BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1941.

I.—ALIPHATIC.

Direct determination of oxygen in organic compounds by hydrogenation. II. Cracking mechanism on platinum–silica gel catalyst. K. Morikawa, T. Kimoto, and R. Abe (*Bull. Chem. Soc. Japan*, 1941, **16**, 33—39).—The production of H_2O, CO_2, and CO by passing H_2 and the vapours of sucrose, $H_2C_2O_4$, BzOH, anthraquinone, and $Na_2C_2O_4$ over Pt–SiO_2 gel, varying the temp. (800—950°) and rate of H_2 flow, has been studied. High temp. gives a high proportion of CO. The vapours from H_2O or $NaHCO_3$ when passed with H_2 over Pt–SiO_2 gel containing free C give 95% of CO. It is concluded that in the cracking process the following reactions occur: $C + CO_2 = 2CO$; $C + H_2O = CO + H_2$; $CO_2 + H_2 = CO + H_2O$. A. Li.

Separation of pure methane from other gaseous hydrocarbons by selective adsorption.—See B., 1941, II, 69.

Preparation of ββ- and γγ-dimethylpentane. H. Soroos and H. B. Willis (*J. Amer. Chem. Soc.*, 1941, **63**, 881).—Prep. of CH_2EtBu^{γ} from $Bu^{\gamma}Cl$–$MgPr^{\alpha}Cl$ (27%) or –$MgPr^{\alpha}Br$ (29%) and of CMe_2Et_2 from CMe_2EtCl–MgEtCl (43%) or –MeEtBr (41%) is reported (cf. Wibaut *et al.*, A., 1939, II, 237; Edgar *et al.*, A., 1929, 789). R. S. C.

Isomerising action of cyclising catalysts.—See A., 1941, I, 216.

ξ-Bromo-βζκ-trimethyl-*n*-pentadecane. P. G. Smith and C. E. Schweitzer (*J. Amer. Chem. Soc.*, 1941, **63**, 882).—$Pr^{\beta}\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot COMe$ and Na–$Pr^{\beta}OH$ give the alcohol, b.p. 146—148°/1 mm., and thence by PBr_3 in light petroleum *ξ-bromo-βζκ-trimethyl*-n-*pentadecane*, b.p. 138—140°/1 mm. R. S. C.

Estimation of unsaturated hydrocarbons by bromine addition. S. J. Green (*J. Inst. Petroleum*, 1941, **27**, 66—71).—In the Br′–OBr′ method for brominating olefines, the amount of excess reagent is crit. since inhibition of bromination occurs when low [Br] are used. The Lewis and Bradstreet titration technique is preferred to the Francis method as it appears to avoid this inhibition effect. If Br no. is accepted as a guide to the degree of unsaturated compounds, the conditions of the reaction must be very precisely specified. The % of unsaturated compounds cannot be determined unless the mol. wts. and nature of the olefines present can be determined. T. C. G. T.

Catalytic polymerisation of normally gaseous olefines.—See B., 1941, II, 106.

Polymerisation of olefines. II. Co-polymerisation of *sec.*- and *tert.*-butyl alcohols by sulphuric acid. F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski, and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 756—757).—Addition of $Bu^{\gamma}OH$ to *sec.*-BuOH in 75% (wt.) H_2SO_4 at 64° results in union of Bu^{γ} with *sec.*-Bu (75%) and Bu^{γ} (25%). The products, $CHBu^{\gamma}{:}CHMe$ (**I**) (40%), $CMePr^{\beta}{:}CHMe$ (35%) [formed by rearrangement of (**I**)], and di*iso*butylenes (25%), are identified by fractionation and subsequent ozonisation. R. S. C.

[Catalytic] polymerisation of unsaturated hydrocarbons.—See A., 1941, I, 215.

Structure of additive compounds of metallic halides and unsaturated hydrocarbons. S. L. Varschavski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 29, 315).—$CH_2{:}CHCl$ is produced when $CHCl{:}CH\cdot HgCl$ (obtained by passing C_2H_2 into saturated aq. NaCl containing $HgCl_2$) is treated with 40% HBr or conc. HCl. The results support the views of Freidlina and Nesmejanov (A., 1940, II, 246). W. McC.

[Photometric] determination of small traces of solvent vapours in air.—See A., 1941, I, 178.

Formation of trichloroacetic acid from perchlorethylene by atmospheric oxidation. K. C. Bailey and W. S. E. Hickson (*J.C.S.*, 1941, 145).—Exposure of C_2Cl_4 with a trace of H_2O to sunlight for 4 months yields $CCl_3\cdot CO_2H$ (extracted by H_2O). A. Li.

Derivatives of allylic chlorides. Reactions of methallyl chloride involving the double linking. J. Burgin, G. Hearne, and F. Rust (*Ind. Eng. Chem.*, 1941, **33**, 385—388).—Hydration of $CH_2{:}CMe\cdot CH_2Cl$ (**I**) to $OH\cdot CMe_2\cdot CH_2Cl$ (**II**) (63% yield) is effected by 80% H_2SO_4 at 5—10° for 2·5 hr. $CMe_2{:}CHCl$ (**III**) and 90% H_2SO_4 at −10° to 0° give (**II**) (66% yield). Other acids, *e.g.*, 85% H_3PO_4, 70% HNO_3, $PhSO_3H$, or 60% $HClO_4$ (very effective, apart from explosion danger), can be used, but each has a sp. optimum temp. and concn. range. (**I**) and 80% H_2SO_4 (or H_3PO_4) at 40° give (**III**) (85% yield) (equilibrium reaction); the passage of the vapour over activated Al_2O_3 gives a similar result. (**III**), b.p. 68·1°, is purified by refluxing with 10% KOH–EtOH, which hydrolyses (**I**). Chlorination of (**I**) or (**III**) at room temp. affords ~70% yield of isomeric dichloro*iso*butenes, $CH_2{:}C(CH_2Cl)_2$ and $CHCl{:}CMe\cdot CH_2Cl$, in approx. equal amounts. Direct chlorohydrination of (**I**) by dil. Cl_2–H_2O at 30° (apparatus is described) (Cl_2 bubbled into aq. solution gives a poor result) affords ~70% of $OH\cdot CMe(CH_2Cl)_2$, b.p. 69°, with small amounts of trichloro*tert.*-butyl alcohols, unsaturated dichlorides, tetrachloro*iso*butanes, and $CMeCl(CH_2Cl)_2$. Mechanisms of reactions are given. $CH_2{:}CMe_2$ is more reactive to HCl or Cl_2 than is (**I**); for hydration, 65% H_2SO_4 is the max. concn. possible to avoid excessive polymerisation. A. T. P.

Nitration of hydrocarbons.—See B., 1941, II, 106.

Preparation of unsaturated higher alcohols. VII. S. Komori (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 428—430B).—A series of Cr_2O_3–Fe_2O_3 catalysts are shown to accelerate the hydrogenation of the Et ester of rice oil or erucic acid to docosenol at ~313—340°/80—100 atm. Fe_2O_3 alone is less satisfactory but utilisable if its proportion is high. H. W.

Catalytic dehydrogenation and condensation of aliphatic alcohols. V. I. Komarewsky and J. R. Coley (*J. Amer. Chem. Soc.*, 1941, **63**, 700—702).—In presence of Cr_2O_3 at 400—425°, *n*-hexyl, -heptyl, and -octyl alcohol give the ketone according to the equation, $2CH_2R\cdot OH \rightarrow COR_2 + CO + 3H_2$, but at 475—525° less ketone and ~2·5% of phenol [PhOH, *o*-cresol, and *m*-2-xylenol (by rearrangement of o-$C_6H_4Et\cdot OH$), respectively] are obtained. Cr_2O_3–Al_2O_3 (A., 1939, II, 49) is thus a true "complex action" catalyst. R. S. C.

Synthetic glycerin [and allyl alcohol] from petroleum [propylene].—See B., 1941, II, 69.

Preparation of pentaerythritol.—See B., 1941, II, 106.

Halogenation in reactive solvents. VII. Chlorination of olefines in reactive solvents with *tert.*-butyl hypochlorite. C. F. Irwin and G. F. Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 858—860; cf. A., 1940, II, 295).—(*a*) *cyclo*Hexene, (*b*) $CH_2{:}CHBu^{\alpha}$, and (*c*) $(CHEt{:})_2$ with Cl_2 in MeOH give (*a*) 17·6 and 82·3, (*b*) 31·6 and 68·3, and (*c*) 34·7 and 65·2% of dichloride and chloro-ether, $CHRCl\cdot CHR'\cdot OMe$, respectively, the proportions being determined from the Cl-content of the product. Olefines and ROH [R = *n*-alkyl, OAc, or (in C_6H_6) Ph] in presence of $Bu^{\gamma}OCl$ (and, if R = alkyl, a little p-$C_6H_4Me\cdot SO_3H$ as catalyst) at a suitable controlled temp. (5—60°) give only (35·5—77·7%) the chloro-ether. Thus are obtained $CH_2Cl\cdot CHMe\cdot OMe$, b.p. 100—101°/743 mm., *β-chloro-γ-methoxy-γ-methylbutane*, b.p. 134—135°/749 mm., *β-chloro-γ-methoxy*-n-*pentane*, b.p. 75—77°/100 mm., 1-*chloro*-2-*methoxy*cyclo*hexane*, b.p. 73—74°/20 mm., *γ-chloro-δ-*

methoxy-n-*hexane*, b.p. 94—95°/98 mm., *β-chloro-γ-ethoxy*-n-*pentane*, b.p. 69—70°/50 mm., *β*-methoxy-, b.p. 123°/100 mm., *-ethoxy*-, b.p. 98°/28 mm., -n-*propoxy*-, b.p. 104—105°/20 mm., and -n-*butoxy*-n-*heptyl chloride*, b.p. 128—129°/30 mm., $(Cl\cdot[CH_2]_2)_2O$, $Cl\cdot[CH_2]_2\cdot OAc$, *β-chloroisopropyl acetate*, b.p. 147—149°/745 mm., *γ-chloro-β-acetoxy-β-methylbutane* (22·4%), b.p. 99—101°/100 mm. (with 47·5% of $CMeCl{:}CMe_2$, b.p. 91—92°/741 mm.), *β-chloro-γ-acetoxy*-n-*pentane*, b.p. 73—75°/20 mm., *γ-chloro-δ-acetoxy*-n-*hexane*, b.p. 124—126°/100 mm., *α-chloro-β-acetoxy*-n-*heptane*, b.p. 119—120°/20 mm., *β-phenoxy*-n-*propyl chloride*, b.p. 110—113°/22 mm., and *β-phenoxy*-n-*heptyl chloride*, b.p. 138—140°/8 mm. R. S. C.

[Kinetics of] synthesis of diethyl acetal.—See A., 1941, I, 171.

Use of Bunte salts in synthesis. I. Preparation of mercaptals. H. E. Westlake, jun., and G. Dougherty (*J. Amer. Chem. Soc.*, 1941, **63**, 658—659).—RHal and $Na_2S_2O_3$ in boiling 50% EtOH give $SR\cdot SO_3Na$ (not isolated), which, after removal of the EtOH, with R'CHO in boiling aq. HCl give 46—77% of $CH_2(S\cdot CH_2Ph)_2$, $CHPh(S\cdot CH_2Ph)_2$, $CH_2(SBu)_2$, $CHMe(SBu)_2$, $CH_2(SEt)_2$, and *formaldehyde di-(β-hydroxyethyl) mercaptal*, b.p. 52—54°/5 mm. R. S. C.

Anhydrides of normal aliphatic saturated monobasic acids. J. M. Wallace, jun., and J. E. Copenhaver (*J. Amer. Chem. Soc.*, 1941, **63**, 699—700).—The following are prepared by boiling RCO_2H in $AcOH-Ac_2O$: heptoic, m.p. −10·8°, octoic, m.p. 0·9±0·1°, nonoic, m.p. 14·8°, decoic, m.p. 24·7±0·2°, undecoic, m.p. 36·7°, lauric, m.p. 42·1±0·1°, *tridecoic*, m.p. 49·9±0·2°, myristic, m.p. 53·5±0·1°, *pentadecoic*, m.p. 60·6°, palmitic, m.p. 63·9°±0·1°, *margaric*, m.p. 67·6°, and stearic, m.p. 70·7°, anhydride. There is little evidence of alternation in m.p. above C_5. R. S. C.

Methacrylic resins. I. Polymerisation of methyl methacrylate. R. Inoue (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 448—449B).—$CH_2{:}CMe\cdot CO_2Me$ (purification described) is sealed into hard glass tubes, which are then placed in a thermostat for polymerisation in the absence of light. The amount of polymeride (**I**) is determined by dissolving the weighed sample in $COMe_2$ or C_6H_6 and pptg. (**I**) by MeOH. (**I**) is then dried at ~80° for a week and then weighed. The rate of polymerisation accelerates with time to a max., after which it decreases continuously. From the val. dx/dT at 10% yield of (**I**) and polymerisation temp. T° K. the apparent heat of activation is ~12·5 kg.-cal. The degree of polymerisation of (**I**) formed at various stages during a polymerisation is almost the same; it increases with decreasing temp. o polymerisation. H. W.

Direct esterification of higher fatty acids with glycerol. V. Esterification of two-component fatty acid mixture into monoglyceride. S. Kawai (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 428B).—Complete esterification occurs when equimol. mixtures of stearic (**I**) and oleic acid (**II**), (**I**) and lauric acid (**III**), and (**II**) and (**III**) are heated for ~60 min. at 220—250° with glycerol (1·4 mols. per mol. of acid). The products contain considerable amounts of di- and tri- in addition to mono-glycerides. In the esterification of (**I**) + (**II**) and (**I**) + (**III**) the formation of mono-olein (**IV**) or monolaurin (**V**) predominates over that of monostearin whilst with (**II**) + (**III**) the production of (**V**) appears readier than that of (**IV**). H. W.

Ester interchange between oils and glycerol. III. Experiments on sperm-head oil and kurokozame oil. S. Kawai (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 427B).—Addition of Zn and oleic acid accelerates the interchange resulting in the rapid formation of the oils of higher OH vals.; judging from these vals. ester interchange occurs in the glyceride structure and in the wax ester compositions and therefore produces a considerable amount of free higher alcohols (*A*). The portion of the product insol. in EtOH appears to consist mainly of triglycerides and unchanged esters whilst the sol. portions (*B*) contain predominatingly mono- (and also di-)glycerides and *A* and *B* are suitable materials for the manufacture of sulphonated oil etc. H. W.

Isomeric structure of the C_{18} unsaturated [fatty] acids from their Raman and infra-red spectra. J. W. McCutcheon, M. F. Crawford, and H. L. Welsh (*Oil and Soap*, 1941, **18**, 9—11).—A study of the Raman and infra-red spectra of highly purified specimens of the Et esters of the respective acids has led to the conclusion that all the double linkings of the naturally occurring oleic, linoleic (as also of *β*-linoleic acid), and linolenic acids have the *cis*-configuration, whilst the esters of elaidic and linelaidic acid (prepared by the method of Kass and Burr, A., 1939, II, 297) contain only *trans*-linkings. An alternative explanation, consistent with the above conclusions, is suggested for the experimental results obtained by Bertram and Kipperman (B., 1935, 1149), which were interpreted by them as indicating a *trans*-structure of oleic acid. E. L.

Influence of solvents on auto-oxidation of methyl linoleate. T. R. Bolam and W. S. Sim (*J.S.C.I.*, 1941, **60**, 50—56).—In the auto-oxidation of Me linoleate at 75° in absence of solvent, or in solution in AcOH or a hydrocarbon solvent, a peroxide group is formed at one double linking and a ketol at the other. The peroxide undergoes change, probably as the result of polymerisation, and the ketol group is enolised to an extent depending on the conditions. In AcOH the initial rate of oxidation and the rate of change of peroxide are ≫ in hydrocarbons or in absence of solvent, the hydrocarbons acting simply as diluents. With chloroacetic acids, the initial rate of absorption is still further increased, the effect being the more marked the greater is the degree of substitution. The rate of absorption is not increased in alcoholic solution, so that factors other than the polar or non-polar nature of the solvent are involved. Since the max. rate of absorption occurs at an earlier stage in AcOH than in hydrocarbons, the rate of oxidation is probably determined by the concn. of free peroxide. Volatile oxidation products are formed to a very limited extent.

Catalysis by ascorbic acid.—See A., 1941, I, 215.

Manufacture of lævulic acid.—See B., 1941, II, 107.

Catalytic oxidation of benzene [to maleic acid].—See B., 1941, II, 107.

Oxidation processes in platinum oxalates.—See A., 1941, I, 217.

Condensation of bromoacetaldehyde with malonic acid. N. S. Vulfson and M. M. Schemjakin (*Compt. rend. Acad. Sci., U.R.S.S.*, 1940, **29**, 206—207).—Condensation of $CH_2Br\cdot CHO$ (**I**) with $CH_2(CO_2H)_2$ (**II**) in presence of piperidine at room temp. and subsequently at 105—115° gives a small amount of the *β-lactone*, $CH_2Br\cdot CH<\begin{matrix}CH(CO_2H)\\O\end{matrix}>CO$ (*Ag* salt), hydrolysed by alkali to (**I**) and (**II**). H. W.

Mechanism of the primary photodissociation of organic molecules.—See A., 1941, I, 173.

Production of formaldehyde in a high- and low-frequency arc.—See A., 1941, I, 172.

Catalysis by activated copper sulphide.—See A., 1941, I, 215.

Production of acraldehyde.—See B., 1941, II, 73.

Formation of polyhydroxydialdehydes. I. Xylotrihydroxyglutardialdehyde and its derivatives. K. Iwadare (*Bull. Chem. Soc. Japan*, 1941, 16, 40—44).—Oxidation $[Pb(OAc)_4$ in $C_6H_6]$ of 1 : 2-*iso*propylidene-*d*-glucofuranose yields 1 : 2-iso*propylidene*-d-*xylotrihydroxyglutardialdehyde* (**I**), b.p. 132—136°/0·01—0·02 mm., $[\alpha]_D^{16}$ +20°±3° in EtOH [*monophenylhydrazone*, m.p. 140·5—141° (corr.), $[\alpha]_D^{10}$ −41°±1° in $CHCl_3$; *monosemicarbazone*, m.p. 209—209·5° (corr.; decomp.)], hydrolysed (0·1N-H_2SO_4) to *xylotrihydroxyglutardialdehyde* (**II**) [*bisphenylhydrazone*, m.p. 126·5—127·5° (corr.); *bis*-p-*nitrophenylhydrazone*, m.p. 191—192° (corr.; decomp.). (**I**) and (**II**) with $SrCO_3$ and aq. Br yield *Sr* 1 : 2-iso*propylidene*-d-*xyluronate* and d-*xyluronate*, respectively. A. Li.

