and D. B. Melville (with K. Folkers, D. E. Wolf, R. Mozingo, J. C. Keresztesy, and S. A. Harris) (*J. Biol. Chem.*, 1943, **146**, 475—485; cf. A., 1942, II, 387).—Biotin (I) is converted into its Me ester, which with Raney


(I.)

Ni in boiling 90% EtOH gives *dethiobiotin Me ester* [*Me* ε : 5-(4-*methylglyoxazolid*-2-*one*)*hexoate*] (**II**), m.p. 69—70°, $[\alpha]_D^{20}$ +2·6° in $CHCl_3$, converted by HCl at 200° in a sealed tube into the *dethiodiaminocarboxylic acid dihydrochloride* (*ζη-diaminononoic acid dihydrochloride*), m.p. 180—182°, $[\alpha]_D^{29}$ +4·04° in MeOH. The corresponding *sulphate* (**III**), m.p. 242—243°, $[\alpha]_D^{26}$ +7·75° in H_2O, is obtained from (**II**) and aq. $Ba(OH)_2$ at 140°, followed by H_2SO_4. (**III**) and HIO_4–aq. NaOH at room temp. (12 hr.), then at 40° (3 hr.) and 75° (2·5 hr.), give a product, which after sublimation in high vac. yields pimelic acid and a trace of adipic acid. Et ε-bromohexoate and $CHAcNa\cdot CO_2Et$ give, after hydrolysis of the Et ester, b.p. 144—148°/0·9 mm., *η-ketononoic acid*, m.p. 39—40°, b.p. 135°/0·9 mm.; its *Et* ester, b.p. 91—96°/0·4 mm., with EtO·NO–HCl–EtOH at 50°, followed by NH_2OH,HCl–NaOAc, affords *Et ζη-dioximinononoate*, m.p. 107—108°, hydrogenated (Raney Ni at 50—55°/140 atm.; liquid NH_3–MeOH) to *Et ζη-diaminononoate* [*sulphate*, m.p. 274° (decomp.)]. Phenanthrenequinone (**IV**) in EtOH converts the latter into *Et* 2-*methyldibenzoquinoxaline*-3-*hexoate*, m.p. 78—79°; the free *acid*, m.p. 186—187°, obtained by alkaline hydrolysis of the ester, is also obtained when (**III**) is converted into the free acid with $Ba(OH)_2$, followed by reaction with (**IV**). A. T. P.

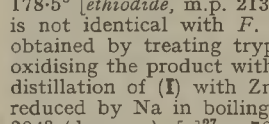
Structure of biotin : formation of thiophenvaleric acid from biotin. D. B. Melville, A. W. Moyer, K. Hofmann, and V. du Vigneaud (*J. Biol. Chem.*, 1943, **146**, 487—492).—The structure of biotin as 2′-keto-3 : 4-glyoxalido-2-tetrahydrothiophenvaleric acid is confirmed. The diaminocarboxylic acid sulphate from biotin and Me_2SO_4–aq. KOH, followed by refluxing the acidified (HCl) mixture, give δ-2-*thienylvaleric acid*, m.p. 40—41°, identical with that obtained by reducing γ-2-thienoylbutyric acid (**I**), m.p. 92—94°, with Zn–HCl. (**I**) is prepared from glutaric anhydride and thiophen (Friedel–Crafts) and is oxidised by alkaline $KMnO_4$ to thiophen-2-carboxylic acid. A. T. P.

Cocarboxylase and related esters. J. Weijlard (*J. Amer. Chem. Soc.*, 1942, **64**, 2279—2282).—Aneurin hydrochloride with $H_4P_2O_7$–$Na_4P_2O_7$ at 150—155° gives the *orthophosphate* ester, RH_2PO_4, $+2H_2O$, m.p. 200—202°, with conc. H_2SO_4 at 150° give the *H sulphate* ester, $RHSO_4$, $+H_2O$, m.p. 258—259° (decomp.), and with HPO_3 or $H_4P_2O_7$–P_2O_5–$NaPO_3$ at ~150° gives the pyrophosphate (cocarboxylase) (**I**), (~10%), $+0·75—1H_2O$, m.p. 238—240°. 4-Methyl-5-hydroxyethylthiazole with $H_4P_2O_7$ at 150—160° gives the *orthophosphate* ester, $+H_2O$, m.p. 162°, but with HPO_2 at 150—155° gives the pyrophosphate ester (*Ag* salt, $RAg_3P_2O_7$, $+0·6HNO_3$, $+3H_2O$), which with 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide (**II**) in liquid paraffin at 110° gives (**I**) (10%), which is also obtained (10%) from 4-methyl-5-β-chloroethylthiazole, (**II**), and $Ag_4P_2O_7$ in liquid paraffin at 110°. R. S. C.

