BRITISH CHEMICAL
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JULY, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

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A II—Organic Chemistry.

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I.—ALIPHATIC.

Chemical behaviour of free ethyl at low temperatures. G. Semerano L. Riccoboni, and F. Callegari (*Ber.*, 1941, **74**, [*B*], 1297—1308).—When $AgNO_3$ (1 mol.) and $PbEt_4$ (1·5—1·6 mols.) interact in EtOH at −80°, some decomp. of AgEt occurs; when this is completed by warming, the gas evolved contains C_2H_6 (53·2), C_4H_{10} (36·2), C_2H_4 (9·9%), and traces of CO_2 and CO. The Et thus yields only C_4H_{10} and $C_2H_6 + C_2H_4$. The deficiency of C_2H_4 is accounted for by interaction thereof with EtOH to yield Et_2O (isolated; cf. C., 1944, Part 3); in MeOH MeOEt is probably similarly formed. The reaction mechanism is discussed. R. S. C.

Manufacture of ethylene.—See B., 1944, II, 125.

Physical data of Δ^{α}-olefines and *n*-paraffins. A. W. Schmidt, V. Schoeller, and K. Eberlein (*Ber.*, 1941, **74**, [*B*], 1313—1324).—M.p., b.p., *d*, *n*, and η are recorded for most of the Δ^{α}-olefines and paraffins containing 5—30 C, including the following: Δ^{α}-C_nH_{2n} in which $n = 9$ m.p. −88°, b.p. 33·5°/11 mm., 10 m.p. −66·3°, b.p. 52°/11 mm., 11 m.p. −49·5°, b.p. 74·8°/11 mm., 12 m.p. −33·6°, b.p. 89—89·5°/11 mm., 13 m.p. −22·2°, b.p. 104°/11 mm., 15 m.p. −4°, b.p. 135·2°/11 mm., 17 m.p. 11°, b.p. 157°/11 mm., and 21 m.p. 35·5°, b.p. 134°/0·04 mm.; *n*-C_nH_{2n+2} in which $n = 8$ m.p. −57·0°, b.p. 124°/11 mm., 11 m.p. −24·8°, b.p. 74°/11 mm., 13 m.p. −5·5°, b.p. 104°/11 mm., 17 m.p. 21·2°, b.p. 157°/11 mm., 21 m.p. 39·4°, b.p. 129°/0·05 mm., 26 m.p. 56·4°, b.p. 169°/0·05 mm., and 30 m.p. 65·5°, b.p. 202°/0·05 mm. The olefines are prepared from MgRHal and $CH_2{:}CH{\cdot}CH_2Br$ in Et_2O. *n*-Octane was prepared by the Wurtz–Fittig reaction (60% yield), *n*-C_nH_{2n+2} ($n = 11$—21) by hydrogenation of C_nH_{2n}, and *n*-$C_{26}H_{54}$ and -$C_{30}H_{62}$ by electrolysis of the K salt in EtOH. R. S. C.

Structure of copolymers of *iso*butylene and isoprene. J. Rehner, jun. (*Ind. Eng. Chem.*, 1944, **36**, 46—51).—O_3 degradation, in $CHCl_3$ or, better, in CCl_4, applied to investigation of the structure of *iso*butylene–isoprene copolymers of various degrees of unsaturation, indicates that the isoprene units are exclusively in the $\alpha\delta$-position as in natural rubber; any units with $\alpha\beta$- or $\gamma\delta$-addition must be $\ll$1% of the isoprene present. No occurrence of the C_5H_8 units in sequences could be detected, and the C_5H_8 must enter the growing chain in a random manner. D. F. T.

Separation of divinylacetylene and ethinylbutadiene ($\Delta^{\alpha\epsilon}$-hexadien-Δ^{γ}- and $\Delta^{\gamma\epsilon}$-hexadien-Δ^{α}-inene).—See B., 1944, II, 126.

Effect of natural inhibitors on the photochemical oxidation of iodoform. K. Weber and M. Czirfusz (*Ber.*, 1941, **74**, [*B*], 1338—1342).—Light-petroleum extracts of oatmeal or cornflour decrease the rate of autoxidation of CHI_3 in light. This is shown not to be due to absorption of the effective light. R. S. C.

Allylic rearrangements. XIV. Hydrolysis of butenyl chlorides.—See A., 1944, I, 157.

Polyene series. XII. Ethynylcarbinols from sorbaldehyde and octatrienal. Poly-carbon anionotropic rearrangements. I. M. Heilbron, E. R. H. Jones, and J. T. McCombie. **XIII. Acetylenyl glycols from polyene aldehydes and their rearrangement with acids.** I. M. Heilbron, E. R. H. Jones, and R. A. Raphael. **XIV. Anionotropic rearrangements of carbinols from condensation of crotonaldehyde with vinyl- and β-methylvinyl-acetylene.** I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon. **XV. Condensation of carbonyl compounds with propenylethynylcarbinol and hex-3-en-5-yn-2-ol.** J. Cymerman, I. M. Heilbron, A. W. Johnson, and E. R. H. Jones. **XVI. Condensation of $\alpha\beta$-unsaturated ketones with 1-hexyne.** J. Cymerman, I. M. Heilbron, and E. R. H. Jones (*J.C.S.*, 1944, 134—136, 136—139, 140—141, 141—144, 144—147; cf. A., 1943, II, 249).—XII. Sorbaldehyde (**I**) in liquid NH_3 with C_2HNa gives *octa-$\delta\zeta$-dien-α-yn-γ-ol* (**II**), b.p. 71—74°/0·5 mm. Octatrienal (**III**) (similar conditions) gives *deca-$\delta\zeta\theta$-trien-α-yn-γ-ol* (**IV**), b.p. 94—96°/1 mm., m.p. 73·5—74·5°. (**II**) undergoes anionotropic rearrangement with H_2SO_4 (N_2 atm.) to give *octa-$\gamma\epsilon$-dien-α-yn-η-ol*, b.p. 62—65°/0·5 mm., unstable in air, which on hydrogenation (PtO_2) and oxidation (CrO_3) yields $COMe{\cdot}C_6H_{13}$-*n*. Similarly (**IV**) gives *deca-$\gamma\epsilon\eta$-trien-α-yn-ι-ol*, m.p. 82—83°, which affords $COMe{\cdot}C_8H_{17}$-*n*. Replacement of an ethenoid by an acetylenic linking has a negligible effect on the location of the absorption max.

XIII. (**I**) $(\ddot{C}{\cdot}MgBr)_2$ (from C_2H_2 and MgEtBr) in N_2 followed by aq. NH_4NO_3 gives *tetradeca-$\beta\delta\kappa\mu$-tetraen-η-yne-$\zeta\iota$-diol* (**V**), m.p. 95—102°. (**III**) (similar conditions) gives *octadeca-$\beta\delta\zeta\mu\xi\pi$-hexaen-$\iota$-yne-$\theta\lambda$-diol* (**VI**), m.p. 154°. (**V**) undergoes anionotropic rearrangement (aq. H_2SO_4, N_2 atm.) to *tetradeca-$\gamma\epsilon\iota\lambda$-tetraen-$\eta$-yne-$\beta\nu$-diol* (**VII**), m.p. 115—116° (sealed tube). Similarly (**VI**) gives *octadeca-$\gamma\epsilon\eta\lambda\nu$-hexaen-$\iota$-yne-$\beta\rho$-diol* (**VIII**), sinters 145°, m.p. 149° (sealed tube). (**VII**) on hydrogenation and oxidation (NaOBr) yields $[CH_2]_{10}(CO_2H)_2$. (**VIII**) on hydrogenation gives *octadecane-$\beta\rho$-diol*, which is oxidised to $[CH_2]_{14}(CO_2H)_2$. (**VII**) and (**VIII**) resemble corresponding polyenes in their light-absorption properties.

XIV. Mg vinylacetylenyl bromide with $CHMe{:}CH{\cdot}CHO$ (**IX**) gives *octa-$\beta\eta$-dien-ϵ-yn-δ-ol* (**X**), b.p. 72—73°/3·5 mm. (*α-naphthylurethane*, m.p. 95—96°), also given by (**IX**) and $CH_2{:}CH{\cdot}C{:}CH$ with Na in liquid NH_3. (**X**) with H_2SO_4 (N_2) is isomerised to *octa-$\gamma\eta$-dien-ϵ-yn-β-ol* (**XI**), b.p. 78°/4 mm. Hydrogenation and subsequent oxidation of (**XI**) yields $COMe{\cdot}C_6H_{13}$-*n*. Methylvinylacetylene and (**IX**) (similar conditions) give *η-methylocta-$\beta\eta$-dien-ϵ-yn-δ-ol* (**XII**), b.p. 62—68°/3 mm. (*α-naphthylurethane*, m.p. 99°), which isomerises to *η-methylocta-$\gamma\eta$-dien-ϵ-yn-β-ol* (**XIII**), b.p. 75—78°/2 mm., 27° (bath)/10^{-4} mm. (*α-naphthylurethane*, m.p. 89°). (**XIII**) is hydrogenated to η-methyloctan-β-ol, b.p. 57°/3 mm. (*α-naphthylurethane*, m.p. 75°), which gives (CrO_3) η-methyloctan-β-one, b.p. 78°/17 mm. (semicarbazone, m.p. 132—133°). Absorption spectra of (**X**), (**XI**), (**XII**), and (**XIII**) are analogous in location and intensity of max. to each other and compounds previously described.

XV. $CHMe{:}CH{\cdot}CH(OH){\cdot}C{:}CH$ condenses (Grignard method) with $COPh_2$, $Pr^{\alpha}CHO$, PhCHO, and (**IX**) respectively to $\alpha\alpha$-diphenylhept-ϵ-en-β-yne-$\alpha\delta$-diol, m.p. 131°, *dec-β-en-ϵ-yne-$\delta\eta$-diol* (**XIV**), b.p. 52° (bath)/10^{-4} mm. [two *bisphenylurethanes*, m.p. 125° and 153° (decomp.); *bis-α-naphthylurethane*, m.p. 194° (decomp.)], α-phenylhept-ϵ-en-β-yne-$\alpha\delta$-diol, b.p. 80—90° (bath)/10^{-4} mm., m.p. 108°, and deca-$\beta\theta$-dien-ϵ-yne-$\delta\eta$-diol (**XV**), b.p. 90—100° (bath)/10^{-4} mm., m.p. 91°. Hex-γ-en-ϵ-yn-β-ol (**XVI**) with $Pr^{\alpha}CHO$, PhCHO, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, COMeEt, (**IX**), and $COPh_2$ respectively yields *dec-γ-en-ϵ-yne-$\beta\eta$-diol* (**XVII**), b.p. 72° (bath)/10^{-4} mm., *α-phenylhept-δ-en-β-yne-$\alpha\zeta$-diol*, b.p. 78° (bath)/10^{-4} mm., *α-(p-anisyl)hept-δ-en-β-yne-$\alpha\zeta$-diol*, b.p. 78° (bath)/10^{-4} mm., m.p. 19—20°, *γ-methylnon-ζ-en-δ-yne-$\gamma\theta$-diol*, b.p. 63° (bath)/10^{-4} mm., *deca-$\gamma\theta$-dien-ϵ-yne-$\beta\eta$-diol* (**XVIII**), b.p. 75° (bath)/10^{-4} mm., and *$\alpha\alpha$-diphenylhept-δ-en-β-yne-$\alpha\zeta$-diol* (**XIX**), b.p. 85° (bath)/10^{-4} mm. Both (**XV**) and (**XVIII**) give deca-$\gamma\eta$-dien-ϵ-yne-$\beta\iota$-diol, b.p. 110—115° (bath)/10^{-4} mm., and (**XIV**) with aq. H_2SO_4 yields (**XVII**). The products from (**XVI**), with the exception of (**XIX**) which dissociates into $COPh_2$, exhibit light-absorption characteristics consistent with the conjugated vinylacetylene chromophore in their mol.

XVI. $CBu^{\alpha}{:}CH$ (converted into $CBu^{\alpha}{:}C{\cdot}MgBr$ by MgEtBr) condenses with $COMe{\cdot}CH{:}CH_2$, $COMe{\cdot}CH{:}CHMe$, mesityl oxide (**XX**), and oct-γ-yn-β-one respectively to give at room temp. *γ-methylnon-α-en-δ-yn-γ-ol* (**XXI**), b.p. 61—61·5°/3·5 mm., *δ-methyldec-β-en-ϵ-yn-δ-ol* (**XXII**), b.p. 62—62·5°/2 mm., *$\beta\delta$-dimethyldec-β-en-ϵ-yn-δ-ol* (**XXIII**), b.p. 69—69·5°/3 mm., and η-methyltrideca-$\epsilon\theta$-diyn-η-ol. (**XXI**), (**XXII**), and (**XXIII**) show no light absorption. With aq. H_2SO_4, (**XXI**) gives *γ-methylnon-β-en-δ-yn-α-ol* (**XXIV**), b.p. 75·5—76°/3·5 mm. (*α-naphthylurethane*, m.p. 69—70°). (**XXIV**) yields H_2–PtO_2) γ-methylnonan-α-ol, b.p. 121°/24 mm. (*α-naphthylurethane*, m.p. 49°), which gives (CrO_3) β-*n*-hexylbutyric acid (p-*toluidide*, m.p. 76—77°). (**XXII**) similarly gives *δ-methyldec-γ-en-ϵ-yn-β-ol* (**XXV**), b.p. 84°/2 mm., 28° (bath)/10^{-4} mm. (*α-naphthylurethane*, m.p. 71°); δ-methyldecan-β-ol, b.p. 104°/12 mm. (*α-naphthylurethane*, m.p. 63°), and δ-methyldecan-β-one, whilst (**XXIII**) yields *$\beta\delta$-dimethyl-γ-en-ϵ-yn-β-ol* (**XXVI**), b.p. 35° (bath)/10^{-4} mm. (**XVI**) condenses with (**XX**) to give *$\beta\delta$-deca-$\beta\eta$-dien-ϵ-yne-$\delta\iota$-diol*, b.p. 60° (bath)/10^{-4} mm., which undergoes some rearrangement with aq. H_2SO_4. The anionotropic rearrangements above are easier than those for related *sec.* carbinols; it is suggested that this is due to the inductive effect of the *tert.* Me group which facilitates the separation of the hydroxylic anion. The isomerisation products (**XXIV**), (**XXV**), and (**XXVI**) exhibit light-absorption characteristic of the vinylacetylene chromophore. D. G.

$\beta\gamma\delta\epsilon$-Di*iso*propylidene-*DL*-xylitol. R. M. Hann, A. T. Ness, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 73—76).—$\beta\gamma\delta\epsilon$-Di*iso*propylidene-*DL*-xylitol (modified prep.; cf. Tipson *et al.*, A., 1943,

II, 149), m.p. 33—34° (*α-acetate*, m.p. 45—46°; *α-benzoate*, m.p. 61—62°), gives an *α-p*-toluenesulphonate (I), m.p. 77—78° (*loc. cit.*, 70—71°), which with NaI in $(CH_2Ac)_2$ at 60° gives the *α-iodide*, m.p. 57—59°, reduced by H_2–Raney Ni in $Ba(OMe)_2$–MeOH at 27°/810 mm. to *α-deoxy-βγδε-diisopropylidene*-DL-*xylitol* (II), b.p. 88—90°/6—7 mm. (II) consumes 3 HIO_4 in H_2O at 25°. Boiling 20% AcOH hydrolyses (II) to *α-deoxy*-DL-*xylitol*, a syrup, which reduces 2·87 $NaIO_4$ in H_2O at 25°, giving 0·91 MeCHO. These facts prove the structure of (I). *αβγδ*-Dibenzylidene-*D*-sorbitol *εζ*-di-*p*-toluenesulphonate with NaI in $COMe_2$ at 100° gives 2 p-$C_6H_4Me{\cdot}SO_3Na$ and *αβγδ-dibenzylidene*-D-*sorbitoleën*, m.p. 187—188°, $[\alpha]_D^{20}$ +19·0° in $CHCl_3$, reduced by H_2–Raney Ni to *αβγδ-dibenzylidene-εζ-deoxy*-D-*sorbitol*, m.p. 184—185°, $[\alpha]_D^{20}$ +39·4° in $CHCl_3$, whence it appears that p-$C_6H_4Me{\cdot}SO_2$ esterified to contiguous primary and *sec.* OH are both removed by NaI (cf. *loc. cit.*).
R. S. C.

Isomerisation of trialkyl phosphites. G. M. Kosolapov (*J. Amer. Chem. Soc.*, 1944, **66**, 109—111).—Interaction of Et_3PO_3 with Bu^aBr (at 150°), n-$C_6H_{13}Br$ (at 133° and 150°), or $(CH_2Br)_2$ (at 150°) is followed by measuring the rate of evolution of EtBr. According to the proportions of the reactants, $(CH_2Br)_2$ reacts according to the equation, $2Et_3PO_3 + (CH_2Br)_2 \rightarrow 2EtBr + CH_2[PO(OEt)_2]_2$, or $Et_3PO_3 + (CH_2Br)_2 \rightarrow EtBr + (OEt)_2PO{\cdot}[CH_2]_2{\cdot}Br$ (I). (I) is, however, not isolated because of its instability. An induction period occurs in all the reactions, during which $PRBr(OEt)_3$ accumulates; this is shortened by rise in temp.
R. S. C.

Purification of ethers.—See B., 1944, II, 126.

Sulphur linkage in vulcanised rubbers. Reaction of methyl iodide with sulphur compounds.—See B., 1944, II, 187.

Carbon–carbon cleavage in the hydrogenolysis by Raney nickel catalyst of ethylenedithiol and its ethers. H. R. Snyder and G. W. Cannon (*J. Amer. Chem. Soc.*, 1944, **66**, 155—156).—Hydrogenation (Raney Ni) of $(CH_2{\cdot}SR)_2$ gives (*a*) $2RH + C_2H_6$ and (*b*) $2RH + 2CH_4$. The following yields of C_2H_6 and CH_4, respectively, are recorded: R = $[CH_2]_2{\cdot}CH(NH_2){\cdot}CO_2H$ 66, 34, $\begin{matrix}NPh{\cdot}CO\\ CO{-}NH\end{matrix}\!\!>\!CH{\cdot}[CH_2]_2$ 56, 44, $OH{\cdot}[CH_2]_2$ 100, 0, Ph 77, 23, and H 86, 14%.
R. S. C.

Action of nitric acid on ethyl *iso*dehydracetate. L. Panizzi (*Gazzetta*, 1942, **72**, 423—429).—5-Carbethoxy-4 : 6-dimethylcumalin (Et *iso*dehydracetate), $CO_2Et{\cdot}C\!\!<\!\!\begin{matrix}CMe{:}CH\\ CMe{-}O\end{matrix}\!\!>\!CO$, with HNO_3 (*d* 1·52) gives its 3-NO_2-derivative (I) (cf. Angeli, A., 1893, i, 197), reduced by $SnCl_2$–HCl–Et_2O to the stannichloride of 3-*amino-5-carbethoxy*-4 : 6-*dimethylcumalin*, m.p. 80—81° (*Bz* derivative, m.p. 128—129°), which with conc. aq. NH_3 gives a *product*, $C_{10}H_{15}O_5N$, m.p. 203—205° (decomp.), regarded as $CO_2Et{\cdot}CHAc{\cdot}CMe{:}C(NH_2){\cdot}CO_2H$ or $CO_2Et{\cdot}CHAc{\cdot}CHMe{\cdot}C(:NH){\cdot}CO_2H$. With $NHPh{\cdot}NH_2$–AcOH at the b.p., (I) gives Et 1-phenyl-3 : 5-dimethylpyrazole-4-carboxylate, CO_2, and $MeNO_2$.
E. W. W.

Esterification under the catalytic influence of acid chlorides. K. Freudenberg and W. Jakob (*Ber.*, 1941, **74**, [*B*], 1001—1002).—Small amounts of AcCl, $ClCO_2Et$, $SOCl_2$, or n-$C_{17}H_{35}{\cdot}COCl$ cause very rapid esterification of acids with alcohols at $\not>20°$. Examples are the Me and Et esters of veratric, *p*-nitrobenzoic, and stearic acid. Polyacrylic acid is thus 40% esterified; $OH{\cdot}CHPh{\cdot}CO_2Me$ is not thus formed. A mol. compound of the acid chloride with, probably, the acid is formed, which reacts faster with the alcohol than with H_2O; thus, ethylene glycol monopalmitate is formed only if an excess of glycol is present and the dipalmitate cannot be obtained. The method is preferable to that using HCl.
R. S. C.

Chemical morphology of liquids. III. Liquid-crystalline aliphatic monocarboxylic acids. C. Weygand, R. Gabler, and J. Hoffmann (*Z. physikal. Chem.*, 1941, **B**, **50**, 124—127).—$\Delta^{\alpha\gamma}$-Nonadienoic acid, prepared by condensation of $CHBu^a{:}CH{\cdot}CHO$ with $CH_2(CO_2H)_2$ followed by decarboxylation, passes above 23° into a characteristic nematic phase, becoming clear at 49°. The melt may be supercooled to ~10°, and still lower with small drops, but no smectic phase appears. It is suggested that the diene group adjacent to the CO_2H plays the same rôle as the C_6H_6 ring in the mesomorphic *p-n*-alkylbenzoic acids, conferring rigidity on a considerable length of the dimeric acid mol., and that such rigidity, provided that the m.p. is sufficiently low, will result in mesomorphic properties. The mesomorphic states of the many *p*-derivatives of C_6H_6, of sterol derivatives, and of Tl and alkali-metal soaps are discussed in the light of this concept.
W. R. A.