Synthesis of acetone from acetylene.—See B., 1941, II, 105.

Action of fluorine on organic compounds. X. Vapour-phase fluorination of acetone. N. Fukuhara and L. A. Bigelow (*J. Amer. Chem. Soc.*, 1941, **63**, 788—791).—Apparatus for vapour-phase fluorination of volatile org. compounds is described. $COMe_2$ and F_2-N_2 at ≮60° give exothermally COF_2, CF_4, mono-, b.p. 78° (lit. 72·5°) [semicarbazone, m.p. 132° (decomp.)], and *hexa-fluoroacetone*, m.p. −129°, b.p. −28° [*semicarbazone*, $+H_2O$ and anhyd., m.p. 153° (decomp.)], $CF_3\cdot COF$, b.p. −59° (derived amide, m.p. 74—75°), *oxalyl fluoride*, b.p. 28° [with MeOH and then liquid NH_3 gives $(CO\cdot NH_2)_2$], (?) O_2F_2, and other products. A free-radical mechanism is proposed. R. S. C.

Qualitative chemical identification of the natural sugars. W. E. Militzer (*J. Chem. Educ.*, 1941, **18**, 25—28).—Procedures for carrying out numerous well-known tests are given. The tests are arranged in a systematic scheme for identifying the sugars. L. S. T.

Industrial uses of cane sugar. I. Catalytic effects of pyridine on the acetylation of sucrose. M. Amagasa and T. Yanagita (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 444—445B).—At 130—140° C_5H_5N is a very active catalyst of the action of Ac_2O on sucrose, giving a higher yield of sucrose octa-acetate than can be obtained by use of anhyd. NaOAc. The progress of acetylation can be accurately followed by thermometric titration. H. W.

Chemistry of galactogen from *Helix pomatia*. *l*-Galactose as a component of a polysaccharide of animal origin. D. J. Bell and E. Baldwin (*J.C.S.*, 1941, 125—132; cf. A., 1941, III, 111).—Galactogen (**I**) hydrolysate after removal of *d*-galactose yields by the method of Moore and Link (A., 1940, II, 244) 2-dl-*galactobenziminazole*, m.p. 233°. A fraction of the methanolysis product of methylated (**I**) yields 2 : 3 : 4 : 6-*tetramethyl*-dl-*galactoseanilide*, $[\alpha]_D$ −2° in $COMe_2$, m.p. (and mixed m.p. with synthetic product) 179—181°. It is concluded that (**I**) is composed of units having 7 galactose radicals, 3 "backbone" radicals of *d*-galactose and 4 side-chains, 3 of *d*- and one of *l*-galactose. The structure of the unit is discussed. A. Li.

Separation of trimethylamine from mixture with mono- and di-methylamine.—See B., 1941, II, 107.

Aldol condensations with aliphatic Schiff's bases. W. S. Emerson, S. M. Hess, and F. C. Uhle (*J. Amer. Chem. Soc.*, 1941, **63**, 872).—When Pr^aCHO and NH_2Bu^a are heated at 20 mm., N-n-*butylidene*-n-*butylamine* (85%), b.p. 140—145°, distils. When boiled, this gives 65% of γ-n-*butylimino-methyl*-Δγ-n-*heptene* (**I**), b.p. 217—220°, hydrolysed by boiling 6N-HCl to $CHPr^a{:}CEt{\cdot}CHO$. Formation of (**I**) occurs by way of $NHBu^a{\cdot}CHPr^a{\cdot}CHEt{\cdot}CH{:}NBu^a$. R. S. C.

Synthesis of *N*-trimethylglycylcholine. T. S. Work (*J.C.S.*, 1941, 190—191).—$Br{\cdot}[CH_2]_2{\cdot}O{\cdot}CO{\cdot}CH_2Br$, or (poor yield) *β-bromoethyl chloroacetate*, b.p. 112—114°/22 mm. (from $CH_2Cl{\cdot}COCl$ and $CH_2Br{\cdot}CH_2{\cdot}OH$ at ≯50°), with NMe_3 in a sealed tube yields the *dibromide*, m.p. 238°, of trimethylglycylcholine [*dipicrate*, m.p. 244°; aurichloride, m.p. ~250° (decomp.); *platinichloride*, m.p. indefinite]. The crude dichloride is similarly obtained from $Cl{\cdot}[CH_2]_2{\cdot}O{\cdot}CO{\cdot}CH_2Cl$. A. Li.

Reduction of fatty acid amides at high pressures. II. Reduction of anilides. S. Ueno, S. Takase, and Y. Tajima (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 58—59B).—Lauric, myristic, or palmitic acid and NH_2Ph at 200° give the corresponding *anilides*, m.p. 75°, 84°, or 87°, respectively, hydrogenated at ~280°/~100—200 atm. for ~3 hr. to *di*-n-*dodecyl*-, m.p. 53°, -*myristyl*-, m.p. 56°, or -*cetyl-amine*, m.p. 64°, respectively. A. T. P.

Ethylenediamine. IV. Monoalkyl derivatives. S. R. Aspinall (*J. Amer. Chem. Soc.*, 1941, **63**, 852—854; cf. A., 1940, II, 289).—70% aq. $(CH_2{\cdot}NH_2)_2$ and EtOAc at room temp. give $NH_2{\cdot}[CH_2]_2{\cdot}NHAc$ (60%) [with a little $(CH_2{\cdot}NHAc)_2$], converted (Schotten–Baumann) into $NHAc{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO_2Ph$, m.p. 103° (lit. 105°), which with RHal and KOH in boiling EtOH gives $SO_2Ph{\cdot}NR{\cdot}[CH_2]_2{\cdot}NHAc$, whence conc. HCl liberates (80% yields) $NH_2{\cdot}[CH_2]_2{\cdot}NHR$. Examples are R = Me, b.p. 115—116°/757 mm. [dipicrate, m.p. 220°; *Bz*$_2$, m.p. 112°, and $(SO_2Ph)_2$ derivative, m.p. 94°], Et, b.p. 129—131°/759 mm. [*dipicrate*, m.p. (anhyd. and + solvent) 195°; *Bz*$_2$, m.p. 120°, and $(p\text{-}C_6H_4Br{\cdot}SO_2)_2$ derivative, m.p. 126°], and CH_2Ph, b.p. 100°/4 mm. [dipicrate, m.p. 222° (decomp.); Bz$_2$, m.p. 188°, and $(p\text{-}C_6H_4Br{\cdot}SO_2)_2$ derivative, m.p. 198°. R. S. C.

Amino-acid constituent of ox brain kephelin.—See A., 1941, III, 343.

Glycyl-*l*-methionine. W. C. Hess and M. X. Sullivan (*J. Amer. Chem. Soc.*, 1941, **63**, 881—882).—*Chloroacetyl*-l-*methionine* (prep. by $CH_2Cl{\cdot}COCl$ in N-NaOH), m.p. 105—107°, and 25% aq. NH_3 at 70° give 57—64% of *glycyl*-l-*methionine*, m.p. 140—145°. R. S. C.

Introduction of substituted vinyl groups. VII. Alkylidene- and substituted vinyl-alkylmalononitriles. A. C. Cope and K. E. Hoyle (*J. Amer. Chem. Soc.*, 1941, **63**, 733—736; cf. A., 1940, II, 85).—With a little piperidine in C_6H_6 (exothermic reaction) or piperidine and AcOH or NH_4OAc–AcOH in boiling C_6H_6 or without other catalyst in AcOH at 100°, *cyclo*hexanone (**I**) and $CH_2(CN)_2$ give cyclo*hexylidenemalononitrile* (**II**), b.p. 137—138°/10 mm., whence O_3 in C_5H_{12} regenerates (**I**). With NH_4OAc–C_6H_6 or piperidine in AcOH, $CH_2(CN)_2$ and the appropriate ketone give *α-ethylpropylidene*- (**III**), b.p. 122—125°/23 mm., *α-methylbutylidene*- (**IV**), b.p. 110—113°/12 mm., and iso*propylidene-malononitrile* (**V**), b.p. 107—108°/23 mm. The cryst. products previously considered to be (**II**) and (**V**) are dimerides. The monomeric products polymerise when boiled or kept with piperidine [(**V**) so rapidly that it cannot be alkylated (see below)], and a dimeride, m.p. 168—170° (softens at 158°), of (**V**) is isolated. Treatment of (**II**), (**III**), or (**IV**) with $NaOPr^\beta$–$Pr^\beta OH$ at 50° and then with EtI, first at 0° and then at the b.p., gives *ethyl*cyclo*hexenyl*-, b.p. 153—154°/20 mm., *ethyl-α-ethylpropenyl*-, b.p. 128—130°/29 mm., and *ethyl-α-methylbutenylmalononitrile*, b.p. 121—124°/24 mm., identified by conversion into the derived barbituric acids. The Na derivative of (**IV**) with EtI, EtBr, or Et_2SO_4 in $Pr^\beta OH$ or EtOH gives the imino-ether, $CHEt{:}CMe{\cdot}CEt(CN){\cdot}C(OEt){:}NH$, b.p. (impure) 142·5—143°/26 mm. R. S. C.

Manufacture of mono- and di-methylformamides.—See B., 1941, II, 107, 108.

Grignard reductions. IX. Reduction of acid halides. F. C. Whitmore, J. S. Whitaker, W. A. Mosher, O. N. Breivik, W. R. Wheeler, C. S. Miner, jun., L. H. Sutherland, R. B. Wagner, T. W. Clapper, C. E. Lewis, A. R. Lux, and A. H. Popkin (*J. Amer. Chem. Soc.*, 1941, **63**, 643—654).—Interaction of RCOCl with MgR′Hal proceeds by independent reactions: (*a*) → CORR′ → CHRR′·OH, and (*b*) RCOCl + MgR′Hal → $MgHal_2$ + RCHO + olefine, followed by RCHO + MgR′Hal → $CH_2R{\cdot}OH$ + MgHal·OH + olefine and RCHO → CHRR′·OH. $CH_2Bu^\gamma{\cdot}CMeBu^\gamma{\cdot}COCl$ with $MgBu^\gamma Cl$ or $CMe_2Et{\cdot}MgCl$ gives ~70% of $CH_2Bu^\gamma{\cdot}CMeBu^\gamma{\cdot}CHO$, but owing to further reaction ≯ traces of other aldehydes are obtained. Free Mg has no effect on the reaction; RCOCl and RCOBr react similarly, but RCOI gives by-products ($CHEt_2{\cdot}COHal$–$MgBu^\gamma Cl$). MgR′Cl, MgR′Br, and MgR′I give similar results. Essentially the same reactions occur whether RCOCl is added to MgR′Hal or vice versa, but in the latter case $CH_2R{\cdot}OH$ is obtained as ester. Lowering the temp. increases slightly the amount of ketone isolated. Et and Bu esters are formed in small amount by interaction of RCOCl with the solvent Et_2O or Bu_2O in presence of $MgCl_2$. Some RCO_2CHRR' is also formed. Increasing the concn. of MgR′Hal slightly increases the yield of $CH_2R{\cdot}OH$ ($MgBu^\gamma Cl$–$CHEt_2{\cdot}COCl$). Reduction to $CH_2R{\cdot}OH$ is best obtained by adding RCOCl gradually with stirring to 2—3 mols. of MgR′Hal. Branching or larger size of R or R′ greatly increases the amount of reduction. RCO_2Na is not reduced by $CMe_2Et{\cdot}MgCl$ (a good reducing agent) in Et_2O. Addition of $CHEt_2{\cdot}COCl$ (134·5) to $MgBu^\gamma Cl$ gives $CHEt_2{\cdot}CHBu^\gamma{\cdot}OH$ (**I**) (88·3), b.p. 131—132°/150 mm. (*α-naphthylurethane*, m.p. 101—102°), $CHEt_2{\cdot}CH_2{\cdot}OH$ (**II**) (21·7), b.p. 103°/150 mm., and C_2Me_6 (21·7 g.). $CHEt_2{\cdot}CHO$ and $MgBu^\gamma Cl$ in Et_2O give (**I**) and a little (**II**). $CHEt_2{\cdot}COBu^\gamma$ [prepared from (**I**) by $K_2Cr_2O_7$], b.p. 120·5—121°/150 mm., and $MgBu^\gamma Cl$ in boiling Et_2O (not at 25°) give 38% of (**I**). Addition of $CHEtBu^a{\cdot}COCl$ to $MgBu^\gamma Cl$ gives 64% of $CHEtBu^a{\cdot}CHBu^\gamma{\cdot}OH$ (**III**), b.p. 105°/17 mm. (*phenylurethane*, m.p. 96—97°), and 29·6% of $CHEtBu^a{\cdot}CH_2{\cdot}OH$ (**IV**), b.p. 133—134°/150 mm. [oxidised by CrO_3 to $CHEtBu^a{\cdot}CO_2H$ (anilide, m.p. 88·5—89·5°)]. The acetate, b.p. 170°/150 mm., of (**III**) at 480—500° gives $CEtBu^a{:}CHBu^\gamma$, oxidised by O_3 to $Bu^\gamma CHO$ and $COEtBu^a$. Addition of $CHEtBu^a{\cdot}COCl$ to $MgBu^\gamma Cl$ and MgI_2 gives 42·8% of (**III**) and 19·3% of (**IV**). Addition of $Bu^\gamma COCl$ to $MgBu^\beta I$ gives 74% of $CH_2Bu^\gamma{\cdot}OH$, and of $CH_2Bu^\gamma{\cdot}COCl$, b.p. 94°/100 mm., to $MgBu^\gamma Cl$ gives 67% of $Bu^\gamma{\cdot}[CH_2]_2{\cdot}CHBu^\gamma{\cdot}OH$ (**V**), m.p. 58—59° [acetate, b.p. 152°/150 mm.; proof of structure as for (**III**)], and 13·5% of $Bu^\gamma{\cdot}[CH_2]_3{\cdot}OH$. Addition of $MgBu^\gamma Cl$ to (*a*) Pr^aCOCl or (*b*) $Pr^\beta COCl$ gives (*a*) 21% of $COPr^aBu^\gamma$, 11·6% of $Bu^aCO_2Bu^a$, and 36·8% of $Pr^aCO_2CHPr^aBu^\gamma$, and (*b*) 45% of $Pr^\beta CO_2CHPr^\beta Bu^a$, b.p. 131°/100 mm., 19% of $Pr^\beta CO_2Bu^\beta$, and 17·7% of $COPr^\beta Bu^\gamma$. Addition of $Bu^\gamma COCl$ to $CH_2Bu^\gamma{\cdot}MgCl$ gives 87% of $Bu^\gamma{\cdot}[CH_2]_2{\cdot}COBu^\gamma$, b.p. 108—110°/150 mm. [reduced by $Al(OPr^\beta)_3$ to (**V**) (cf. lit.)], and a trace of $CH_2Bu^\gamma{\cdot}OH$. With (*a*) $MgBu^\gamma Cl$ or (*b*) $CMe_2Et{\cdot}MgCl$, $COMePr^\beta$ gives (*a*) $CHMePr^\beta{\cdot}OH$ (29%) and $COPr^\beta{\cdot}CH_2{\cdot}CMePr^\beta{\cdot}OH$ (**VI**)