VII.—ALKALOIDS.

Formation of nicotine in plants grafted on tobacco.—See A., 1943, III, 292.

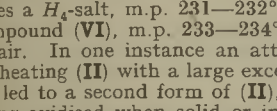
***Alstonia* alkaloids. I. Degradation of alstonine to β-carboline bases and the reduction of tetrahydroalstonine with sodium and butyl alcohol.** N. J. Leonard and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 556—572; cf. Sharp, A., 1934, 538, 1117; 1938, II, 463).—The composition, $C_{21}H_{20}O_3N_2$, is confirmed for alstonine (**I**) from *A. constricta*, F. Muell, by analyses of the *sulphate dihydrate*, m.p. 195—196°, decomp. 208°, $[\alpha]_D^{25}$ +127°±2° in H_2O, *sulphate tetrahydrate*, m.p. 203—204°, $[\alpha]_D^{25}$ +120°±2° in H_2O, H sulphate, m.p. 243—244° (decomp.), $[\alpha]_D^{25}$ +120°±2° in H_2O, *platinichloride*, m.p. 220—221° (decomp.), hydrochloride, m.p. 278—279° (decomp.), $[\alpha]_D^{25}$ +141°±2° in H_2O, nitrate, m.p. 252—254° (decomp.), hydriodide, m.p. 270° (decomp.), and *perchlorate*, m.p. 239—240°. (**I**) is hydrogenated (PtO_2 but not Pd in abs. MeOH) to tetrahydroalstonine (**II**), m.p. 230—231°, $[\alpha]_D^{20}$ −110°±2° in $CHCl_3$, $[\alpha]_D^{27}$ −88°±2° in C_5H_5N, which is not formed by attempted reduction of salts of (**I**) or (**I**) in AcOH in presence of PtO_2. (**II**) gives a colour similar to that of yohimbine in the Adamkiewicz test. Fusion of (**I**) with KOH gives harman (**III**), prisms or needles, m.p. 239—241° [further identified as the picrate, m.p. 257—258° (decomp.), aurichloride, m.p. 229·5—230° (decomp.), and CHPh: derivative, m.p. 204—205°], but no volatile amine; a pure compound has not been isolated from the considerable basic fraction. Similar treatment of (**II**) affords (**III**), norharman, *base A*, $C_{17}H_{16}N_2$, m.p. 171·5—172·5° [*picrate*, m.p. >267° (decomp.)], which in HCl–EtOH shows a marked blue fluorescence and is probably a β-substituted carboline, base *B*, considered tentatively to be $C_{16}H_{16}N_2$ or $C_{16}H_{18}N_2$ on the basis of analysis of its *picrate*, m.p. 261° (decomp.), which also gives a strong blue fluorescence, and base *C*, considered tentatively to be $C_{17}H_{18}N_2$ on the basis of analysis of the *picrate*, m.p. 203·5—205·5° (decomp.). Indole-2-carboxylic acid is isolated from the acidic products of the fusion but a pure individual could not be isolated from the neutral fraction, which appears to contain indole derivatives. Thermal decomp. of (**I**) yields a series of bases all apparently derived from β-carboline although none has been definitely identified. These are base *D*, $C_{17}H_{18}N_2$, readily isolated by taking advantage of the very sparing solubility of its *picrate*, m.p. 254—256°, in EtOH, which appears to be isomeric with base *C*; base *E*, $C_{18}H_{20}N_2$ or $C_{19}H_{22}N_2$ (*picrate*, m.p. 193·5—195°), not identical with Sharp's alstyrine, and *base* F, $C_{13}H_{12}N_2$, m.p. 79—81° [*picrate*, m.p. 261—262·5° (decomp.); *hydrochloride*, m.p. ~275° (decomp.), becomes brown at 227°; *methiodide*, m.p. 283—284° (decomp.)]. The ultra-violet absorption spectrum of *F* closely resembles that of 2-ethyl-β-carboline (**IV**). γ-Aminobutaldehyde Et$_2$ acetal, NPhEt·NH_2, and fused $ZnCl_2$ afford 1-*ethyltryptamine*, b.p. 170—171°/2 mm. (*phthalimide*, m.p. 149—150°; *picrate*, m.p. 178·5—180·5°), converted by dil. H_2SO_4 and 40% CH_2O at 70° and subsequently by boiling dil. H_2SO_4 into 1-ethyl-2 : 3 : 4 : 5-tetrahydro-β-carboline, isolated as the *picrate*, m.p. 224—225°, and p-$NO_2\cdot C_6H_4\cdot CO$ derivative, m.p. 146—148°; the base is dehydrogenated by Pd-black at 160—170° to (**IV**), m.p. 41—42° (*picrate*, m.p. 227—228°; *methiodide*, m.p. 293—295°), not identical with *F*. Norharman ethiodide, m.p. 198—199°, is treated with an excess of NaOH and the ppt. is dried over P_2O_5 at room temp. and then at 100°, after which it is repeatedly treated with evaporating PhMe, thus giving 3-*ethyl*-β-iso*carboline*, m.p. 176·5—178·5° [*ethiodide*, m.p. 213·5—215°, also prepared from (**IV**)], which is not identical with *F*. 2-Ethyl-β-carboline, m.p. 193—195°, is obtained by treating tryptophan with EtCHO in dil. H_2SO_4 and oxidising the product with $K_2Cr_2O_7$. The product obtained by the distillation of (**I**) with Zn dust appears identical with *F*. (**II**) is reduced by Na in boiling BuOH to *hexahydroalstanol*, m.p. 282—284° (decomp.), $[\alpha]_D^{27}$ −78°±3° in C_5H_5N [*picrate*, m.p. 237—238° (decomp.); *acetate*, m.p. 95—96°, and its *picrate*, m.p. 223—224·5° (decomp.)]. CO_2Me of (**II**) is reduced to $CH_2\cdot OH$ and 2 H are added but the exact relationship of initial and final substances is not clear. The ultra-violet absorption suggests that the compound is an αβ-disubstituted indole. The formula for (**I**) may be partly resolved as in (*A*). (**I**) is inactive in doses of 35 mg. per day in birds infected with avian malaria. M.p. are corr. H. W.