Shellac. XIII. Transformation of aleuritic into hexadecenoic acid. W. Nagel and W. Mertens (*Ber.*, 1941, **74**, [*B*], 976—982).—Me *iso*propylidenealeuritate, an oil, prepared from Me aleuritate, $COMe_2$, and a little H_2SO_4 at room temp., with p-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N at room temp. gives the oily *o-p*-toluenesulphonate (I), which with NaOMe–MeOH at 70—75° yields *aleuritic acid o-Me ether* [*θι-dihydroxy-o-methoxypalmitic acid*] (80%), m.p. 76° (*Me* ester, m.p. 65°). With NaI in $COMe_2$ at ~70°, (I) gives the *o*-I-ester, which with Zn and H_2SO_4 and then boiling 3N-KOH gives *θι*-dihydroxypalmitic acid (II), m.p. 89—90°. The Me ester thereof with p-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N gives an oily ester, converted by NaI–$COMe_2$ and then Zn dust in AcOH into *Me* Δ^9-n-*hexadecenoate*, b.p. 181—183°/15 mm. Δ^9-n-*Hexadecenoic acid* (III), m.p. 33°, obtained therefrom by 2N-KOH, gives a dibromide, m.p. ~30°, and is converted by $KMnO_4$–KOH into (II) (~40%). Ag_2O oxidises (II) (0·6) in boiling C_6H_6 to azelaic (0·25) and heptoic acid (0·03 g.). (III) is accompanied by an isomeric oily acid, oxidised by $KMnO_4$ to a $(OH)_2$-acid, m.p. 125°. (III) may be identical with hypogaic acid.
R. S. C.

Unsaturated synthetic glycerides. III. Unsaturated symmetrical mixed diglycerides. B. F. Daubert and H. E. Longenecker (*J. Amer. Chem. Soc.*, 1944, **66**, 53—55).—Glyceryl α-esters and CPh_3Cl in quinoline at 100° give *glyceryl α-CPh_3 ether α′-dodecoate* (I), m.p. 47·0°, *α′-tetradecoate*, m.p. 56·0°, α′-palmitate, m.p. 62·0°, and α′-stearate, m.p. 66·0°, converted by oleyl chloride in quinoline–$CHCl_3$ at room temp. into the *β-oleates*. Hydrolysis of these products by HCl in light petroleum at ~5° involves migration, yielding *glyceryl* α-n-*dodecoate*, m.p. 32·0°, α-n-*tetradecoate*, m.p. 41·0°, α-palmitate, m.p. 46·0°, and α-stearate, m.p. 54·0°, *α′-oleate*, structures of which are proved by hydrogenation. *Glyceryl* α-n-*dodecoate α′-stearate*, m.p. 62·0°, is also obtained from (I) by way of *glyceryl α-CPh_3 ether β*-n-*dodecoate α′-stearate*, m.p. 25·0°.
R. S. C.

Long-chain acids containing a quaternary carbon atom. III. W. H. Hook and (Sir) R. Robinson (*J.C.S.*, 1944, 152—154; cf. A., 1944, II, 17).—Et α-methylhexylidenecyanoacetate (I) treated with n-$C_5H_{11}{\cdot}MgBr$ in presence of Cu_2I_2 gives *Et α-cyano-ββ-di*-n-*amylbutyrate* (II), b.p. 137—139°/0·3 mm., and *Et α-cyano-β-methyloctoate*, b.p. 90—92°/0·1 mm. (II), after boiling with H_2SO_4–AcOH–H_2O, and decarboxylation (160°/vac.), yields *ββ-di*-n-*amylbutyric* [*β-methyl-β*-n-*amyloctoic*] *acid*, b.p. 125—130°/0·3 mm. *Et α-methyldecylidenecyanoacetate*, b.p. 146—148°/0·25 mm. (from $COMe{\cdot}C_9H_{19}$-n and $CN{\cdot}CH_2{\cdot}CO_2Et$), with $MgBu^aBr$ and Cu_2I_2 gives *Et α-cyano-β-n-butyl-β*-n-*nonylbutyrate*, b.p. 150—160°/0·2 mm., which on hydrolysis and decarboxylation gives β-n-*butyl-β*-n-*nonylbutyronitrile* (III), b.p. 130—136°/0·3 mm., and a little *β-methyldodecoamide*, m.p. 87°. (III) after hydrolysis and treatment with MeOH and H_2SO_4 yields *Me β*-n-*butyl-β*-n-*nonylbutyrate* (IV), b.p. 116—120°/0·1 mm. The hydrolysis also gives *β*-n-*butyl-β*-n-*nonylbutyramide*, b.p. 165—180°/0·45 mm., which yields (IV) on hydrolysis. Alkaline hydrolysis of (IV) gives *β*-n-*butyl-β*-n-*nonylbutyric acid*, b.p. 155—157°/0·3 mm. (I) with n-$C_7H_{15}{\cdot}MgBr$ yields *Et α-cyano-β*-n-*amyl-β*-n-*heptylbutyrate*, b.p. 155—158°/0·12 mm., which affords β-n-*amyl-β*-n-*heptylbutyronitrile*, b.p. 123—126°/0·25 mm., *Me β*-n-*amyl-β*-n-*heptylbutyrate*, b.p. 115—117°/0·2 mm., and *β*-n-*amyl-β*-n-*heptylbutyric acid*, b.p. 144—149°/0·45 mm. Similarly *Et α-methyloctylidenecyanoacetate*, b.p. 165—168°/13 mm., with n-$C_7H_{15}{\cdot}MgBr$ gives *Et α-cyano-ββ-di*-n-*heptylbutyrate*, b.p. 168—172°/0·5 mm., *ββ-di*-n-*heptylbutyronitrile*, b.p. 145—150°/0·5 mm., *Me ββ-di*-n-*heptylbutyrate*, b.p. 135—140°/0·4 mm., and *ββ-di*-n-*heptylbutyric acid*, b.p. 168—172°/0·6 mm. *Et α*-n-*propyliso*hexylidenecyanoacetate, b.p. 120—125°/0·4 mm. (from $COPr^a{\cdot}C_5H_{11}$-*iso*), with $CH_2Bu^{\beta}{\cdot}MgI$ gives *Et α-cyano-β*-n-*propyl-ββ-diiso*amylpropionate, b.p. 140—145°/0·7 mm., *β*-n-*propyl-ββ-diiso*amylpropionitrile, b.p. 115—118°/0·8 mm., *Me β*-n-*propyl-ββ-diiso*amylpropionate, b.p. 100—108°/0·3 mm., and *β*-n-*propyl-ββ-diiso*amylpropionic acid, b.p. 138—145°/0·3 mm. (*amide*, m.p. 52—53°). Of the above, the C_{18} acids are most active bactericidally, but not more so than diheptylacetic acid. The prep. of *θ-keto-ζ-methyl-ζ*-n-*amyltridecane*, b.p. 165—170°/19 mm., is also described.
D. G.

Linear superpolyesters from dilinoleic acid. J. C. Cowan and D. H. Wheeler (*J. Amer. Chem. Soc.*, 1944, **66**, 84—88).—Superpolymers (*i.e.*, mol. wt. >10,000) are obtained by heating dilinoleic acid (I) with $OH{\cdot}[CH_2]_{10}{\cdot}OH$, and hydrogenated dilinoleyl glycols. Owing to loss of $(CH_2{\cdot}OH)_2$, this glycol gives superpolymers only by glycolysis in presence of p-$C_6H_4Me{\cdot}SO_3H$. Superpolymers from (I) are essentially similar to those from hydrogenated (I), so that the unsaturation plays no vital rôle. They are sol. in $CHCl_3$ and are converted into cross-linked, non-cryst. solids by long exposure to air or by heating at 290—300°. Determination of mol. wt. by end-group assay or η gives concordant results, except at very high mol. wts. when end-group assay has a large experimental error.
R. S. C.

Chemistry of *Phytomonas tumefaciens*. II. Composition of acetone-soluble fat. S. F. Velick and R. J. Anderson. **III. Phytomonic acid, a new branched-chain fatty acid.** S. F. Velick (*J. Biol. Chem.*, 1944, **152**, 523—531, 533—538).—II. *P. tumefaciens* (I), grown on a medium in which sucrose is the main source of C, contains 6·4% of lipins and 41·7% of $COMe_2$-sol. fat, m.p. 9°. The latter contains ~70% of free fatty acids, which after hydrolysis with boiling KOH–EtOH (N_2) afford palmitic acid (II), and (mainly) liquid acids which are reduced (H_2–PtO_2), esterified (CH_2N_2), and hydrolysed to stearic acid (III) + some (II), and a little of an *acid* (IV), $C_{20}H_{40}O_2$, m.p. ~15° (liquid Me ester). The presence of glycerol in the H_2O-sol. constituents after hydrolysis suggests that the fat is a mixture of free fatty acids and neutral glycerides. In the unsaponifiable fraction, some Ph_2O, m.p. 28° (Br_2-derivative,

m.p. 55·6—56°), is isolable, but is not found in organisms grown under slightly different conditions.

III. The hydrolysis product (boiling 5% aq. H_2SO_4 under N_2) of the phosphatide from (I) is reduced (H_2–PtO_2–EtOH), (II) + (III) are removed, and a branched-chain acid, "*phytomonic acid*," m.p. 24° (*hydrazide*, m.p. 56·6°), identical with (IV), is isolated through its Me ester. It is probably a homologue of tuberculostearic acid.

A. T. P.

Use of potassium *tert*-amyloxide for the alkylation of acetoacetic ester and its alkyl substitution products. W. B. Renfrow, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 144—146).—KO·CMe_2Et–CMe_2Et·OH is approx. as efficient as NaOEt–EtOH for condensation of *n*-AlkBr (Alk = Et or Bu) with $CH_3Ac·CO_2Et$, but is superior for branched-chain AlkBr (Alk = Pr^{β} 50%, Bu^{β} 61%, *iso*-C_5H_{11} 72% yield), and much superior for alkylation of CHRAc·CO_2Et ($CEt_2Ac·CO_2Et$ 75%, $CBu^{\alpha}_2Ac·CO_2Et$ 70% yield). Superiority of KO·CMe_2Et is due to the stronger base hindering the reverse Claisen equilibrium and depressing dissociation of the enolates. R. S. C.

Acidity and diazomethane reaction of *C*-methylacetoacetic ester. F. Arndt, L. Loewe, and B. Beyer (*Ber.*, 1941, **74**, [*B*], 1460—1464).—The rate of reaction of COR·CH_2·CO_2Et with CH_2N_2 depends on the amount of enol in the equilibrium mixture, which parallels the acidity of the enol. The inductive effect of R is the primary factor. When *O*-methylation is slow, formation of the γ-ethylene oxide (and thence the *C*-Me derivative) occurs. CHMeAc·CO_2Et (I) reacts very slowly with CH_2N_2 in Et_2O, but in Et_2O–MeOH gives, more quickly, a mixture of (II), estimated by its OMe content to contain 1 part of OMe·CMe:CMe·CO_2Et and 4 parts of *Et βγ-epoxy-αβ-dimethyl*-n-*butyrate* (III). Treating (II) with conc. aq. HCl–Et_2O at −20° (2 hr.) and then room temp. (1 hr.) gives *Et β-hydroxy-α-methyl-β-chloromethyl*-n-*butyrate* (IV), b.p. 98—100°/8 mm., which with 2·5% aq. KOH–Et_2O gives pure (III), b.p. 62—63°/5 mm., whence Ac_2O and a little $FeCl_3$ at room temp. and then 100° give *Et β-acetoxy-α-methyl-β-acetoxymethyl*-n-*butyrate* (V), b.p. 88—91°/2 mm. (III) and (IV), but not (V), give abnormally high OMe vals. (I) gives a less acid enol than does $CH_2Ac·CO_2Et$ (VI). When the Na derivative of (VI) is treated with MeI in PhMe, unchanged (VI) is removed from the product in Et_2O by aq. NH_3 and the (I) is then extracted by N-NaOH at 0° and immediately recovered therefrom by cold 10% H_2SO_4 under Et_2O; the Et_2O residue contains a little $CMe_2Ac·CO_2Et$. The yield of (I) depends largely on the loss in alkali. Pure (I) has b.p. 59°/5 mm. R. S. C.

***r*-α-Hydroxy-ββ-dimethyl-γ-butyrolactone (pantolactone).** J. H. Ford (*J. Amer. Chem. Soc.*, 1944, **66**, 20—21).—OH·CH_2·CMe_2·CHO (? its dimeride, 4-*hydroxy*-5 : 5-*dimethyl*-2-β-*hydroxy*-tert.-*butyl*-1 : 3-*dioxan*), m.p. 78—81°, with NaCN and then HCl in aq. $CaCl_2$, finally at 100°, gives a solid solution, m.p. 89·8—91·0°, b.p. 117—121°/10 mm., α 0, of the *d*- and *l*-forms of pantolactone.

R. S. C.

Branched-chain fatty acids. II. Synthesis in the C_{19}- and C_{25}-series. Preparation of keto-esters. J. Cason and F. S. Prout (*J. Amer. Chem. Soc.*, 1944, **66**, 46—50; cf. A., 1942, II, 297).—CH_2Bu^{β}·MgBr and $CdCl_2$ in Et_2O–N_2 at 0° and then room temp. give $Cd(CH_2Bu^{\beta})_2$, which with $CO_2Me·[CH_2]_2·COCl$ (I) in C_6H_6 exothermally and then at the b.p. gives $CH_2Bu^{\beta}·CO·[CH_2]_2·CO_2Me$ (73·5%; 42·5% obtained in Et_2O), b.p. 116·5—117°/8 mm., and a little $CO_2Me·[CH_2]_2·CO_2Et$. $Cd(CH_2Bu^{\beta})_2$ and ground $(CH_2·CO)_2O$ in boiling C_6H_6 give $CH_2Bu^{\beta}·CO·[CH_2]_2·CO_2H$ (30·8%), b.p. 152—153°/4 mm., and fractions, b.p. 100—111°/4 mm. and 147—150°/4 mm. $Cd(CH_2Bu^{\beta})_2$ and $CO_2Et·[CH_2]_8·COCl$ give similarly *Et ι-keto-ν-methyl*-n-*tetradecoate* (85%), b.p. 180—182°/3 mm. $CdMe_2$ gives similarly $COMe·[CH_2]_4·CO_2Et$ (II) (86·5%) [semicarbazone, m.p. 104·8—107° (lit. 107°)] and $COMe·[CH_2]_8·CO_2Et$ (III) (89·6%) (*semicarbazone*, m.p. 110·7—112·8°). Hydrolysis of crude (I) yields the derived acid, dimorphic, m.p. 59° (immediate), partly resolidifies, remelts at 60° (cf. lit.), $[CH_2]_8(CO_2H)_2$ (IV), and *dodecane-βλ-dione*, m.p. 67·4—67·8° [obtained by further interaction of (III) with $CdMe_2$]. $Zn(CHMePr^{\alpha})_2$ and (I) in Et_2O at −5° to −7° give *γ-keto-δ-methyl*-n-*octoate* (21·5%), b.p. 130·5—130·7°/21 mm. $Cd(CH_2·CHMeEt)_2$ and (I) in Et_2O give 24—27% of crude $CHMeEt·CH_2·CO·[CH_2]_2·CO_2Me$, b.p. 132—134°/16 mm., which by hydrolysis yields the derived acid [*semicarbazone*, m.p. 137—138° (decomp.)] and by Zn–Hg in aq. HCl gives $CHMeEt·[CH_2]_4·CO_2H$, b.p. 98—105°/1—2 mm. (*amide*, m.p. 90·4—91·6°). $COMe·[CH_2]_4·CO_2Et$ and MgEtI in Et_2O–N_2 give an alcohol, which by I at 180—190° and then H_2–PtO_2 in EtOH yields $CHMeEt·[CH_2]_4·CO_2Et$ (V), b.p. 125·5—127·5°/36 mm. Na–EtOH reduces (V) to $CHMeEt·[CH_2]_5·OH$, b.p. 108—111°/22 mm., which with anhyd. HBr gives the bromide, b.p. 105—108°/21 mm. Similar reactions yield *Et ι-keto-o-methyl*-n-*octadecoate* (VI) (76·5%), b.p. 192—195°/2 mm., and a fraction, b.p. 130°/2 mm., whence hydrolysis yields (IV) and n-*hexadecane-γξ-dione*, an oil. Hydrolysis of (VI) yields the derived *acid*, m.p. 52·7—54·1°, and Clemmensen reduction gives *Et o-methyl*-n-*octadecoate* (78·6%), b.p. 170—175°/1·5 mm., hydrolysed to the derived *acid* (VII), m.p. 49·9—50·6° (*amide*, m.p. 92·5—93°; *tribromoanilide*, m.p. 106·2—106·9°). Attempts to prepare (VII) starting from $CHMeEt·CH_2·OH$ yielded the less sol. $Pr^{\beta}·[CH_2]_{15}·CO_2H$ owing to the presence of $CHMePr^{\alpha}·OH$ as impurity. n-$C_{18}H_{37}$·MgBr and (II) in Et_2O at 0° and then the b.p. give a OH-ester (VIII) (and a little $C_{36}H_{74}$), which with I at 180—190° and then PtO_2–H_2–EtOH yields *Et ε-methyl*-n-*tetracosoate* (29·2%), b.p. 211—214°/~0·5 mm., and thence the derived acid, m.p. 57·5—60·5° (*amide*, m.p. 83·9—85·3°; *tribromoanilide*, m.p. 94·4—97·2°). Hydrolysis of (VIII) by KOH–EtOH gives *ε-hydroxy-ε-methyl*-n-*tetracosoic acid*, m.p. 46—47·3°. Similar methods lead to *Et ι-methyl*-n-*tetracosoate*, b.p. 218—222°/~0·5 mm., and the derived *acid*, m.p. 50·5—51·5° (amide, m.p. 77·5—78·5°; *tribromoanilide*, m.p. 84·2—84·8°). M.p. are corr.

R. S. C.

Kinetics of transformation of 2-ketopolyhydroxy-acids.—See A., 1944, I, 157.

Alkali antimonyl citrates. Y. Volmar and G. Geottelmann (*Compt. rend.*, 1942, **215**, 417—418).—The action of a mixture of a normal citrate (I) and citric acid (II) (mol. ratio 1 : 5) on $Sb(OH)_3$ gives *salts* $(CO_2H·CH_2)_2C(CO_2R)·O·Sb<^{O}_{O·CO}>C(CH_2·CO_2H)_2,H_2O$ in which R = K, Na, or NH_4. With a mixture of (I) and (II) in equimol. ratio the *product* is

$$\begin{matrix}CO_2H·CH_2\\CO_2R·CH_2\end{matrix}>C(CO_2R)·O·Sb<^{O}_{CO·O}>C<\begin{matrix}CH_2·CO_2H\\CH_2·CO_2R\end{matrix},H_2O$$

(R = K, Na, or NH_4). A dialkali salt could not be obtained. The antimonyl citrates are very stable, very sol. in H_2O to acid solutions, and very sparingly sol. in org. media. They can be heated with H_2O at 110° without undergoing hydrolysis; Sb is not immediately pptd. from them by H_2S. Mineral acids and alkalis decompose them with formation of $Sb(OH)_3$. They are very sensitive to ultra-violet light, Sb being liberated. H. W.

β-Acetyl-δε-*iso*propylideneascorbic acid. C. S. Vestling and M. C. Rebstock (*J. Biol. Chem.*, 1944, **152**, 585—591).—Acetylation of δε-*iso*propylideneascorbic acid, m.p. 221·6° (decomp.), $[\alpha]_D^{28\cdot5}$ +22° in H_2O, by a rapid stream of keten in anhyd. $COMe_2$ at room temp. is followed by indophenol titration. The resulting *β-acetyl-δγ-iso*propylideneascorbic acid (I), m.p. 115—116°, $[\alpha]_D^{27}$ +27·4° in MeOH, does not react readily with CH_2N_2 in MeOH at −40° or in dioxan at 13°. Hydrolysis of (I) in 3% HPO_3 at 70° and pH 1·9 indicates a pseudo-first-order reaction. A linear rate of decomp. of (I) is noted during 2 hr., equiv. to 0·1% per min. Hydrolysis is ~75% in 1 hr., and during the 2nd hr. oxidative decomp. occurs at such a rate as to make it impossible to obtain accurate vals.

A. T. P.

Raman spectra of vitamin-*C* and its oxidation products.—See A., 1944, I, 142.

Preparation of *d*-galacturonic acid and *l*-galactonic acid and derivatives thereof.—See B., 1944, II, 128.