(18%) (semicarbazone, m.p. 116°), *iso*-C_4H_{10} (63·6%) and -C_4H_8 (34·6%) with recovered $COMePr^\beta$ (46%) and C_2Me_6 (trace), and (*b*) $CHMePr^\beta$·OH (49%), $COPr^\beta$·CH:$CMePr^\beta$ (**VII**) (35·6%), $COMePr^\beta$ (2%), and no gas. Dehydration of (**VI**) by boiling with I gives (**VII**), which with O_3 gives $COMePr^\beta$ and (?) $Pr^\beta CO$·CHO. $CHEt_2$·CHBu$^\gamma$·OH, b.p. 123—124°/100 mm., gives the acetate, b.p. 90°/16 mm., and thence at 490—520° 70% of $CHEt_2$:CHBu$^\gamma$, b.p. 99°/20 mm., which with O_3 gives Bu$^\gamma$CHO and $COEt_2$. With MgBu$^\gamma$Cl, (*a*) $(CH_2Bu^\gamma)_2CH$·COCl, (*b*) *n*-$C_{11}H_{23}$·COCl, and (*c*) CH_2Bu^γ·CMeBu$^\gamma$·COCl give (*a*) $(CH_2Bu^\gamma)_2CH$·CH_2·OH (60%), m.p. 44°, b.p. 108°/17 mm. (3 : 5-dinitrobenzoate, m.p. 101—102°), and $(CH_2Bu^\gamma)_2CBu^\gamma$·OH (17%), b.p. 97—101°/5 mm. (3 : 5-*dinitrobenzoate*, m.p. 96—97°), (*b*) *n*-$C_{11}H_{23}$·CHBu$^\gamma$·OH (67%), b.p. 149°/7 mm. [3 : 5-dinitrobenzoate, m.p. 64°; oxidised to *n*-$C_{11}H_{23}$·COBu$^\gamma$, b.p. 155°/20 mm. (*semicarbazone*, m.p. 79°)], *n*-$C_{12}H_{25}$·OH (13·7%), and *n*-$C_{11}H_{23}$·CO_2CHBu$^\gamma$·$C_{11}H_{23}$-*n* (10·4%), m.p. 69—70°, and (*c*) CH_2Bu^γ·CMeBu$^\gamma$·CHO (62·5%), b.p. 101—104°/14 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 153°; oxidation by CrO_3 or air (less rapidly than that of PhCHO) gives the acid, m.p. 128°], and CH_2Bu^γ·CMeBu$^\gamma$·CH_2·OH (19·7%), b.p. 113—114°/16 mm. Addition of Pr^βCHO to CMe_2Et·MgCl gives 84% of Bu^βOH, and of CMe_2Et·MgCl to Pr^βCOCl gives 44% of $Pr^\beta CO_2Bu^\beta$. By addition to CMe_2Et·MgCl, $CHEt_2$·COCl gives $CHEt_2$·CH_2·OH (**VIII**) (74·5%) and $CHEt_2$·CH(OH)·CMe_2Et (**IX**) (7·8%), b.p. 150—152°/150 mm. (*phenylurethane*, m.p. 71—72°; α-naphthylurethane, m.p. 85°), $CHEtBu^\alpha$·COCl gives $CHEtBu^\alpha$·OH (74·5%), b.p. 82°/20 mm., and $CHEtBu^\alpha$·CH(OH)·CMe_2Et (15·7%), b.p. 125—137°/25 mm. (*phenylurethane*, m.p. 91—92°), $CHEt_2$·CHO gives (**VIII**) (67%) and (**IX**) (21%), Bu$^\gamma$COCl gives CH_2Bu^γ·OH (97·5%), *n*-$C_{11}H_{23}$·COCl gives *n*-$C_{12}H_{25}$·OH (54·8%) and *n*-$C_{11}H_{23}$·CH(OH)·CMe_2Et, b.p. 190°/25 mm. (phenylurethane, m.p. 150—151°), CH_2Bu^γ·CMeBu$^\gamma$·COCl gives CH_2Bu^γ·CMeBu$^\gamma$·CHO (**X**) (78%) and CH_2Bu^γ·CMeBu$^\gamma$·CH_2·OH (19%) [90% obtained from (**X**)], CHPh:CH·CHO gives only CMe_2Et·CHPh·CH_2·CHO (10%), b.p. 160—165°/24 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 130—131°), and mesityl oxide (**XI**) gives COMe·CH_2·CMe_2·CMe_2Et (**XII**) (16·2%), b.p. 118—120°/35 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 114°), a C_{11}-diene (8·3%), b.p. 75°/35 mm., $COMeBu^\beta$ (4%), and a trace of CMe_2:CH·CHMe·OH. (**XII**) yields $CHBr_3$ and CMe_2Et·CMe_2·CH_2·CO_2H, m.p. 41—42° (*anilide*, m.p. 153°). With MgBu$^\gamma$Cl in Bu_2O, AcCl gives CHMeBu$^\gamma$·OAc (11%), COMeBu$^\gamma$ (10%), Bu^αOAc (2%), (**XI**) (5%), and C_2Me_6. With CMe_2Et·MgCl in Et_2O, AcCl gives CMe_2:CMe·COMe (9%), b.p. 73—83°/56 mm. (semicarbazone, m.p. 185·5—187·5°), COMe·CMe_2Et (9%), and EtOAc (4%). CH_2Bu^γ·CHMe·COCl and MgBu$^\gamma$Cl give CH_2Bu^γ·CHMe·CHBu$^\gamma$·OH (67%), b.p. 102—106°/22 mm. [3 : 5-*dinitrobenzoate*; with CrO_3–AcOH gives (?) CH_2Bu^γ·CHMe·COBu$^\gamma$ (51%), b.p. 87—90°/16—18 mm., and 10% of CH_2Bu^γ·CHMe·CO_2H (10%)], and CH_2Bu^γ·CHMe·CH_2·OH (21%), b.p. 78—80°/22 mm. (3 : 5-*dinitrobenzoate*, m.p. 72·5—73·5°; α-naphthylurethane, m.p. 70°; also obtained from CH_2Bu^γ·CHMe·CO_2Et by Na–PhMe–EtOH and from CH_2Bu^γ·CHMe·MgCl by CH_2O). Addition of CH_2Ph·COCl to MgBu$^\gamma$Cl gives CH_2Ph·CHBu$^\gamma$·OH (14·9%), b.p. 128°/20 mm. (*phenylurethane*, m.p. 82·5—85·5°), CH_2Ph·CO_2CHBu$^\gamma$·CH_2Ph (20%), and Ph·$[CH_2]_2$·OH (9·2%), but $CHPh_2$·COCl gives 67·5% of $CHPh_2$·CH_2·OH. CH_2Bu^γ·COCl and MgBu$^\gamma$Cl give 48·5% of CH_2Bu^γ·CHBu$^\gamma$·OH and 5% of CH_2Bu^γ·OH. Bu$^\gamma$COCl and CH_2Bu^γ·COCl with MgBu$^\gamma$Cl give ~1% of RCHO. CEt_3·COCl with MgBu$^\gamma$Cl gives 89·5% of CEt_3·CH_2·OH, b.p. 75°/13 mm. (α-naphthylurethane, m.p. 133—134°); CBu^α_3·COCl, b.p. 137—138°/12 mm., gives CBu^α_3·CH_2·OH (88·5%), b.p. 114—118°/3 mm. (phenylurethane, m.p. 77°). R. S. C.

II.—HOMOCYCLIC.

Synthesis of multi*cyclo*pentyls. G. E. Goheen (*J. Amer. Chem. Soc.*, 1941, **63**, 744—749).—*cyclo*Pentanol (prep. from the ketone in 94% yield by H_2–Raney Ni at 60—80°/1000—1600 lb.) and PBr_3 at 0° give the bromide (**I**), b.p. 136·7—137·7°. 1-Chloro-Δ^2-*cyclo*pentene (**II**) (prep. from the diene by dry HCl at −25°), b.p. 25—29°, and the Grignard reagent from (**I**) give 1-*cyclo*pentyl-Δ^2-*cyclo*pentene (**III**) (73·2%), b.p. 185—186°, which with fuming HBr at room temp. gives 3-*bromodi*cyclo*pentyl* (**IV**) (89·3%), b.p. 96°/1 mm., and with H_2–Raney Ni in EtOH at 100°/1800—1900 lb. gives di*cyclo*pentyl (62%), b.p. 190—190·5°/761·8 mm. The Grignard reagent from (**IV**) with (**II**) in Et_2O at 0° gives 44% of (**III**), 30% of 3-$\Delta^{2'}$-cyclo*pentenyldi*cyclo*pentyl* (**V**), b.p. 140—141°/10 mm., and 14% of 3 : 3′-di(*cyclo*pentyl)di*cyclo*pentyl (**VI**), b.p. 183—185°/3 mm., 369—370°/761 mm. Addition of NaOEt–EtOH to *cyclo*pentanone at room temp. gives 36% of 2-*cyclo*pentylidene-, b.p. 102—103°/5 mm., and 46·3% of 2 : 5-di-(*cyclo*pentylidene)-*cyclo*pentanone (**VII**), m.p. 82°. H_2–Raney Ni in EtOH at 160—170°/1500 lb. converts (**VII**) into 1 : 3-di(*cyclo*pentyl)*cyclo*pentanol (87%), m.p. 68—69° [at 70—90° di(*cyclo*pentyl)*cyclo*pentanone is obtained], which with $ZnCl_2$ gives 1 : 3-*di*(cyclo*pentyl*)Δ^1-cyclo*pentene* (79·5%), b.p. 125—127°/1 mm., 300—301°/760 mm., reduced by H_2–Raney Ni in *iso*-C_6H_{14} at 135—140°/2200—2300 lb. to 3-cyclo*pentyldi*cyclo*pentyl* (**VIII**), b.p. 147—148°/12 mm., 296—297°/761 mm. An *isomeride*, b.p. 158°/16 mm., 293—294°/760 mm., of (**VIII**) is obtained by similar reduction of (**V**). (**VI**) is also obtained from the Grignard reagent of (**IV**) by AgBr. Physical consts. of the polycyclic hydrocarbons are recorded and discussed. R. S. C.

Determination of carotene in presence of lycopene.—See A., 1941, III, 407.

Palm oil carotenoids. I. Lipoid pigments from "Sherbro" palm oil.—See A., 1941, III, 315.

Copper [benzene] hydrogenation catalysts.—See A., 1941, I, 215.

Hydrogen fluoride as a condensing agent. XIV. Alkylation. J. H. Simons and G. C. Bassler (*J. Amer. Chem. Soc.*, 1941, **63**, 880—881; cf. A., 1941, II, 125).—Yields obtained from C_6H_6 and (*a*) CMe_2EtF, (*b*) C_5H_{10}–HF, or (*c*) C_5H_{10}–CMe_2EtF–HF, and from PhMe and *cyclo*hexene, *cyclo*hexanol, *cyclo*hexyl fluoride, chloride, bromide, or iodide in HF show that an aliphatic fluoride does not react in absence of HF, that olefines react at least as readily as do fluorides, that increase in the at. wt. of the halogen decreases the yield, and that alcohols react very readily. R. S. C.

Styrene substitutes and their polymerides. I. Methylstyrene and its polymeride. E. Matsui (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 88—89B).—$(CH_2)_2O$–PhMe–$AlCl_3$ at ~10° afford β-*p*-tolylethyl alcohol, b.p. 231—232°/766 mm., 112—115°/8·5 mm., dehydrated by 10% KOH to *p*-methylstyrene, b.p. 67·5—68·5°/28 mm. Polymerides of the latter, hardened at 165—170° without catalyst for 11—30 hr., show little difference from polystyrene in appearance, although they are somewhat brittle. A. T. P.

Synthesis of *m*-di-β-phenylethylbenzene and its relationship to carcinogenic hydrocarbons. K. Sisido (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 55—56B).—*m*-$C_6H_4(CH_2Br)_2$, CH_2PhCl, and Na refluxed in PhMe afford *m*-di-β-phenylethylbenzene, m.p. 56°. A. T. P.

Action of aluminium chloride on β-phenylethyl chloride. K. Sisido and S. Kato (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 450—451B).—The action of $AlCl_3$ on Ph·$[CH_2]_2$·Cl (**I**) in CS_2 at 0° and subsequently at room temp. gives a red-violet elastic mass, m.p. >300°. Without solvent at 60—70° the product is a colourless, brittle mass, m.p. >300°. Both products are oxidised by $K_2Cr_2O_7$ and H_2SO_4 to *p*-$C_6H_4(CO_2H)_2$ suggesting the presence of long, linear chain mols. without branching or net formation. H. W.

Catalytic dehydrogenation of tetrahydronaphthalene and 1 : 2 : 3 : 4-tetrahydro-2-naphthol in the liquid phase. H. Adkins and W. A. Reid (*J. Amer. Chem. Soc.*, 1941, **63**, 741—744).—Liquid-phase dehydrogenation of tetrahydronaphthalene (**I**) (best prepared by H_2–Cu chromite ar 200°/150—200 atm.) by Raney Ni at 350°/30—60 atm. (N_2) gives 78% of $C_{10}H_8$; at 300° a 35 : 25 : 40 equilibrium mixture of (**I**), dihydronaphthalene, and $C_{10}H_8$ is set up. (**I**) is stable in presence of Cu chromite at 350°. 1 : 2 : 3 : 4-Tetrahydro-2-naphthol (similarly prepared) is dehydrogenated by Raney Ni at 250°, giving mainly $C_{10}H_8$, and in presence of Cu chromite at 300° gives 70% of β-$C_{10}H_7$·OH and >1% of $C_{10}H_8$. C_2H_4 polymerises in steel at 350° giving products of b.p. >112°/2 mm., and decomposes in presence of Raney Ni at 300—350°; it is thus useless as H acceptor for the above dehydrogenations. R. S. C.

7-Methylcholanthrene and 5 : 1′-dimethyl-1 : 2-benzanthracene. W. E. Bachmann and S. R. Safir (*J. Amer. Chem. Soc.*, 1941, **63**, 855—857).—5-Keto-1′-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene (**I**) and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give the 5-*OH*-compound (93%), m.p. 128·5—129°, which with HCl–$CaCl_2$–C_6H_6 at 5° gives the chloride, m.p. 127—127·5°, whence condensation with $CHNa(CO_2Et)_2$ in EtOH–C_6H_6 at, successively, room temp., 60°, and the b.p., followed by hydrolysis (KOH) and decarboxylation (190°), gives 1′-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*-5-*acetic acid*, m.p. 145—145·5°. The derived (PCl_5–C_6H_6) chloride with $SnCl_4$–C_6H_6 at ~15° gives 97% of 1-*keto*-7-*methyl*-2a : 3 : 4 : 5-*tetrahydrocholanthrene*, m.p. 193·5—194°, reduced (Zn–Hg–PhMe–HCl–AcOH) to 7′-*methyl*-2a : 3 : 4 : 5-*tetrahydrocholanthrene* (99%), m.p. 90—98°, which with Pd–C–N_2 at 310° gives 7-*methylcholanthrene*, m.p. 147—148° (vac.; preheated at 135°) [*picrate*, m.p. 151—152° (vac.; preheated at 135°)]. MgMeI and (**I**) in Et_2O–C_6H_6 at 0° give an oily carbinol, which with Pd–C–N_2 at 310° gives 5 : 1′-*dimethyl*-1 : 2-*benzanthracene*, m.p. 106—107° [*picrate*, m.p. 150—150·5° (vac.)]. R. S. C.

***sec.* and *tert.* Amines from nitro-compounds.** W. S. Emerson and C. A. Uraneck (*J. Amer. Chem. Soc.*, 1941, **63**, 749—751).—Hydrogenation of $PhNO_2$ (1 mol.) and Pr^aCHO (1 mol.) in presence of a little $NHMe_3Cl$ and Raney Ni in 95% EtOH gives 63% of $NPhBu^a_2$; 69% is obtained from a 1 : 3 mixture in presence of AcOH and PtO_2 in 95% EtOH. By the latter method, $NPhEt_2$ (70%), $NPhPr^a_2$ (34%), and α-$C_{10}H_7$·NEt_2 (40%), b.p. 155—165°/30 mm. (*picrate*, m.p. 152—154°), and (from $MeNO_2$) $NMeEt_2$ (92%), $NMeBu^a_2$ (56%), b.p. 155—163° (*hydrochloride*, m.p. 131—131·5°; *picrate*, m.p. 86—87·5°), and $NMePr^a_2$ (45%), b.p. 110—122° (*picrate*, m.p. 92—93°), are obtained. Ketones give *sec.* amines, *e.g.*, $NHPhPr^{\beta}$ (53%) and $NHMePr^{\beta}$ (59%) from $COMe_2$ with $PhNO_2$ and $MeNO_2$, respectively. The reaction mechanism is probably: $RNO_2 \rightarrow {}^+NH_2R{\cdot}OH$ (+R′CHO) → $OH{\cdot}{}^+NHR{\cdot}CHR'{\cdot}OH \rightarrow OH{\cdot}N^+{:}CHR' \rightarrow OH{\cdot}N^+HR{\cdot}CH_2R'$ (+R′CHO) → $OH{\cdot}CHR'{\cdot}N^+R(OH){\cdot}CH_2R' \rightarrow {}^+NHR(CH_2R')_2$. In conformity therewith, $CH_2Ph{\cdot}NPh{\cdot}OH$ and Pr^aCHO (2 mols.) give 38% of $NPhBu^a{\cdot}CH_2Ph$, whereas only 3% thereof is obtained from $NHPh{\cdot}CH_2Ph$. R. S. C.

***sec.* and *tert.* Amines from azo-compounds.** W. S. Emerson, S. K. Reed, and R. R. Merner (*J. Amer. Chem. Soc.*, 1941, **63**, 751—752).—$(NPh{:})_2$ (1 mol.), RCHO (2·5 mols.), NaOAc, and H_2 (3—4 mols. absorbed)–Raney Ni in EtOH at 45 lb. give $NHPh{\cdot}CH_2R$, amines in which R = Pr^a (71%), *n*-hexyl (74%), and Ph (49%) being obtained. If $(NPh{:})_2$ carries an *o*- or *p*-activating group (OH, NMe_2), *tert.* amines are formed. Thus, *p*-$NMe_2{\cdot}C_6H_4{\cdot}N{:}NPh$ and Pr^aCHO give *p*-$NMe_2{\cdot}C_6H_4{\cdot}NBu^a_2$ (76%), b.p. 150—175°/20 mm. (*picrate*, m.p. 121—122°), and $NHPhBu^a$ (73%), *p*-$OH{\cdot}C_6H_4{\cdot}N{:}NPh$ gives *p*-$OH{\cdot}C_6H_4{\cdot}NBu^a_2$ (46%) (*benzoate*, m.p. 232—233°), and 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}N{:}NPh$ gives 1-*NN*-di-*n*-butylamino-β-naphthol (41%), unstable, m.p. 106—107° (*hydrochloride*, m.p. 225—227°). $(NHPh)_2$ is probably formed as intermediate. R. S. C.

Sulphonamide [derivatives]. II. Diphenyl derivatives. A. Novelli and J. C. Somaglino (*J. Amer. Chem. Soc.*, 1941, **63**, 854—855).—*p*′-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$-*p* and Sn–HCl at ≯55° give the *p*′-NH_2-compound, m.p. 262—263° (decomp.). 4′-*Nitrodiphenyl*-4-*sulphonanilide*, m.p. 182—183°, gives similarly the 4′-NH_2-*anilide*, m.p. 182—183°. R. S. C.

Abnormal reaction in the Sommelet aldehyde synthesis. R. C. Fuson and J. J. Denton (*J. Amer. Chem. Soc.*, 1941, **63**, 654—656).—2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH_2Cl$ (**I**) and $(CH_2)_6N_4$ in boiling $CHCl_3$ give the impure *salt*, $C_{16}H_{25}N_4Cl$, decomposed by boiling H_2O to NN′-*di*-(2 : 4 : 6-*trimethylbenzyl*)*methylenediamine* (**II**), m.p. 151·5—152°, and by boiling HCl–EtOH to 2 : 4 : 6-*trimethylbenzylamine hydrochloride* (**III**), m.p. 315° (decomp.). In boiling aq. HCl, (**II**) gives CH_2O and (**III**); in boiling AcCl and in BzCl at 120—150°, *acet*-, m.p. 186·5—187°, and *benz*-2 : 4 : 6-*trimethylbenzylamide*, m.p. 153·5—154°, respectively, are formed. With boiling aq. CH_2O and later boiling aq. NH_3–CH_2O, (**III**) gives (**II**). 2 : 4 : 6 : 1-$C_6H_2Me_3Br$ and CuCN in C_5H_5N at 220—230° give 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CN$, m.p. 50—52°, which with H_2–Raney Ni in EtOH at 150°/2200 lb. followed by HCl gives (**III**). *o*-$C_6H_4(CO)_2NK$ and (**I**) at 170—180° give *phthal*-2′ : 4′ : 6′-*trimethylbenzylimide*, m.p. 209·5—210°, hydrolysed to (**III**) (as hydrobromide) by boiling HBr–Ac_2O–AcOH. R. S. C.