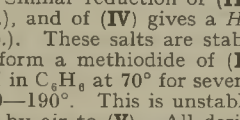

(A.)

***Alstonia* alkaloids. II. New alkaloid, alstoniline, from *A. constricta*.** W. L. Hawkins and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 573—580).—The isolation is described of *alstoniline* (**I**), decomp. 372°, a minor alkaloid of *A. constricta* in which it occurs to the extent of 0·02—0·05% of the bark. It exists also as the cryst. *monohydrate* (**II**), $C_{22}H_{18}O_3N_2,H_2O$, decomp. 356°. Derivatives of (**I**) fall into two groups depending on whether or not this H_2O is present. (**II**) is obtained by neutralising the *hydrochloride* (**III**)

which contains 1 H_2O and decomposes over a wide range when heated without melting, whereas (**I**) is derived by neutralising the anhyd. *sulphate* (**IV**), m.p. 260—264° (decomp.). All derivatives of (**II**) (*e.g.*, the *picrate*, decomp. 294°) retain 1 H_2O whereas compounds derived from (**I**) may or may not be anhyd. (*e.g.*, anhyd. *picrate*, explosive decomp. >350°; anhyd. *methiodide*, decomp. without melting over a wide temp. range). (**I**) is transformed into (**II**) by crystallisation from 95% EtOH. The similarity between the ultra-violet absorption curves of (**I**) and (**II**) indicates that hydration does not involve a basic change in the arrangement of the double linking of the two substances. Aeration of a solution of (**II**) in EtOH for several hr. gives a cryst. product, $C_{22}H_{18}O_4N_2,H_2O$, m.p. 212—213°, provisionally named *alstoniline oxide* (**V**). Reduction (PtO_2) of (**II**) leads to the absorption of 2 H_2, the colour of the solution changing from dark orange-red to a strongly fluorescent yellow. On exposure to air in the working up of the product, the absorbed 2 H_2 is removed and 1 O is absorbed with production of (**V**). Attempts to isolate the reduced base by crystallisation under N_2 were fruitless. Similar reduction of (**III**) gives a H_4-salt, m.p. 231—232° (decomp.), and of (**IV**) gives a H_8-compound (**VI**), m.p. 233—234° (decomp.). These salts are stable to air. In one instance an attempt to form a methiodide of (**II**) by heating (**II**) with a large excess of MeI in C_6H_6 at 70° for several hr. led to a second form of (**II**), m.p. 189—190°. This is unstable, being oxidised when solid or in solution, by air to (**V**). All derivatives of (**I**) are optically inactive. (**II**) gives a negative result with Ehrlich's reagent. The colour changes of (**VI**) in the Adamkiewicz reaction as modified by Harvey *et al.* are similar to those observed with tetrahydroalstonine and indicate the probable presence of a tetrahydro-β-carboline ring system. (**II**) gives an entirely different colour series with this reagent. The presence of 2 OMe in (**V**) is indicated by analysis. *A. constricta* and several of its alkaloid fractions have been found to be inactive in avian malaria. M.p. are corr. H. W.