Plant growth substances. XXXIII. Constitution of biotin from egg-yolk. F. Kögl, J. H. Verbeek, H. Erxleben, and W. A. J. Borg (*Z. physiol. Chem.*, 1943, **279**, 121—139).—In relationship to the sulphohexoic acid (I) obtained from biotin, the degradation of β-sulphohexoic acid (II) by alkali fusion is studied. Δ^{α}-*n*-Hexenoic acid, prepared from Et α-bromohexoate and quinoline at 185° and subsequent hydrolysis of the unsaturated ester, adds NH_4HSO_3 to form the NH_4 salt of (II) (*m-toluidine* salt, m.p. 145°). With 50% KOH at 170° the SO_2 is removed. The product is hydrogenated (PtO_2), heated at 200°, and again hydrogenated. The *n*-hexoic acid produced is identified as *p*-phenylphenacyl ester, m.p. 72°. (I) with KOH at 225° (lower temp. does not remove SO_2) and subsequent hydrogenation affords $CHMePr^{\beta}·CO_2H$, identified as the *p*-phenylphenacyl ester, m.p. 73°. The γ-sulpho-acid was synthesised by the following stages. $CH_2Ph·SNa$ + $CH_2Br·CH:CH_2$ gives *CH_2Ph allyl sulphide* (III), b.p. 110—155°/13 mm. Addition of HBr to (III) affords *β-bromo-α-benzylthiolpropane* (IV), b.p. 98·5—99°/0·05 mm. With $CHNa(CO_2Et)_2$ (IV) gives *Et α-carbethoxy-γ-benzylthiol-β-methyl*-n-*butyrate* (V), b.p. 147°/0·007 mm., converted by way of the Na compound of (V) with MeI into *Et α-carbethoxy-γ-benzylthiol-αβ-dimethyl*-n-*butyrate* (VI), b.p. 136°/0·003 mm. [also obtainable from (III) and $CHMe(CO_2Et)_2$]. Hydrolysis of (VI) gives the free *acid* (VII), m.p. 120°, decarboxylated to *γ-benzylthiol-αβ-dimethyl*-n-*butyric acid* (VIII). Fission of (VIII) with Na in NH_3 affords γ-thiol-αβ-dimethyl-*n*-butyric acid, an oil, the Ba salt of which is oxidised by Br to *Ba γ-sulpho-αβ-dimethyl*-n-*butyrate* (IX) (*m*-toluidine salt, m.p. 103—105°). The *anhydride* of (IX), b.p. (bath)/0·02—0·03 mm., forms an *aniline* salt of the anilide, m.p. 168°. SO_2 is not removed from (IX) by alkali fusion below 270°; (IX) is therefore excluded as a possibility for (I). $CHPr^{\beta}(CO_2H)_2$, $NHMe_2$, and CH_2O afford *dimethylaminomethyliso*propylmalonic *acid*, m.p. 112·5°, which when boiled in slightly acid solution gives *α-methylene-β-methylbutyric acid* (X), b.p. 98°/18 mm. (p-*phenylphenacyl* ester, m.p. 76—77°). With AcSH (X) yields as an oil, later cryst., the *acetylthiol* compound (XI), b.p. 120—123°/0·65 mm., which with 10% aq. NaOH gives *β-methyl-α-thiolmethyl*-n-*butyric acid* (XII), b.p. 92—94°/0·7 mm., m.p. 40°. With Br–$BaCO_3$ (XII) affords *β-methyl-α-sulphomethyl*-n-*butyric acid* (XIII) (m-*toluidine* salt, m.p. 153—154°), which with 50% KOH loses SO_2 only at 225—230°. (XI) is resolved by means of cinchonidine, the salt fraction cryst. from $COMe_2$ having $[\alpha]_D$ −78·9° in EtOH; the acid is an oil, $[\alpha]_D$ −4·17° in $CHCl_3$. It is converted as above into

optically active (**XIII**), with no measurable rotation. The *m*-toluidine salt, m.p. 156°, gives no m.p. depression with the corresponding product from (**I**). When heated with $SOCl_2$ in C_6H_6, (**XIII**) gives the *anhydride* (**XIV**), b.p. 113°/0·02 mm. (**XIV**) with NH_2Ph in C_6H_6 affords the *aniline* salt of the *anilide* (**XV**), m.p. 223° (micro), 248° (ordinary method, quick heating). The corresponding optically active *component* has m.p. 234—235° (micro), 250—251° (ordinary). With CH_2N_2, (**XV**) or the free anilide yields the *Me* ester (**XVI**), m.p. 134°, of the anilide. The optically active Me ester has m.p. 135°, [α] +2·12° in $COMe_2$. By similar treatment (**I**) gives the anilide aniline salt [cf. (**XIV**)], m.p. 224—225°, and the Me ester [cf. (**XV**)], m.p. 135°, and the respective mixed m.p. showed no depression. The constitution $\begin{matrix} NH\cdot CH(CO_2H)\cdot CH\cdot S\cdot CH_2 \\ | \qquad\qquad\qquad | \\ CO\cdot NH\text{———}CH\text{—}CHPr^{\beta} \end{matrix}$ is assigned to biotin from egg yolk (now termed α-biotin). J. H. B.

Decomposition of chloral hydrate by piperidine. L. Yang and P. F. Hu (*J. Chinese Chem. Soc.*, 1943, **10**, 190—193).—$CCl_3\cdot CH(OH)_2$ (**I**) is decomposed by piperidine (**II**) at 25°; with (**II**) in excess, the reaction is unimol., but with equal concn. of (**I**) and (**II**) or with excess of (**I**), reaction is bimol. It is probable that with excess of (**II**), the formation of the adduct, (**I**) + (**II**), is instantaneous, and the reaction rate represents mainly the decomp. of the adduct. In excess of (**I**), addition is slower than decomp. A. T. P.

Reaction of acetaldehyde with ethyl bromide at 400°.—See A., 1944, I, 157.

Derivatives of aldol and crotonaldehyde. III. Constitution of paraldol. E. Späth and H. Schmid (*Ber.*, 1941, **74**, [*B*], 859—866).—Removing volatile ingredients at 100°/10 mm. from commercial aldol, keeping the residue at 18°, and then treating with Et_2O gives paraldol (**I**), m.p. ~95—97° (decomp.; vac.), which at the b.p., 125° (bath)/15 mm., regenerates aldol, whence (**I**) is rapidly re-formed on keeping. With Ac_2O–C_5H_5N at 18° or, better, keten in boiling Et_2O, (**I**) gives its diacetate (**II**), b.p. 120—125° (bath)/1 mm. With H_2–Pd-black in warm AcOH, (**II**) gives 4-methyl-2-β-acetoxy-*n*-propyl-1 : 3-dioxan, b.p. 80—85° (bath)/1 mm. (and AcOH), hydrolysed by 3% NaOH–MeOH at room temp. to 4-*methyl*-2-*β-hydroxy*-n-*propyl*-1 : 3-*dioxan*, m.p. −62° to −59°, b.p. 90° (bath)/8 mm., which is also obtained from aldol, $OH\cdot CHMe\cdot[CH_2]_2\cdot OH$, and HCl at 50° (proof of structure). 0·05N-HCl–EtOH–H_2O at 70·0° hydrolyses 1 Ac of (**II**) in ~4 min., but the second Ac only very slowly, 0·58 OAc surviving after 85 min. With NH_2OH–MeOH at 18° (**II**) gives a 1 : 1 mixture of aldoxime and acetylaldoxime. (**I**) is, therefore, considered to be 4-*hydroxy*-6-*methyl*-2-*β-hydroxy*-n-*propyl*-1 : 3-*dioxan*; the OAc which is readily removed from (**II**) is the semi-acetal group at $C_{(4)}$. R. S. C.

Higher primary alkylamines and their reaction with carbon disulphide. T. Wagner-Jauregg, H. Arnold, and H. Rauen (*Ber.*, 1941, **74**, [*B*], 1372—1378).—Higher NH_2Alk are not obtained from AlkHal by liquid NH_3 but are prepared by *o*-$C_6H_4(CO)_2NK$ (**I**), followed by N_2H_4. With CS_2 in cold EtOH they give 70—75% of amine dithiocarbamates, but after prolonged boiling give excellent yields of thiocarbamides, by means of which they can be characterised. Turpin's method (A., 1888, 1174) gives only thiocarbamides. Use of $Hg(OAc)_2$ and CS_2 in boiling EtOH gives the alkylthiocarbimides. Thus are obtained cryst. cetylamine, oleylamine (from oleyl bromide, b.p. 180—200°/0·15 mm.), cryst., b.p. ~175°/0·2 mm. (*hydrochloride*, m.p. 161—165°; *cinnamoyl* derivative, m.p. 77—78·5°), hydnocarpylamine, chaulmoogrylamine, cryst., b.p. 185°/0·1 mm., *cetylamine* N-*cetyldithiocarbamate*, m.p. 100—101°, s-*dicetyl*-, m.p. 88—89°, s-*dioleyl*-, m.p. 67—69°, and s-*dihydnocarpylthiocarbamide*, m.p. 65—66°, *cetyl*-, cryst., b.p. 180—194°/0·35 mm., and *oleyl-thiocarbimide*, b.p. 200—210°/0·4 mm., N-*oleyl*-, m.p. 72—75°, b.p. 260—270°/0·4 mm., *N*-hydnocarpyl-, m.p. 57°, and *N*-chaulmoogryl-phthalimide, cryst. R. S. C.

Preparation of unsymmetrical secondary aliphatic amines. K. N. Campbell, A. H. Sommers, and (Miss) B. K. Campbell (*J. Amer. Chem. Soc.*, 1944, **66**, 82—84).—Adding RCHO gradually to NH_2R' and KOH at 0° gives 52—83% of $NPr^{\alpha}{:}CHMe$, b.p. 74—81°, *ethylidene-butylamine*, b.p. 98—106°, NEt:CHEt, b.p. 70—76°, *propylidene*-n-*butylamine*, b.p. 118—127°, n-*butylidene-ethylamine*, b.p. 100—108°, -n-, b.p. 120—124°, and -iso-*propylamine*, b.p. 100—111°, and -cyclo-*hexylamine*, b.p. 78—88°/20 mm., $NPr^{\alpha}{:}CHPr^{\beta}$, b.p. 108—114°, iso*amylidene*-n-*propylamine*, b.p. 130—139°, and -n-*butylamine*, b.p. 90—96°/100 mm. Hydrogenation (PtO_2 or, more slowly, Pd–C) of the aldimines in EtOH at 2—3 atm. gives 33—63% of $NHEtPr^{\alpha}$, b.p. 77—80°/738 mm. (α-naphthylthiocarbamide, m.p. 122—123°; *hydrochloride*, m.p. 223—224°), $NHEtBu^{\alpha}$, b.p. 109°/737 mm. (α-naphthylthiocarbamide, m.p. 125°; *hydrochloride*, m.p. 197°), $NHPr^{\alpha}Bu^{\alpha}$, b.p. 92—93°/200 mm. [α-naphthylthiocarbamide, m.p. 136—137°; *hydrochloride*, m.p. 267—268° (decomp.)], $NHPr^{\alpha}Bu^{\beta}$, b.p. 83—84°/200 mm. [α-naphthylthiocarbamide, m.p. 143—144°; *hydrochloride*, m.p. 278—282° (decomp.)], $NHPr^{\alpha}\cdot C_5H_{11}$-*iso*, b.p. 106—107°/200 mm. [α-naphthylthiocarbamide, m.p. 137—138°; *hydrochloride*, m.p. 264—265° (decomp.)], $NHPr^{\beta}Bu^{\alpha}$, b.p. 121°/733 mm. (α-naphthylthiocarbamide, m.p. 91·5—92·5°; *hydrochloride*, m.p. 195—196°), $NHBu^{\alpha}\cdot C_5H_{11}$-*iso*, b.p. 64—65°/14 mm. (α-naphthylthiocarbamide, m.p. 117·5—118·5°; *hydrochloride*, decomp. 290°), and *cyclo*hexyl-*n*-hexylamine, b.p. 87—90°/12 mm. [α-naphthylthiocarbamide, m.p. 107—108°; *hydrochloride*, m.p. 278—283° (decomp.)]. Reduction occurs in presence of Raney Ni, but yields no *sec.* amine. R. S. C.

Availability of ε-acetyl-*l*-lysine and ε-methyl-*dl*-lysine for growth.—See A., 1944, III, 490.

Invert soaps. IX. Azinium salts. O. Westphal (*Ber.*, 1941, **74**, [*B*], 1365—1372).—$NRR'\cdot NH_2$, in which R is a short-chain and R′ a long-chain alkyl, react with MeHal or EtHal to give $NH_2\cdot NMeRR'$}Hal (*A*) etc. MeI and EtI react exothermally; EtBr reacts best in EtOH during several hr.; EtCl reacts only in EtOH at 100° and causes some substitution to give inseparable mixtures. Addition of Alk_2SO_4 or $CH_2Br\cdot CO_2Alk$ is quant. *A* are sparingly sol. in H_2O; supersaturated solutions may form gels. *A* are surface-active and ppt. proteins. Against lactic acid bacteria they are approx. as effective as are NR_4X, max. effectiveness occurring at R′ = octyl. $NR_2\cdot NHR'$ are also approx. as effective, but the max. occurs at R′ = $C_{12}H_{25}$. Against staphylococci also *A* are about as effective as NR_4X or $NR_2\cdot NHR'$, but the max. occurs at R′ = $C_{12}H_{25}$. $NRR'\cdot NH\cdot CO\cdot CH{:}CH\cdot CO_2H$ is effective in acid, but not in alkaline, solution. $NR_2\cdot NHR'$ are prepared by interaction of $NR_2\cdot NH_2$ with AlkCl. The following are described: NNN-*tri*-n-*hexylhydrazinium chloride* (prep. from $C_6H_{13}Cl$ and N_2H_4 in EtOH at 150°), m.p. 65°; N-*methyl*-N-n-*dodecylhydrazine hydrochloride*, m.p. 70—72°; N-*methyl*-N-*ethyl*-N-n-*dodecyl*-, m.p. 82°, and -*cetyl-hydrazinium bromide*, m.p. 94°; NN-*dimethyl*-N-n-*dodecyl*-, m.p. 96°, and -*cetyl-hydrazinium iodide*, m.p. 163—164·5° (decomp.) (corresponding *methosulphate*, m.p. 99—100°); *N*-methyl-*N*-*n*-dodecyl-*N*-allylhydrazinium chloride and bromide, oils; N-*cyano*-N-*methyl*-N-n-*dodecylhydrazinium bromide*, m.p. 71—72°; *N*-methyl-*N*-cetylhydrazine, m.p. ~36°, b.p. 173°/3 mm.; N-*methyl*-N-*carbethoxymethyl*-N-*cetylhydrazinium bromide*, m.p. 68—69°; NN-*diethyl*-N′-n-*cetyl*-, b.p. 107—109°/13 mm., and -N′-n-*dodecyl-hydrazine*, b.p. 172—174°/11 mm. *n*-$C_{12}H_{25}\cdot MgCl$ and $NEt_2\cdot CH_2\cdot CN$ in Et_2O give, after hydrolysis, diethyltridecylamine, b.p. 169°/12 mm. (*hydrochloride*, m.p. 77—79°). $C_{12}H_{25}\cdot NMe\cdot NH_2$ and $(CH\cdot CO)_2O$ in boiling C_6H_6 give *H* N-*malein*-N′-*methyl*-N′-n-*dodecylhydrazide*, m.p. 69·5—70·5°. M.p. are m.p. (micro). R. S. C.

αζ-Diamino-βγ-δε-dimethylenemannitol. W. N. Haworth, R. L. Heath, and L. F. Wiggins (*J.C.S.*, 1944, 155—157).—Mannitol with fuming HCl (sealed tube at 95°) gives αζ-dichloromannitol (**I**), m.p. 174°, and other compounds not yet investigated. (**I**) condenses with CH_2O to *αζ-dichlorodimethylenemannitol* (**II**), m.p. 156°, with a little of an *isomeride*, m.p. 96°, $[\alpha]_D$ −18·2°. (**II**) is also obtained by treating (**I**) with paraformaldehyde and H_2SO_4. (**II**), fused with *o*-$C_6H_4(CO)_2NK$ in presence of glycerol, gives (20% yield) *αζ-diphthalimidodimethylenemannitol* (**III**), m.p. 277°, hydrolysed (hydrazine method) to *αζ-diaminodimethylenemannitol monohydrate* (**IV**), m.p. 48—52°, $[\alpha]_D^{18}$ +67·7° in $CHCl_3$. (**II**) with NH_3 in MeOH (autoclave at 150°), followed by aq. $Ba(OH)_2$ (N_2), yields 60% of (**IV**). (**IV**) gives *αζ-diaminodimethylenemannitol dihydrochloride* (**V**), m.p. 220—224° (decomp.), reconverted into (**IV**) by aq. $Ba(OH)_2$. Crystallising (**IV**) from dry EtOAc–Et_2O yields the anhyd. *diamine* (hygroscopic), m.p. 50°. (**IV**) gives *αζ-bis*-N-*salicylideneaminodimethylenemannitol*, m.p. 191—192°, *αζ-bis*-p-*benzenesulphonamidodimethylenemannitol*, m.p. 249—251°, and several salts: *oxalate*, m.p. 280° (decomp.), *adipate* (**VI**), m.p. 205°, *sebacate* (**VII**), m.p. 162°, *dimethylene*-l-*idosaccharate*, decomp. 270—300°. (**VI**) and (**VII**) when heated above their m.p. give polymers which do not give oriented fibres when cold-drawn. With *o*-$C_6H_4(CO)_2O$ (**IV**) gives (**III**), and with $CH_2Ac\cdot CO_2Et$ a *compound*, $C_{20}H_{32}O_8N_2$, m.p. 120°, $[\alpha]_D^{15}$ +67·2° in $CHCl_3$ (structure suggested). Hydrolysis of (**V**) (10% HCl) gives *αζ-diaminomannitol dihydrochloride*, m.p. 238—240° (decomp. 302—305°). (**II**), with KOH in EtOH, or fused with Na, yields di(methylenedioxy)-$\Delta^{\alpha\epsilon}$-hexadiene, m.p. 80°, $[\alpha]_D^{20}$ +281·5° in $CHCl_3$. This reaction supports the suggestion that the $\cdot CH_2\cdot$ groups bridge C_β–C_δ and C_γ–C_ϵ. D. G.

Degradation of amino-acids in the animal organism. I. *l*-Alanine.—See A., 1944, III. 426.

Action of amino-acids on α-ketohexonates. K. Maurer and K. Knoevenagel (*Ber.*, 1941, **74**, [*B*], 1003—1006).—Me α-ketogluconate with $NH_2\cdot CHMe\cdot CO_2Et$ or $NH_2\cdot CH_2\cdot CO_2Et$ in MeOH in absence of air gives the NH_2-ester salt, and thence by KOH the K salt (33 and 41%, respectively), of *iso*ascorbic acid. Similar reactions occur with (i) $NH_2\cdot[CH_2]_2\cdot CO_2Et$ or arginine, and (ii) Me or Et α-ketogulonate. The primary products could not be crystallised. The reaction could not be followed by changes in α or by I-titration; yields thus recorded average 60—100%. R. S. C.

Aliphatic carbodi-imides. III. E. Schmidt and W. Striewsky (*Ber.*, 1941, **74**, [*B*], 1285—1296; cf. A., 1943, II, 219).—The stability of NR:C:NR′ towards storage and Na is increased by increase in mol. wt. and still more so if R or R and R′ are *sec.* Prep. of NR:C:NR′ is much improved by use of moist HgO, which reduces the amount of carbamide obtained as by-product. The

following are described: di-*n*-, b.p. 53—54°/10 mm., and -iso*propyl*-, b.p. 36—37°/10 mm., N-n-*propyl*-N'-iso*propyl*-, b.p. 45°/10 mm., -N'-cyclo*hexyl*-, b.p. 105—106°/10 mm., and -N'-*γ-dimethylamino*-n-*propyl*-, b.p. 99—101°/10 mm. (*methiodide*, m.p. 98·5—99·5°), N-iso*propyl*-N'-cyclo*hexyl*-, b.p. 97—98°/10 mm., -N'-n-*dodecyl*-, b.p. 169—170·5°/10 mm., and -N'-*γ-dimethylamino*-n-*propyl*-, b.p. 91—92°/10 mm. (*methiodide*, m.p. 108—109°), and N-*methoxymethyl*-N'-*γ-dimethylamino*-n-*propyl*-, b.p. 105—106°/10 mm. (*methiodide*, m.p. 89—90°), -*carbodi-imide*; N-n-*propyl*-N'-iso*propyl*-, m.p. 90—91°, -N'-cyclo*hexyl*-, m.p. 88·5—89·5° (~103° after re-solidification), and -N'-*γ-dimethylamino*-n-*propyl*-, an oil (*picrate*, m.p. 155·5—156·5°), NN'-*di*iso*propyl*-, m.p. 141—141·5° (lit. 161°), N-iso*propyl*-N'-cyclo*hexyl*-, m.p. 139—140°, -N'-n-*dodecyl*-, m.p. 74·5—75·5°, and -N'-*γ-dimethylamino*-n-*propyl*-, m.p. 79—80° (*picrate*, m.p. 158—159°), and N-*methoxymethyl*-N'-*γ-dimethylamino*-n-*propyl*-, m.p. 56·5—58·5°, -*thiocarbamide*. OH·[CH$_2$]$_2$·NH$_2$ and CH$_2$:CH·CH$_2$·NCS in cold CHCl$_3$ give N-*β-hydroxyethyl*-N'-*allylthiocarbamide*, m.p. 77·5—78·5°, which with HgO in H$_2$O gives, by ring-closure of the carbodi-imide, 2-allylimino-oxazolidine, b.p. 104—105°/10 mm. (*picrate*, m.p. 146—147°). N-*γ-Hydroxy*-n-*propyl*-N'-*allylthiocarbamide*, m.p. 58—59°, with moist HgO in Et$_2$O or C$_6$H$_6$ gives similarly 2-*allyliminotetrahydro*-1 : 3-*oxazine*, b.p. 101·5—103°/10 mm. (*picrate*, m.p. 132—133°). R. S. C.

Acrylonitrile. V. Cyanoethylation of aldehydes. H. A. Bruson and T. W. Reiner (*J. Amer. Chem. Soc.*, 1944, **66**, 56—58; cf. A., 1943, II, 122, 153).—CHEt$_2$·CHO or CHEtBu·CHO with CH$_2$:CH·CN in 50% KOH at 55—58° gives *γ-aldehydo-γ-ethyl*-n-*hexonitrile* (I) (76·6%), b.p. 128°/4 mm., or -n-*octonitrile* (II) (79·5%), b.p. 140—142°/5 mm., respectively, hydrolysed by boiling 10% NaOH to *γ-aldehydo-γ-ethyl*-n-*hexoic* (III), b.p. 142°/3 mm., and -n-*octoic acid* (IV), b.p. 157°/4 mm. Air, H$_2$O$_2$, or KMnO$_4$ oxidises (III) and (IV) to *αα-diethyl*-, m.p. 84°, and *α-ethyl-α*-n-*butyl-glutaric acid* (V), m.p. 81—82°, respectively. The CHO of (I) and (II) resists alkali but is oxidised in air; thus, (I) yields *γ-carboxy-γ-ethyl*-n-*hexonitrile*, m.p. 88°. H$_2$–Raney Ni converts (II) and (IV) in aq. NaOH into the *lactones*, b.p. 101°/2·5 mm. and (VI) 124°/3·5 mm., of γ-hydroxy-methyl-γ-ethyl-*n*-hexoic and -*n*-octoic acids, respectively.
CHPr$^{\alpha}$:CEt·CHO and CH$_2$:CH·CN give, with migration of H, *γ-aldehydo-γ-ethyl-*Δ$^{\delta}$-n-*octenonitrile*, b.p. 138—140°/6 mm., and -n-*octenoic acid* (VII), b.p. 154°/4 mm. Hydrogenation of (VII) gives (VI) and oxidation gives (V). R. S. C.