***cis*-Azo-compounds. IV. Reactions with diphenylketen.** A. H. Cook and D. G. Jones (*J.C.S.*, 1941, 184—187).—*cis*-$(NPh{:})_2$ reacts rapidly with $CPh_2{:}CO$ (**I**) in light petroleum at room temp. to give 4-*keto*-1 : 2 : 3 : 3-*tetraphenyldimethylene*-1 : 2-*di-imine* (**II**), m.p. 175°, also obtained (more conveniently) by irradiation of a mixture of *trans*-$(NPh{:})_2$ and (**I**) in light petroleum, and (in small yield) from *trans*-$(NPh{:})_2$ and (**I**) at 125—130°/42 hr. in CO_2. Boiling 10% MeOH–NaOMe and (**II**) give *trans*-$(NPh{:})_2$; decomp. of (**II**) at 190° gives this and $NPh{:}CPh_2$. (**I**) when irradiated with the *trans*-azo-compounds, or, in the first two cases, when treated with the *cis*-azo-compounds in light petroleum, similarly yields 4-*keto*-3 : 3-*diphenyl*-1 : 2-*di*-m-*tolyl*-, m.p. 118°, -p-*tolyl*-, m.p. 172°, -o-*tolyl*-, m.p. 162°, and -β-*naphthyl-dimethylene*-1 : 2-*di-imine*, m.p. 222°. *p*-$NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$ with (**I**) in C_6H_6 or with $CHPh_2{\cdot}COCl$ yields p-*diphenylacetamidoazobenzene*, m.p. 194°. *cis*- or (more slowly) *trans*-*p*-$C_6H_4Cl{\cdot}N_2{\cdot}CN$ with (**I**) in light petroleum yields 4-*keto*-1-*cyano*-2-p-*chlorophenyl*-3 : 3-*diphenyldimethylene*-1 : 2-*di-imine*, m.p. 121° (on one occasion the *cis*-cyanide afforded an isomeride, m.p. 266°), hydrolysed (aq. EtOH–NaOH) to α-β′-*cyano*-α′-p-*chlorophenylhydrazinodiphenylacetic acid*, m.p. 288° (decomp.). A. Lt.

Positional influence of chlorine and of the nitro-group on colour of azo-dyes. Colorimetric evidence for the mesomeric and inductive effects.—See B., 1941, II, 138.

Catalytic decomposition of phenylhydrazine in presence of uracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 761).—Uracil, thymine, and 4-methyluracil are unchanged in boiling $NHPh{\cdot}NH_2$, which is catalytically decomposed into NH_2Ph, C_6H_6, NH_3, and N_2. R. S. C.

Synthesis of phenol by partial-pressure evaporation.—See B., 1941, II, 135.

Alkylnitrophenols. W. H. Hartung and H. F. Koehler (*J. Amer. Chem. Soc.*, 1941, **63**, 872—873).—Condensation of PhOH with *sec.*-$C_6H_{13}{\cdot}OH$ and *tert.*-$C_5H_{17}{\cdot}OH$ by $ZnCl_2$ and treatment of the product in C_6H_6 with 1 : 1-HNO_3–H_2O at <5° gives x-*nitro*-y-sec.-*hexyl*-, b.p. 165—185°/2 mm., and -y-tert.-*octyl-phenol*, b.p. 157—168°/1 mm. Neither product is fungicidal. The product of nitration of *sec.*-hexyl-*m*-cresol decomposes when distilled. R. S. C.

Compounds related to natural œstrogens; γ-*cyclo*pentyl- and γ-2-methyl*cyclo*pentyl-δ-*p*-hydroxyphenyl-Δγ-hexene. H. Minlon (*Contr. Biol. Lab. Sci. Soc. China*, 1940, **15**, 17—27).—*cyclo*Pentyl bromide and $CNaEt(CO_2Et)_2$ in PhMe give Et_2 *cyclo*pentylethylmalonate, b.p. 146—152°/17 mm.; the free *acid*, m.p. 168—169°, when heated at 160—180° under reduced pressure affords α-*cyclo*pentylbutyric acid (**I**), b.p. 136—139°/15 mm. The chloride, b.p. 97—99°/15 mm., of (**I**) and PhOMe–$AlCl_3$–CS_2 at room temp. afford p-*methoxy*-α-*cyclo*pentylbutyrophenone, b.p. 132—133°/0·09 mm., which with MgEtBr yields δ-*cyclo*pentyl-γ-*p*-anisylhexan-γ-ol, b.p. 139—143°/0·5 mm., converted by PBr_3–$CHCl_3$ at 0° and then at room temp. into γ-*cyclo*pentyl-δ-p-*anisyl*-Δγ-*hexene*, b.p. 123—125°/0·3 mm., and thence (KOH–EtOH at 200°) into γ-*cyclo*pentyl-δ-p-*hydroxyphenyl*-Δγ-*hexene*, b.p. 127—129°/0·17 mm. 2-Methyl*cyclo*pentanone and $CHBrEt{\cdot}CO_2Et$–Zn–C_6H_6 afford Et α-(1-hydroxy-2-methyl*cyclo*pentyl)butyrate, b.p. 122—130°/16 mm., dehydrated by $SOCl_2$–C_5H_5N and then hydrolysed by 10% KOH–EtOH to α-(2-methyl-Δ¹-*cyclo*pentenyl)butyric acid, b.p. 148—152°/18 mm., hydrogenated (Pd; $COMe_2$) at room temp. and pressure to α-(2-*methyl*cyclo*pentyl*)*butyric acid*, b.p. 139—141°/16 mm. The chloride, b.p. 98—100°/16 mm., of the latter is converted into p-*methoxy*-α-2-*methyl*cyclo*pentylbutyrophenone*, b.p. 142—145°/0·12 mm., and thence (by MgEtBr) into the carbinol, b.p. 145—149°/0·3 mm., and (PBr_3) γ-2-*methyl*cyclo*pentyl*-δ-p-*anisyl*-Δγ-*hexene*, b.p. 124—127°/0·17 mm., demethylated to the corresponding p-*OH*-compound, b.p. 132—134°/0·1 mm. *p*-$OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ (**II**) and MgEtBr yield β-keto-α-*p*-anisylbutan-α-ol, b.p. 173—175°/16 mm., converted by MgEtBr into α-*p*-anisyl-β-ethylbutane-αβ-diol, m.p. 78—79°, and thence (H_2SO_4) δ-*p*-anisylhexan-γ-one (*semicarbazone*, m.p. 131—132°; *oxime*, m.p. 114—115°), which does not react with Mg *cyclo*pentyl bromide (**III**). (**II**) and (**III**) afford cyclo*pentyl* α-*hydroxy*-p-*methoxybenzyl ketone*, m.p. 71—72° (*semicarbazone*, m.p. 162—163°), reduced by $SnCl_2$–HCl–EtOH at 100° (bath) to *cyclo*pentyl *p*-methoxybenzyl ketone,

m.p. 54—55° (*semicarbazone*, m.p. 151—152°), which could not be ethylated. A. T. P.

2-Methyl-1 : 4-naphthaquinol hydrogen succinate. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1941, **63**, 882).—2-Methyl-1 : 4-naphthaquinol (1 mol.) and $(CH_2{\cdot}CO)_2O$ (4 mols.) at 140° give the (mono-)*H succinate*, m.p. 176—178°, showing vitamin-*K* activity in doses of 2 μg. R. S. C.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1941, III, 132.

Synthesis of unsaturated substances from β-ionone and substituted vinylacetylenes. A. F. Thompson, jun., N. A. Milas, and I. Rovno (*J. Amer. Chem. Soc.*, 1941, **63**, 752—755).—Addition of β-ionone (**I**) to $CH_2{:}CH{\cdot}C{:}C{\cdot}MgBr$ in boiling Et_2O gives 59% of α-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-γ-*methyl*-$\Delta^{\alpha\zeta}$-n-*heptadien*-Δ^δ-*inen*-γ-*ol* (**II**), b.p. 155—160°/2 mm., obtained also in 11—20% yield from $CH_2{:}CH{\cdot}C{:}CH$ and (**I**) by $CMe_2Et{\cdot}OK$–$CMe_2Et{\cdot}OH$ at −10°. With tetrahydroionone both methods give 80% of η-2 : 6 : 6-*trimethyl*cyclo*hexyl*-ε-*methyl*-Δ^α-*hepten*-Δ^γ-*inen*-ε-*ol* (**III**), b.p. 155—160°/2 mm. H_2–Pd–$CaCO_3$ reduces (**II**) and (**III**) in abs. EtOH to α-2 : 6 : 6-trimethyl-Δ^1-*cyclo*hexenyl-γ-methyl-$\Delta^{\alpha\delta\zeta}$-heptatrien-γ-ol (**IV**), b.p. 155—160°/2 mm., and η-2 : 6 : 6-trimethyl*cyclo*hexyl-ε-methyl-$\Delta^{\alpha\gamma}$-heptadien-ε-ol, b.p. 150—155°/2 mm., respectively, both of which are further hydrogenated (PtO_2) to α-2 : 6 : 6-*trimethyl*cyclo*hexyl*-γ-*methyl*-n-*heptan*-γ-*ol*, b.p. 145—150°/2 mm. $CH{:}C{\cdot}CMe{:}CH_2$ and $CH{:}C{\cdot}CMe{:}CHMe$ give similarly α-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-γζ-*dimethyl*-$\Delta^{\alpha\zeta}$-n-*hepta*-, b.p. 165—170°/2 mm., and -*octa*-*dien*-Δ^δ-*inen*-γ-*ol*, b.p. 170—175°/2 mm., α-2 : 6 : 6-trimethyl-Δ^1-*cyclo*hexenyl-γζ-dimethyl-$\Delta^{\alpha\delta}$-hepta- (**V**), b.p. 165—170°/2 mm., and -octa-trien-γ-ol (**VI**), b.p. 170—175°/2 mm., η-2 : 6 : 6-*trimethyl*cyclo*hexyl*-βε-*dimethyl*-Δ^α-*hepten*-Δ^γ-*inen*-ε-*ol*, b.p. 165—170°/2 mm., θ-2 : 6 : 6-*trimethyl*cyclo*hexyl*-γζ-*dimethyl*-Δ^β-*octen*-Δ^δ-*inen*-ζ-*ol*, b.p. 170—175°/2 mm., η-2 : 6 : 6-trimethyl*cyclo*hexyl-βε-dimethyl-$\Delta^{\alpha\gamma}$-heptadien-ε-ol, b.p. 160—165°/2 mm., θ-2 : 6 : 6-trimethyl*cyclo*hexyl-γζ-dimethyl-$\Delta^{\beta\delta}$-octadien-ζ-ol, b.p. 165—170°/2 mm., α-2 : 6 : 6-*trimethyl*cyclo*hexyl*-γζ-*dimethyl*-n-*heptan*-γ-*ol*, b.p. 155—160°/2 mm., and -*n*-octan-γ-ol, b.p. 160—165°/2 mm. (**IV**), (**V**), and (**VI**) have no vitamin-*A* activity. Attempts to rearrange them to primary alcohols failed. R. S. C.

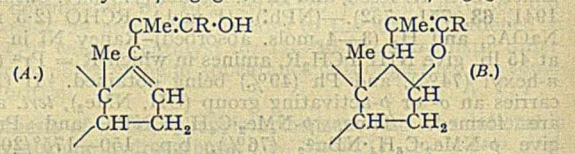
Sponge sterol. A. Mazur (*J. Amer. Chem. Soc.*, 1941, **63**, 883—884).—*Spongila lacustris* yields mixed sterols, whence, by acetylation and adsorption on Al_2O_3, a *sterol*, $C_{29}H_{50}O$, m.p. 136·5—137°, $[\alpha]_D$ −41·8° in $CHCl_3$ (*acetate*, m.p. 137°, $[\alpha]_D$ −47·6° in $CHCl_3$; *benzoate*, m.p. 137·5°, $[\alpha]_D$ −17·1° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 200°, $[\alpha]_D$ −18·3° in $CHCl_3$; hydrogenated to stigmastanol), and another sterol (impure) are obtained. R. S. C.

Lanosterol. II. Oxidation of lanosterol with chromic acid. III. Action of selenium dioxide and of perbenzoic acid on lanosterol. L. J. Bellamy and C. Dorée (*J.C.S.*, 1941, 172—176, 176—181; cf. A., 1936, 1505).—II. Lanosterol (**I**) with CrO_3 in H_2O–AcOH–C_6H_6 at room temp. gives 40% of lanostenone (**II**), and an isomeride, *lanostenone*-B, m.p. 78° (2 : 4-dinitrophenylhydrazone, m.p. 191°; tetrahydrocarbazole derivative, m.p. 178°, from $NHPh{\cdot}NH_2$), reduced (Na + EtOH) to (**I**). (**II**) is reduced (Na + EtOH) to α-dihydrolanosterol, or [$Al(OPr^\beta)_3$ in $Pr^\beta OH$] to lanosterol-*E*, m.p. 143° (*acetate*, m.p. 164°). Vigorous oxidation (CrO_3) of (**I**) gives an acid, $C_{25}H_{46}O_2$, m.p. 81—82° (Et ester, m.p. 64°), unaffected by Br, H_2 (Pd–C), or BzO_2H. Lanosteryl acetate (**III**) with CrO_3–H_2O–AcOH yields the acetate (**IV**), m.p. 164°, $[\alpha]_D^{20}$ +44° in $CHCl_3$, of lanosterol-*D*, m.p. 145°, oxidised [as for (**I**)] to lanostenone-*D*, m.p. 105° (tetrahydrocarbazole derivative, m.p. 128°). Hydrogenation (Pd–C, AcOH) of (**IV**) yields dihydrolanosteryl-*D* acetate, m.p. 218°. (**I**) is unaffected by $Al(OBu^\gamma)_3$ in $COMe_2$.

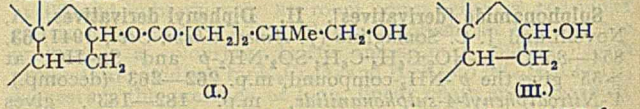
III. (**III**) with SeO_2 in boiling EtOH yields the *monoacetate*, m.p. 110°, of a *diol*, $C_{30}H_{50}O_2$, m.p. 143—144° (*diacetate*, m.p. 132°) (with a small amount of an isomeric *diol*, m.p. 152°). (**III**) must therefore contain a CH_2 group adjacent to the active double linking. α-Dihydrolanosteryl acetate with SeO_2 in boiling AcOH yields the *acetate* (**V**), m.p. 167°, of γ-*lanosterol* (? α-dihydroagnosterol), m.p. 141°, oxidised (CrO_3) to γ-*lanostenone*, m.p. 124° (tetrahydrocarbazole derivative, m.p. 228°). Hydrogenation (Pd–C, AcOH) of (**V**) yields α-dihydrolanosteryl acetate. (**III**) with BzO_2H in $CHCl_3$ at 0° yields an oxide, m.p. 185°, hydrolysed (aq. EtOH–HCl) to *lanostenetriol*, m.p. 130° (*diacetate*, m.p. 104°). (**II**) with BzO_2H affords an *oxide*, m.p. 92°, converted by EtOH–HCl into *dehydrolanostenone*, $C_{30}H_{46}O$, m.p. 126° (tetrahydrocarbazole derivative, m.p. 228°; oxime, m.p. 183°), which is hydrogenated (Pd–C) to α-*iso*dihydroagnostenone, m.p. 124° (tetrahydrocarbazole derivative, m.p. 202°; oxime, m.p. 164°). The significance of these results is discussed; (**I**) is a tetracyclic, doubly unsaturated alcohol probably related to the triterpenes. A. Li.

Sterols. CXIX. Sapogenins. XLVII. Pregnanetriols from ψ-sapogenins. R. E. Marker, D. L. Turner, R. B. Wagner, P. R. Ulshafer, H. M. Crooks, jun., and E. L. Wittle (*J. Amer. Chem. Soc.*, 1941, **63**, 779—782).—ψ-Tigogenin with CrO_3–AcOH at 28° gives (cf. following abstract) a non-cryst. product, converted by H_2–PtO_2–AcOH and subsequent hydrolysis into allo*pregnane*-3(β) : 16 : 20(β)-*triol*, m.p. 286—288°, and by acid or alkali into $CO_2H{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CO_2H$ and Δ^{16}-*allo*pregnene-3 : 20-dione. ψ-Sarsasapogenin and its diacetate or dihydro-ψ-sarsasapogenin diacetate with CrO_3–AcOH at 20—30°, followed by H_2–PtO_2 and then KOH–EtOH, give *pregnane*-3(β) : 16 : 20(β)-*triol*, m.p. 236—240° (*triacetate*, m.p. 145—148°). *epi*-ψ-Sarsasapogenin diacetate gives similarly *pregnane*-3(α) : 16 : 20(β)-*triol*, m.p. 203—206° (*triacetate*, m.p. 175—177°). *epi*-ψ-Tigogenin diacetate gives allo*pregnane*-3(α) : 16 : 20(β)-*triol*, m.p. 263—265° (*triacetate*, m.p. 181°). ψ-Deoxysarsasapogenin acetate or dihydro-ψ-deoxysarsasapogenin gives Δ^{16}-*pregnen*-20-*one*, m.p. 129—131°, identified by hydrogenation (H_2–Pd–$BaSO_4$–EtOH–Et_2O) to pregnan-20-one. Δ^{16}-*allo*Pregnen-3(β)-ol-20-one with $Al(OPr^\beta)_3$–$Pr^\beta OH$ and then 8% KOH–MeOH gives Δ^{16}-allo*pregnene*-3(β) : 20(β)-*diol*, m.p. 188—190° (*diacetate*, m.p. 102—104°), hydrogenated (PtO_2 in Et_2O–MeOH containing a little AcOH; 45 lb.) to *allo*pregnane-3(β) : 20(β)-diol (**I**). Similar reduction of $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one gives $\Delta^{5:16}$-*pregnadiene*-3(β) : 20(β)-*diol*, m.p. 169—171° (*diacetate*, m.p. 121°), hydrogenated to (**I**). R. S. C.

Sterols. CXVII. Sapogenins. XLVI. Structure of ψ-sapogenins. R. E. Marker, D. L. Turner, R. B. Wagner, P. R. Ulshafer, H. M. Crooks, jun., and E. L. Wittle (*J. Amer. Chem. Soc.*, 1941, **63**, 774—777).—ψ-Sapogenins probably exist in tautomeric forms (*A*) and (*B*), the former accounting for formation of diketo-acids and certain other oxidations, and the latter accounting for the following reactions. Diacetates of dihydro-ψ-tigogenin at 30° and of ψ-tigogenin at



15° with CrO_3–AcOH give the same *product* (**I**), $C_{31}H_{48}O_7$, m.p. 102—104°, converted (hydrolysis and dehydration) by boiling 2% KOH–EtOH, K_2CO_3–EtOH, or 10% HCl–EtOH into Δ^{16}-*allo*pregnen-3(β)-ol-20-one, by Na–$Pr^\beta OH$ into *allo*pregnane-3(β) : 20(α)-diol (**II**), by CrO_3 in 90% AcOH at



25° into 3-hydroxyætio*allo*bilianic acid, and by $Al(OPr^\beta)_3$–$Pr^\beta OH$ or H_2–PtO_2–AcOH at 70°/30 lb. (later hydrolysis by 2% KOH–EtOH) into an allo*pregnane*-3 : 16 : 20-*triol* (**III**), m.p. 285—288° (*triacetate*, m.p. 161—163°). ψ-Diosgenin diacetate and CrO_3–AcOH at 15° (no protection of the C:C) give similarly a *product*, $C_{31}H_{46}O_7$, m.p. 84—86°, and thence by acid or alkali $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one, by Na–$Pr^\beta OH$ a product converted by H_2–PtO_2–AcOH into (**II**), by H_2–PtO_2 in Et_2O at 30 lb. into (**I**), by H_2–PtO_2 in AcOH at 70°/45 lb. into (**III**), and by $Al(OPr^\beta)_3$–$Pr^\beta OH$ followed by hydrolysis (2% MeOH–KOH) into a Δ^5-*pregnene*-3 : 16 : 20-*triol*, m.p. 281—285° (*triacetate*, m.p. 143°), which with H_2–PtO_2–AcOH also gives (**III**). R. S. C.