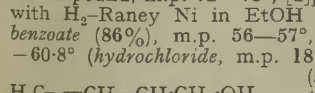
Structure of monocrotaline. VII. Structure of retronecine and related bases. R. Adams, M. Carmack, and J. E. Mahan. **VIII. Proof of primary and *sec.* hydroxyl groups in retronecine.** R. Adams and K. E. Hamlin, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2593—2597, 2597—2599; cf. A., 1941, II, 154).—VII. Relative basic strengths of retronecine (**I**) and its derivatives and chemical reactions indicate the annexed structure. Retronecanol (**II**) and CNBr in Et_2O give an oily additive compound, which, when kept at 2° or better (28%)


(I.)


(III.)

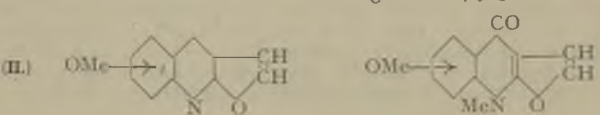
boiled in C_5H_5N, give the 1′-*CN*-derivative (**III**), m.p. 94·5—95° (corr.), hydrolysed by hot 15% H_2SO_4 to 4-methyl-2 : 3 : 5 : 6-tetrahydropyrrolidino-3′ : 2′-2 : 3-pyran, an oil [*picrate*, m.p. 121·5—122·5° (corr.)], which with CNBr regenerates (**III**) and with MeI–$COMe_2$ gives 4 : 1′-*dimethyl*-2 : 3 : 5 : 6-*tetrahydropyrrolidino*-3′ : 2′-2 : 3-*pyran hydrobromide*, m.p. 195—196° (corr.). The following p*K*H are recorded (cf. A., 1943, II, 102): (**I**) 8·94, platynecine (**IV**) 10·22, deoxyretronecine (**V**) 9·55, retronecanol (**VI**) 10·91, anhydroplatynecine (**VII**) 9·42, heliotridane (**VIII**) 11·48, heliotridene (**IX**) 10·60, and iso*retronecanol* (**X**) (see below) 10·88. In accordance with (**I**) etc., Kuhn–Roth determinations show no CMe in (**I**), (**IV**), (**VII**), or (**X**) and 0·40—0·69 CMe in (**V**), (**VI**), (**VIII**), and (**IX**).

VIII. The presence of primary and *sec.* OH in (**I**) is proved. Platynecine benzoate, new m.p. 118—119°, $[\alpha]_D^{29}$ −88·6°, gives the Cl-compound, m.p. 72—73°, $[\alpha]_D^{29}$ −14·5° (cf. A., 1936, 1277), which with H_2–Raney Ni in EtOH at 2—3 atm. gives iso*retronecanol benzoate* (86%), m.p. 56—57°, b.p. 161·5—162·5°/1·2 mm., $[\alpha]_D^{28}$ −60·8° (*hydrochloride*, m.p. 181—182°, $[\alpha]_D^{28}$ −48·6°), and thence (aq. NaOH) (**X**) [= 1-*hydroxymethylpyrrolizidine*] (74%), m.p. 39—40°, b.p. 115—116°/1—2 mm., $[\alpha]_D^{27}$ −78·2° [*methiodide*, m.p. 281—282° (decomp.); *picrate*, m.p. 194—195° (decomp.)]. With CrO_3–AcOH, added gradually, this gives 1-*carboxypyrrolizidine*, m.p. 228—229° (decomp.), $[\alpha]_D^{23}$ −65·8° [*picrate*, m.p. 220—221° (decomp.)], which with CH_2N_2 gives the Me betaine [*chloroaurate*, m.p. 224—225° (decomp.); *picrate*, m.p. 194—195° (decomp.)]. Al(OBu$^\gamma$)$_3$–*cyclo*hexanone–PhMe at the b.p. oxidises (**II**) to *retronecanone* (30%), unstable, b.p. 95—96°/15 mm., $[\alpha]_D^{30}$ −96·7° [*picrate*, m.p. 195° (decomp.); *semicarbazone*, m.p. 209—210° (decomp.); *oxime*, m.p. 167—168°, $[\alpha]_D^{26}$ −76·0°]. M.p. are corr. [α] are in EtOH.


(X.)

R. S. C.

Argentine plants. V. Identification and characterisation of alkaloids in *Fagara coco* (Gill), Engl. V. Deulofeu, R. Labriola, and F. De Langhe (*J. Amer. Chem. Soc.*, 1942, **64**, 2326—2328; cf. A., 1942, II, 275).—Leaves and twigs (10 kg.) of this plant yield skimmianine (previously called β-fagarine) (13 g.), α- (**I**), $(OMe)_2C_{15}H_{12}O_2$:NMe (7 g.), dimorphic, m.p. 163° and 169°, [α] 0, and γ-fagarine (**II**), $C_{13}H_{11}O_3N$ (6 g.), m.p. 142° (*picrate*, m.p. 177°; *picrolonate*, m.p. 174—175°). The structure of (**II**) is as shown, for with MeI at 100—105° it gives iso-γ-*fagarine* (**III**), m.p.