II.—SUGARS AND GLUCOSIDES.

Blood-sugars. IV. Effect of mercury on the reducing power of dilute solutions of glucose. M. Lora Tamayo and J. M. Piñar Miura (*Anal. Fís. Quím.*, 1940, **36**, 132—140).—Dil. solutions of glucose are oxidised by HgCl$_2$ in NaOH to AcOH and H$_2$C$_2$O$_4$. Acid solutions remain unchanged. F. R. G.

Formation of anhydro-derivatives by the action of alkali on mononitrate acetates of glucose and methylglucoside. E. K. Gladding and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, **66**, 76—81).—In the sugar series, the behaviour of nitrates towards alkali resembles that of halides, methane- or *p*-toluene-sulphonates: fission is normally >CH·O·NO$_2$ → >CH·OH + HNO$_3$, but, if the NO$_2$ is "blocked," some reaction CH$_2$R·O·NO$_2$ → RCHO + HNO$_2$ occurs. *α-D*-Glucopyranose 2 : 3 : 4 : 6-tetra-acetate 1-nitrate (I), m.p. 148—149° (corr.), $[\alpha]_D^{20}$ +148° in CHCl$_3$, is obtained by nitrating *β*-glucose penta-acetate in CHCl$_3$; the NO$_2$ is as labile towards alkali as are the Ac; with NaOMe–MeOH it gives 75% of a CHCl$_3$-sol. material which, after re-acetylation, on one occasion crystallised to an inseparable mixture, on another yielded 28% of *β*-methylglucoside tetra-acetate (II), and probably consists of a 1 : 1 mixture of (II) and glucosan<1 : 5>*β*<1,6> triacetate (III); with NaOH in aq. dioxan it gives 33% of (III), 4·5% of HNO$_3$, and ~66% of a gum. The NO$_2$ of *β*-methylglucoside 3 : 4 : 6-triacetate 2-nitrate (IV) is removed rather faster than is that of (I); with NaOH in aq. dioxan it gives only 2·3% of HNO$_3$ with 84% of mixed anhydromethylhexosides, $[\alpha]_D^{20}$ −111° to −106° in H$_2$O (a fraction having m.p. 127—136° was isolated), containing ≯6% of methylhexosides. Consecutive methylation, nitration, and treatment with boiling BaCO$_3$–MeOH converts *D*-glucosan<1,5>*β*<1,6> into 2 : 3 : 4-trimethyl-*β*-methyl-*D*-glucopyranosidyl 6-nitrate (50%), m.p. 52—54° (corr.), $[\alpha]_D^{15}$ −7° in CHCl$_3$, which is more stable towards alkali than is (I) or (IV); NaOH in 50% aq. MeOH at 60° yields 75% of 2 : 3 : 4-trimethyl-*β*-methylglucoside, 20% of HNO$_3$, and 20% of an acidic, methylated tar. R. S. C.

α-Methylglucopyranoside 2 : 3 : 4-triacetate 6-nitrate and β-methylpyranoside 3 : 4 : 6-triacetate 2-nitrate. E. K. Gladding and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, **66**, 153—154).—*α*-Methylglucoside 6-CPh$_3$ ether 2 : 3 : 4-triacetate (modified prep.), new m.p. 143—145° (corr.), with P$_2$O$_5$–HNO$_3$ at 3—5° gives *α-methylglucoside* 2 : 3 : 4-*triacetate* 6-*nitrate* (88%), m.p. 112—113° (corr.), $[\alpha]_D^{20}$ +132° in CHCl$_3$, also obtained from the 6-iodide by AgNO$_3$ (excess) in hot MeCN and converted thereinto by NaI in (CH$_2$Ac)$_2$. *β*-Methylglucoside 3 : 4 : 6-triacetate (modified prep.) gives similarly its 2-*nitrate*, m.p. 117—118° (corr.), $[\alpha]_D^{25}$ −1° in CHCl$_3$. R. S. C.

Glucose 6-fluorohydrin and its derivatives. B. Helferich and A. Gnüchtel (*Ber.*, 1941, **74**, [*B*], 1035—1039).—*α*-Methylglucoside tetramethanesulphonate and KF in boiling H$_2$O (30% yield) or, better, MeOH at 100° (tube) give *α-methylglucoside* 6-*fluoride* 2 : 3 : 4-*trimethanesulphonate*, m.p. 133—134°, $[\alpha]_D^{22}$ +93·1° in C$_5$H$_5$N, but the MeSO$_2$ cannot be removed without affecting the F. *α*-Methylglucoside 2 : 3 : 4-triacetate 6-methanesulphonate and KF give only glucose and derivatives of anhydroglucose. 3 : 5-Benzylidene-1 : 2-*iso*propylideneglucopyranose 6-methanesulphonate and KF,2H$_2$O in MeOH at 100° give 3 : 5-*benzylidene*-1 : 2-iso*propylideneglucofuranose* 6-*fluoride* (96%), m.p. 104—105° (corr.), $[\alpha]_D^{21}$ +14·2° in C$_6$H$_6$, whence H$_2$SO$_4$–MeOH–H$_2$O at the b.p. and then Ac$_2$O–C$_5$H$_5$N at 100° gives *glucose* 6-*fluoride* 1 : 2 : 3 : 4-*tetra-acetate* (45%), m.p. 125—126°, $[\alpha]_D^{19}$ +20·1° in C$_5$H$_5$N. H$_2$SO$_4$–MeOH–H$_2$O then yields *glucose* 6-*fluoride* (>60%), sinters ~145°, m.p. 155°, $[\alpha]_D^{19}$ +85·8° → +46·8° in H$_2$O, whilst HBr in AcOH and then AcOH–CHCl$_3$ gives 1-*bromoglucose* 6-*fluoride* 2 : 3 : 4-*triacetate* (I), m.p. 127—128° (corr.), $[\alpha]_D^{21}$ +234° in CHCl$_3$. PhOH and Ag$_2$O in quinoline convert (I) into *phenyl-β*-d-*glucoside* 6-*fluoride* 2 : 3 : 4-*triacetate*, m.p. 167—168° (corr.), $[\alpha]_D^{19}$ −8·2° in CHCl$_3$, and thence (NaOMe) *phenyl-β*-d-*glucoside* 6-*fluoride*, m.p. 148—149° (corr.), $[\alpha]_D^{21}$ −79·0° in H$_2$O. Vanillin, (I), and NaOH in aq. COMe$_2$ at room temp. give *vanillyl-β*-d-*glucoside* 6-*fluoride*, m.p. 181—182° (corr.), $[\alpha]_D^{19}$ −48·6° in C$_5$H$_5$N, by way of its *triacetate*, m.p. 166—167° (corr.), $[\alpha]_D^{20}$ −35·7° in CHCl$_3$. R. S. C.

Glucoside of a γ-hydroxy-carboxylic acid. B. Helferich, W. Richter, and H. Flechsig (*Ber.*, 1941, **74**, [*B*], 1019—1022).—Aceto-bromoglucose, CMe$_2$:CH·[CH$_2$]$_2$·CHMe·OH, CaSO$_4$, and Ag$_2$O in CHCl$_3$ give mixed diastereoisomerides, whence ~11% of *ζ-methyl-β*-Δ$^{\epsilon}$-n-*heptenylglucoside tetra-acetate*, m.p. 93—94°, $[\alpha]_D^{20}$ −2·8° in CHCl$_3$, is obtained. With boiling NaOMe–MeOH this gives the free *glucoside* (I), m.p. 78—79°, $[\alpha]_D^{18}$ −23° in H$_2$O, and with O$_3$–AcOH, followed by Zn dust in Et$_2$O–AcOH, gives *γ-glucosidoxy*-n-*valeraldehyde tetra-acetate* (~65%), m.p. 128—129°, $[\alpha]_D^{23}$ −0·5° in CHCl$_3$ (*semicarbazone*, m.p. 108—109°, $[\alpha]_D^{20}$ −2·3° in CHCl$_3$; 2 : 4-dinitrophenylhydrazone, m.p. 170°), oxidised by KMnO$_4$–COMe$_2$ at ~2° to *γ-glucosidoxy*-n-*valeric acid tetra-acetate* (60%), m.p. 92—93°, *α* 0 (*Me* ester, m.p. 85—86°, *α* 0). The rate of hydrolysis of (I) by emulsin is reduced to about one seventh by conversion into the aldehyde. R. S. C.

Nature of erythroamylose particles and of higher dextrins produced by α-diastase.—See A., 1944, III, 432.

Relation of starch–iodine absorption spectra to the structure of starch and starch components. R. R. Baldwin, R. S. Bear, and R. E. Rundle (*J. Amer. Chem. Soc.*, 1944, **66**, 111—115).—The position of the max. and val. of ε$_{max.}$ of the absorption spectra of starch–I complexes (0·01% solution) differentiate amyloses from amylopectins, but cannot be used to analyse whole starch owing to variation among amyloses and amylopectins from different starches. The amount of I bound increases as the [KI] decreases, becoming 1 I per ~6 glucose units at infinitely small [KI]. Increase in chain-length of amylose or in length of the unbranched portion of amylopectin shifts the max. to longer λ and increases ε; both phenomena, particularly ε, may be used to determine mol. wts. and degrees of branching, giving vals. in agreement with other methods. The spectrometric method shows higher vals. for bound I than does potentiometric titration, owing to rapid removal of I from the ends of the helices during the titration. R. S. C.

Effect of acid hydrolysis on activity of polysaccharides in enzymic synthesis of starch.—See A., 1944, III, 500.

Influence of dextrin on synthetic action of plant phosphorylase.—See A., 1944, III, 500.

Cellulose and liquid hydrogen chloride. Influence of morphological structure and crystal lattice structure on the reaction and activity of cellulose. M. Ulmann and K. Hess (*Ber.*, 1941, **74**, [*B*], 1465—1473).—The reaction velocity of ramie cellulose (I) with liquid HCl at −15° to 20° is given, up to 66% completion, by $dx/dt = K(a - x)/l$, in which l measures diffusion of HCl into the (I); l can be represented as $K'\sqrt{t}$, whence for the whole reaction $K = 0{\cdot}5\sqrt{t}\log_e a(a - x)$. After 66% completion of the reaction (for which $K = 0{\cdot}058$), the velocity suddenly increases, proceeding then to 100% completion. When ground in a "swinging" mill, (I) reacts much faster ($K = 0{\cdot}103$) up to 58% completion; a similar sudden increase in reaction rate then occurs. The non-reducing portion remaining from partly reacted ground (I) consists of unchanged (I) and H$_2$O-sol. cellulose (II); the amount of (II) is const. (25%) until shortly after the sudden increase in velocity but then falls gradually to approx. nil. When ground (I) is boiled in H$_2$O for 1 hr. and the suspension is then evaporated and dried at 105°, a "recryst." cellulose (III) is obtained, which reacts with HCl initially at the same rate ($K = 0{\cdot}060$) as does natural (I); a sudden increase in velocity occurs after 40% completion; 8% of (II) is also formed from (III), this amount remaining const. for a long time. (III) may also be prepared without heating, by drying the H$_2$O-treated (I) with EtOH and Et$_2$O. The amount of reaction is determined by the Bertrand reducing val.; results by Willstätter

and Schudel's method are more erratic. The *X*-ray diagram of (I) remains normal up to 66% reaction and thereafter is that of an amorphous substance; *X*-ray diagrams of (II) and (III) are both the same as that of "cellulose hydrate." The following interpretations are offered. The effect of grinding on the initial velocity, being reversible by H_2O, is due to lattice distortion; subdivision proceeds only to the individual fibrils. Also formation of (II), largely reversible by H_2O, occurs from lattices deformed by grinding. The sudden increase in velocity is due to HCl penetrating through less reactive layers (which react more slowly) and suddenly exposing normally reactive portions. R. S. C.

Cellulose–water adsorption isotherm.—See A., 1944, I, 153.

Study of the amorphous portion of dry, swollen cellulose by an improved thallous ethoxide method. A. G. Assaf, R. H. Haas, and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, **66**, 59—65).—The no. of accessible OH in cellulose is determined by treatment with TlOEt in a solvent and then with MeI–C_6H_6 and determining the OMe in the product. When hydrocarbons (n-C_7H_{16}, -$C_{10}H_{22}$, -$C_{16}H_{34}$) are used as solvent, the % OMe is const., but when ethers [Et_2O, Pr_2O, Bu_2O, $(C_5H_{11})_2O$] are used, the % OMe ∝ the mol. vol. of the solvent ether. The % "amorphous" cellulose is defined as the % wetted by an ether of zero mol. vol., estimated by extrapolation from the ether graph. Thallation in alcohols is probably accompanied by swelling but confirms the results within ±10%. Unswollen linters contains only 0·25—0·5% of amorphous cellulose, but swollen linters contains up to 27±2%; the corresponding colloidal surfaces are 10—520 × 10^4 sq. cm. per g. R. S. C.

III.—HOMOCYCLIC.

Spectroscopic evidence for conjugation in *cyclo*propane systems. I. M. Klotz (*J. Amer. Chem. Soc.*, 1944, **66**, 88—91).—Hyperconjugation of a *cyclo*propane ring with an ethylenic linking causes some absorption due to resonance, so that absorption spectra are intermediate between those of systems containing C·C·C:C or C:C·C:C. Examples are Δ^6-*i*-cholestadiene, *i*-cholesteryl Me ether, *i*-cholestenone, and carone. The same principle may apply to terpenes containing *cyclo*butane rings. R. S. C.

Poly*cyclo*pentyls. J. von Braun and (Frl.) J. Reitz-Kopp (*Ber.*, 1941, **74**, [*B*], 1105—1110).—n-*Heptyl*-Δ^2-cyclo*pentene*, b.p. 102°/15 mm., is obtained (Grignard) from n-$C_7H_{15}Br$ and Δ^2-*cyclo*pentenyl chloride (I) in nearly 50% yield and is freed from halogen by Na at 100°. With fuming HBr (excess) at 100° or room temp. it gives 3-*bromo*-n-*heptyl*cyclo*pentane* (II) (>70%), b.p. 97—102°/0·2 mm., which reacts more slowly than does the Et analogue with Mg (A., 1937, II, 404), yielding after treatment with solid CO_2 3-n-*heptyl*cyclo*pentane*-1-*carboxylic acid* (22%), b.p. 186—188°/13 mm., and 3 : 3′-*di*-n-*heptyldi*cyclo*pentyl* (III) (~10%), b.p. 230°/13 mm. ~30% of (II) is obtained from (I) by Na wire and a little EtOAc in Et_2O at room temp. and then the b.p. 3-*cyclo*Pentenyl-1-ethyl*cyclo*pentane, b.p. 75—85°/12 mm. [obtained (34%) from Mg 3-ethyl*cyclo*pentyl bromide and (I)], with fuming HBr at room temp. gives 3-bromo-3′-ethyldi*cyclo*pentyl (IV) (77%), b.p. 135°/16 mm., which with Mg and then CO_2 gives impure 3-ethyldi*cyclo*pentyl-3′-carboxylic acid, b.p. ~130°/0·1 mm., and 3 : 3′-*diethylquater*cyclo*pentyl* (~10%), b.p. 160—170°/0·3 mm. [obtained in 20% yield from (IV) by Na]. The similarity in reactions of (II) and (IV), which contain the same no. of C, is noted. Mg 3-di*cyclo*pentylyl bromide and (I) give, after treatment with Na, Δ^2-*tri*cyclo*pentylene* [3-$\Delta^{2''}$-cyclo*pentenyldi*cyclo*pentyl*] (V) (nearly 20%), b.p. 139—140°/10 mm., and quater*cyclo*pentyl (12%), b.p. 205—207°/9 mm. H_2–Pd in MeOH reduces (V) to *tri*cyclo*pentyl* (92%), b.p. 144°/12 mm. HBr converts (V) into 3-*bromotri*cyclo*pentyl* (~50%), b.p. 182°/10 mm., yielding with Na in Et_2O *hexa*cyclo*pentyl* (almost 40%), b.p. 235°/0·1 mm., of which 10% is obtained having m.p. 143—146°. *d* and *n* of poly*cyclo*pentyls increase regularly, but the b.p. show signs of alternation. In the above compounds the *cyclo*pentyl nuclei are united in the 1 : 3-positions. R. S. C.

Reactions of *cyclo*hexane and decahydronaphthalene under hydrogenation-cracking conditions.—See B., 1944, II, 125.

Chlorination of *cyclo*hexane.—See B., 1944, II, 128.

Rubber, polyisoprenes, and allied compounds. VI. Mechanism of halogen-substitution reactions and the additive halogenation of rubber and of dihydromyrcene. G. F. Bloomfield. **VII. Action of nitric oxide thereon.** G. F. Bloomfield and (in part) G. A. Jeffrey (*J.C.S.*, 1944, 114—120, 120—124; cf. A., 1943, II, 289).—Chlorination of peroxide-free *cyclo*hexene (I) by Cl_2 or SO_2Cl_2 gives substituted and additive derivatives, the former retaining full unsaturation. (I) with Cl_2 yields *cyclo*hexene, mono- (II), 1 : 2-di- (III), and tri-chloro*cyclo*hexane, b.p. 52—53°/0·01 mm. Comparison of the reactions of (II) and 1-chloro*cyclo*hexene (from *cyclo*hexanone and PCl_5) towards $AgNO_3$ in EtOH and to ICl suggests that (II) is a mixture of 3- (IV) and 4-chloro*cyclo*hexene (20%). SO_2Cl_2 with (I) in presence of peroxide gives (III) but with peroxide-free (I) in presence of quinol gives (III) and (IV) and the *chloride* of 2-*chloro*cyclo*hexyl sulphite*, b.p. 74°/0·002 mm., which with H_2O yields 2-chloro*cyclo*hexanol and *bis*-(2-*chloro*cyclo*hexyl*) *sulphite* (?), m.p. 92°. SO_2Cl_2 and (I) with a little I at 80° give (III) and (IV). SO_2Cl_2 (1 mol. per 4 :) and dihydromyrcene (V) in presence of Bz_2O form the *dichloride*, b.p. 55—56°/0·2 mm., but SO_2Cl_2 (2 mol.) and (V) (1 mol.) give (Bz_2O present) the *tetrachloride*, b.p. 82—90°/0·002 mm., m.p. 50°. Rubber (VI) with SO_2Cl_2 and Bz_2O gives *polyisoprene dichloride*, $(C_5H_8Cl_2)_n$, indistinguishable from material obtained from (VI) and $PhICl_2$. (V) with $(CH_2{\cdot}CO)_2NBr$ (VII) gives *monobromodihydromyrcene*, b.p. 54°/0·1 mm. (VI) and (VII) (0·5 Br per C_5H_8 unit) yield a *compound*, $(C_{10}H_{15}Br)_n$, without formation of HBr. (VI) gives an entirely additive reaction with Br at 0° (if a little EtOH is present in the solvent, *e.g.*, $CHCl_3$, used) and a method based on Br addition can be used for determination of rubber hydrocarbon. The reaction mechanism of chlorination of (VI) is discussed, and it is suggested that provision of Cl in free radical form is necessary for a wholly additive reaction. The reaction of mol. Cl_2 or Br is explained by formation of an activated dihalide, further products being determined by the nature of the olefinic system and the experimental conditions.

VII. In the reaction of NO with (I), 1-methyl*cyclo*hexene (VIII), (V), and (VI) the general characteristics of a free-radical chain mechanism are exhibited. The induction period (15—30 min.) varies with the light intensity. N_2 which is formed stops the reaction, but if removed >1 mol. of NO per : is absorbed, 1/3—1/4 vol. of N_2 being evolved per vol. of NO absorbed. Products contain N (generally linked to C) in various states of combination with O. It is suggested that NO is converted into higher oxides of N (in the liquid phase only) by a mechanism involving the hydrocarbon, and HNO_2 or N_2O_3 was detected. The apparatus used is described. (I) (1 mol.) absorbs NO (1·6 mols.) to give the ψ-nitrosite, m.p. 153° (decomp.), for which a bimol. structure is confirmed by *X*-ray examination, a mixture of 1-nitro*cyclo*hexene (giving adipic acid on oxidation, and *cyclo*hexanoneoxime on reduction) and 3-nitro*cyclo*hexene (?), and an *oil* (IX), $C_6H_{10}O_{3\cdot6}N_{1\cdot6}$, containing N and O added or substituted at the original :. (IX) gives a *compound*, $C_6H_8O_3N_2$, m.p. 107—108°, with KOH, and on oxidation ($KMnO_4$) gives adipic acid and a neutral oil. (V) (1 mol.) absorbs NO (0·73 mol.) and evolves N_2 (0·22 mol.) giving a *nitrodihydromyrcene* (?), b.p. 60—70°/0·001 mm., and a *solid*, $C_{10}H_{18}O_{3\cdot3}N_{1\cdot8}$. (VIII) gives a *nitromethyl*cyclo*hexene* (?), b.p. 50°/0·01 mm., and a viscous residue. The properties of the products obtained from (VI) for absorption of various amounts of NO are tabulated. No definite compounds were isolated. D. G.

***cis–trans*-Isomerisation and *cis*-peak effect in the α-carotene set and in other stereoisomeric sets.** L. Zechmeister and A. Polgár (*J. Amer. Chem. Soc.*, 1944, **66**, 137—144).—The ethylenic linkings of carotene etc. are numbered serially, no. 1 being that in the β-ionone ring. *cis*-Linkings are indicated by prefixes, *e.g.*, 3 : 6-di-*cis*- indicates that ethylenic linkings nos. 3 and 6 are *cis*. In α-carotene (I), nos. 3, 5, 6, 7, and 9 can be *cis* and 32 stereoisomerides are possible. By boiling or illumination in light petroleum, by treating in light petroleum with I (in light), 10% HI, or 37% HCl, or by melting, (I) gives varying amounts of the following neo-α-carotenes, listed in order of decreasing adsorption affinity with absorption max. (A. in light petroleum) in parentheses: U (4715, 4415), V (4655, 4370), W (4705, 4410), X (4635, 4350), Y (4675, 4370), all *trans*-α-carotene (4770, 4465), A (4685, 4390), B (4665, 4370), C (4725, 4425), D (4600, 4320), and E (4615, 4335). U, m.p. 65° (corr.), $[\alpha]^{25}_{Cd}$ +221°±5% in C_6H_{14}, and W, m.p. 97° (corr.), $[\alpha]^{25}_{D}$ +365° in light petroleum, are obtained cryst. (photomicrographs). Absorption data (partly new) are interpreted to indicate the following configurations: U 9-*cis*, W 3-*cis*, V 3 : 9-di-*cis*, X (? 7 :)9-di-*cis*, C 6- or 5-*cis*, B 5 : 9- or 6 : 9-di-*cis*, A and B being chosen from 5 : 9-, 6 : 9-, and 3 : 6-di-*cis*; neolutein A 6- or 5-*cis*, B 3- or 9-*cis*; neolycopene A 6-*cis*., B 1 : 6- or 3 : 6-di-*cis*. R. S. C.