Alkamine esters of di*cyclo*hexylacetic and related acids.—See B., 1941, III, 133.

Preparation of benzoic acid of high purity. F. W. Schwab and E. Wichers (*J. Res. Nat. Bur. Stand.*, 1940, **25**, 747—

757).—Fractional distillation in a vac., recrystallisation from H_2O or pure C_6H_6, fractional freezing, oxidation of purified PhMe followed by recrystallisation from H_2O, and hydrolysis of purified BzCl have been compared as methods for producing pure BzOH. Eight recrystallisations from C_6H_6, fractional freezing, and hydrolysis of BzCl each yield products of purity $\nless$99·999%. The f.p. of pure BzOH is assigned tentatively as 122·36±0·01°. J. W. S.

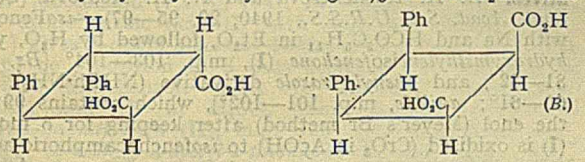
Hippuric acid derivatives.—See B., 1941, III, 133.

Preparation of lower monoalkylaminoethyl aminobenzoates.—See B., 1941, III, 132.

Preparation of hydroxynaphthoic acids. J. Cason (*J. Amer. Chem. Soc.*, 1941, **63**, 828—832).—1 : 3 : 8-NH_2·$C_{10}H_5(SO_3H)_2$, Zn dust, and a little *n*-C_6H_{13}·CHMe·OH in boiling aq. NaOH give 1 : 3-NH_2·$C_{10}H_6$·SO_3Na (81—87%), converted by KCN at ~500° into 1 : 3-NH_2·$C_{10}H_6$·CN (10—13%), new m.p. 125·5—126°, which in 70% H_2SO_4–AcOH (1 : 4) gives 4 : 2-NH_2·$C_{10}H_6$·CO_2H (**I**), new m.p. 215—216°, and in 10% H_2SO_4 at 195±5° gives 4 : 2-OH·$C_{10}H_6$·CO_2H (90·5%), m.p. 225—226° (lit. 182—183°) [acetate, m.p. 211·5—212·5° (lit. 168°)], also obtained with difficulty from (**I**). 4-*Acetoxy*-2-*naphthoyl chloride* (prep. by PCl_5), m.p. 96—98°, remelting at 99·0—99·5°, with H_2–Pd–$BaSO_4$ and a little S-quinoline in boiling xylene gives 4-*acetoxy*-2-*naphthaldehyde* (51%), m.p. 113·2—114·2° [*semicarbazone*, m.p. ~230° (decomp.), obtained in 73·5% yield from the crude reaction product; Wolff–Kishner reduction fails], hydrolysed by boiling N-H_2SO_4 to 4-*hydroxy*-2-*naphthaldehyde*, m.p. 169·5—170°, which with H_2–Cu chromite in abs. EtOH at 140° yields 3 : 1-$C_{10}H_6$Me·OH, m.p. 87—90°, remelts at 91°. 1 : 6-NH_2·$C_{10}H_6$·SO_3Na gives similarly 5 : 2-NH_2·$C_{10}H_6$·CN (**I**) (~10%), new m.p. 143·5—144°, and thence 5 : 2-NH_2·$C_{10}H_6$·CO_2H (**II**), new m.p. 234—236° (decomp.) [Ac derivative, m.p. 291—292° (gas)]. 10% H_2SO_4 and (**I**) at 220±5° give 67% of 5 : 2-OH·$C_{10}H_6$·CO_2H, new m.p. 215—216° (acetate, new m.p. 215—216°), but at 180° give (**II**). 2 : 6-NH_2·$C_{10}H_6$·SO_3Na gives 6-*amino*-2-*naphthonitrile* (1·5%), m.p. 199·0—199·5°, and thence 6 : 2-OH·$C_{10}H_6$·CO_2H, new m.p. 243—244° (acetate, new m.p. 223—224°). 5 : 1-OH·$C_{10}H_6$·CO_2H, new m.p. 237—240° (decomp.) (acetate, m.p. 205—206°), is similarly obtained (53—57%). M.p. are corr. R. S. C.

Fluoranthenecarboxylic acids.—See B., 1941, II, 137.

Spatial structure of two new diphenyl*cyclo*butanedicarboxylic acids; μ- and ω-truxinic acids. M. M. Schemjakin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 199—201; cf. A., 1940, II, 87).—The monoanilide of μ-truxinic acid is unchanged when heated at 270° or boiled with 10% HCl for 2·5 hr.; it is readily hydrolysed by boiling 5% KOH–H_2O. The



monochloride, new m.p. 139°, of ω-truxinic acid is smoothly converted by NH_2Ph in dry C_6H_6 into the *monoanilide*, m.p. 108—111° (decomp.) and 169—173° after re-solidification. It is readily hydrolysed by boiling aq. KOH and is converted when heated alone or with 10% HCl into the *anil*, m.p. 179°. μ- and ω-Truxinic acid are (*A*) and (*B*) respectively. H. W.

Properties of μ-truxinic acid. M. M. Schemjakin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 202—205).—The most characteristic property of μ-truxinic acid (**I**) is the difference in character between the two CO_2H. (**I**), m.p. 196°, dissolves in aq. Na_2CO_3 with formation of a Na H salt and with NH_3 in Et_2O gives the *NH_4H* salt, m.p. 150—160° (decomp.). (**I**) is unchanged by boiling Ac_2O. The Me ester, m.p. 196° (A., 1940, II, 87), is the Me H ester (**II**), since it is obtained by short treatment of the monochloride (**III**) with MeOH and is converted by MeOH–H_2SO_4 or NaOH–Me_2SO_4 into the Me_2 ester (**IV**), m.p. 183°. (**I**) is isomerised to ω-truxinic acid (**V**) at 240—245°. (**II**), (**III**), (**IV**), and μ-truxinmonoanilide (**VI**) are partly transformed into (**V**) when boiled with 5—10% aq. NaOH until dissolution is complete; with boiling 10% HCl, (**V**) is the sole product [except from (**VI**), which hydrolyses only with difficulty]. (**III**) and NaOMe in boiling MeOH afford Me_2 ω-truxinate, m.p. 133°, also obtained with the β-ester from (**IV**) at 260°. H. W.

Preparation of symmetrical diaryls by the action of reducing agents on diazotised amines. Reducing agents. E. R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball, and E. R. Read (*J. Amer. Chem. Soc.*, 1941, **63**, 730—733).—Diphenic acid is obtained in 90% yield from *o*-CO_2H·C_6H_4·N_2Cl by Cu_2O–NH_3 ($\nless$1 atom of Cu). CuCl–HCl gives *o*-C_6H_4Cl·CO_2H. Cu^{II}–NH_3 gives no Ph_2 derivative. R. S. C.

Lactones of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1941, III, 133.

Condensation of malonanilic acid with aldehydes. II. With *o*-, *m*-, and *p*-hydroxybenzaldehyde. III. With *o*-, *m*-, and *p*-nitrobenzaldehyde. P. I. Ittyerah and K. C. Pandya (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 119—121, 122—125; cf. Mehra *et al.*, A., 1938, II, 365; 1939, II, 478).—II. Malonanilic acid (**I**) and *o*-OH·C_6H_4·CHO at 100° (not at 60°) yield coumarin-3-carboxylanilide, m.p. 247°, also obtained in presence of a base. (**I**) and *m*- or *p*-OH·C_6H_4·CHO afford m-, m.p. 209°, or p-*hydroxybenzylidenemalononanilic acid*, m.p. 239—240° (in 52% and 18% yield). *Benzylidenemalononanilic acid*, m.p. 238°, is obtained in 86% yield from PhCHO and (**I**) at 100°.

III. (**I**) and *o*-, *m*-, or *p*-NO_2·C_6H_4·CHO at 100° give a mixture of substituted cinnamanilide and benzylidenemalononanilic acid, reaction proceeding least rapidly with the *o*-compound, probably owing to the presence of a H bond. p-, m.p. 240° (decomp.) (*Ag* salt, decomp. 231°), and m-*nitrobenzylidenemalononanilic acid*, m.p. 226° (decomp.) (*Ag* salt, decomp. 211°), are new. H. W.

Interconversion of mixed benzoins. R. P. Barnes and V. J. Tulane (*J. Amer. Chem. Soc.*, 1941, **63**, 867—868).—Both *p*-OMe·C_6H_4·CO·CHPh·OAc and *αβ-diacetoxy*-4-*methoxystilbene*, m.p. 127°, are obtained by boiling Ac_2O–KOAc from *p*-OMe·C_6H_4·CH(OH)·COPh, *p*-OMe·C_6H_4·CO·CHPh·OH (**I**), or *p*-OMe·C_6H_4·CO·CHPhBr. The enediol is an intermediate in the last two cases, (**I**) being the stable form favoured by resonance. R. S. C.

Δ^2-*cyclo*Hexenone and related substances. F. C. Whitmore and G. W. Pedlow, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 758—760).—Addition of MgRX to Δ^2-*cyclo*hexenone (**I**) results in 1 : 2- and 1 : 4-addition, reduction, and formation of complex products in the following proportions: R = Me, X = Br 38, 15, 0, 18; Et, Br 52, 24, 0, 13; Pr^{β}, Cl, 10, 44, 12, 16, and Bu^{γ}, Cl 0, 70, 0, 14. *iso*Phorone with MgMeBr and MgEtBr gives no 1 : 4-addition and only 8% with $MgPr^{\beta}Br$. (**I**) and its 2 + 3-Me derivative are prepared (yields 37 and 2 + 20%, respectively) from *cyclo*hexene and 1-methyl*cyclo*hexene, respectively, by CrO_3–AcOH. Compounds of the following probable constitution are described: 1-methyl-, b.p. 63—65°/20 mm. {and thence by $CuSO_4$ a diene, b.p. 106·5—107°/738 mm. [maleic anhydride adduct, m.p. 65—66°; with $KMnO_4$ gives $(CH_2(CO_2H)_2)$]}, and 1-*iso*propyl-Δ^2-*cyclo*hexenol, b.p. 72—74°/13 mm.; 3 : 3 : 5 : 5-tetramethyl-, m.p. 37—38°, and 3 : 5 : 5-trimethyl-1-ethyl-Δ^2-*cyclo*hexenol, m.p. 49—50°; 3 : 5 : 5-trimethyl-3-*iso*propyl-*cyclo*hexanone, b.p. 115°/20 mm. [semicarbazone, m.p. 199—200° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 154—155°]; 3-*tert.*-butyl*cyclo*hexanone, b.p. 96—98°/20 mm. [semicarbazone, m.p. 207—208° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 158—159°]. A polymeric product was obtained from (**I**) and $\Delta^{1:3}$-*cyclo*hexadiene. R. S. C.

Reaction of *cyclo*pentadiene and keten. B. T. Brooks and G. Wilbert (*J. Amer. Chem. Soc.*, 1941, **63**, 870—871).—Contrary to Smith *et al.* (A., 1939, II, 116), keten and *cyclo*pentadiene in PhMe at 100° give Δ^2-*di*cyclo[0, 2, 3]*heptene*-6 (or 7)-*one*, b.p. 157·5—159° (*semicarbazone*, m.p. 222°), hydrogenated (Pd–aq. EtOH) to di*cyclo*[0, 2, 3]heptan-6-one, b.p. 164—165° (semicarbazone, m.p. 216°), which with boiling 1 : 1 conc. HNO_3–H_2O gives glutaric acid. R. S. C.

Naphthalene series. VIII. Preparation and properties of 2 : 4-dipropionyl- and 4-acetyl-2-propionyl-1-naphthol. IX. Properties of 4-propionyl-1-naphthol and preparation of 4-propyl-1-naphthol. R. D. Desai and A. Hamid (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 126—131, 132—136).—VIII. Gradual addition of EtCOCl to 2 : 1-COEt·$C_{10}H_6$·OH and anhyd. $ZnCl_2$ in $PhNO_2$ gives an almost quant. yield of 2 : 4-*dipropionyl*-1-*naphthol* (**I**), m.p. 103°, less advantageously obtained by use of $AlCl_3$ and (**V**) (below). (**I**) does not give

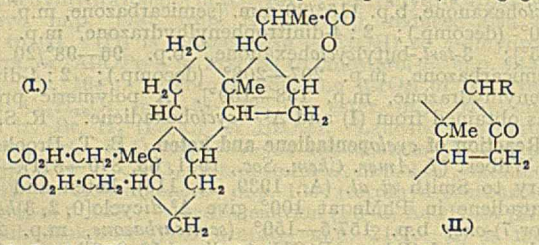
a picrate. It is converted by Br in glacial AcOH into 4-*propionyl*-2-*α*-*bromopropionyl*-1-*naphthol*, m.p. 100°, converted by hot 5% NaOH into a neutral *compound*, $C_{16}H_{14}O_3$, m.p. 254°, and an acidic *product*, $C_{16}H_{14}O_3$, m.p. 133°. (**I**) with HNO_3 (*d* 1·5) (1 mol.) in cold, glacial AcOH gives 4-nitro-2-propionyl- (**II**), m.p. 162°, 2-nitro-4-propionyl- (**III**), m.p. 100°, and 2 : 4-dinitro-1-naphthol (**IV**), m.p. 138°; with 2 mols. of acid the products are (**III**) and (**IV**). (**I**) and anhyd. $ZnCl_2$ in boiling AcOH or $EtCO_2H$ give 2 : 1-COEt·$C_{10}H_6$·OH. (**I**) is converted by Ac_2O and anhyd. NaOAc at 170—180° into 6-*propionyl*-2 : 3-*dimethyl*-1 : 4-*α*-*naphthapyrone*, m.p. 168°, hydrolysed by boiling 5% NaOH to 1-*hydroxy*-4-*propionyl*-2-*naphthoic acid*, m.p. 205°; this passes above its m.p. into 4 : 1-COEt·$C_{10}H_6$·OH (**V**), m.p. 188°, and is reduced (Clemmensen) to 1-*hydroxy*-4-*propyl*-2-*naphthoic acid*, m.p. 174°, decarboxylated to 4 : 1-$C_{10}H_6Pr^{\alpha}$·OH. 2 : 1-COEt·$C_{10}H_6$·OH, AcCl, and anhyd. $ZnCl_2$ in $PhNO_2$, or EtCOCl, 4 : 1-$C_{10}H_6$Ac·OH, and $AlCl_3$ give 4-*acetyl*-2-*propionyl*-1-*naphthol* (**VI**), m.p. 142°, in 80% or 75% yield. (**VI**) does not form a picrate. When heated with $ZnCl_2$ in AcOH or $EtCO_2H$ it affords 2 : 1-COEt·$C_{10}H_6$·OH. (**VI**) and Br in $CHCl_3$ yield 4-*bromoacetyl*-2-*propionyl*-1-*naphthol*, m.p. 158°, converted by 5% NaOH or NaOMe into an acidic *product*, $C_{15}H_{14}O_4$, m.p. 108°. With 1 mol. of fuming HNO_3 in cooled glacial AcOH, (**VI**) gives (**II**), (**IV**), and 2 : 1-NO_2·$C_{10}H_6$·OH. (**VI**) is converted by Kostanecki's reaction into 6-*acetyl*-2 : 3-*dimethyl*-1 : 4-*α*-*naphthapyrone*, m.p. 189°, hydrolysed in alkaline solution to 1-*hydroxy*-4-*acetyl*-2-*naphthoic acid*, m.p. 219—220°, which passes at 200° into 4 : 1-$C_{10}H_6$Ac·OH.

IX. (**V**), m.p. 188°, is best obtained by addition of EtCOCl to *α*-$C_{10}H_7$·OH and anhyd. $ZnCl_2$ in well-cooled $PhNO_2$; inferior results are obtained with $(EtCO)_2O$ or $AlCl_3$. (**V**) gives an *acetate*, m.p. 92°, a *picrate*, m.p. 158°, and a *semicarbazone*, m.p. 223°. $ZnCl_2$ in glacial AcOH or $EtCO_2H$ transforms (**V**) into 4 : 2 : 1-COEt·$C_{10}H_5$Ac·OH, 2 : 1-$C_{10}H_6$Ac·OH, *α*-$C_{10}H_7$·OH, and 2 : 1-COEt·$C_{10}H_6$·OH. With differing amounts of Br in $CHCl_3$ (**V**) gives 2-*bromo*-4-*propionyl*-, m.p. 111°, and 2-*bromo*-4-*α*-*bromopropionyl*-, m.p. 132°, -1-*naphthol*. With 1 mol. of fuming HNO_3, (**V**) yields 2-*nitro*-4-*propionyl*-1-*naphthol*, m.p. 100°, accompanied by 2 : 1-NO_2·$C_{10}H_6$·OH and (**IV**), which is the sole product when 2 mols. of HNO_3 are used. (**V**) is reduced (Clemmensen) to 4-*propyl*-1-*naphthol* (**VII**), b.p. 150°/6 mm. (*picrate*, m.p. 138°), and (?) 4-*propyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthol*, b.p. 126—128°/6 mm. (**VII**) and $ZnCl_2$ in boiling AcOH afford 2-*acetyl*-4-*propyl*-1-*naphthol*, m.p. 185°. (**VII**) couples with PhN_2Cl to 2-*benzeneazo*-4-*propyl*-1-*naphthol*, m.p. 186°, and 4-*propyl*-1 : 2-*naphthaquinone*-2-*phenylhydrazone*, m.p. 150°.