179°, and with $KMnO_4$ in hot $COMe_2$ gives γ-*fagaraldehyde* [2-*hydroxy*-4 : x-*dimethoxyquinoline*-3-*aldehyde*], m.p. 185° (*phenylhydrazone*, m.p. 207°), and thence ($KMnO_4$–$COMe_2$) γ-*fagaric acid*, m.p. 215° [also obtained similarly from (**II**)], which in boiling dil. HCl yields 2 : 4-*dihydroxy*-x-*methoxyquinoline*, m.p. 250° [*NO*-derivative, m.p. 216—217° (decomp.)]. (**I**) differs in behaviour and structure. R. S. C.

VIII.—ORGANO-METALLIC COMPOUNDS.

Composition of magnesium alkyl chloride solutions in ethyl ether. C. R. Noller and A. J. Castro (*J. Amer. Chem. Soc.*, 1942, **64**, 2509—2510).—Previous views (A., 1940, II, 300) are incorrect, since distribution of the Cl in $MgBu^\alpha Cl$–Et_2O depends on access of traces of H_2O. R. S. C.

Condensations by sodium. XXI. Sodium *n*-octyl and *n*-decyl. A. A. Morton, J. B. Davidson, and R. J. Best. **XXII. General theory of the Wurtz reaction. The initial step.** A. A. Morton, J. B. Davidson, and H. A. Newey. **XXIII. General theory of the Wurtz reaction. II. Second phase.** A. A. Morton, J. B. Davidson, and B. L. Hakan. **XXIV. Pyrolysis of sodium amyl.** A. A. Morton and H. A. Newey. **XXV. Reactions of sodium amyl with naphthalene, acenaphthene, and decahydronaphthalene.** A. A. Morton, J. B. Davidson, T. R. P. Gibb, jun., E. L. Little, E. F. Clarke, and A. G. Green (*J. Amer. Chem. Soc.*, 1942, **64**, 2239—2240, 2240—2242, 2242—2247, 2247—2250, 2250—2253; cf. A., 1941, II, 123).—XXI. NaC_8H_{17}-*n* and $NaC_{10}H_{21}$-*n* resemble NaC_5H_{11}. Bubbling CO_2 into *n*-$C_8H_{17}Cl$ (**I**) and Na in light petroleum at −10° gives *n*-C_8H_{17}·CO_2H (49%), *n*-C_7H_{15}·$CH(CO_2H)_2$ (15%), and *n*-$C_{18}H_{34}$ (7%); yields are 23, 26, and 6%, respectively, if CO_2 is passed over the surface; the supernatant solution alone gives no acid. With PhMe and Na at 72°, (**I**) gives 51% of *n*-$C_9H_{19}Ph$, but with C_6H_6 gives only C_8H_{18} (68%), BzOH (33%), and traces of CPh_3·OH and (?) *n*-$C_8H_{17}Ph$, and with PhOMe gives a little PhOH and acid. *n*-$C_{10}H_{21}Cl$ with Na and CO_2 or PhMe gives similarly *n*-$C_{10}H_{21}$·CO_2H (28·4%) + *n*-C_9H_{19}·$CH(CO_2H)_2$ (2·3%) or *n*-undecylbenzene (74%), b.p. 296°±1° (p-*sulphonamide*, m.p. 95·7—96·2°), respectively.

XXII. It is not necessary to assume existence of free radicals for formation of NaAlk compounds. The yield of NaC_5H_{11}-*n* from Na (1 atom) and *n*-$C_5H_{11}Cl$ (1 mol.) in *n*-C_8H_{18} is raised to 72% by very rapid stirring. Primary AlkCl and Na produce insol., jelly-like coatings, readily penetrated by AlkCl and removed or burst by newly formed NaAlk; *sec.*-AlkCl give solid, impenetrable coatings which prevent further reaction. AlkCl give good yields of NaAlk as the halide can penetrate the coating of NaAlk without reacting with it; such reaction deposits NaCl which stops further formation of NaAlk. Thus, high yields of NaAlk depend on presence of an excess of finely divided Na, absence of a protective coating on it, and an unreactive C–halogen linking. The assumption that the Na acts as a trap for alkyl radicals is negatived by the relatively large size of the Na particles and by the fact that the yield of NaC_5H_{11}-*n* is the same whether $C_5H_{11}Cl$ is added to Na or vice versa. Interaction of activated Na with $Bu^\alpha Cl$ in light petroleum at 18—20° and pouring the mixture on to CO_2 gives 42·2% of $Bu^\alpha CO_2H$ and 3·3% of $CHPr^\alpha(CO_2H)_2$.