Alkylation of *o*- and *p*-xylene. D. Nightingale and J. R. Janes (*J. Amer. Chem. Soc.*, 1944, **66**, 154—155).—With $Bu^{\gamma}Cl$–$FeCl_3$ or $Bu^{\gamma}OH$–BF_3, *o*-xylene gives good yields of 1 : 2 : 4-$C_6H_3Me_2Bu^{\gamma}$ (oxidised to 2 : 4 : 1-$C_6H_3MeBu^{\gamma}{\cdot}CO_2H$). *p*-Xylene does not condense with $Bu^{\gamma}OH$–80% H_2SO_4, $Bu^{\gamma}Cl$–$FeCl_3$, or $CMe_2{:}CH_2$–$FeCl_3$, and with $Bu^{\gamma}OH$–BF_3 gives an inseparable mixture. PhMe is readily alkylated by $CMe_2{:}CH_2$–$FeCl_3$. R. S. C.

Delay in the heat-polymerisation of styrene caused by *p*-benzoquinone. J. W. Breitenbach and K. Horeischy (*Ber.*, 1941, **74**, [*B*], 1386—1389).—When styrene is heated with 2 mol.-% of *p*-O:C_6H_4:O (I) at 120°, quinhydrone can be isolated from the product. Polymerisation is not prevented by (I) but leads to products of quite low η and mol. wt., which invalidates the conclusions of Foord (A., 1940, I, 167). R. S. C.

Alkylation by olefines in presence of aluminium chloride. I. S. I. Lurie and A. J. Golovatscheva (*J. Gen. Chem. Russ.*, 1943, **13**, 189—194).—*m*-Xylene and $CMe_2{:}CH_2$ at 12—14° in presence of $AlCl_3$ in EtBr afford 1 : 2 : 4-$C_6H_3Me_2Bu^{\gamma}$ in 18% yield. Various activators (HCl, $CHCl_3$, CCl_4) raise the yield, the most active being CCl_4 (60%). With alkoxybenzenes the ·CH: groups act as promoters

of the reaction, rendering the presence of added activators unnecessary. R. T.

Hydrolytic rupture of carbon linkings. VI. Substituted stilbenes. M. M. Schemjakin and N. I. Oranski (*J. Gen. Chem. Russ.*, 1943, **13**, 175—183).—Substituted stilbenes are hydrolysed by aq. alkalis as follows: $CHR{:}CHR' + H_2O \rightarrow R{\cdot}CHO + R'Me$ [$R = R' = Ph$, o-$NO_2{\cdot}C_6H_4{\cdot}$, 2 : 4-$C_6H_3(NO_2)_2$, 2 : 4-$NO_2{\cdot}C_6H_3{\cdot}SO_3H$; $R = o$-$NO_2{\cdot}C_6H_4$, $R' = 2 : 4$-$C_6H_3(NO_2)_2$; $R = Ph$, $R' = 2 : 4$-$C_6H_3(NO_2)_2$]. The velocity of the reaction rises with increasing asymmetry of the mol. R. T.

Physical data of αα-diphenyl-alkenes and -alkanes and αααω-tetraphenylalkenes. A. W. Schmidt and C. Hartmann (*Ber.*, 1941, **74**, [*B*], 1325—1332).—By interaction of $MgPhBr$ with RCO_2Et or $X(CO_2Et)_2$ and subsequent dehydration by $KHSO_4$ are prepared *αα-diphenyl-Δ^α-n-butene*, b.p. 108—110°/4 mm., *-octene*, m.p. −5·5° to −6°, b.p. 133—134°/0·05 mm., *-dodecene*, m.p. 5—6°, b.p. 170—171°/0·05 mm., *-hexadecene*, m.p. 25·5°, b.p. 196—197°/0·04 mm., and *-octadecene*, b.p. 202—203°/0·04 mm., $(CPh_2{:}CH{\cdot}[CH_2]_n)_2$ in which $n = 1$ m.p. 108°, and 2 m.p. 113° (lit. 92—93°), *ααικ-tetraphenyl-Δ^αι-n-decadiene*, m.p. 113°, and *ααοσ-tetraphenyl-Δ^αρ-n-octadiene*, m.p. 77°. H_2–Pd–$BaSO_4$ in Et_2O or EtOH then yields αα-diphenyl-*n*-butane, b.p. 103—104°/0·05 mm., -octane, m.p. −5° to −4°, b.p. 143—145°/0·1 mm., and -hexadecane, m.p. 26°, b.p. 211—213°/0·1 mm., and *αα-diphenyl-n-hexadecan-α-ol*, m.p. 48—49°. *n*, *d*, and *η* are also recorded for the hydrocarbons. R. S. C.

Magnetic investigations of organic substances. XXI. Diradicaloid terphenyl derivatives. XXII. Diradicaloid quaterphenyl derivative. E. Müller and H. Pfanz (*Ber.*, 1941, **74**, [*B*], 1051—1074, 1075—1083).—XXI. *p*-$C_6H_4Ph_2$, *p*-$C_6H_4Ph{\cdot}COCl$, and $AlCl_3$ at 190—200° give, after sublimation of the product, 4 : 4″-*di-p-phenylbenzoyl-p-terphenyl* (20%), m.p. 406—408°. This is finely powdered, stirred in molten $C_{10}H_8$–N_2, diluted with C_6H_6, and treated with *p*-$Li{\cdot}C_6H_4Ph$–Et_2O–N_2 at 25—30° [at 70° much (*p*-$C_6H_4Ph)_2$ is formed], thus yielding 4 : 4″-*bis-(α-hydroxydi-p-xenylmethyl)-p-terphenyl* (58%), sinters from ~140°, m.p. 165—175°, resolidifies, remelts at ~283—286° (violet-blue in H_2SO_4), which with gaseous HCl in boiling C_6H_6–AcOH gives the *dichloride* (54%), sinters from 165°, m.p. 185°, resolidifies, remelts at ~294—296°, whence Cu-bronze or "mol." Ag in C_6H_6–N_2 at 80° yields 4 : 4″-*p-terphenylenebisdi-p-xenylmethyl* (I) (peroxide). Similarly are prepared 4 : 4″-dibenzoyl-, m.p. 296—297°, 4 : 4″-*bis-(α-hydroxy-α-p-xenylbenzyl)*-, sinters 100°, m.p. 150—~245° (greenish-blue in conc. H_2SO_4), 4 : 4″-*bis-(α-chloro-α-p-xenylbenzyl)*- (prep. by gaseous HCl in, successively, MeOH–C_6H_6, AcCl–C_6H_6, and AcCl–C_6H_6–Et_2O), sinters from 270°, m.p. 282—283°, 4 : 4″-*bis-α-hydroxybenzhydryl-* (II), +C_6H_6, sinters 130°, m.p. ~160—165°, and solvent-free, m.p. 207·5—209·5° (reddish-violet in H_2SO_4), and 4 : 4″-*bis-α-chlorobenzhydryl-*, m.p. 248—249°, -*p-terphenyl* and 4 : 4″-*p-terphenylenebis-phenyl-p-xenylmethyl* (III) (peroxide) and *-diphenylmethyl* (IV), sinters 135—140°, m.p. 165—200° (N_2) (di- or poly-meric *peroxide*). Structures are confirmed by absorption spectra of Ph_2, *p*-$C_6H_4Ph_2$, $CPh_3{\cdot}OH$, *p*-$C_6H_4(CPh_2{\cdot}OH)_2$ [max. at ~2640 A. (log ε 3·12)], (*p*-$OH{\cdot}CPh_2{\cdot}C_6H_4{\cdot})_2$ [max. at 2630 A. (log ε 4·52)], and (II) [max. at 2920 A. (log ε 4·7)] in dioxan; changes in $\lambda_{max.}$ are regular. $\chi_{mol.}$ are recorded for the diketones, dicarbinols, dichlorides, (I), (III), and (IV) in C_6H_6, and for solid (I) and (IV). (I), (III), and (IV) are paramagnetic in C_6H_6 at 18° and 80° and when solid. For (I) the apparent % of diradical in 1·8% C_6H_6 solution is 53—54±5 at 18° and 80°; for (III) and (IV) it is less and varies with concn. and temp.; heats of dissociation are (I) 0±2·5, (III) −8·3±2·5, and (IV) −9·5±2·5 kg.-cal. $\mu_{eff.}$ are (I) 0·78 at −183° to 0·81 at 20° and (IV) 0·51 at −183° to 20°, rising to 0·65 at 120°, and then falling to 0·35 at 180°. The compounds, (I), (III), and (IV) are held to be "diradicaloid," *i.e.*, prevented from acting as 100% free radicals by the fact that free rotation around a long X in $CR_2{\cdot}X{\cdot}CR_2$ prevents completely planar configuration. (IV) is ∢ dimeric in C_6H_6, which is considered to be due to association to large rings.

XXII. 4 : 4‴-*p*-Quaterphenylenebisdiphenylmethyl (V) is diradicaloid. By the methods described above (*p-p'*-$C_6H_4Ph)_2$ (VI) gives 4 : 4‴-*dibenzoyl-* (49%), m.p. 357—359°, 4 : 4‴-*bis-α-hydroxybenzhydryl-* (VII), sinters ~120°, m.p. 220—221°, and 4 : 4‴-*bis-α-chlorobenzhydryl-p-quaterphenyl*, m.p. 263—264°, and (V). (VII) is greenish-blue in H_2SO_4 and has an absorption max. at 3090 A. χ are recorded for (VI) and the products. (V) is paramagnetic, has heat of dissociation −7·3±2·5 kg.-cal., $\mu_{eff.}$ 0·81 at 20° and 1·23 at 80°, and in C_6H_6 an apparent diradical content 15·5±3% at 20° and 19·0±3% at 80°. (V) is magnetically anisotropic. It is very highly electrified by friction; the charge is dissipated when the surrounding air is ionised by Ra. R. S. C.

***pp'*-Diphenyl diradical of the triphenylmethyl type. III.** W. Theilacker (*Ber.*, 1941, **74**, [*B*], 1353—1359).—Polemical against Müller (cf. preceding abstract). Association of *pp'*-diradicals, $\cdot C_6H_4{\cdot}C_6H_4{\cdot}$, to dimerides is extremely improbable on steric grounds. Dissociation of such radicals (if formed) is more complicated than Müller assumes, since partial dissociation to $\cdot[C_6H_4]_4{\cdot}$ gives a paramagnetic mol. The solids are probably long-chain structures formed by polymerisation. R. S. C.

Syntheses of compounds related to vitamin-*K*. I. Synthesis of 2-methylnaphthalene. E. J. H. Chu and Z. I. Shen (*J. Chinese Chem. Soc.*, 1943, **10**, 119—113).—PhMe, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ yield *p*-$C_6H_4Me{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 126·2—127·3°, reduced (Clemmensen) to *p*-$C_6H_4Me{\cdot}[CH_2]_3{\cdot}CO_2H$, m.p. 56°, convertible through the chloride by $AlCl_3$ in PhMe at room temp. into 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 33°, and thence (Clemmensen) 6-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 94—96°/10 mm. (some 3 : 4 : 3′ : 4′-*tetrahydro-7 : 7′-dimethyl-1 : 1′-dinaphthyl*, m.p. 162—163°, is isolated); S at 215—230° then gives 2-$C_{10}H_7Me$ (overall yield, 6%). A. T. P.

Triterpenes. LXXXVI. Birch-tar oil.—See A., 1944, II, 165.

New route to polycyclic compounds having an angular methyl group. Synthesis of *iso*chrysofluorene. N. N. Chatterjee and H. B. Roy (*J. Indian Chem. Soc.*, 1943, **20**, 329—330).—Et 2-methyl-*cyclo*hexanone-2-carboxylate with 1-$C_{10}H_7{\cdot}MgBr$ gave *Et 1-α-naphthyl-2-methyl*cyclo*hexanol-2-carboxylate*, b.p. 220—225°/6 mm., dehydrated ($SOCl_2$–C_5H_5N–Et_2O) to *Et 1-α-naphthyl-2-methyl-Δ^6-*cyclo*hexene-2-carboxylate*, b.p. 210—220°/6 mm., which was reduced (H_2, PtO_2, EtOH) very slowly to *Et 1-α-naphthyl-2-methyl*cyclo*hexane-2-carboxylate*, b.p. 208—210°/6 mm. The free *acid*, b.p. 235—245°/7 mm., was converted into its acid chloride, which with $AlCl_3$ gave *methylhexahydro*peri*benzanthrone* (I), b.p. 215—225°/4 mm. Reduction of (I) (HI and red P) gave *methylhexahydro*iso*chrysofluorene* (not isolated pure), which with Se gave *iso*chrysofluorene, m.p. 84° (picrate, m.p. 110—111°). D. G.

Perylene and its derivatives. LIV. Molecular compound of perylene with two molecules [four atoms] of iodine, $C_{20}H_{12},2I_2$. M. Pestemer and E. Treiber (*Ber.*, 1941, **74**, [*B*], 964—975).—Dependence of the saturation concn. on the composition of the solid phase in the system, perylene (I)–I–C_6H_6 or –$CHCl_3$, shows the existence of a *compound*, $C_{20}H_{12},4I$, forming mixed crystals with excess of I, in the solid phase (cf. Brass *et al.*, A., 1933, 57; 1939, II, 207). The solubilities and additivities of absorption spectra prove that the compound is ∢95% dissociated in solution. Absorption spectra are recorded for (I) and I in C_7H_{16} and in C_6H_6, and for Br, 3 : 9- and 3 : 10-dibromoperylene in *cyclo*hexane. R. S. C.

Fission of amines by alkali metals. E. Stoelzel (*Ber.*, 1941, **74**, [*B*], 982—986).—Amines, NRR'_2, are cleaved by K or K–Na in Et_2O at room temp. to $KR + KNR'_2$; products are identified by interaction with CO_2. Thus, $NPh_2{\cdot}CPh_3$, $NMe_2{\cdot}CPh_3$, or $NH_2{\cdot}CPh_3$ gives $CPh_3{\cdot}CO_2H$; $NPh_2{\cdot}CH_2Ph$ gives $NPh_2{\cdot}CO_2H$ and $NHPh_2$; *benzhydryldimethylamine* (prep. from $CHPh_2Br$ by $NHMe_2$ and then Na–Hg in C_6H_6–EtOH), m.p. 72°, or $NH_2{\cdot}CHPh_2$ gives $CHPh_2{\cdot}CO_2H$. R. S. C.

Analogues of pantothenic acid. IV. Aryl derivatives of pantoyltaurine. J. Barnett, D. J. Dupré, B. J. Holloway, and F. A. Robinson (*J.C.S.*, 1944, 94—96).—$CHPhCl{\cdot}CH_2{\cdot}NH_2,HCl$ (from $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2,HCl$ and $SOCl_2$) with Na_2SO_3 at 100° gives *α-phenyltaurine* (I), m.p. 258°. The Na salt of (I) with pantothenolactone gives the Na salt of *β-(α′γ′-dihydroxy-β′β′-dimethylbutyramido)-α-phenylethanesulphonic acid* (II). *β-Hydroxy-αα-diphenylpropaldehyde*, m.p. 137—139° (from $CHPh_2{\cdot}CHO$ and CH_2O), is converted into its cyanohydrin, which is hydrolysed to dl-*α-hydroxy-ββ-diphenyl-γ-butyrolactone*, (III), two forms, m.p. 141° and 174°. (III) with the Na salt of taurine gives *β-(αγ-dihydroxy-ββ-diphenylbutyramido)ethanesulphonic acid* (IV). Pantothenolactone gives *mono-p-toluenesulphonylpantothenolactone*, m.p. 114—115°, which with the Na salt of taurine gives the Na salt of *β-(α-p-toluenesulphonyl-γ′-hydroxy-β′β′-dimethylbutyramido)ethanesulphonic acid* (V). (II), (IV), and (V) showed no bacteriostatic activity *in vitro* or *in vivo*. Prep. of *α-hydroxy-β-phenyl*iso*valeric acid*, m.p. 94—95°, is described. D. G.

Action of nitrous acid on 4-dimethylaminodiphenyl. J. Guiteras (*Anal. Fis. Quím.*, 1940, **36**, 354—359).—The derivative, m.p. 112—115°, of García Banús *et al.* (A., 1922, i, 333) is *p*-$C_6H_4Ph{\cdot}NMe{\cdot}NO$ (m.p. 115—116°) (with HNO_2 gives the 3-NO_2-derivative); 3-nitro-4-dimethylaminodiphenyl (I), m.p. 70—71°, is also formed. *p*-$C_6H_4Ph{\cdot}NMe_2$ or (I) with AcOH–HNO_2 yields 3 : 5-*dinitro-*, m.p. 104—105°, reduced by Na_2S to 3-nitro-5-amino- [*hydrochloride*, m.p. 175—180° (decomp.)], by $SnCl_2$ to 3 : 5-*diamino-4-dimethylamino-*, m.p. 113—115° (oxidised by CrO_3 to BzOH), and converted by HNO_2 into 3 : 5-dinitro-4-nitrosomethylamino-diphenyl, m.p. 121—122°. The nitration of bases by HNO_2 is considered to take place through a quinonoid form, which has been isolated in the case of (*p*-$NMe_2{\cdot}C_6H_4)_2$, and subsequent nitration. Quinol with $C_6H_{11}{\cdot}O{\cdot}NO$ gives quinhydrone and benzoquinone. F. R. G.

Intramolecular transformations among completely substituted benziminophenylthiocarbamides and thiobenzoylguanidines. H. Rivier and M. Langer (*Helv. Chim. Acta*, 1943, **26**, 1722—1740).—$PhCS{\cdot}NPh{\cdot}C(:NPh){\cdot}NPhR$ is converted by heat into $NPh{:}CPh{\cdot}NPh{\cdot}CS{\cdot}NPhR$ when R = Et. Change occurs in the reverse direction when R = Me. The mechanism of the reactions is discussed. Carbodiphenylimide (I) (trimeric) is converted by an

equimol. quantity of NHPhAlk at room temp. into 2-*methylanilino*-1 : 2 : 3 : 4 : 5 : 6-*hexaphenyldihydro*isomelamine, NPh<C(:NPh)·NPh / C(:NPh)·NPh>C(NHPh)·NPhMe, m.p. 144—145°, and the corresponding *Et* compound, m.p. 149—150°. At ~110° the corresponding products are NN′N″-*triphenyl*-N-*methyl*- (**II**), m.p. 128—129° (*hydrochloride*, m.p. 216—217°), and -N-*ethyl*-, m.p. 89—90° (*hydrochloride*, m.p. 205—206°), -*guanidine*. Nascent (**I**) and NHPhMe give an isomeride (**III**), m.p. 115—116° (rapid), ~127° (slow heating) (hydrochloride, m.p. 205—206°), of (**II**). (**II**) or (**III**) is transformed by BzCl in alkali or $CHCl_3$–C_5H_5N into N″-*benzoyl*-NN′N″-*triphenyl*-N-*methylguanidine*, m.p. 194—195°; the corresponding *Et* compound has m.p. 109—110°. PhCSCl and (**II**) (Schotten–Baumann) give N″-*thiobenzoyl*-NN′N″-*triphenyl*-N-*methylguanidine* (**IV**), m.p. 182—183° (*hydrochloride*, decomp. ~160°; picrate, m.p. 188—189°), also obtained from chlorodiphenylmethylamidine and PhCS·NHPh in $CHCl_3$ containing C_5H_5N. N″-*Thiobenzoyl*-NN′N″-*triphenyl*-N-*ethylguanidine* (**V**), m.p. 130·5—131°, and its hydrochloride are described. Since either base is readily regenerated from its hydrochloride there is no transformation under the influence of HCl under these conditions. Addition of NPh:CPhCl in $CHCl_3$ (free from EtOH) to a solution of NPh:C(SH)·NPhMe in $CHCl_3$ containing C_5H_5N at room temp. gives N′-N-*phenylbenzimino*-N′N″-*diphenyl*-N″-*methylthiocarbamide* (**VI**) (+C_6H_6 or +Et_2O), m.p. 96—98°; the corresponding *Et* compound (**VII**) has m.p. 131—132° (also +1C_6H_6, m.p. 89—91°). In the initial absence of C_5H_5N these reactants give isomerides of (**VI**) and (**VII**) (as red hydrochlorides); C_5H_5N then gives (**IV**) and (**VII**) [or $(NPh:CPh)_2S$] respectively. NPh:CCl·NPhMe and NPh:CPh·SNa give (**VI**). *Chloro*-NN′-*diphenyl*-N-*ethylamidine* b.p. 196—200°/10 mm., m.p. 58—59°, under similar conditions affords (**VII**). (**VI**) is also obtained from NPh:CPh·NHPh and NPhMe·CSCl in $CHCl_3$ (free from EtOH) at 30—35°; with the crude chloride in boiling $CHCl_3$ the product is triphenyldimethyldithiobiuret, m.p. 204—205°. (**VII**) is obtained analogously from NPhEt·CSCl. (**VI**) and (**VII**) afford yellow hydrochlorides from which the bases are readily regenerated by C_5H_5N, showing that under the experimental conditions there is no transformation under the influence of HCl. (**IV**) is unchanged by boiling C_6H_6 whereas under these conditions (**V**) is partly converted into (**VII**). (**VI**) remains unchanged in boiling C_6H_6 whereas at 180—200° it is converted into (**IV**). N′-N-*Phenylbenzimino*-N′-*phenylthiocarbamyl chloride*, m.p. 112—113°, is prepared from NPh:CPh·NHPh and $CSCl_2$ in $CHCl_3$. M.p. are corr. H. W.