H. W.

Sterols. CXIV. Sapogenins. XLIII. Oxidation products from tigogenin. R. E. Marker, D. L. Turner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1941, **63**, 763—767).—Marker's formula for the side-chain of steroidal sapogenins is supported by the following reactions. Gitogenin lactone and CrO_3 in 90% AcOH at 25° or tigogenone and AcOH–HNO_3 (*d* 1·5) at 90° give the lactone 2 : 3-diacid (**I**), m.p. 244—245° (Windaus *et al.*, A., 1925, i, 1438; +0·5H_2O, m.p. 238°). Tigogenin

(I.)



(II.)

and CrO_3–AcOH at 90—95° give gitogenoic 2 : 3-diacid (**II**) (R = ·CHMe·CO·$[CH_2]_2$·CHMe·CO_2H), +0·5H_2O, m.p. 216—219° (also obtained from gitogenic acid) (with some 3-dehydrotigogenin lactone), which with fuming HNO_3 at room temp. gives 16-ketobisnor*alloiso*lithobilianic acid (**II**) (R = CHMe·CO_2H) (cf. *loc. cit.*), m.p. 295—298° (decomp.), reduced by H_2–PtO_2–EtOH–Et_2O to (**I**). Dihydrotigogenin diacetate and CrO_3 in AcOH at 90—95° give tigogenin lactone, 3-dehydrotigogenoic acid, and 3-*hydroxyætio*allo*bilianic acid* (**III**), m.p. 244—247° (decomp.) (oxidised by CrO_3 to the known 3-CO-acid). Tigogenoic acid (**IV**) with NH_2OH,HCl and KOAc in MeOH at 130° gives a *dioxime*, brown at 230°, decomp. 250° (gas), with KOH in boiling aq. EtOH gives *anhydrotigogenoic acid*, m.p. 256—258°, and with H_2–PtO_2 at 45 lb. in AcOH gives *anhydrotetrahydrotigogenoic acid*, m.p. 203—205°, also obtained by oxidation (CrO_3–AcOH) of dihydrotigogenin monoacetate followed by hydrolysis (EtOH–KOH). Oxidation by CrO_3 in AcOH and subsequent hydrolysis converts the acetate of (**IV**) into (**III**). R. S. C.

Sterols. CXVIII. Action of selenious acid on Δ^5-pregnenediol and on Δ^5-androstenediol. R. E. Marker, H. M. Crooks, jun., and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1941, **63**, 777—779).—Δ^5-Pregnene-3(*β*) : 20(*α*)-diol (prep. from $\Delta^{5:16}$-pregnadien-3(*β*)-ol-20-one by Na–EtOH), m.p. 174—176°, gives a *diacetate*, m.p. 144—146°, which with SeO_2 and NaOAc in boiling C_6H_6–AcOH gives a product, hydrolysed to Δ^5-*pregnene*-3 : 4 : 20-*triol*, m.p. 207—210° (*triacetate*, m.p. 153—154°). With boiling conc. HCl–EtOH this gives Δ^4-*pregnen*-20(*α*)-*ol*-3-*one*, m.p. 158—160° (*acetate*, m.p. 138—140°), whence CrO_3 in AcOH at room temp. gives progesterone. Δ^5-Androstene-3 : 17-diol diacetate, SeO_2, and NaOAc in C_6H_6–AcOH give similarly Δ^5-*androstene*-3 : 4 : 17-*triol*, m.p. 258—261° (*triacetate*, m.p. 155—156°), and thence by HCl–AcOH testosterone, which is isolated as semicarbazone, m.p. 225° (decomp.), and regenerated therefrom by $H_2C_2O_4$ in 75% EtOH. R. S. C.

III.—TERPENES.

Solvent effects in addition reactions. II. Addition of hydrogen bromide and chloride to α-pinene. G. F. Hennion and C. F. Irwin (*J. Amer. Chem. Soc.*, 1941, **63**, 860—862).—As indicated previously (A., 1939, I, 476), co-ordination between HHal and the solvent greatly decreases the rate of reaction of the acid. Relative reaction rates for *α*-pinene and HBr are $CHCl_3$ > xylene > C_7H_{16} > $PhNO_2$ > dioxan > $EtOBu^{\alpha}$ > Et_2O and for HCl are $CHCl_3$ > xylene > $PhNO_2$ ≫ MeOH > dioxan > $EtOBu^{\alpha}$ > Et_2O. R. S. C.

Condensation of amino-acids with terpenes. I. Glycine and limonene nitrosochloride. C. F. Krewson (*J. Amer. Pharm. Assoc.*, 1941, **30**, 47—49).—Glycine (1 mol.) and limonene nitrosochloride (1 mol.) in 85% EtOH, heated at 50° for several hr., and then steam-distilled, yield a volatile oil containing carvone, carvoxime, and various unidentified fractions; the residue yielded 3·1% (calc. on glycine used) of *limonenenitrolaminoacetic acid hydrochloride* [*N*-(2-keto-1-$\Delta^{8(9)}$-*p*-menthenyl)glycine oxime hydrochloride], m.p. 141·0—141·5° (uncorr.) (*Cu* derivative, $Cu[C_{10}H_{15}(N{\cdot}OH){\cdot}NH{\cdot}CH_2{\cdot}CO_2]_2{\cdot}CuCl_2$). The mechanism of the formation of the reaction products is discussed.

F. O. H.

***iso*Fenchone. Hydroxymethylene*iso*fenchone and its derivatives.** A. K. Rushentzeva and N. K. Kedrova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 95—97).—*iso*Fenchone with Na and $HCO_2C_5H_{11}$ in Et_2O, followed by H_2O, yields *hydroxymethylene*iso*fenchone* (**I**), m.p. 103—104° [*Bz*, m.p. 81—82°, and *phenylpyrazole* derivative ($NHPh{\cdot}NH_2$), m.p. 60—61°; *anilide*, m.p. 101—102°], which contains 99% of the enol (Meyer's Br method) after keeping for 6 months. (**I**) is oxidised (CrO_3 in AcOH) to *iso*fenchocamphoric acid.

A. Lt.

Triterpene group. VIII. Minor triterpenoid constituents of *Manila elemi* resin (continued). (Miss) I. M. Morice and J. C. E. Simpson (*J.C.S.*, 1941, 181—184).—By adsorption on Al_2O_3, *ψ*-*taraxastanediol* (**I**), $C_{30}H_{52}O_2$, m.p. 270—272°, $[\alpha]_D^{23}$ −10·9° (*monoacetate*, m.p. 281—284°, $[\alpha]_D^{23}$ −1·5°), has been isolated from the resin; it is the precursor of *ψ*-taraxasterol. (**I**) is a saturated dihydric alcohol containing C·OH, and it is converted (HCO_2H) by dehydration into *ψ*-taraxasteryl acetate, which with BzO_2H gives the *oxide*, m.p. 265—267°, a reaction not shown by the acetate of (**I**). From the resin were isolated small amounts of *diol A*, $C_{30}H_{48}O_2$ (?), m.p. 234—236°, $[\alpha]_D^{22}$ −70°±10° (*diacetate*, m.p. 211—212°, $[\alpha]_D^{19}$ +35°), and *alcohol B*, $C_{30}H_{54}O_2$ (?), m.p. 252—254°, $[\alpha]_D^{19}$ −17° (*monoacetate*, m.p. 227—229°, $[\alpha]_D^{23}$ −39°). All [*α*] in $CHCl_3$. F. R. S.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Action of ultra-violet light on lignin. L. V. Forman (*Paper Trade J.*, 1940, **111**, *TAPPI Sect.*, 266—272).—Lignin (**I**) in the form of solvent-extracted sprucewood meal undergoes

drastic colour change when irradiated with ultra-violet light, and its OMe content is decreased. The effect of "native" (I), though appreciable, is not so great. Extraction of irradiated (I) with EtOH removes a no. of degradation products) among them being vanillin (II) and a product (OMe 10·6%, similar to native (I). Filter-paper impregnated with an EtOH solution of (II) discolours very rapidly when exposed to ultra-violet light; dehydrodivanillin is probably formed. H. A. H.

V.—HETEROCYCLIC.

2-Cyanoacetylcoumarone-5-sulphonyl chloride.—See B., 1941, II, 104.

Cannabis indica. **VII. Relation between chemical constitution and hashish activity.** P. B. Russell, A. R. Todd, S. Wilkinson, A. D. Macdonald, and G. Woolfe (*J.C.S.*, 1941, 169—172).—The following compounds prepared from the corresponding coumarin and MgMeI have been tested pharmacologically: 5″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran*, b.p. 150—160°/10^{-3} mm. (*acetate*, b.p. 150°/10^{-3} mm.) [from 6-*hydroxy*-5′-*methyl*-7-n-*amyl*-3 : 4-cyclo*hexenocoumarin*, m.p. 188° (*acetate*, m.p. 119—120°)], and the 6″-*hydroxy*-2 : 2-*dimethyl* compound, b.p. 158—165°/10^{-3} mm. [from 5-*hydroxy*-7-n-*amyl*-3 : 4-cyclo*hexenocoumarin*, m.p. 180° (*acetate*, m.p. 80°)]; 5-*hydroxy*-2 : 2 : 4 : 7-*tetramethyl*-Δ^3-*chromen*, m.p. 97° (not tested); 5-*hydroxy*-2 : 2 : 4-*trimethyl*-7-n-*amyl*-Δ^3-*chromen*, b.p. 140—150°/10^{-1} mm. [from 5-*hydroxy*-4-*methyl*-7-n-*amylcoumarin*, m.p. 185° (*acetate*, m.p. 97°)]; 5-*hydroxy*-2 : 2 : 7-*trimethyl*-, b.p. 140—150°/10^{-1} mm. [from 5-*hydroxy*-7-*methyl*-3 : 4-cyclo*pentenocoumarin*, m.p. 254° (*acetate*, m.p. 131°)], and 5-*hydroxy*-2 : 2-*dimethyl*-7-n-*amyl*-3 : 4-cyclo*penteno*-Δ^3-*chromen*, m.p. 78° [from 5-*hydroxy*-7-n-*amyl*-3 : 4-cyclo*pentenocoumarin*, m.p. 176° (*acetate*, m.p. 65—66°)]. The question of chemical constitution and hashish activity is discussed. All b.p. are at bath temp. F. R. S.

Constitution of natural tannins. VII. Colouring matters derived from β-naphthaldehyde. A. Russell and J. C. Speck (*J. Amer. Chem. Soc.*, 1941, **63**, 851—852; cf. A., 1939, II, 557).—2-$C_{10}H_7$·CHO and the appropriate COPhMe derivative in AcOH give 2-*phenyl*-, decomp. 118°, 2-o-*anisoxy*-, decomp. 110°, 2-2′ : 4′-*di*-, decomp. 132°, and 2-2′ : 3′ : 4′-*tri-methoxy-phenyl*-1-α-*naphthopyrylium chloride* (I), decomp. 121°. 2-o- and 2-p-*Hydroxy*- and 2-2′ : 4′-*dihydroxy-phenyl*-1-α-*naphthopyrylium chloride* (all decomp. ~200°) are obtained as benzoates and liberated therefrom by boiling conc. HCl–EtOH. Hydrolysis of (I) by $AlCl_3$ in boiling PhCl gives the $(OH)_3$-compound, decomp. ~200°. R. S. C.

Dismutation of some disulphides. IV. F. S. Fowkes and E. W. McClelland (*J.C.S.*, 1941, 187—190).—5 : 5′-Dichloro-2 : 2′-dithiobenzoic acid (I) with Ac_2O and KOAc (130°; 4 hr.) gives 5-*chloro*-3-*acetoxy*-1-*thionaphthen*, m.p. 67°; the Cl in the *p*-position to S thus decreases the tendency of a 2 : 2′-dithiobenzoic acid to undergo dismutation. CH_2Ac_2 and (I) in H_2SO_4 afford 5-*chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen* (II), m.p. 166° (*Ac* derivative, m.p. 132°); 3-*acetoxy*-2-*acetyl*-1-*thionaphthen* has m.p. 127°. NHPh·NH_2 and (II) yield the *hydrazone*, m.p. 162°, which with conc. H_2SO_4 is converted into 8-*chloro*-1-*phenyl*-3-*methyl*-4 : 5-*thionaphthenopyrazole*, m.p. 135°; (II) and H_2O_2–AcOH give 5-*chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen* 1 : 1-*dioxide*, m.p. 265°. 5-Chloro-3-hydroxy-1-thionaphthen and NHPh·NH_2 afford 10-*chlorothionaphthindole*, m.p. 222°. The 3-Ac derivative with H_2O_2–AcOH yields 5-*chloro*-3-*acetoxy*-1-*thionaphthen* 1 : 1-*dioxide*, m.p. 164°, under mild conditions, but under more vigorous conditions it gives the 3-*hydroxy-dioxide*, m.p. 194°, the *phenylhydrazone*, m.p. 290—292°, of which could not be indolised. Thus the Cl substitution of hydroxythionaphthens has no marked effect on their reactivity. 2 : 2′-Dithiobenzoic acid undergoes dismutation in neutral media. F. R. S.

α-Coumarilyl- and α-thionaphthenoyl-acetates etc.—See B., 1941, II, 109, 132.

Condensation of 6-amino-2-hydroxypyridine with *p*-acetamidobenzenesulphonyl chloride. M. A. Phillips (*J.C.S.*, 1941, 291—293).—6-Amino-2-hydroxypyridine sulphate in C_5H_5N with one equiv. of *p*-NHAc·C_6H_4·SO_2Cl gives mainly 6-*amino*-2-*pyridyl* p-*acetamidobenzenesulphonate* (I) and some 6-p-*acetamidobenzenesulphonamido*-2-*pyridyl* p-*acetamidobenzenesulphonate* (II), m.p. 222°. Hydrolysis (HCl) of (I) yields 6-*amino*-2-*pyridyl* p-*aminobenzenesulphonate*, m.p. 148°, and treatment with NaOH affords 6-amino-2-hydroxypyridine. Further treatment of (I) with *p*-NHAc·C_6H_4·SO_2Cl leads to (II), which with NaOH gives 6-*hydroxy*-2-(p-*aminobenzenesulphonamido*)*pyridine*, m.p. 239—240°. F. R. S.

Piperidine derivatives.—See B., 1941, III, 80.

Chromic acid oxidation of quinoline homologues. Oxidation of *Bz*-ethylquinolines to quinolyl methyl ketones. R. A. Glenn and J. R. Bailey [with, in part, W. N. Axe] (*J. Amer. Chem. Soc.*, 1941, **63**, 641—643).—Oxidation of 8-alkylquinolines by $K_2Cr_2O_7$ is more rapid than that by CrO_3, owing to catalysis (proved experimentally) of the latter reaction by $KHSO_4$. Max. yields of acid are obtained by using < theoretical amount of oxidant. The following yields of 8-carboxylic acid and 8-Ac derivative, respectively, are obtained by (*a*) CrO_3–$KHSO_4$–H_2SO_4 and (*b*) $K_2Cr_2O_7$–H_2SO_4 from the bases named: 2 : 3 : 8-trimethyl- (*a*) 85, 0, 2 : 3-dimethyl-8-ethyl- (*a*) 56, 12, (*b*) 50, 0, 2 : 4-dimethyl-8-ethyl- (*a*) 0, 36, (*b*) 30, 0, 2 : 3-dimethyl-8-*n*-propyl- (*a*) 83, 0, 2 : 3 : 4 : 8-tetramethyl- (*a*) 86, 0, 8-ethyl- (*b*) 40, 40, 2-methyl-8- or -6-ethyl- (*b*) 0, 75, 3-methyl-8-ethyl- (*b*) 0, 80, 2 : 4-dimethyl-6-ethyl- (I) (*b*) 0, 30, 2 : 3 : 4-trimethyl-8-ethyl- (*b*) 25, 50, 3-methyl-2 : 8-diethyl- (II) (*b*) 10, 55, and 3-methyl-2 : 6-diethyl-quinoline (III) (*b*) 0, 85%. The following are described: *semicarbazones* of 2-methyl-6-, m.p. 262°, 3-methyl-8-, m.p. 226—227°, 2 : 3-dimethyl-8-, m.p. (+H_2O) 239°, 2 : 4-dimethyl-6-, m.p. (+$2H_2O$) 251°, 2 : 4-dimethyl-6-, m.p. (+$2H_2O$) 262°, 2 : 3 : 4-trimethyl-8-, m.p. (+$2H_2O$) 258—259°, 3-methyl-2-ethyl-8-, m.p. 243°, and 3-methyl-2-ethyl-6-, m.p. 251°, -acetylquinoline; 3-methyl-2-ethylquinoline-8-carboxylic acid, new m.p. 223°; (I) (from boiling *p*-C_6H_4Et·NH_2 and CH_2Ac_2 and, later, H_2SO_4 at 100°), b.p. 299—300°/742 mm. (*picrate*, m.p. 190—191°); (II) (from *o*-C_6H_4Et·NH_2 and EtCHO), m.p. 18·5—19·5°, b.p. 298°/754 mm. (*picrate*, m.p. 194—195°); (III), b.p. 313·5°/748 mm. (*picrate*, m.p. 152—153°). R. S. C.

Nitrogen compounds in petroleum distillates. XIX. Isolation from Californian petroleum, and synthesis, of 2 : 3 : 8-trimethyl-4-ethylquinoline. XX. Isolation of 2-methyl-8-ethylquinoline from Californian petroleum; proof of its structure by degradation and synthesis. R. A. Glenn and J. R. Bailey (*J. Amer. Chem. Soc.*, 1941, **63**, 637—638, 639—641; cf. A., 1940, II, 357).—XIX. The fraction, b.p. 308—313°, of the bases previously (A., 1939, II, 24) obtained from Californian petroleum yields, by countercurrent extraction, 2 : 3 : 4-trimethyl-8-ethyl-, 2 : 3 : 4 : 8-tetramethyl-, and 2 : 3 : 8-*trimethyl*-4-*ethyl-quinoline* (I), b.p. 310—311°/748 mm. [*picrate*, m.p. 178°; *nitrate*, m.p. 161° (decomp.); *phthalone*, m.p. 158° (red Na salt)]. $K_2Cr_2O_7$–H_2SO_4 oxidises (I) to 2 : 3-*dimethyl*-4-*ethylquinoline*-8-*carboxylic acid*, m.p. 178°, converted by distillation with soda–lime into 2 : 3-*dimethyl*-8-*ethylquinoline* (II), b.p. 302°/749 mm. (*picrate*, m.p. 220—221°). Condensation of $COEt_2$ and paraldehyde by dry HCl at 0° and subsequent interaction with NH_2Ph or *o*-C_6H_4Me·NH_2 and conc. HCl at 100° gives (II) and (I), respectively. (I) is the first base isolated from petroleum to contain in the *Py*-nucleus an alkyl other than Me.