XXIII. Free radicals have no part in the second phase (NaAlk + AlkHal → Alk_2) of the Wurtz reaction. When the alkyl chains of $NaCH_2R$ and R′·$[CH_2]_2$·Hal are sterically adjacent during interaction, prototropic change leads to RMe and CHR′:CH_2; this distribution of paraffin and olefine predominates in the products from NaC_8H_{17}–EtHal and –PrHal, NaC_5H_{11}–AlkHal (12 examples), NaC_6H_{13}–$C_5H_{11}Cl$ and –$C_8H_{17}Cl$. The relative amounts are, however, somewhat obscured by the change, NaAlk + Alk′Hal → NaAlk′ + AlkHal, which occurs most readily with iodides and least readily with chlorides. When this change occurs readily, the yield of symmetrical Alk_2 should be high; this is so for interaction of NaC_5H_{11} with AlkHal. Free radicals, if formed, should give the same relative amounts of products independently of their source; this is not the case for NaC_8H_{17} with MeCl, MeBr, or MeI. Reputed analogies requiring free radical mechanisms are false analogies.

XXIV. Heating NaC_5H_{11} at 110—120° before interaction with CO_2 reduces the amount of *n*-C_5H_{11}·CO_2H formed, a large fall in yield occurring at 80—90°; heating at 80—120° leads to some tarry acids; H_2O-sol. acids are also formed (max. at 90—100°), containing >1 CO_2H per C_5-unit, the CO_2H being attached to a remote C.

XXV. $C_{10}H_8$ with NaC_5H_{11}-*n* or NaC_8H_{17}-*n* and then CO_2 in light petroleum at 72° (N_2) gives α- + β-$C_{10}H_7$·CO_2H (14, 17),

1 : 3- + 1 : 8- + 2 : 6-$C_{10}H_5(CO_2H)_2$ (10, 15), and $C_{10}H_5(CO_2H)_3$ (2, 5%, respectively). Acenaphthene and NaC_5H_{11}–CO_2 give the 1 : 5-*dicarboxylic acid* (~50%), m.p. 292—294° (Et_2 ester), converted by CaO–Cu-bronze at 280° into the 5-CO_2H-compound and by $KMnO_4$ at 50—60° into 1 : 4 : 8-$C_{10}H_5(CO_2H)_3$. Decahydronaphthalene and NaC_5H_{11}–CO_2 very readily give the (? 1 : 4 : 5 : 8-)$(CO_2H)_4$-compound, m.p. 61—62° (*dianhydride*, m.p. ~300°); impure (?) amyl derivatives were obtained by alkylation. R. S. C.

IX.—PROTEINS.

Electrophoretic study of the proteins in rubber latex serum. C. P. Roe and R. H. Ewart (*J. Amer. Chem. Soc.*, 1942, **64**, 2628—2632).—Serum from unpreserved rubber latex (from Florida or Sumatra) contains seven electrophoretically distinct proteins, for five of which the relation between electrophoretic mobility and pH is determined. Preservation by NH_3 rapidly alters the proteins, reducing the separable components to two. Dry protein is obtained from rubber-free latex serum by sublimation in vac. without much alteration in electrophoretic properties. Modifications in procedure necessary for study of rubber latex are recorded. R. S. C.

Catalysed hydrolysis of amide and peptide bonds in proteins. J. Steinhardt and C. H. Fugitt (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 315—327).—The rate of hydrolysis of amide and peptide linkings in wool and ovalbumin by strong acids of high mol. wt. is ≫ by HCl, and the relative efficiencies of various acids as hydrolysing agents are in the same order as the affinities of their anions for the protein (cf. B., 1941, II, 338). Among compounds $RO{\cdot}SO_3H$ where R = alkyl, those containing 14 C atoms show max. hydrolytic action. Addition of n-$C_{12}H_{25}{\cdot}O{\cdot}SO_3Na$ (I) increases the hydrolytic breakdown produced by HCl, small amounts of the salt favouring decomp. of amide rather than peptide linkings. The effect of temp. on the rate of hydrolysis is decreased by addition of (I) to HCl. The mechanism of the catalysis and practical applications are discussed. C. S. W.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

New crystalline compounds of heparin. D. A. Scott, A. F. Charles, and A. M. Fisher (*Trans. Roy. Soc. Canada*, 1942, [iii], **36**, V, 49—51).—Ba-heparin in H_2O with excess of piperidine, *iso*-$C_5H_{11}{\cdot}NH_2$, and n-$C_5H_{11}{\cdot}NH_2$ yields cryst. compounds which after drying over NaOH retain all the activity of the heparin (cat blood), and contain respectively 8·3, 6·1, and 6·8% of N. They undergo no apparent change when heated at 110° for 1 hr. Na- and NH_4-heparin yield similar compounds. No analyses are given. A. Li.