***anti*-α-Hydroxylamino-γ-oximino-αε-di-*p*-anisyl-Δ$^{\delta}$-pentene, m.p. 156—157° (corr.).**—See C., 1944, 64.

Synthesis of chloro-ortho-esters of silicic acid. J. N. Volnov and A. Mischelevitsch (*J. Gen. Chem. Russ.*, 1943, **13**, 213—216).—The following esters were obtained from $SiCl_4$ and the appropriate OH-compound in Et_2O: *trichlorothymoxysilan*, b.p. 122—124°/23 mm., *dichlorodithymoxysilan*, b.p. 195—200°/3 mm., *chlorotrithymoxysilan*, b.p. 251—255°/7—8 mm. *trichlorocarvacryloxysilan*, b.p. 108—111°/4 mm., and *trichloro*-o-*anisyloxysilan*, b.p. 134—136°/30 mm. R. T.

Dipole moments of friedelin, cerin, isomerides of friedelinol, and isomerides of γ-(α-naphthyl)-α-chloro-Δ$^{\alpha}$-propene.—See A., 1944, I, 142.

Syntheses of 2 : 4 : 6-trialkylresorcinols from products of the Nidhone process. I. 2 : 4 : 6-Triethylresorcinol. S. D. Limaye (*Rasāyanam*, 1943, **1**, 246—250).—2 : 1 : 3-$C_6H_3Et(OH)_2$ gives (Ac_2O–NaOAc at 155—160°) its *diacetate*, m.p. 70—71°, which with $AlCl_3$ at 150° yields 4 : 6-*diacetyl*-2-*ethylresorcinol*, m.p. 110°, reduced (Clemmensen) to 2 : 4 : 6-*triethylresorcinol* (**I**), m.p. 85°. 2 : 4 : 1 : 3-$C_6H_2Et_2(OH)_2$ with AcOH–$ZnCl_2$ at 140° gives 6-*acetyl*-2 : 4-*diethylresorcinol*, m.p. 115°, giving (**I**) on reduction. 4 : 6 : 1 : 3-$C_6H_2Ac_2(OH)_2$ with AcCl and $AlCl_3$ at 110° gives 2 : 4 : 6-*triacetylresorcinol*, m.p. 136°, also reduced to (**I**). D. G.

Migration of radicals during a Grignard reaction. αα-Di-*p*-hydroxyphenyl-ββ-diethylethylene. Z. Földi and I. Demjén (*Ber.*, 1941, **74**, [*B*], 930—934).—Anisoin and $SOCl_2$ at 50° give *chlorodeoxyanisoin* (**I**), m.p. 80—82°, which with MgEtBr gives (p-OMe·C_6H_4)$_2$CH·CEt_2·OH (**II**), m.p. 84—85°, b.p. 164—167°/~0·01 mm., converted by $POCl_3$ alone at room temp. into (p-OMe·C_6H_4)$_2$C:CEt_2 (**III**), m.p. 90—92°, or by $POCl_3$ in PhMe at 100° into (p-OMe·C_6H_4·CEt:)$_2$, m.p. 121—123° (cf. Peteri, A., 1940, II, 306; von Wessely *et al.*, *Monatsh.*, 1940, **73**, 132). Structures are proved as follows. CrO_3–AcOH at room temp. and then 100° oxidises (**I**) to anisil; with MgMeI, (**II**) gives 80—85% of CH_4, and with CrO_3–AcOH gives (p-OMe·C_6H_4)$_2$CO; KOH–EtOH at 200° converts (**III**) into (p-OH·C_6H_4)$_2$C:CEt_2, m.p. 170—173°, and H_2–Pd–C in EtOH gives (p-OMe·C_6H_4)$_2$CH·$CHEt_2$, b.p. 115—124°/~0·01 mm. With a little H_2SO_4 and distillation at ~0·01 mm., (**II**) yields (**III**). PBr_5 converts (**II**) into an oily bromide, which with boiling KOH–EtOH yields (**III**). R. S. C.

Natural stilbenes. III. Synthesis of resveratrole. E. Späth and K. Kromp. **IV. Synthesis of pinosylvin.** E. Späth and F. Liebherr. **V. Synthesis of pinosylvin monomethyl ether.** E. Späth and K. Kromp (*Ber.*, 1941, **74**, [*B*], 867—869, 869—872, 1424—1428).—III. 3 : 5 : 1-$(OH)_2C_6H_3$·CHO (**I**) and p-OH·C_6H_4·CO_2Na in Ac_2O at 160° give, after keeping in aq. NaOH–N_2 at room temp., 3 : 5-*dihydroxy*-α-p-*hydroxyphenylcinnamic acid* (46%), m.p. 284—286° (decomp.), decarboxylated to resveratrole (Takaoka, A., 1940, II, 328) (CH_2N_2 gives the Me_3 ether = pterostilbene) by Cu-bronze in quinoline at 220° (4 min.).

IV. 3 : 5 : 1-$(OAc)_2C_6H_3$·CO_2H and $SOCl_2$ at 60—70° give the acid *chloride*, m.p. 89·5—90°, converted by H_2–Pd–$BaSO_4$ in xylene at 160° into (**I**), m.p. 161—162° (decomp.) (lit., 145—146°) (*diacetate*, m.p. 53·5—54·5°). CH_2Ph·CO_2Na (**II**) and (**I**) in Ac_2O at 100° and then 160° give 3 : 5-*diacetoxy*-α-*phenylcinnamic acid* (46%), m.p. 197·5—198·5°, converted by Cu-bronze in quinoline at 260° and then 240° into an oil which with boiling 5% aq. NaOH–N_2 gives pinosylvin.

V. 3 : 5 : 1-$(OH)_2C_6H_3$·CO_2Me and Me_2SO_4 in MeOH–NaOMe at 20° and then the b.p. give 3-*hydroxy*-5-*methoxybenzoic acid* (36%), m.p. 203—204° (and a small amount of the Me_2 ether ester), converted by boiling AcCl into the *acetate*, m.p. 151·5—152·5°, which with $SOCl_2$ at 75° gives 3-*acetoxy*-5-*methoxybenzoyl chloride*. H_2–Pd–$BaSO_4$ in xylene at 160° then gives 3 : 5 : 1-OH·C_6H_3(OMe)·CHO, m.p. 130—131°, which with (**II**) in Ac_2O at 160° and then aq. KOH–N_2 at 20° gives 3-*hydroxy*-5-*methoxy*-α-*phenylcinnamic acid* (**III**), m.p. 200—201°, and a small amount of an isomeric *acid* (**IV**), m.p. 181—182°. With Cu-bronze in quinoline at 240° and then 220°, (**III**) gives an oil, isomerised by short heating at 350°/vac. (not other methods) into pinosylvin Me ether (67% yield), m.p. 121·5—122°, which is obtained directly by decarboxylation of (**IV**). R. S. C.

Structure of hydroxyazo-dyes according to their absorption spectra. Spectroscopic analysis of acyloxyazo-compounds. P. Ramart-Lucas (*Compt. rend.*, 1942, **215**, 468—470).—Spectra of (:NPh)$_2$, p-OAc·C_6H_4·N_2Ph, p-NPhAc·N:C_6H_4:O, and 4 : 1 : 3-OAc·C_6H_3Me·N_2Ph are recorded; the spectrum of the *O*-Ac derivatives is very close to that of (:NPh)$_2$. The structure of acyloxyazo-compound is therefore determinable from their spectra. H. W.

Action of montmorillonite clays on vitamin-*A*. Mesomerism in the carotenoid group. P. Meunier (*Compt. rend.*, 1942, **215**, 470—473).—Montmorillonite clays become blue by the adsorption of vitamin-*A* from non-polar solvents (C_6H_6, light petroleum, *cyclo*hexane, and even $CHCl_3$). Other clays behave similarly after treatment with HCl or H_2SO_4. The colour is very persistent, particularly if the clay is soaked in the solvent. It can easily be removed by a trace of a polar solvent (EtOH, $COMe_2$, Et_2O). If the latter is removed and a polar solvent used again, the blue colour reappears. It is considered that mesomerism between the ψ-quinonoid and ψ-benzenoid forms is caused by the reaction of widely differing reagents, all of which have incomplete octets, on carotenoids in non-polar media. A trace of polar solvent causes the disappearance of mesomerism (and the colour reaction in consequence) by a mutual attraction of the dipoles; the mol. -*A* is detached in one of its forms. The colour with the clays is thus brought into line with that given by $SbCl_3$. H. W.

Contact synthesis of *o*-methylbenzyl alcohol from crotonaldehyde and ethyl alcohol. J. A. Gorin and K. N. Tscharskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 131—135).—A mixture of CHMe:CH·CHO and EtOH passed over the dehydrating component of Lebedev's catalyst (A., 1934, 168) at 350° gives o-C_6H_4Me·CH_2·OH in 5% yield. R. T.

Phenol–formaldehyde resins. II. Quinonemethide as intermediate product in the hardening of phenol resins. V. Reactions of *p*-hydroxymethyl groups during hardening. VI. Oxido-reduction processes during heating of polymeric quinonemethides. K. Hultzsch (*Ber.*, 1941, **74**, [*B*], 898—904, 1533—1538, 1539—1543).—II. Heating 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (**I**) at 175° in CO_2 gives H_2O, an oil, and a resin containing a di- or tri-meride, m.p. 200° (**II**), of 1 : 3 : 5 : 2-CH_2:$C_6H_2Me_2$:O and much (2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2)$_2$O (**III**), m.p. 100° (*diacetate*, m.p. 85·5°). At 190—200° (**III**) gives (**II**) and at 225° gives (2 : 3 : 5 : 1-OH·$C_6H_2Me_2$)$_2$$CH_2$ (**IV**) (does not condense with paraformaldehyde at 200—240°). Heating (**II**) to 240° in CO_2 causes darkening and formation of (2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2)$_2$ (**V**), m.p. 168° (diacetate, m.p. 124°; Br_4-derivative, m.p. 258°), and a tetracyclic resin, but no H_2O or CH_2O. Heating (**I**) rapidly to 235° in CO_2 gives H_2O, CH_2O, (**IV**), (**V**), and 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CHO. Quinonemethides are considered to be intermediates in the hardening of (**I**) etc., reacting by disproportionation and diene addition.

V. Hardening of 4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (**VI**) proceeds similarly to that of (**I**) by way of the quinonemethide, but is slower and requires a higher temp.; it is, however, very rapid if other mols. have free *p*-positions. 68% of (**VI**), m.p. 105°, with very little (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$)$_2$$CH_2$ (**VII**) is obtained from 1 mol. each of 2 : 6 : 1-$C_6H_3Me_2$·OH (**VIII**), 30% CH_2O, and 10% NaOH in the cold. (**VI**) is partly unchanged by distillation at 1 mm., but ~50% is resinified, giving, *inter alia*, (**VII**), m.p. 175°. Heating (**VI**) at 230—240° in CO_2 gives H_2O, CH_2O (a little), 4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CHO, mesitol (a trace), (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2)$_2$, (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH:)$_2$ (**IX**), an *isomeride*, m.p. 224—226°

[gives the known (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·$CHBr)_2$, m.p. 178—186° (decomp.)], of (**IX**), and a resin (mol. wt. 584) (cf. Adler *et al.*, A., 1943, II, 130).

VI. Hardening of *o*-hydroxybenzyl alcohols containing no free *o*- or *p*-position is held to proceed entirely by way of *o*-quinonemethides, which dimerise to coumaran derivatives and thence, by oxidation and reduction, give all the products hitherto isolated. Similarly *p*-hydroxybenzyl alcohols give *p*-quinonemethides, which dimerise to stilbene derivatives, whence all isolated products are derived by oxidation and reduction. Isolation of mesitol after heating (**I**) is described. 2-Hydroxy-5-*cyclo*hexyl-3-methylbenzyl alcohol gives 4-*cyclo*hexyl-2 : 6-*dimethylphenol*, m.p. 78—79°, also obtained from (**VIII**) by *cyclo*hexanol and 72% H_2SO_4 at 60—70°; 2 : 3 : 5 : 1-OH·C_6H_2MeBu$^{\gamma}$·CH_2·OH gives 2 : 6-*dimethyl*-4-tert.-*butylphenol*, m.p. 81—82°, also obtained from (**VIII**) by Bu$^{\gamma}$OH and 72% H_2SO_4 at 60—70°. R. S. C.

Cyclic compounds containing sulphur.—See A., 1944, II, 154.

9 : 10-Dialkyl-9 : 10-dihydrophenanthrenediols and related compounds. E. J. H. Chu and Z. I. Shen (*J. Chinese Chem. Soc.*, 1943, **10**, 116—118).—Phenanthraquinone and MgAlkBr give 9 : 10-*di*-n-*hexyl*- (64%), m.p. 93·3—94·3°, -*di*-n-*heptyl*- (80%), m.p. 78·6—78·8°, and -*di*-n-*octyl*-9 : 10-*dihydrophenanthrene*-9 : 10-*diol* (69%), m.p. 92·3—93·2°, which yield oils on attempted rearrangement. The 9 : 10-Bu^{α}_2 analogue (78%), m.p. 134·5—136·5°, is rearranged by boiling AcOH–I to 10 : 10-*di*-n-*butyl*-9-*phenanthrone* (94%), m.p. 71·8—72·8°, reduced (Clemmensen) to 9 : 9-*di*-n-*butyl*-9 : 10-*dihydrophenanthrene* (10%), m.p. 76° (cf. Bachmann *et al.*, A., 1932, 745). A. T. P.

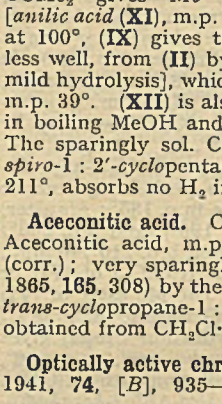
Mercapturic acids. IV. Synthesis of *p*-fluorophenyl-*l*-cysteine and its conversion into *p*-fluorophenylmercapturic acid *in vitro* and *in vivo*. S. H. Zbarsky and L. Young (*J. Biol. Chem.*, 1944, **152**, 599—602).—Cysteine Cu' mercaptide (A., 1944, II, 76) and *p*-C_6H_4F·N_2HSO_4 at 0°, then at 60—70°, afford, after purification with Sn–aq. HCl at 100° (bath), p-*fluorophenyl*-l-*cysteine* (**I**), decomp. 180—183°, $[\alpha]_D^{22}$ +13° in 0·1N-NaOH. Successive treatment of (**I**) with 0·1N-NaOH and Ac_2O at 0° gives p-*fluorophenylmercapturic acid*, m.p. 158—159°, $[\alpha]_D^{24}$ −20° in EtOH, which is isolated (14—15% conversion) from the urine of rats fed on a diet containing (**I**). A. T. P.

1 : 1-Diphenylindane and its derivatives. 1 : 1-Diphenyl-3-indanyl- and -3-indenyl-acetic acids. P. E. Gagnon, L. Gravel, and L. P. Amiot (*Canad. J. Res.*, 1944, **22**, B, 32—44).—1 : 1-Diphenylindane (**I**) (improved prep.) with Br (1 mol.) in boiling CS_2 gives the 3-*Br*-derivative (**II**), m.p. 87—88°, converted by MeOH, EtOH, piperidine, *p*-toluidine, and NH_2Ph into 3-*methoxy*- (**III**), m.p. 101—102°, 3-*ethoxy*-, m.p. 70—71°, 3-*piperidino*-, m.p. 108—109° (*hydrochloride*, m.p. 253—255°), 3-p-*toluidino*-, m.p. 124—125° (*hydrochloride*, m.p. 218—219°), and 3-*anilino*-1 : 1-*diphenylindane*, m.p. 125—126° (*hydrochloride*, m.p. 213—214°), respectively. With aq. KOH or K_2CO_3, (**II**) gives 1 : 1-diphenylindene (**IV**), m.p. 90—91°, and a little *di*-(1 : 1-*diphenyl*-3-*indanyl*) *ether*, m.p. 192—195°, while (**III**) and boiling 48% HBr yields (**IV**). (**II**) with $CHNa(CO_2Et)_2$ in boiling PhMe gives *Et* 1 : 1-*diphenyl*-3-*indanylmalonate*, b.p. 268°/1 mm.; the *malonic acid*, m.p. 160° (*Ag* salt; *di*-p-*nitrobenzyl* ester, m.p. 73—75°), at 170—180° gives 1 : 1-*diphenyl*-3-*indanylacetic acid* (**V**), m.p. 173—174° [*Ag* salt; p-*nitrobenzyl* ester, m.p. 172—173°; *amide* (**VI**), m.p. 181—182°; *anilide*, m.p. 171—172°]. Boiling $SOCl_2$ and (**VI**) yield 1 : 1-*diphenyl*-3-*indanylacetonitrile*, m.p. 120—121°, reduced (Na, EtOH) to β-1 : 1-*diphenyl*-3-*indanylethylamine* (*hydrochloride*, m.p. 180—185°). (**VI**) and Et_2O–EtOH–HCl give a *hydrochloride*, m.p. 191—192°. 3 : 3-Diphenylindanone with CH_2Br·CO_2Et (Reformatsky) gives *Et* 3-*hydroxy*-1 : 1-*diphenyl*-3-*indanylacetate*, m.p. 93—94°, dehydrated (HCl in PhMe) to *Et* 1 : 1-*diphenyl*-3-*indenylacetate* (**VII**), m.p. 80—81° [free *acid* (**VIII**), m.p. 178—179° (*Ag* salt; p-*nitrobenzyl* ester, m.p. 142—143°)]. Reduction (H_2, PtO_2, AcOH) of (**VIII**) [or (**VII**) and subsequent hydrolysis] gives (**V**). D. G.

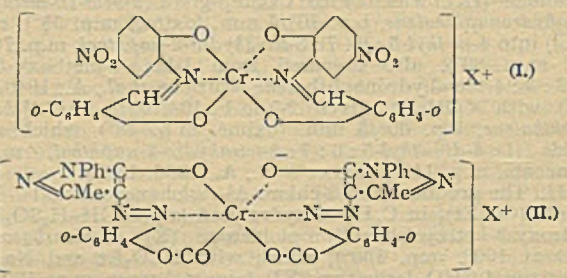
αα'α'-Ditetramethyleneadipic [ethylene-αβ-bis*cyclo*pentane-1 : 1'-dicarboxylic] acid. Ring-contraction by oxidation. C. Mannich (*Ber.*, 1941, **74**, [*B*], 1007—1014).—*cyclo*Pentane*spiro*-1' : 2-*cyclo*pentanone*spiro*-3 : 2''-*cyclo*hexanone (A., 1943, II, 373) with 30% H_2O_2 in AcOH gives exothermally (cooling) *αα-α'α'-ditetramethyleneadipic acid* (**I**) (87%), m.p. 220°, sublimes 205—210°, the structure of which follows from proof that it is symmetrical (below) and from the facts that it (i) resists dehydrogenation by Pt-asbestos at 300—500°, Br at 165° (partial decomp.; complete at 195°), or Se at 300° [gives a small amount of 1-β-*cyclo*pentylethyl*cyclo*pentane-1-*carboxylic acid*, m.p. 35—36° (amorphous *Ag* salt), and CO_2], (ii) is partly decomposed but not decarboxylated by Cu-bronze in acridine–N_2 at 300°, (iii) is 50% decomposed and 50% unchanged by Br and red P at 100°, (iv) does not undergo condensation to a ketone, and (v) in boiling Ac_2O gives a dimeric *anhydride* (**II**), m.p. 187° [hydrolysed to (**I**) by alkali but unaffected by boiling MeOH]. With boiling $SOCl_2$–C_6H_6 and then NH_3–MeOH at 0°, (**I**) gives the *diamide* (77%), m.p. 245—246°. With CH_2:CH·CH_2·NH_2 (**III**) in C_6H_6 at 45°, (**II**) gives the *mono*- (**IV**) (~50%), dimorphic, m.p. 84° (resolidifies, remelts 103°) and 103°, and the *di-allylamide* (**V**), m.p. 205°. The *mono*- (**VI**) (~50%), m.p. 93°, and *di*-n-*propylamide* (**VII**), m.p. 218°, are similarly prepared. The N-*propyl*-N'-*allyldiamide*, m.p. 213°, is prepared from (**IV**) by $SOCl_2$ at 40° and then NH_2Pr^{α}–EtOH at 0° or from (**VI**) by $SOCl_2$ and then (**III**); a mixture of (**V**) and (**VII**) shows a sharp m.p. (214—215°), so that this proof of symmetry is invalid. Me_2SO_4–NaOH converts (**I**) into the Me_2 ester (**VIII**), m.p. 88°; HCl–EtOH at room temp. gives the Et_2 ester, b.p. 189—190°/4 mm. The Na_2 salt of (**I**) with CH_2PhCl in boiling MeOH gives the $(CH_2Ph)_2$ ester (**IX**), m.p. 91°. Boiling KOH–90% MeOH converts (**VIII**) into the *Me H* ester (**X**) (50%), m.p. 85°, which with boiling $SOCl_2$–C_6H_6 and then NH_2Ph–$COMe_2$ gives *Me αα'α'-ditetramethyleneadipanilate*, m.p. 115° [*anilic acid* (**XI**), m.p. 163°]. With Na and a little H_2O in CH_2Ph·OH at 100°, (**IX**) gives the *CH_2Ph H* ester, m.p. 105° [also obtained, less well, from (**II**) by CH_2Ph·OH] [*anilide*, m.p. 96°, gives (**XI**) by mild hydrolysis], which with CH_2N_2 gives the *CH_2Ph Me* ester (**XII**), m.p. 39°. (**XII**) is also obtained from the K salt of (**X**) by CH_2PhCl in boiling MeOH and is converted into (**X**) by H_2–Pd–C in MeOH. The sparingly sol. Ca salt of (**I**) at 470—550° gives *cyclo*pentane-*spiro*-1 : 2'-*cyclo*pentanone, b.p. ~165°/13 mm. (*semicarbazone*, m.p. 211°, absorbs no H_2 in presence of Pd–C). R. S. C.