XX. The fraction, b.p. 258—264°, of the bases obtained as above yields by distillation and crystallising the picrates 2-*methyl*-8-*ethylquinoline* (III), b.p. 263·0—263·5°/755 mm. [*picrate*, m.p. 169°; *phthalone*, m.p. 246° (red Na salt); *nitrate*, m.p. 143° (decomp.)], and a base, $C_{12}H_{13}N$ (*picrate*, m.p. 153·0—153·5°). SeO_2 converts (III) in boiling EtOH into 8-ethylquinoline-2-aldehyde (*semicarbazone*, m.p. 189—190°), oxidised by H_2O_2–$COMe_2$ (90%) or Ag_2O–EtOH (8% yield) to 8-*ethylquinoline*-2-*carboxylic acid*, m.p. 121°, which, when fused alone, gives 8-*ethylquinoline* (IV), b.p. 256° [*picrate*, m.p. 146° (decomp.); *nitrate*, m.p. 146°], also obtained with some quinoline from *o*-C_6H_4Et·NH_2, $PhNO_2$, $FeSO_4$, H_3BO_3, glycerol, and H_2SO_4. *o*-C_6H_4Et·NH_2, MeCHO, $ZnCl_2$, and HCl give 22% of (III). $K_2Cr_2O_7$–H_2SO_4 oxidises (III) to 8-acetyl-2-methylquinoline (46%) [*picrate*, m.p. 182° (decomp.); *semicarbazone*, m.p. 209°], stable to $K_2Cr_2O_7$ but oxidised by NaOBr to 2-methylquinoline-8-carboxylic acid. $K_2Cr_2O_7$–H_2SO_4 oxidises (IV) to 8-acetylquinoline (40%) (semicarbazone, new m.p. 225°) and quinoline-8-carboxylic acid (40%). R. S. C.

Quinoline "sulphanilamides."—See B., 1941, III, 109.

Synthesis of analgesics. P. V. A. Raman (*J. Indian Chem. Soc.*, 1940, **17**, 715—720).—Homopiperonylamine (**I**) is condensed with Et furoate at 100° and the crude amide is cyclised with $POCl_3$ in boiling PhMe to 6 : 7-*methylenedioxy*-1-2′-*furyl*-3 : 4-*dihydro*isoquinoline, m.p. 95—96° [*picrate*, m.p. 206° (decomp.); *methiodide* (**II**), m.p. 238° (decomp.)]. (**II**) is reduced by Zn dust and dil. H_2SO_4 at 100° to 6 : 7-methylenedioxy-1-2′-furyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, isolated as the *picrate*, m.p. 100° (decomp.). *Me* 7-*methoxycoumarone*-2-*carboxylate*, m.p. 79°, and (**I**) at 100° afford 7-*methoxy*-2-*coumaronylhomopiperonylamide*, m.p. 86°, cyclised ($POCl_3$ in boiling PhMe) to 6 : 7-*methylenedioxy*-1-7′-*methoxy*-2′-*coumaronyl*-3 : 4-*dihydro*isoquinoline, m.p. 140—142° [*picrate*, m.p. 220° (decomp.); *methiodide* (**III**), m.p. 190—191° (decomp.)]. Reduction (Zn dust and dil. H_2SO_4) of (**III**) gives 6 : 7-methylenedioxy-1-7′-methoxy-2′-coumaronyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, an oil, isolated as the *picrate*, m.p. 185—187° (decomp.). 9-Phenanthroyl chloride and (**I**) in conc. KOH yield the non-cryst. 6 : 7-methylenedioxy-1-9′-phenanthryl-3 : 4-dihydro*iso*quinoline [*picrate*, m.p. 145—147° (decomp.)]; the corresponding methiodide is reduced to the non-cryst. 6 : 7-methylenedioxy-1-9′-phenanthryl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, isolated as the *picrate*, m.p. 105—108° (decomp.). Et β-2-furylpropionate and (**I**) at 100° afford β-2-*furylpropionylhomopiperonylamide*, m.p. 92°, and (**I**) and Et β-2-5′-phenylfurylpropionate give β-2-5′-*phenylfurylpropionylhomopiperonylamide*, m.p. 104·5°, neither of which could be satisfactorily cyclised. H. W.

Amino-alcohols derived from carbazole. II. L. Ruberg and L. Small (*J. Amer. Chem. Soc.*, 1941, **63**, 736—741; cf. A., 1938, II, 380).—3-Acetyl-9-methylcarbazole, paraldehyde, and the appropriate sec. amine in boiling abs. EtOH–N_2 give 3-ω-*dimethylamino*-, m.p. 72·5—73° (*hydrochloride*, m.p. 193·5—194·5°), 3-ω-tetrahydroquinolino-, an oil (*hydrochloride*, sinters at 198·5°, m.p. 201—202°; *picrate*, sinters at ~170°, m.p. 177·5—178·5°), and 3-ω-diethylamino-propionyl-9-methylcarbazole, an oil (*hydrochloride*, sinters at ~162°, m.p. 167—168·5°; *picrate*, sinters at ~134°, m.p. 143—143·5°), the hydrochlorides of which with H_2–PtO_2 in MeOH give 9-*methyl*-3-γ-*hydroxy*-α-*dimethylamino*-, m.p. 122·5—123° [*picrate*, sinters at >145°, m.p. 157·5—158·5° (gas)], -γ-tetrahydroquinolino-, amorphous [*hydrochloride*, sinters at >177°, m.p. 187° (gas)], and -γ-diethylamino-propylcarbazole [*hydrochloride* (**I**), sinters at >129°, m.p. 132—134°]. Conversion of (**I**) into the oily base and treatment thereof with HCl–EtOH–Et_2O gives a *hydrochloride*, $C_{20}H_{25}N_2Cl$, sinters at ~184°, m.p. 189—190·5°. 9-Acetylcarbazole, $CH_2Cl{\cdot}COCl$, and $AlCl_3$ in CS_2 give 94% (cf. lit.) of the 2-$CH_2Cl{\cdot}CO$ derivative, sinters at 178°, m.p. 181—183°, hydrolysed by 20% aq. H_2SO_4 in boiling EtOH to 2-chloroacetylcarbazole (**II**), m.p. 208—210°, the structure of which is proved by fusion with KOH to give the 2-carboxylic acid. With Me_2SO_4–KOH, (**II**) gives 2-*chloroacetyl*-9-*methylcarbazole*, m.p. 173·5—175°. With $NHEt_2$ in C_6H_6 at 100° (tube), (**II**) gives 2-ω-*dimethylaminoacetylcarbazole*, m.p. 134—136° (decomp.; sinters at >126°; air), 155·5—156·5° (no decomp.; sinters at >150°; vac.) [*hydrochloride*, +0·5H_2O, m.p. 190·5—193° (decomp.; sinters at >100°); *picrate*, m.p. 164—165° (sinters at 160°)], reduced as hydrochloride by H_2–PtO_2–60% EtOH or, better, 5% Na–Hg in HCl–aq. EtOH to 2-α-*hydroxy*-β-*diethylaminoethylcarbazole*, m.p. 151—152° [*hydrochloride*, m.p. 182·5—184°; *styphnate*, sinters at >174°, m.p. 179—180° (decomp.); N-*oxide*, sinters at >176°, m.p. 181° (gas)]. R. S. C.

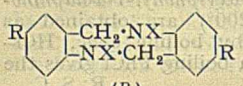
Retene field. XI. Synthesis of retopyridines (naphthaquinolines) from 3-aminoretene. (Miss) S. A. Cassaday and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 703—708; cf. A., 1939, II, 206).—γ-Keto-γ-3-retyl-*n*-butyric acid (modified prep.) gives an *oxime*, m.p. 165—166°, and an *Et* ester, m.p. 92·5—93°, the *oxime*, m.p. 105—106°, of which with PCl_5 in Et_2O gives *Et* 3-*retylsuccinamate*, m.p. 168—169°, and thence (KOH–$Pr^{\alpha}OH$ or HCl–AcOH–H_2O) 3-aminoretene (**I**) (11 g. from 100 g. of retene) [*hydrochloride*, m.p. 267—273° (vac.); Ac derivative, new m.p. 240—241°], the less advantageous prep. of which from 3-acetylretene is modified. With $PhNO_2$, glycerol, $FeSO_4$, and H_2SO_4 at 140—145° and later 160—170°, (**I**) gives 7-*methyl*-3-iso*propylnaphtha*[2 : 1-g]*quinoline* [6′-*methyl*-6-iso*propylnaphtha*-1 : 2-7′ : 6′-*quinoline*] or 6-*methyl*-10-iso*propylnaphtha*[1 : 2-f]-*quinoline* [7′-*methyl*-6-iso*propylnaphtha*-1′ : 2-5′ : 6′-*quinoline*], m.p. 87·5—88·5° [*picrate*, m.p. 277—279° (decomp.); *hydrochloride*, +3H_2O (tenaciously held), m.p. 96—101°], which resists reduction. With paraldehyde in conc. HCl at 100°, (**I**) gives 7 : 10-*dimethyl*-3-iso*propylnaphtha*[2 : 1-g]- or 3 : 6-*dimethyl*-10-iso*propylnaphtha*[1 : 2-f]-*quinoline*, m.p. 110—111° [*hydrochloride*, +3H_2O (tenaciously held), m.p. 258—261°; *picrate*, m.p. 221—226° (decomp.)]. With PhCHO and $AcCO_2H$ in boiling EtOH, (**I**) gives 5-*keto*-4-3′-*retylimino*-2-*phenyl*-1-3′-*retylpyrrolidine*, m.p. 218—219° [*picrate*, m.p. 234·5—235·5° (decomp.)], which with NH_2OH,HCl and $BaCO_3$ in boiling MeOH gives 5-*keto*-4-*oximino*-2-*phenyl*-1-3′-*retylpyrrolidine*, m.p. 208—209°. With PhCHO in boiling EtOH, (**I**) gives the *CHPh*: derivative, m.p. 88—89°. M.p. are corr. R. S. C.

Barbituric acids.—See B., 1941, III, 108.

Direct synthesis of 1 : 2 : 4 : 5-tetra-substituted iminazoles. F. Lions and E. Ritchie (*J. Proc. Roy. Soc. N. S. Wales*, 1940, **74**, 365—372).—OH·CHMe·NH_2, Ac_2, and NH_2Me in EtOH at room temp. give 1 : 2 : 4 : 5-*tetramethylglyoxaline*, m.p. 58° (*picrate*, m.p. 189°). A similar interaction of the respective α-diketone, primary amine, and aldehyde-ammonia affords: 1-n-*butyl*-, b.p. 145—146°/28 mm. (*picrate*, m.p. 145°), 1-*phenyl*-, b.p. 170—174°/29 mm. (*picrate*, m.p. 122°), 1-p-*tolyl*-, b.p. 176—180°/20 mm. (*picrate*, m.p. 123°), 1-(β-*phenylethyl*)-, b.p. 209—212°/28 mm. (*picrate*, m.p. 164°), and 1-*benzyl*-2 : 4 : 5-*trimethylglyoxaline*, m.p. 81° (*picrate*, m.p. 127°); 1-*benzyl*-2-*methyl*-4 : 5 : 6 : 7-*tetrahydrobenziminazole*, m.p. 76° (*picrate*, m.p. 143°), and 2-methyl-4 : 5 : 6 : 7-tetrahydrobenziminazole, m.p. 220° (picrate, m.p. 184°) (cf. Hartmann *et al.*, A., 1939, II, 37); 1-*benzyl*-2-n-*propyl*-4 : 5-*dimethylglyoxaline*, b.p. 194—196°/19 mm. A. T. P.

Pyrazolone derivatives.—See B., 1941, II, 172.

Analogues of Troeger's base and related compounds. T. R. Miller and E. C. Wagner (*J. Amer. Chem. Soc.*, 1941, **63**, 832—836).—*p*-$C_6H_4R{\cdot}NH_2$, $(p\text{-}C_6H_4R{\cdot}NH)_2CH_2$, $(p\text{-}C_6H_4R{\cdot}\dot{N}{\cdot}CH_2)_3$ (R = OMe or OEt), 6-methoxy-3-*p*-anisyl- or 6-ethoxy-3-*p*-phenetyl-1 : 2 : 3 : 4-tetrahydroquinazoline with 39% CH_2O or conc. HCl at room temp. give the Troeger bases (*A*), 6-*methoxy*-3-p-*anisyl*-, m.p. 172—172·5° (corr.) [*hydrochloride*, +2H_2O, m.p. 115—120°, and anhyd., m.p. 213—215°; picrate, m.p. 207·5—208·5° (corr.)], and 6-*ethoxy*-3-p-*phenetyl*-1 : 2′-*methylene*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, m.p. 131·5—132° (corr.) [*hydrochloride*, +2H_2O, m.p. 135—137°, and anhyd. m.p. 236—240° (corr.); picrate, m.p. 196·5—197·5°], converted by aq. HNO_2 into *nitrosoamines* (*B*) [X = NO; R = OMe, m.p. 207·5—208·5° (decomp.), and OEt, m.p. 184—186° (corr.)], and by boiling Ac_2O into CH_2O and *compounds* (*B*) [X = Ac; R = OMe, m.p. 298—300° (decomp.), and OEt, m.p. 232·5—233·5° (corr.)], respectively. However, *p*-$C_6H_4R{\cdot}NH_2$, $(p\text{-}C_6H_4R{\cdot}NH)_2CH_2$, $(p\text{-}C_6H_4R{\cdot}\dot{N}{\cdot}CH_2)_3$, 2 : 5 : 1-$NH_2{\cdot}C_6H_3R{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4R$-*p* (R = Cl or Br), or the derived tetrahydroquinazoline gives 6-*chloro*-3-p-*chlorophenyl*- (**I**), m.p. 135—136° [*hydrochloride*, m.p. 273—274° (decomp.); picrate, m.p. 188—189° (corr.); *phenylurethane*, m.p. 141—142° (corr.)], and 6-*bromo*-3-p-*bromophenyl*- (**II**), m.p. 139·5—140·5° [*hydrochloride*, m.p. 276—278° (decomp.); *picrate*, m.p. 203·5—204·5° (corr.); *phenylurethane*, m.p. 159·5—160·5° (corr.)], -1-*hydroxymethyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, whence red P and boiling 57% HI yield >1 mol. of *p*-$C_6H_4Hal{\cdot}NH_2$. (**I**) and (**II**) are considered to be intermediates in the formation of (*A*) (cf. A., 1935, 1118), although attempts to achieve this conversion failed. In two experiments a substance, m.p. 121°, was obtained instead of (**IV**). R. S. C.



(*B*.)

Adamkiewicz, Hopkins and Cole, and Rosenheim tests for tryptophan. Investigation of the configuration of the organic molecule responsible for the colour formation and its bearing on the constitution of yohimbine; action of formaldehyde on tryptophan. D. G. Harvey, E. J. Miller, and W. Robson (*J.C.S.*, 1941, 153—159).—If to an aq. solution of 2 : 3 : 4 : 5-tetrahydro-β-carboline-4-carboxylic acid (**I**), conc. H_2SO_4 containing a trace of an oxidising agent is added so that the two liquids do not mix, the play of colours at their zone of contact resembles that obtained when tryptophan (**II**) is subjected to the modified Adamkiewicz procedure. Hence (**I**) may be used to test conc. H_2SO_4 for the presence of oxidising agents. The colour reaction has been carried out with several compounds and only those possessing the struc-

ture of (I) give it. The following have been prepared: *Me 2-methyl-2 : 3 : 4 : 5-tetrahydro-β-carboline-4-carboxylate hydrochloride*, m.p. 264° (decomp.), *2-hydroxymethyl-*, m.p. 234°, *3-methyl-* (+H_2O), m.p. 208°, *2 : 3-dimethyl-*, m.p. 243—245°, and *2-phenyl-3-methyl-2 : 3 : 4 : 5-tetrahydro-β-carboline-4-carboxylic acid* (+H_2O), m.p. 219°, and *2 : 3 : 4 : 5-tetrahydro-β-carboline-2 : 4-dicarboxylic acid*, m.p. ~270° (decomp.). The reaction with (II) involves the formation of (I) or a derivative thereof and then oxidation to the blue pigment. Yohimbine (III) behaves like (I) towards conc. H_2SO_4 containing an oxidising agent. Therefore probably the CO_2Me in (III) is at $C_{(5)}$ and not at $C_{(16)}$ as postulated by Hahn *et al.* (A., 1934, 667). F. R. S.

Fluorescence of purines and pyrimidines.—See A., 1941, I, 193.

Cu and Co tetra-(4)-pyridylphthalocyanines.—See B., 1941, II, 77.

αβ-Unsaturated amino-ketones. IV. Mechanism of the reaction of α-bromo-αβ-unsaturated ketones with *sec.* amines. N. H. Cromwell (*J. Amer. Chem. Soc.*, 1941, **63**, 837—839; cf. A., 1941, II, 110).—The mechanism previously proposed for the reaction of CHR:CBr·COR′ with NHR_2 is confirmed, but the course of the reaction is partly dependent on the nature of the base. α-Bromo-α-piperidino-β-phenylpropiophenone (1 mol.) and morpholine (2 mols.) in boiling EtOH give *α-piperidino-β-morpholino-β-phenylpropiophenone* (I), *forms*, m.p. 174—175° and 155—157°, and CHPh:C(NC_5H_{10})·COPh (II), m.p. 102—103°. Hydrolysis of (I) by 15% H_2SO_4 gives ω-piperidinoacetophenone (*hydrochloride*, m.p. 226—227°), PhCHO, and morpholine (not isolated). In boiling EtOH (I) does not yield (II) and the two products thus arise by independent reactions. Piperidine and α-bromo-α-morpholino-β-phenylpropiophenone in boiling EtOH give mixtures (*a*) CHPh:CR·COPh (acid hydrolysis gives 80—85% of COPh·CO·CH_2Ph), and (*b*) NC_5H_{10}·CHPh·CHR·COPh (hydrolysis gives mixed CH_2R·COPh), in which R = piperidino and morpholino. R. S. C.

Thiazole "sulphanilamides."—See B., 1941, III, 133.

Cyanine dyes.—See B., 1941, II, 110, 140, 170.

Gelsemine. II. Bromination and nitration. T. Q. Chou and T. T. Chu (*J. Amer. Chem. Soc.*, 1941, **63**, 827—828; cf. A., 1940, II, 360).—Gelsemine and Br in $CHCl_3$ at <0° give *dibromo-*, m.p. 309° (decomp.), converted by dil. aq. Na_2CO_3 into *bromo-gelsemine*, m.p. >320°. Dihydrogelsemine and HNO_3–H_2SO_4 at −7°, later 5°, give *dinitrogelsemine*, m.p. 257—258° (decomp.), $[\alpha]_D^{23}$ +6·6° [*nitrate*, m.p. 219—221° (decomp.), $[\alpha]_D^{22}$ −61·7° in MeOH; *methiodide*, m.p. 255—256°, $[\alpha]_D^{18}$ −68·5° in MeOH]. R. S. C.