Barbaloin. L. N. Owen and J. L. Simonsen (*J. Amer. Chem. Soc.*, 1942, **64**, 2516—2517).—Hydrolysis of barbaloin (I) by borax does not give MeOH (Rosenthaler, *Pharm. Acta Helv.*, 1934, **9**, 9; Cahn *et al.*, A., 1932, 1252). The mol. wt. (521) of barbaloin Me ether, determined by *X*-ray analysis, establishes the formula, $C_{21}H_{17}O_2(OMe)_7$. (I) is thus the corresponding $(OH)_7$-compound. R. S. C.

Penillic acid, an optically active acid from penicillin. W. M. Duffin and S. Smith (*Nature*, 1943, **151**, 251).—In aq. solution at pH 2, penicillin affords *penillic acid*, decomp. 175°, extracted with BuOH but not Et_2O, and recryst. from H_2O. It shows a pale blue fluorescence in ultra-violet light, gives a deep bluish-purple colour with ninhydrin, possesses some of the properties of an NH_2-acid, but does not react to $FeCl_3$ like penicillamine. A. A. E.

Penicillamine, a characteristic degradation product of penicillin. E. P. Abraham, E. Chain, W. Baker, and (Sir) R. Robinson (*Nature*, 1943, **151**, 107).—*Penicillamine*, $C_6H_{11}O_4N$,HCl (but conceivably $C_6H_9O_3N$,HCl,H_2O), is obtained by hydrolysing Ba penicillin at 100° for 1 hr. with 0·1N-H_2SO_4 and separating by means of $HgCl_2$. It is optically inactive. Three proton-binding centres at pH 2·0, 7·9, and 10·5, respectively, may be an acidic OH, the basic group, and a weakly acidic OH; N is present as NH_2 and the substance gives an intense bluish-purple ninhydrin reaction. A typical α-NH_2-acid structure is improbable. Unusual behaviour (detailed) suggests relationship to an NH_2-sugar and ascorbic acid. A. A. E.

XI.—ANALYSIS.

Review of organic microchemistry. L. T. Hallett (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 956—993).—The applications of micromethods to the following are reviewed and discussed in detail: synthesis and purification of org. substances, including recrystallisation, sublimation, chromatographic separation, extractions; physical methods, including weighing and determination of consts.; the use of the microscope, and analysis for elements and sp. groups. Throughout stress is laid on special micro-apparatus, and many designs are given in detail. An entensive bibliography is appended. J. D. R.

Identification of very small amounts of liquids.—See A., 1943, I, 101.

Preparation of "N/10-bromine."—See A., 1943, I, 98.

Semimicro-determination of chlorine, bromine, and iodine in organic compounds. E. W. Peel, R. H. Clark, and E. C. Wagner (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 149—151).—The sample is fused in the Parr bomb with Na_2O_2, KNO_3, and sucrose, lactose, or BzOH, and Cl determined gravimetrically as AgCl. If Br or I is to be determined BrO_3' or IO_3' is reduced with N_2H_4 and determined as AgBr or AgI. Liquids are weighed into gelatin capsules for analysis. J. D. R.

Micro-determination of sulphur and halogens by melting with potassium.—See A., 1943, I, 98.

Iodoform reaction by methods of microscopy. H. F. Schaeffer (*J. Chem. Educ.*, 1942, **19**, 15—16).—The technique of carrying out the reaction on hanging drop and ordinary slides is described. L. S. T.

Analytical data for the systems carbon tetrachloride–acetic acid–benzene and carbon tetrachloride–tetrachloroethylene. W. R. McMillan and H. J. McDonald (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 114—116).—The ternary system C_6H_6–CCl_4–AcOH is analysed by titration of the AcOH with standard NaOH; during the titration the C_6H_6–CCl_4 phase separates and is centrifuged and analysed by n determination. Alternatively the sample may be analysed by measurement of d and n. The binary system CCl_4–$C_2H_2Cl_4$ is analysed by n determinations. J. D. R.

Acraldehyde determination in presence of formaldehyde and acetaldehyde by the polarographic method. R. W. Moshier (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 107—109).—$CH_2{:}CH{\cdot}CHO$ is determined polarographically in presence of CH_2O and MeCHO in LiCl solution buffered to pH 7·0—8·0 with Li_3PO_4. During the determination the temp. must be held const. to ±0·05°. J. D. R.

Quantitative drop analysis. XVII. Gasometric determination of amino-nitrogen. J. Sandkuhle, P. L. Kirk, and B. Cunningham (*J. Biol. Chem.*, 1943, **146**, 427—432; cf. A., 1941, II, 276).—A modification of the Van Slyke gasometric method for determination of μg. quantities of amino-N is described; 0·5 μg. of N can be estimated, and 2 μg. or greater amounts with accuracy. The method is applicable to protein hydrolysates. A. T. P.