Aceconitic acid. C. Grundmann (*Annalen*, 1943, **555**, 77—80).—Aceconitic acid, m.p. 220—221° (corr.) [Me_3 ester, m.p. 56—57° (corr.); very sparingly sol. *Ba* salt], obtained by Baeyer (*Annalen*, 1865, **165**, 308) by the action of Na on CH_2Br·CO_2Et, is identified as *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid. Lower yields are obtained from CH_2Cl·CO_2Et. H. W.

Optically active chromium lakes. P. Pfeiffer and S. Saure (*Ber.*, 1941, **74**, [*B*], 935—941).—For hexaco-valent, tetrahedral compounds (*A*), there are 6 optically active *cis*- and 4 optically active *trans*-isomerides, plus 5 corresponding racemates. However, if R = R', there are only two active (+ its racemate) forms and one, inactive *trans*-form. The Cr compounds described below were obtained in only one configuration. The Na salt [(**I**), X = Na] with H_2SO_4 in aq. MeOH gives the yellowish-brown *complex* [(**I**), X = H],



(*A*.)



(I.)

(II.)

which gives no cryst. quinine salt but with CHPhMe·NH_2 gives the *dl*-base *dl*-acid *salt* and with the *d*-base gives a *salt*, $[M]_D$ −2196° in 50% EtOH, whence dil. H_2SO_4 yields the l-*complex* [(**I**), X = H], α ~0 in 50% EtOH, $[M]_D$ −2196° as Na salt in 50% EtOH. The Na salt [(**II**), X = Na] gives similarly the *substance* [(**II**), X = H] which with strychnine yields *salts*, $[M]_D$ +820° and −1438°, and thence *substances* [(**II**), X = H], $[M]_D$ (as Na salt) +1109° and −693°, respectively, in 50% EtOH. R. S. C.

Preparation of retinene *in vitro*.—See A., 1943, III, 405.

Alkylation by olefines in presence of aluminium chloride. II. S. I. Lurie and A. J. Golovatscheva (*J. Gen. Chem. Russ.*, 1943, **13**, 195—201).—Butylation of COMeR (R = Ph, 2 : 4-$C_6H_3Me_2$, 2 : 5- and 2(4) : 4(2)-OMe·C_6H_3Me) by means of CH_2:CMe_2 in CS_2 in presence of $AlCl_3$ does not take place, suggesting that the CO group inactivates the mol. R. T.

Ring enlargement in cyclanes. Methyl*cyclo*pentane, *cyclo*heptane, and indane series. (Mlle.) B. Tchoubar (*Compt. rend.*, 1942, **215**, 224—225).—2-Methyl*cyclo*pentanone is converted into its *cyanohydrin*, b.p. 134—135°/35 mm., which is hydrogenated (PtO_2) to 2-*methyl*-1-*aminomethyl*cyclo*pentanol*, b.p. 105°/15 mm. (*hydrochloride*, m.p. 157°). This is deaminated ($NaNO_2$–dil. AcOH) exclusively to 3-methyl*cyclo*hexanone (semicarbazone, m.p. 178°). Rupture of the ring occurs only between $C_{(1)}$ and $C_{(2)}$. 3-*Methyl*cyclo*pentanone cyanohydrin*, b.p. 122—124°/19 mm., is hydrogenated to 3-*methyl*-1-*aminomethyl*cyclo*pentanol*, b.p. 115°/20 mm., deaminated to 3- and 4-methyl*cyclo*hexanone (semicarbazones, m.p. 178° and 198°, respectively), fission occurring mainly between C·C on the substituted side of the ring. cyclo*Heptanone cyanohydrin*, b.p. 138—139°/15 mm., affords 1-*aminomethyl*cyclo*heptanol*, b.p. 14° (?)/18 mm. (*hydrochloride*, m.p. 185°), deaminated to *cyclo*octanone, b.p. 90°/12 mm. (semicarbazone, m.p. 164—165°). 2-Indanone is converted through the H sulphite into the *cyanohydrin*, m.p. 121°, and thence into the NH_2-alcohol, which is deaminated directly to 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (semicarbazone, m.p. 215°). H. W.

Syntheses in the santonin series. I. 4-Alkyl-$\Delta^{2:5}$-*cyclo*hexadienones. II. 2-Keto-1 : 10-dimethyl-$\Delta^{1(9):3}$-hexahydronaphthalene. III. Santonin. (Miss) K. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Rasāyanam*, 1943, **1**, 233—237, 237—243, 243—245).—I. Et Δ^{α}-nonenoate, HCO_2Et, and Na in Et_2O give *Et γ-formyl-Δ^{α}-nonenoate* (**I**), b.p. 120°/8 mm. (*p*-nitrophenylhydrazone, m.p. 113°), oxidised (cold aq. $KMnO_4$ + $MgSO_4$) to *n*-amylmalonic acid (**II**). (**I**) with $CH_2(CO_2H)_2$ in C_5H_5N–piperidine at 100° (bath) gives *Et H γ-n-amyl-$\Delta^{\alpha\delta}$-pentadiene-αε-dicarboxylate*, b.p. 130°/4 mm., and thence (alkali) the free *acid* (**III**). With $Ba(OH)_2$ at 180° (**III**) gives 4-n-*amyl-$\Delta^{2:5}$*-cyclo*hexadienone*, b.p. 194°/713 mm. (*oxime*, m.p. 48°; p-*nitrophenylhydrazone*, m.p. 99°), oxidised to (**II**) and converted by conc. HCl at room temp. (21 days) into *p-n*-amylphenol. Similarly Et hexenoate gives *Et γ-formyl-Δ^{α}-hexenoate*, b.p. 65°/8 mm. (p-*nitrophenylhydrazone*, m.p. 71°), *Et H γ-ethyl-$\Delta^{\alpha\delta}$-pentadiene-αε-dicarboxylate*, b.p. 80°/8 mm. (free *acid*), and 4-*ethyl-$\Delta^{2:5}$*-cyclo*hexadienone* (**IV**), b.p. 160°/713 mm. (p-*nitrophenylhydrazone*, m.p. 83°). (**IV**) with fuming HCl followed by Br gives 4 : 2 : 3 : 6 : 1-C_6HEtBr_3·OH, m.p. 57—58°.

II. 2-Formyl*cyclo*hexanone (**V**), $CH_2(CO_2H)_2$, and C_5H_5N–piperidine give *β-2-keto*cyclo*hexylacrylic acid*, two forms, probably geometric isomerides, b.p. 120°/20 mm. (**VI**) (*semicarbazone*, m.p. 185°; *Me* ester, b.p. 100°/40 mm., and its *semicarbazone*, m.p. 195°), and b.p. 200°/20 mm. (**VII**) (*semicarbazone*, m.p. 225°; *Me* ester, b.p. 210°/40 mm., and its *semicarbazone*, m.p. 225°). Oxidation ($KMnO_4$) of (**VI**) or (**VII**) gives *cyclo*hexanone-2-carboxylic acid. The Me ester of (**VI**) with $CH_2Br·CO_2Et$ gives (Reformatsky) a OH-ester, b.p. 144°/30 mm.; hydrolysis (EtOH–KOH) and dehydration (Ac_2O) gives (poor yield) *β-2-carboxymethylene*cyclo*hexylacrylic acid*, m.p. 86°, which gives a trace of (?) (**VIII**) (below) on distillation with $Ba(OH)_2$. (**V**) with $COMe_2$ and NaOEt in EtOH gives 2-*keto-$\Delta^{1(9):3}$-hexahydronaphthalene* (**VIII**), b.p. 105°/25 mm. (semicarbazone, m.p. 115°; oxime, m.p. 72°). With boiling conc. HCl (**VIII**) gives 5 : 6 : 7 : 8-tetrahydro-2-naphthol, m.p. 62°. (**V**) with COMeEt gives 2-*keto*-1-*methyl-$\Delta^{1(9):3}$-hexahydronaphthalene*, b.p. 85°/5 mm. (oxime, m.p. 52°; *p*-nitrophenylhydrazone, m.p. 92°), which with HCl gives 1-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol*, m.p. 78° (benzoate, m.p. 91°). (**V**) (Na salt) with MeI in C_6H_6 at 60° gives 2-formyl-2-methyl*cyclo*hexanone (**IX**), which with $COMe_2$ gives 2-*keto*-10-*methyl-$\Delta^{1(9):3}$-hexahydronaphthalene*, b.p. 70°/5 mm. (oxime, m.p. 55°), converted (HCl) into 4-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol*, m.p. 70° (*benzoate*, m.p. 89°), also prepared from 1-keto-7-methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (Ruzicka *et al.*, A., 1940, II, 184). (**IX**) with COMeEt gives 2-*keto*-1 : 10-*dimethyl-$\Delta^{1(9):3}$-hexahydronaphthalene*, b.p. 60°/5 mm. (oxime, m.p. 48°), which with HCl yields 1 : 4-*dimethyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol*, m.p. 108° (benzoate, m.p. 119°) (Fieser *et al.*, A., 1936, 1503).

III. The product from 3-chloro-Δ^2-*cyclo*hexenone and $CMeNa(CO_2Et)_2$ in C_6H_6 is hydrolysed (aq. EtOH–H_2SO_4) to α-(2-hydroxy-3-keto*cyclo*hexyl)propiolactone (**X**) (*semicarbazone*, loses H_2O at 100°, m.p. 150°), which with HCO_2Et and Na in Et_2O gives the 4-CHO-derivative (**XI**) (*semicarbazone*, m.p. 199°) of (**X**). The Na derivative of (**XI**) with MeI in C_6H_6 at 60° affords the 4-Me derivative of (**XI**), which with COMeEt and NaOEt gives santonin (**XII**), m.p. 171° (semicarbazone, m.p. 203°), identical (mixed m.p.) with natural (**XII**). The synthetic (**XII**) was optically active (lævorotatory); this is claimed to be the first example of an abs. asymmetric synthesis. D. G.

Syntheses in the naphthalene group. IV. Cyclisation of phenylbenzylpyrotartaric [α-(α′β′-diphenylethyl)succinic] acid. W. Borsche and F. Sinn (*Annalen*, 1943, **555**, 70—77; cf. A., 1937, II, 18).—Cyclisation of α-(α′β′-diphenylvinyl)succinic acid (**I**) [prep. from COPh·CH_2Ph and $(CH_2·CO_2Et)_2$ described] gives mixtures of compounds from which only very small amounts of individuals can be isolated. (**I**) is reduced by Na–Hg at 100° to a mixture (**II**) of isomerides (racemates of the potentially active and *meso*-forms) from which *α-(α′β′-diphenylethyl)succinic acid* (**III**), m.p. 186—187°, is readily isolated. It is also obtained by hydrogenation (Pd–C in EtOH) of the Et_2 ester of (**I**) and hydrolysis of the product. (**III**) gives (CH_2N_2) a Me_2 ester and is converted by boiling AcCl into an *anhydride* (**IV**), m.p. 102—103°, re-converted by KOH–MeOH into (**III**). Treatment of (**III**) with NaOAc and boiling Ac_2O affords predominatingly an *anhydride* (**V**), m.p. 133—134°, hydrolysed (KOH–MeOH) to iso-*α′β′-diphenylethylsuccinic acid* (**VI**), m.p. 150—151°, or (+1 C_6H_6), m.p. 96° (decomp.) and 151° after resolidification. (**VI**) and CH_2N_2 give a *Me_2* ester, m.p. 114·5—115·5°, also obtained from (**V**) and boiling MeOH containing fuming HCl. 1-*Keto*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylacetic acid* (**VII**), m.p. 171° [*oxime*, m.p. 151°, softens ~135°; non-cryst. Me ester (2 : 4-*dinitrophenylhydrazone*, m.p. 169—171°)], is obtained from (**III**) and H_2SO_4 in Et_2O at 0°, from the chloride of (**III**) with $AlCl_3$ [with an *isomeride*, m.p. 204—205°) (previous sintering)], from (**IV**) and $AlCl_3$ with an *isomeride*, m.p. 142—145°, from (**V**) and $AlCl_3$, and from the non-cryst. residue from (**III**) and H_2SO_4 in Et_2O at 0°. The best method is from the chloride (yield 65—70%). (**VII**) is characterised as a γ-CO acid by its transformation by N_2H_4,H_2O in boiling MeOH into 3-*keto*-5-*phenylhexahydro*-7 : 8-*benzocinnoline*, m.p. 191°. (**VII**) is dehydrated by conc. H_2SO_4 at room temp. into two *compounds*, $C_{18}H_{14}O_2$, m.p. 199—203° (*monodinitrophenylhydrazone*, m.p. 271°, darkens at 265°) and m.p. 131—135° (*monodinitrophenylhydrazone*, decomp. 230—231°) (cf. Knott, *Diss.*, *Frankfurt*, 1937). Provided the correct constitution has been assigned to (**VII**) the compounds must be partly hydrogenated derivatives of 1 : 2-benzanthracene or 2 : 3-benzphenanthrene. H. W.

2-Alkyl-3-phytyl-1 : 4-naphthaquinones.—See B., 1944, III, 100.

IV.—STEROLS AND STEROID SAPOGENINS.

Sex hormones and sterols. XVII. Side-chains of β- and γ-sitosterol. W. Dirscherl and H. Nahm (*Annalen*, 1943, **555**, 57—69).—Examination of the oxidation products of β- (**I**) and γ- (**II**) -sitosterol proves that the side-chain ·CHMe·$[CH_2]_2$·CHEtPr$^{\beta}$ is present in each. Optically it exerts a positive action in (**I**) and a negative effect in (**II**). In the two cases it differs in configuration at $C_{(24)}$, possibly also at $C_{(20)}$ and $C_{(17)}$. The yield of COMe·$[CH_2]_2$·Bu$^{\beta}$ obtained by the gradual addition of CrO_3 in 50% AcOH to cholesteryl acetate in boiling AcOH is materially improved by the addition of moderate amounts of $K_2S_2O_8$; "ceroyd" and SeO_2 appear ineffective and $K_2S_2O_8$ alone gives no ketone. Under similar conditions β-sitosteryl acetate affords $COMe_2$ and *ζ-methyl-ε-ethylheptan-β-one*, b.p. 80—92°/16 mm., $[\alpha]_D^{20}$ +2·54°±0·04°, 3·11±0·3° +3·11±0·3° in Et_2O (2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°; *semicarbazone*, m.p. 141—142°, $[\alpha]_D^{23}$ +1·28°±0·6° in EtOH, $[\alpha]_D^{29}$ +4·5°±1° in $CHCl_3$), the structural identity of which with synthetic *dl*-COMe·$[CH_2]_2$·CHEtPr$^{\beta}$ is established röntgenographically. Similar treatment of the acetate of (**II**) leads to $COMe_2$ and (−)-ζ-methyl-ε-ethylheptan-β-one, $[\alpha]_D^{21}$ −2·4°±0·4° in Et_2O (*semicarbazone*, m.p. 140—142°). H. W.

Formation of cholestenone from cholesterol dibromide by removal of hydrogen bromide with collidine. F. Galinovsky (*Ber.*, 1941, **74**, [*B*], 1048—1049).—Boiling cholesterol dibromide in collidine and subsequent chromatography yields Δ^4-cholestenone. R. S. C.

Metabolism of steroids. IV. Ketonic acids derived from cholic acid. G. A. D. Haslewood (*Biochem. J.*, 1944, **38**, 108—111; cf. A., 1943, II, 199).—The series of six possible acids obtainable by oxidation to CO of one or two >CH·OH of cholic acid is completed by the prep. of 12-*hydroxy*-3 : 7-*diketocholanic acid* (**I**), m.p. 165—166° (with apparent change in η at 175°). Et 3 : 12-dihydroxy-7-ketocholanate (**II**), m.p. 155—157° (improved prep.), and AcCl–C_5H_5N–C_6H_6 at 0° give *Et* 12-*hydroxy*-7-*keto*-3-*acetoxycholanate* (**III**), m.p. 147—148°, oxidised by CrO_3–aq. AcOH to Et 7 : 12-*diketo*-3-*acetoxycholanate*, m.p. 145—147°. (**III**) and ArCOCl in C_5H_5N at 20°, then at 100°, afford *Et* 7-*keto*-12-p-*nitrobenzoyloxy*-, m.p. 159—160°, and *Et* 7-*keto*-12-3′ : 5′-*dinitrobenzoyloxy*-3-*acetoxycholanate*, m.p. 171—172°, converted by boiling 10N-HCl–EtOH, followed by CrO_3–aq. AcOH, into *Et* 3 : 7-*diketo*-12-p-*nitrobenzoyloxy*- (**IV**), m.p. 160—161°, and -3′ : 5′-*dinitrobenzoyloxy-cholanate*, m.p. 203—204°, respectively. The latter could not be hydrolysed without formation of highly coloured products, but (**IV**) and boiling KOH–MeOH give an acid, esterified (EtOH–H_2SO_4) to *Et* 12-*hydroxy*-3 : 7-*diketocholanate*, m.p. 168—169°, which with boiling aq. HCl–$COMe_2$ gives (**I**), with CrO_3–AcOH yields Et dehydrocholate, m.p. 218—220°, and with N_2H_4,H_2O–NaOEt–EtOH at 195—210°, followed by CrO_3, affords 12-ketocholanic acid. (**II**) and BzCl–C_5H_5N–C_6H_6 at 16—18° give *Et* 12-*hydroxy*-7-*keto*-3-*benzoyloxycholanate*, m.p. 138—139°, oxidised to *Et* 7 : 12-*diketo*-3-*benzoyloxycholanate*, m.p. 167—168°, and converted by boiling aq. K_2CO_3–EtOH into (probably) 12-*hydroxy*-7-*keto*-3-*benzoyloxycholanic acid*, m.p. 250—251° (decomp.). Me triacetylcholate and boiling 10N-HCl–MeOH, followed by CrO_3–aq. AcOH, give *Me* 3-*keto*-7 : 12-*diacetoxycholanate*, m.p. 190—191°, convertible by N_2H_4,H_2O–NaOEt–EtOH at 200—210° into 7 : 12-dihydroxycholanic acid, m.p. 205°. A. T. P.

Sapogenin derivatives.—See B., 1944, III, 101.

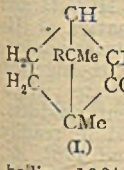
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Synthesis of safranic acid. G. Wendt (*Ber.*, 1941, **74**, [*B*], 1242—1251).—Safranal resists oxidation to the acid by air or $AgNO_3$–NaOH, and its oxime in warm Ac_2O gives a nitrile, b.p. 86°, which resists hydrolysis. *β-cyclo*Geranic acid (**I**) (prep. from *β-cyclo*citral by shaking in air), m.p. 93—94° (p-*$C_6H_4Br·CO·CH_2$* ester, m.p. 103—104°), is much more slowly hydrogenated (PtO_2; AcOH) than is its α-isomeride; similarly, the latter, but not (**I**), readily adds Br. With Br–CCl_4 in light or with C_5H_5N,H_2SO_4–Br, (**I**) gives the 3-*Br-acid* [3-*bromo*-2 : 6 : 6-*trimethyl-Δ^2-tetrahydrobenzoic acid*] (**II**) (65—70%), m.p. 97—98°, converted by boiling H_2O or NaOH–H_2O–MeOH into the 3-*OH-acid* (**III**) (80—90%), m.p. 184° [*Me* ester, b.p. ~100° (bath)/0·01 mm.] (Kuhn–Roth determination yields 1·2 AcOH) (cf. Tiemann, A., 1901, i, 158). With CrO_3 (≡5 O) in H_2SO_4–AcOH–H_2O at 20°, (**I**) gives $CO_2H·CMe_2·[CH_2]_2·CO_2H$, AcOH, and CO_2, but with CrO_3 (≡1 O) gives 3-keto-2 : 6 : 6-trimethyl-Δ^1-tetrahydrobenzoic acid, m.p. 192° [*semicarbazone* m.p. 240° (decomp.)] (cf. *loc. cit.*), which proves the structure of (**II**) and

(III). With H_2SO_4–HCO_2H, (III) gives a *CHO* derivative, m.p. 179° (decomp.). In C_5H_5N or collidine at 160°, (II) gives *safranic* [2 : 2 : 6-*trimethyl*-2 : 3-*dihydrobenzoic*] *acid* (IV), m.p. 63—64°, b.p. 85—90°/0·001 mm. (p-C_6H_4Br·*CO*·CH_2 ester, m.p. 102°). The structure of (IV) is proved by the resemblance of its absorption spectrum (max. at 291 mμ. in EtOH) to that of 2 : 3-dihydro-*o*-toluic acid (max. at 283 mμ.); the corresponding aldehydes show similarly max. at 323 and 317 mμ., respectively. In presence of Pt–SiO_2 in AcOH, (IV) absorbs 1 H_2 fast and a second mol. more slowly; partial hydrogenation yields (I). With HBr–$CHCl_3$, (III) gives 4-bromo-2 : 6 : 6-trimethyl-Δ^1-tetrahydrobenzoic acid, which is decarboxylated by warm H_2O. NaOH–KOH and a little H_2O at 210° convert (II) into a *dehydro*cyclo*geranic acid*, $C_{10}H_{14}O_2$, m.p. 130°, of unknown structure. (III) and (IV) have no termone action on cells of *Chlamydomonas eugametos* f. *synoica*. R. S. C.