Optical activity of quinine and some of its salts in mixtures of water and ethyl alcohol. J. C. Andrews and B. D. Webb (*Ind. Eng. Chem.* [*Anal.*], 1940, **13**, 232—233).—Data are given of the variation in optical activity of quinine, its dihydrochloride and sulphate in various mixtures of H_2O–EtOH, and on the change of rotation as the base is treated with increasing proportions of HCl and H_2SO_4, each in that concn. of aq. EtOH which gives the max. α for each salt. J. D. R.

Alkaloids of Chinese Hanfongchi. III. Hanfongchine *C*. C. F. Hsu (*J. Chinese Chem. Soc.*, 1940, **7**, 123—128).—The aq. NH_3 extract after removal of hanfongchine *A* and *B* when conc. and extracted with hot C_5H_{11}·OH yields *hanfongchine* C, a phenol, $C_{13}H_{10}O_2(OH)_2(OMe)_2NMe,4H_2O$ or $C_{27}H_{23}O_5(OH)_4(OMe)_3(NMe)_2,8H_2O$, m.p. 215—217° (decomp.), $[\alpha]_D^{23}$ −12·9° in H_2O [hydrochloride, m.p. 220—222° (decomp., darkening at 214°); methiodide, m.p. 182—184°; aurichloride, m.p. 118° (decomp., contracting at 90°); platinichloride, m.p. 204° (decomp., darkening at 200°)], which gives a green–dark green colour with $FeCl_3$, and other colour reactions. A. Li.

VI—ORGANO-METALLIC COMPOUNDS.

Preparation of 4-acetamido-2-hydroxyphenylarsenoxide. M. A. Phillips (*J.C.S.*, 1941, 192).—*Biscarboxymethyl 4-acetamido-2-hydroxyphenylthioarsinite*, m.p. 160—161°, obtained from Na thiolacetate and 4 : 2 : 1-NHAc·C_6H_3(OH)·AsO_3H_2, when dissolved in 10% NaOH to a neutral solution and mixed with a neutral solution of *p*-benzarsenious acid, gives 4 : 2 : 1-NHAc·C_6H_3(OH)·AsO in 73% yield. F. R. S.

Sulphophenylarsinic acids and their derivatives. IV. Derivatives of *p*-sulphonamidophenylarsinic acid. J. F. Oneto and E. L. Way (*J. Amer. Chem. Soc.*, 1941, **63**, 762; cf. A., 1940, II, 360).—*p*-AsO_3H_2·C_6H_4·SO_2Cl and the appropriate amine in warm H_2O give p-*arsinobenzenesulphon-dimethylamide*, softens at 166—168°, -anilide, -p′-*carboxyanilide*, and -p′-*sulphonamidoanilide*, converted by HI into the derived *di-iodoarsines*, m.p. 132·5—134°, 125—126°, 234—236°, and 195—197°, respectively. Hydrolysis by aq. NH_3 then gives p-*sulphon-dimethylamido-*, anhyd. and +H_2O, -p′-*carboxyanilido-*, +H_2O, -*anilido-*, and -p′-*sulphonamidoanilido-*, +H_2O, -*phenylarsinoxide*. R. S. C.

Relative reactivities of organo-metallic compounds. XXXV. Colour tests for organo-bismuth and other organo-metallic compounds. H. Gilman and H. L. Yablunky (*J. Amer. Chem. Soc.*, 1941, **63**, 839—844; cf. A., 1940, II, 385).—$BiAr_3Cl_2$ with LiAr or MgArHal in C_6H_6 gives a deep purple colour; if the solution is boiled, cooled, and hydrolysed by H_2O, the org. layer is yellow to orange. Organo-metallic compounds more reactive than MgArHal give only the yellow or orange colour after hydrolysis. Less reactive Mg compounds, other types of Bi compounds, and alkyl compounds give no colour. The sensitivity is approx. that of the Michler's ketone test. Steric hindrance (*e.g.*, mesityl groups) may interfere with the test. Application of the test indicates that in the reaction of carbazole with MgMeI migration of MgI occurs on heating prior to carbonation. R. S. C.

VII.—PROTEINS.

Analysis of proteins. XIII. Caseo-phosphopeptone. J. Lowndes, T. J. R. Macara, and R. H. A. Plimmer (*Biochem. J.*, 1941, **35**, 315—320).—Caseo-phosphopeptone, obtained from caseinogen by Levene and Hill's method (A., 1933, 1062) and purified by repeated pptn. of the Pb salt, is an octapeptide containing N 10·56, P 5·77 (N : P ratio 4 : 1) and glutamic acid 26·8% (2 mols. per mol. of octapeptide) but no S, diamino-acids, tyrosine, tryptophan, or threonine. Of the total N 12·6% is amino-N. All the N is converted into NH_2-N in 48 hr. by treatment with 20% HCl and all P is removed by 5·5N-HCl in 48 hr. at 100° (but not by 0·25N-NaOH at 37° in 48 hr. or more). The acidity and the ratio of acidic H to N atoms indicate that, of 6 replaceable H atoms, two are in H_3PO_4 radicals, two in the glutamic acid residues, one in a terminal CO_2H, and one in another CO_2H. Oxidation with KIO_4 after hydrolysis for 36 hr. with 5·5N-HCl indicates the presence of 2 mols. of serine, hydroxyglutamic acid being probably absent. The results and those of Posternak (A., 1928, 1149) and Damodaran and Ramachandran (A., 1941, II, 115) suggest that the octapeptide is probably constituted thus: phosphoserylglutamic–X–X–phosphoserylglutamic–X–X, where X probably represents *iso*leucine (3 mols.) and aspartic acid (1 mol.). W. McC.

Amino-acids of phosphopeptone. C. Rimington (*Biochem. J.*, 1941, **35**, 321—327; cf. A., 1927, 1211).—Re-examination of the material previously obtained suggests that it consists of a nona- ($C_{37}H_{60}O_{33}N_9P_3$) and a deca-peptide ($C_{43}H_{71}O_{34}N_{10}P_3$) which each yield ~4 mols. of dicarboxylic acid per mol. when boiled for 48 hr. with 20% HCl. Hydroxyglutamic acid and threonine are absent but glutamic acid (I) is obtained in low yield. The hydrolysate of the decapeptide yields *iso*leucine (II) and probably contains phosphoserine. At 37°, 1% NaOH removes ~67% of the total P of phosphopeptone as PO_4''', the time-curve of the hydrolysis strongly resembling that for hydrolysis by bone-phosphatase. The decapeptide is possibly formed by the combination of 5 mols. of (I), one mol. of (II), 4 mols. of serine, and 3 H_3PO_4, 12 H_2O being eliminated, and the nonapeptide of the same constituents except (II), 11 H_2O being eliminated. W. McC.

Coupled oxidation of ascorbic acid and hæmoglobin. II. Formation and properties of choleglobin. III. Determination of choleglobin and of hæmoglobin and ascorbic acid consumption. IV. Labile iron of blood: production during choleglobin formation. J. W. Legge and R. Lemberg (*Biochem. J.*, 1941, **35**, 328—338, 339—352, 353—362; cf. A., 1939, III, 650).—II. The prep. of choleglobin (I) and cholehæmochromogen (II) by coupled oxidation of hæmoglobin (from cryst. horse oxyhæmoglobin or washed erythrocytes of sheep, ox, and horse) and ascorbic acid (V) is described. Reduced (I) has an absorption band at 628—630 mμ., increased in strength by

$Na_2S_2O_4$ and by incubation for short periods. After 30 min. incubation the band is replaced by a band at ~670 mμ. due to Fe^{III} choleglobin or oxycholeglobin (III); this change is reversed by $Na_2S_2O_4$. CO causes replacement of the band at 670 mμ. by a band at 628 mμ. due to CO-choleglobin production. CO also reacts with an alkaline solution of (II), shifting the absorption band from 618 to 628 mμ. Alkali converts (I) into denatured globin-cholehæmochromogen and shifts the band to 615—622 mμ. The green insol. pigment (chiefly Fe^{III} cholehæmochromogen) produced by denaturation when coupled oxidation has continued for > ~45 min. shows the absorption band of ferrous (II) at 616—618 mμ. (shifted to 628 mμ. by CO) when reduced with NaOH–$Na_2S_2O_4$. In C_5H_5N, this band is at 619 mμ.; in dil. AcOH and in neutral aq. suspension the band is at 628 mμ. Further oxidation of (I) and (II) occurs when coupled oxidation is continued for several hr., substances having absorption spectra similar to those of verdohæmatin compounds being produced. It is not known whether (I) combines reversibly with O_2 but, if (III) exists, it is more labile than oxyhæmoglobin (IV). Study of the action of H_2O_2 on (IV) in presence of KCN shows that cholehæmatin is distinct from verdohæmatin and that Barkan and Schales' "pseudohæmoglobin" (A., 1938, III, 551) is Fe^{II} denatured globin-cyancholehæmochromogen.

III. A spectrophotometric method of measuring the rate of production of (I) and (II) from hæmoglobin (VI) and methæmoglobin is described. The rate is diminished when AcSH, glutathione, or cysteine replaces (V) but not when reducton replaces it. At first, (I) is the only oxidation product but later other substances in addition to (I) and (II) are produced. At p_H 7·2 and 37° (I) is produced from (VI) in presence of concns. of (V) and glutathione such as occur in the tissues, glutathione increasing the rate of production by more than the val. expected from additive calculation. The reaction velocity is increased, without affecting (V) oxidation, by diminishing O_2 pressure to 15 mm. or by adding inhibitor for Cu [which prevents autoxidation of (V)] and is doubled by changing the p_H from 7·2 to 8·5. The temp. coeff. is high. In air, without shaking, approx. 10 mols. of (V) are oxidised per mol. of (I) produced. (VI) in erythrocytes is protected from rapid oxidation by the low permeability of the cell membrane and by an inhibitor in the stromata. H_2O_2 produces (I) from (VI) even in the absence of reducing substances. The first step in the production is probably transfer of H from (V) to (IV), a Fe^{II} (VI)–H_2O_2 compound being produced. This compound is converted partly into (I) and partly into methæmoglobin.

IV. Of the labile Fe of blood and (VI) solutions, 67% is probably an artefact arising from the oxidation of the prosthetic group of (VI) by the O_2 produced from (IV) by acid. The fraction of the labile Fe split off even in presence of CO is at least partly derived from a bile pigment–(VI) which yields bile acids when treated with acid, a small part only being derived from blood-catalase. The increase in the proportion of labile Fe which occurs during coupled oxidation of (VI) and (V) ∝ the concn. of (I) produced. Incubation of (I) for 16 hr. with 0·1N-HCl liberates ~66% of the Fe, the remainder being found as cholehæmatin in the ppt. of denatured protein. The elimination of Fe from (I) by acid is apparently not inhibited by CO or reducing substances. W. McC.

Some applications of periodic acid to the study of the hydroxyamino-acids of protein hydrolysates. I. Liberation of acetaldehyde and higher aldehydes by periodic acid. II. Detection and isolation of formaldehyde by periodic acid. III. Ammonia split from hydroxyamino-acids by periodic acid. IV. Hydroxyamino-acid fraction of wool. V. "Hydroxylysine." A. J. P. Martin and R. L. M. Synge (*Biochem. J.*, 1941, **35**, 294—314; cf. A., 1940, II, 385).—I. *dl*-Threonine (I) and HIO_4 at room temp. give a max. yield of ~70% of MeCHO (removed by aëration and absorbed in aq. $NaHSO_3$) at p_H ~7 in aq. $NaHCO_3$, independently of the presence of other amino-acids. *dl*-Serine (II) and -alanine, and *l*-cystine, -methionine, -tyrosine, etc., afford no MeCHO. Protein hydrolysates are examined. Volatile aldehydes from wool, casein, and gelatin are converted into the 2 : 4-dinitrophenylhydrazone; MeCHO only is identified. In the case of wheat gluten a little EtCHO is possibly obtained also, but this is not certain, as previous results are unreliable owing to possible confusion arising from the dimorphism of the 2 : 4-dinitrophenylhydrazone of MeCHO. *X*-Ray powder photographs [Miss F. O. Bell] failed to establish with certainty the presence of any derivative other than from MeCHO. A micro-method for the separation of 5% of EtCHO in a mixture with MeCHO, depending on "carrier" distillation using Et_2O as a solvent, is described.

II. No satisfactory method is found for the determination of CH_2O resulting from the action of HIO_4 on serine etc. Conditions for pptn. of CH_2O by dimedon are studied; the presence of other amino-acids seriously lowers the yield.

III. (I) or (II) and HIO_4 in 50% aq. K_2CO_3 at room temp. yield 88% or 83% of 1 mol. of NH_3, respectively. The method is applied to the determination of hydroxyamino-acid content of complete protein hydrolysates. Silk fibroin has, relatively, low (I) and high (II) content.

IV. The hydroxyamino-acid fraction prepared from a wool hydrolysate by the acetylation–benzoylation procedure is investigated. Low recoveries of threonine are obtained; nearly 2% of the N of wool is isolated as optically active serine.

V. The acetylation–benzoylation procedure is applied to the lysine fractions of gelatin and isinglass hydrolysates, when a picrate, explodes at 226—227°, is obtained (Van Slyke *et al.*, A., 1938, III, 757). The "hydroxylysine" is probably αε-diamino-δ-hydroxyhexoic acid; with HIO_4 it affords NH_3 and CH_2O. A. T. P.

VIII.—ANALYSIS.

Rapid determination of the nitrogen content of organic compounds by the Dumas method. T. Nishi (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 432—434B).—Shortening of the time required for an analysis depends mainly on the use of a Therex glass combustion tube which enables partial avoidance of loss of time during heating and cooling. H. W.

Determination of sulphur in organic compounds by hydrogenation. W. Theilacker and W. Schmid (*Angew. Chem.*, 1940, **53**, 255—256; *Gas- u. Wasserfach*, 1940, **83**, 601).—Ter Meulen's method for determining S in org. compounds by catalytic cracking and hydrogenation to H_2S has been improved and simplified. In the examination of substances containing N and halogens the method has the advantage over the method of combustion followed by volumetric determination of the H_2SO_4 formed in that it can be applied to all substances. A weighed sample is slowly evaporated in a stream of H_2 in a quartz or supremax tube, and the vapours are passed at red heat through platinised quartz wool on which S compounds are quantitatively converted into H_2S, which is absorbed in aq. AcOH containing $Zn(OAc)_2$. The ZnS formed is determined iodometrically. R. B. C.

Analytical procedures employing Karl Fischer reagent. VI. Determination of carbonyl compounds. J. Mitchell, jun., D. M. Smith, and W. M. D. Bryant (*J. Amer. Chem. Soc.*, 1941, **63**, 573—574; cf. A., 1939, I, 577).—A new analytical procedure for aldehydes and ketones is given. The H_2O formed in the reaction between CO: compounds and NH_2OH,HCl in presence of C_5H_5N is determined by titration with Karl Fischer reagent. Results for 21 aldehydes and ketones are given; camphor only does not react completely. The effect of interfering substances is discussed. W. R. A.

Iodometric determination of the sum of aldol and *p*-aldol in acetaldehyde. M. Hori (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 52—54).—The method depends on the fact that *p*-aldol is decomposed to aldol by $NaHSO_4$, and that aldol combines with $NaHSO_4$ in acid, and separates again in slightly alkaline solution. J. N. A.

Semimicro-determination of copper reduced by sugars. T. G. Phillips (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 181—183).—A modification of Bertrand's method is described. F. O. H.

Reduction of cystine at the dropping mercury electrode.—See A., 1941, I, 216.

Photocolorimetric determination of tannins. M. Rosenblatt and J. V. Peluso (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 170—181).—The blue colour developed by the Folin–Denis reagent (Na phosphotungstate–phosphomolybdate) was analysed by quartz spectrograph–photometer apparatus and the procedure established for attainment of max. transmission and stability compatible with good sensitivity. The method gives an error ≯0·5%. F. O. H.

INDEX OF AUTHORS' NAMES, A., II.

JUNE, 1941.

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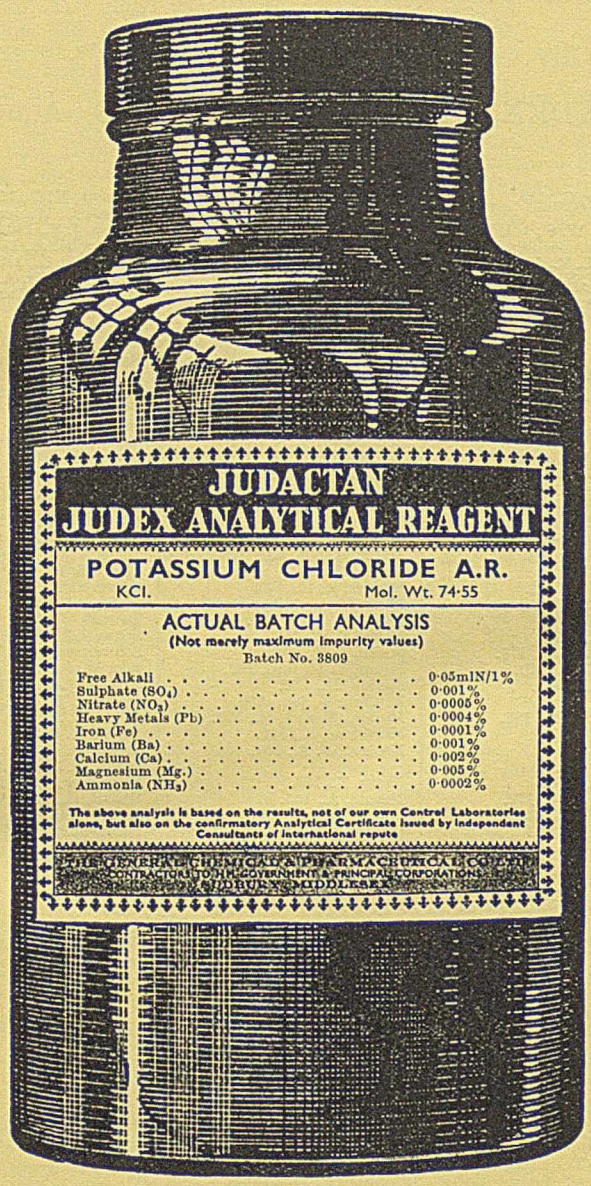
ACTUAL

BATCH

ANALYSIS



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