Colorimetric determination of serine. M. J. Boyd and M. A. Logan (*J. Biol. Chem.*, 1942, **146**, 279—287).—The CH_2O formed by distillation of 1—5 mg. of serine (or of an acid hydrolysate of protein adjusted to the alkaline side of Me-red) with IO_4' is condensed with 1 : 3 : 6-$(OH)_2C_{10}H_4(SO_3H)_2$ and measured colorimetrically with an error of 1—2%. Serine is slowly destroyed by acid hydrolysis and the determination is affected by the presence of carbohydrates unless completely converted into furfuraldehyde derivatives by hydrolysis. The following vals. for serine-N were obtained: horse hæmoglobin 4·42, dog hæmoglobin 4·22, collagen 3·22, ovalbumin 6·27, salmine 3·23, casein 4·75% of the total N. H. G. R.

Possibility of differentiating between small amounts of cerebro-glucosides and -galactosides. J. Brückner (*Z. physiol. Chem.*, 1942, **275**, 73—79).—1 c.c. of 0·01% sugar is mixed with 1 c.c. of orcinol reagent (2% in 20% H_2SO_4) and floated on 3 c.c. of 92% H_2SO_4. The layers are mixed and the colour is observed immediately and after 8, 15, and 30 sec., stabilisation being sufficiently achieved by cooling in ice. Glucose and galactose (I) can thus be identified separately and their relative proportions can be determined in their mixtures. In the investigation of cerebro-galactosides and -glucosides impure preps. and organ extracts can be used provided that the carbohydrates are carefully removed. The lipoid extract of human blood corpuscles shows the reactions of (I) and hence contains a cerebrogalactoside. H. W.

Cryoscopic analysis of styrene, indene, and di*cyclo*pentadiene. E. H. Smoker and P. E. Burchfield (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 128—129).—Cryoscopy offers a precise analytical method for the determination of small quantities of impurities in styrene, indene, and di*cyclo*pentadiene. Depressions of f.p. of these on addition of 0—4% of *p*-xylene are recorded, and molal dispersions are given. J. D. R.

Determination of concentration of chlorophyll. D. I. Saposhnikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 369—371).—Chlorophyll (I) is determined from the width of the band I in the absorption spectrum, measured by a drum spectrometer, and the thickness of the solution layer. The widths of the bands are to each other as the square root of the respective amounts of (I). A. T. P.

INDEX OF AUTHORS' NAMES, A., II.

APRIL, 1943.

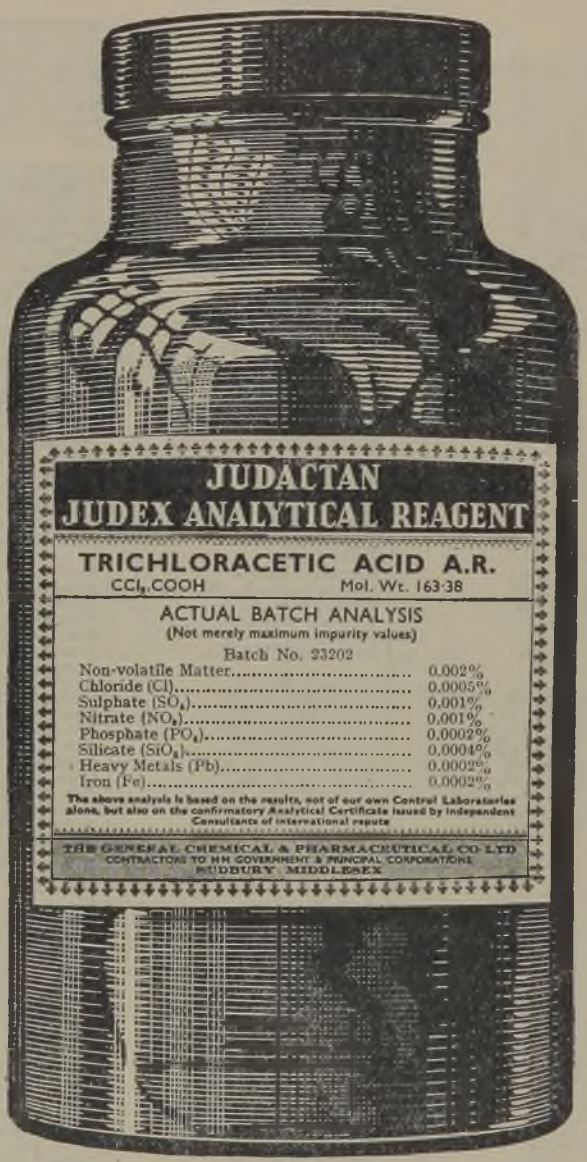
JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



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