Temisin. II. Y. Asahina and T. Ukita (*Ber.*, 1941, **74**, [*B*], 952—963; cf. A., 1940, II, 330).—Temisin (I) is shown to be the 2-*lactone* of α-2 : 6-dihydroxy-4-methyl-4-vinyl-3-*iso*propenyl*cyclo*hexylpropionic acid. Formation of 1 : 7-$C_{10}H_6$MeEt by Se at 270—280° (Nakamura *et al.*, A., 1933, 651; 1934, 1007) is confirmed by mixed m.p. determinations with the product from santonin. Na–*iso*-C_5H_{11}·OH reduces the lactone group of (I), yielding *temisol* [β-2 : 6-*dihydroxy*-4-*methyl*-4-*vinyl*-3-iso*propenyl*cyclo*hexyl*-n-*propyl alcohol*] (II), m.p. 126°, $[\alpha]_D^{16}$ +14·93° in EtOH, which with H_2–PtO_2 in AcOH gives *β-tetrahydrotemisol* [the 4-*ethyl*-3-iso*propyl* compound], m.p. 128—130°, $[\alpha]_D^{16}$ +24·61° in EtOH; this is isomeric at $C_{(3)}$ with α-tetrahydrotemisol, which may indicate presence of 4-CMe_2:. in place of 4-CH_2:CMe· in (II) or its formation by the alkali during the reduction (cf. below); the fact that two C:C survive Na–C_5H_{11}·OH proves that they are not conjugated. Temisone [the *lactone* of α-2-hydroxy-6-keto-4-methyl-4-vinyl-3-*iso*propenyl*cyclo*hexylpropionic acid] (III) with O_3 in $CHCl_3$ yields CH_2O (0·37 mol.) but no $COMe_2$, proving absence of CMe_2:. Hydrolysis of tetrahydrotemisone by warm 0·1N-NaOH gives the oily OH-acid, which is dehydrated by boiling Ac_2O–NaOAc to the *lactone* (IV), m.p. 145°, of the enol form of α-2-*keto*-4-*methyl*-4-*ethyl*-5-iso*propyl*cyclo*hexylidenepropionic acid* (V), m.p. 129—130°. (IV) is unaffected by $KMnO_4$ or Ac_2O–NaOAc, gives a colour with $C(NO_2)_4$ but not with Na nitroprusside, absorbs Br slowly in AcOH, absorbs 3 H_2 (PtO_2; AcOH; to give an oily deoxy-acid), and with hot NaOH–EtOH–H_2O gives (V) and mixed isomeric *cyclo*hexenylpropionic acids, sinter ~75°, m.p. 90°. (V) decolorises $KMnO_4$, does not react with $C(NO_2)_4$, NH_2·CO·NH·NH_2, *p*-NO_2·C_6H_4·NH·NH_2, H_2–PtO_2–AcOH, or NaOI, with boiling Ac_2O–NaOAc regenerates (IV), and with O_3 in cold $CHCl_3$ gives $AcCO_2H$ and *β-methyl-β-ethyl-β′-iso*propyl*adipic acid*, m.p. 134°, $[\alpha]_D^{20}$ +5·94° in EtOH, which proves the cyclic nature of one (*cyclo*hexane) ring. Similarly, (III) with 1 equiv. of 0·1N-NaOH at 100° gives a colourless, oily OH-acid, converted by boiling Ac_2O–NaOAc into the *lactone* (VI), m.p. 79°, $[\alpha]_D^{15}$ −74·83° in C_6H_6, of the enol form of α-2-*keto*-4-*methyl*-4-*vinyl*-5-iso*propenyl*cyclo*hexylidenepropionic acid* (VII), m.p. 162·5°; (VI) is also obtained directly from (III) by Ac_2O–NaOAc. H_2–PtO_2 reduces (VI) in AcOH to an oily acid, boiling NaOH–EtOH–H_2O converts it into (VII) and mixed isomeric cyclo*hexenylpropionic acids*, sinters ~110°, m.p. 125°. Hydrogenation (PtO_2) of (VII) in AcOH gives (V). An excess of NaOH in hot EtOH–H_2O converts (III), with isomerisation, into α-6-*keto*-4-*vinyl*-3-iso*propylidene*-Δ^1-cyclo*hexenylpropionic acid* (VIII), m.p. 108·5°, $[\alpha]_D^{16}$ +162·99° in EtOH [p-*nitrophenylhydrazone*, m.p. 126°; absorbs 3 H_2 (PtO_2; AcOH)], which with O_3 in $CHCl_3$ at 0° gives $COMe_2$, $EtCO_2H$, CO_2H·CHMe·CH_2·CO_2H, CH_2O (0·148 mol.), and presumably, 3 CO_2; these products and the isoprene rule confine the structure of (VIII) to three possibilities, of which one is excluded because formation of the C:C from a β-OH-acid excludes a C:C·C·CO grouping and a second is excluded because the absorption max. of (VIII) at 3180 A. (log ε 4·27) indicates a C:C·C:C·CO. These facts prove the structure of (I) etc. Since hydrolysis and subsequent esterification of (I) causes no re-lactonisation, the free OH and the CHMe·CO are in *trans*-relation. In hot NaOI–NaOH, (III) gives CHI_3 by prior transformation into (VIII) and hydrolysis thereof to $COMe_2$. R. S. C.

Formation of *d*-santenone from π-aldehydocamphor. Configuration of santenone and santenic acid. M. Ishidate and T. Sano (*Ber.*, 1941, **74**, [*B*], 1189—1194).—When *trans*-π-ketocamphor [(I), R = CHO] is kept in air, it rapidly yields, by autoxidation, *iso*ketopinic acid (II) [(I), R = CO_2H] and, by fission, HCO_2H and d-α-*santenone* (III) [(I), R = H], m.p. 56—59°, $[\alpha]_D^{22}$ +11·4° in EtOH [*semicarbazone*, m.p. 235—236° (decomp.)]. Fission also occurs when [(I), R = CHO] is kept in H_2O–N_2, the change being catalysed by O_2 or OH′ and prevented by H_2SO_4. (III) is an optically pure component of Aschan's *dl*-α-santenone (A., 1933, 1166). (II) is stable in boiling C_5H_5N + Cu-bronze and in boiling 10% KOH and is thus not an intermediate in the fission. With $KMnO_4$ in 1% KOH, (III) gives d-cis-α-*santenic acid* (IV), $[CH_2]_2$<CH(CO_2H)–CMe(CO_2H)>CHMe (CO_2H and Me on $C_{(7)}$ all *cis*), m.p. 151—152°, $[\alpha]_D^{23}$ +38·31° in EtOH, which with AcCl at room temp. gives the *anhydride*, m.p. 129—130°, reconverted into (IV) by hydrolysis. (IV) is better obtained by converting (III) by SeO_2 in boiling AcOH into its derived 1 : 2-diketone, *α-santenequinone*, m.p. 73—74°, b.p. 110—112°/12 mm., $[\alpha]_D^{16}$ −75·38° in EtOH, and oxidising this with H_2O_2–EtOH–Na_2CO_3. (IV) cannot be isomerised to the *trans*-acid by, *e.g.*, conc. HCl–AcOH at 190°. R. S. C.


(I.)

Examination of the sesquiterpene alcohol schairol, from *Ferula pyramidata* (Kar. *et* Kir.), Eug. Kov. (*syn. F. paniculata*, LDB). N. P. Kirialov (*J. Gen. Chem. Russ.*, 1943, **13**, 145—154).—Schairol (I), heated with 90% HCO_2H, yields a *hydrocarbon*, $C_{15}H_{24}$, an oil; with Se (7 hr. at 250—280°) it affords an azulene *hydrocarbon*, $C_{15}H_{18}$, b.p. 131—132°/2 mm. (*picrate*, m.p. 111—113°). (I) is oxidised ($KMnO_4$ in aq. $COMe_2$) to a *substance* (II), $C_{15}H_{24}O(OH)_2$, m.p. 221—222°, and a *substance*, $C_{15}H_{25}(OH)_3$, m.p. 102—103°, $[\alpha]_D$ +2·83° in aq. EtOH. (II), heated in a sealed tube with KOH–EtOH (8 hr. at 100°), affords a *substance*, $C_{15}H_{22}O$, b.p. 128—130°/5 mm., $[\alpha]_D$ +14·0° in aq. EtOH, from which a hydrocarbon, possibly cadalene, is obtained by treatment with Se. Hydrogenation of (I) in AcOH solution, using $PdCl_2$ or PtO_2 catalysts, was unsuccessful. The results support the view that (I) is an isomeride of guaiol. R. T.

Sapogenin.—See B., 1944, III, 101.

VI.—HETEROCYCLIC.

Polymerisation processes. IX. Dimeric methyl vinyl ketone. K. Alder, H. Offermanns, and E. Rüden. **X. Dimeric acraldehyde.** K. Alder and E. Rüden. **XI. General scheme of dimerisation of αβ-unsaturated aldehydes and ketones.** K. Alder, H. Offermanns, and E. Rüden (*Ber.*, 1941, **74**, [*B*], 905—920, 920—926, 926—929).—IX. The dimeride of CH_2:CH·COMe is shown to be 6-*acetyl*-2-*methyl*-Δ^2-*dihydropyran* (I). Its ethylenic linking is susceptible to numerous addition reactions. Heating CH_2:CH·COMe with 1% of quinol (to depress formation of higher polymers) at 145° (autoclave) for 22 hr. gives ~55% of (I) with a trimer and other polymers. (:CH·CO)$_2$O and (I) do not react at 200°. 1 H_2 is absorbed by (I) in MeOH in presence of Pd–$CaCO_3$, yielding 2-*acetyl*-6-*methyltetrahydropyran* (II), b.p. 64°/12 mm. (*semicarbazone*, m.p. 175°; p-*OMe*·C_6H_4·*CH*: derivative, m.p. 174—175°). MgPhBr (only 1 mol. consumed) and (II) in Et_2O, later at the b.p., give a carbinol, b.p. 150—170°/11 mm., dehydrated by $KHSO_4$ at 180—190° to 2-*α-phenylvinyl*- [? 2-*α-phenylethylidene*-]6-*methyltetrahydropyran*, b.p. 138—140°/12 mm. With aq. $KMnO_4$–CO_2 at room temp. and then CH_2N_2–Et_2O, (II) gives δ-*n*-hexolactone (proof of ring structure), identified by (i) conversion by NH_3–EtOH at 100° into δ-*hydroxy*-n-*hexoamide*, m.p. 74°, which is also obtained from the synthetic δ-lactone and depresses the m.p. (74°) of the isomeric γ-OH-amide, and (ii) oxidation by HNO_3 to glutaric (III) and succinic (IV) acids. $KMnO_4$–CO_2 and (I) yield (III), which proves the location of the C:C. HNO_3–H_2O [83 (*d* 1·4) : 23 c.c.] and (I) yield, after methylation, $Me_2C_2O_4$, (CH_2·CO_2Me)$_2$, OH·CHMe·CO_2Me (V), the *Me* ester, m.p. 45—46°, of the lactone of α-hydroxyglutaric acid [converted by 57% HI into (III); dihydrazide, m.p. 157—158°), and Me_2 fumarate [derived from (V)]. With NaOBr at 30°, (I) gives exothermally $CHBr_3$ and 2-methyltetrahydropyran-6-carboxylic acid (*Me* ester, b.p. 205—210°; *hydrazide*, m.p. 92—93°) (proof of COMe). 2% HCO_2H at room temp. converts (I) into *n*-octan-γ-ol-βη-dione, b.p. 147°/13 mm. [*disemicarbazone* (VI), m.p. 217°; *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 186°, also obtained by heating (I) with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 in EtOH], probably by way of 2-hydroxy-6-acetyl-2-methyltetrahydrofuran. With aq. NH_2·CO·NH·NH_2,HCl–NaOAc, first warm and then at 0°, (I) gives its *semicarbazone*, m.p. 176°, and, by addition prior to fission, (VI). EtOH or MeOH in AcOH adds exothermally to (I), yielding 2-ethoxy- [*semicarbazone*, m.p. 180°; regenerates (I) and EtOH when distilled at 12 mm.] and 2-methoxy-6-acetyl-2-methyltetrahydropyran (*semicarbazone*, m.p. 183°), respectively. H_2O_2 and (I) in AcOH give exothermally *di*-2-*methyl*-6-*acetyltetrahydro*-2-*pyranyl peroxide*, m.p. 124—125°. With N_2H_4,H_2O and then KOH, (II) gives 2-*methyl*-6-*ethyltetrahydropyran*, b.p. 34—35°/15 mm., and an isomeric, unsaturated alcohol, b.p. 81—82°/13 mm.

X. The dimeride of CH_2:CH·CHO is proved to be 6-*formyl*-Δ^2-*dihydropyran* (VII). It is obtained in 40—45% yield by heating at 170° with 1% of quinol, has b.p. 145—148°, gives a semicarbazone, m.p. 123—124°, and with aq. $KMnO_4$–CO_2 gives (IV) (~100%). H_2–PtO_2 reduces (VII) in MeOH to 2-*formyltetrahydropyran* (VIII), b.p. 156—159° (semicarbazone, m.p. 154°), which with $KMnO_4$–CO_2 and then HNO_3 gives (III) and (IV), and with MgPhBr–Et_2O gives a carbinol, b.p. 150—160°/11 mm., whence $KMnO_4$–CO_2 yields quantitatively (III), (IV), and BzOH. With N_2H_4,H_2O in MeOH at ~50° and then KOH, (VIII) gives 2-*methyltetrahydropyran*, b.p. 104—106° (and a substance, b.p. 160—165°), which is also obtained by dehydrating (by distillation) and then reducing (H_2–PtO_2; MeOH) OH·$[CH_2]_4$·COMe.

XI. The unidirectional 1 : 4 addition of C:C to C:C·C:O during dimerisation of CH_2:CH·COX (X = H or Me) is a general phenomenon. It is reported (without details) also for X = Ph, but in this case the cryst. dimeride can undergo further self-condensation.

Other cases are X = Et and dimerisation of quinonemethides to coumarin derivatives. R. S. C.

New heterocyclic compound with antihæmorrhagic (vitamin-*K*) activity. P. Meunier and C. Mentzer (*Compt. rend.*, 1942, **215**, 259—261).—*o*-OH·C_6H_4·CO_2Me is slowly converted by boiling $(EtCO)_2O$ into *Me o-propoxybenzoate*, b.p. 154°/14 mm., transformed by Na at 165—180° into 2 : 4-*dihydroxy*-3-*methylchroman* (I), m.p. 229—230° (decomp.), which could not be obtained by the action of $NaNH_2$ and MeI on benzotetronic acid. The physiological activity of (I) is ~0·1 of that of 2-methylnaphthaquinone and is in harmony with the hypothesis that the group ·CO·CH:CH_2 ⇌ :C:C(OH)·CH_2· is responsible for antihæmorrhagic activity. H. W.

Chromans.—See B., 1944, II, 101.

Natural chromones. II. Constitution of visnagin (from *Ammi visnaga*). E. Späth and W. Gruber (*Ber.*, 1941, **74**, [*B*], 1492—1500).—Mother-liquors from kellin (A., 1938, II, 111) yield 0·045% of *visnagin*, m.p. 144—145° (oxonium nitrate), which is shown to be 5-*methoxy*-2-*methylfurano*-3′ : 2′-6 : 7-*chromone*. With H_2O_2 in 5% NaOH at 20° it gives $H_2C_2O_4$ and furan-2 : 3-dicarboxylic acid (23%), and in boiling 1% NaOH is hydrolysed to AcOH and *visnagone* [5-*hydroxy*-4-*acetyl*-3-*methoxybenzfuran*] (I), m.p. 109—111° (brownish-green colour with $FeCl_3$), sol. in alkali, whence Ac_2O and NaOAc at 150—155° give 3-*acetylvisnagin*, m.p. 192—193°. In 1 : 1 NaOH–KOH at 205° (I) gives *s*-$C_6H_3(OAc)_3$. Et_2SO_4–20% aq. KOH converts (I) into its *Et ether*, m.p. 153—154°, reduced by Hg–Zn–aq. HCl to 3-*methoxy*-5-*ethoxy*-4-*ethylbenzfuran* (74%), m.p. 54—57°, which with O_3 in $CHCl_3$ at −5° gives 6 : 3 : 2 : 4 : 1-OH·C_6HEt(OMe)(OEt)·CHO (II) (58%), an oil [*p*-*nitrophenylhydrazone*, m.p. 218—220° (decomp.)]. With Et_2SO_4–10% KOH, (II) gives 6 : 4 : 3 : 2 : 1-$(OEt)_2C_6$HEt(OMe)·CHO (III), b.p. 124—126°/0·01 mm. (*semicarbazone*, m.p. 182—183°), whence $KMnO_4$–$COMe_2$–$MgSO_4$ at 50° yields 2-*methoxy*-4 : 6-*diethoxy*-3-*ethylbenzoic acid* (IV), m.p. 118—120° (decomp.; vac.). 2 : 4 : 6 : 1-$(OH)_3C_6H_2$·COMe and Zn–Hg–HCl–H_2O–EtOH give 2 : 4 : 6 : 1-C_6H_2Et$(OH)_3$ (76%), m.p. 123—125°, converted by HCN–HCl–Et_2O into 2 : 4 : 6-*trihydroxy*-3-*ethylbenzaldehyde* (78%), m.p. 174—176°. With EtI and K_2CO_3 in boiling $COMe_2$ this gives the 4 : 6-*Et₂ ether* (76%), m.p. 94—95° [*p*-nitrophenylhydrazone, m.p. 254—256° (decomp.; vac.)], whence Me_2SO_4–20% KOH at 70° yields (III) (*p*-*nitrophenylhydrazone, forms*, m.p. 180—182° and 169—171°), and thence (IV). R. S. C.

Synthesis of chroman derivatives having the ring-system of α-tocopherol. Synthesis of *iso*-α-tocopherol from (IV) ψ-cumene, (V) ψ-cumoquinol monomethyl ether. W. John and (IV) P. Günther, (V) F. H. Rathmann (*Ber.*, 1941, **74**, [*B*], 879—890, 890—898).—The synthesis of α-tocopherol analogues described in Part IV below uses accessible starting materials but requires ⩽3 mols. of Grignard reagent in the last stage; that described in Part V needs only 2 mols. of Grignard reagent, but the starting materials are less accessible.

IV. 2 : 4 : 5 : 1-$C_6H_2Me_3$·CHO [prep. by Gattermann synthesis from ψ-cumene (I) in 70% yield] (32 g.), b.p. 105—110°/0·5 mm., with $COMe_2$ and NaOEt in EtOH at, successively, 0°, room temp., and 35° gives α-2 : 4 : 5-*trimethylphenyl*-Δ^{α}-*buten*-γ-*one* (II) (24 g.), m.p. 51° [*semicarbazone*, m.p. 220° (decomp.)], and a small amount of αε-*di*-2 : 4 : 6-*trimethylphenyl*-$\Delta^{\alpha\delta}$-*pentadien*-γ-*one*, m.p. 165·5°; use of aq. NaOH leads to a difficultly separable 3 : 1 mixture of (II) and α-2 : 4 : 5-*trimethylphenyl*-n-*butan*-α-*ol*-γ-*one*, m.p. 92°. Hydrogenation (Pd-black; EtOH) of (II) gives mainly β-2 : 4 : 5-*trimethylphenylethyl Me ketone* (III), m.p. 55° (semicarbazone, m.p. 185—187°) (and ? isomerides), which with MgMeI gives δ-2 : 4 : 5-*trimethylphenyl*-β-*methyl*-n-*butan*-β-*ol*, m.p. 44° (*dinitrobenzoate*, m.p. 134°; could not be satisfactorily nitrated). Adding crude (III) in light petroleum to KNO_3–H_2SO_4 at −5° and then stirring at room temp. for a few min. gives β-3 : 6-*dinitro*-2 : 4 : 5-*trimethylphenylethyl Me ketone* (IV), m.p. 136·5°, and a very small amount of a *substance*, $C_{13}H_{16}O_6N_2$, m.p. 151°. With $SnCl_2$–conc. HCl–AcOH at ~80°, (IV) gives the diamine stannichloride, which by repeated treatment with CrO_3 in 2N-H_2SO_4 at, successively, 5°, room temp., and 30° yields ~40—45% of 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_3([CH_2]$_2$·COMe):O, m.p. 56°, whence the quinol (V), m.p. 125° (lit., 122°), is best obtained by Zn dust–H_2SO_4–MeOH–H_2O at room temp. CH_2O–HCl converts (I) at 70° into 2 : 4 : 5-*trimethylbenzyl chloride* (VI) (40—45%), b.p. 98—108°/1 mm., and a small amount of *di*(*chloromethyl*)-ψ-*cumene*, m.p. 99—101°. With CHAcNa·CO_2Et in C_6H_6 at room temp. and then the b.p., (VI) gives an oily ester, which by hydrolysis (10% KOH–MeOH at room temp.) and distillation affords crude (III), best purified at the $(NO_2)_2$-stage (IV). *n*-$C_{14}H_{29}$·MgCl (prep. from Mg activated by $C_{14}H_{29}$Br, I, and MeI) (3 mols.) and (V) in Et_2O–C_6H_6–N_2 yield a carbinol, cyclised by boiling 10% *p*-C_6H_4Me·SO_3H–AcOH and by Zn dust and then HBr in AcOH to "iso-α-*tocopherol*" [6-*hydroxy*-2 : 5 : 7 : 8-*tetramethyl*-2-n-*tetradecylchroman*] (VII), m.p. 64°, which is purified by way of its *allophanate*, m.p. 174—175° [absorption max. at 280 mμ. (ε 1740)]; this is separated from $C_{32}H_{66}$ by chromatography and from *cetylurethane*, m.p. 93°, and *cetyl allophanate*, m.p. 153°, by crystallisation. (VII) reduces $AgNO_3$–EtOH and in conc. HNO_3–EtOH gives a red colour. $C_{14}H_{29}$·MgBr yields more hydrocarbon.

V. 1 : 2 : 3 : 6 : 4-OH·C_6HMe$_3$·OMe (VIII), $Zn(CN)_2$, $AlCl_3$, and HCl in C_6H_6 at 0° and then 40° give only small amounts of 3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylbenzaldehyde*, m.p. 107—108°, and thence α-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenyl*-Δ^{α}-*buten*-γ-*one*, m.p. 104°, and β-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenylethyl Me ketone* (IX), m.p. 76°. 40% CH_2O and conc. HCl at room temp. convert (VIII) into 3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylbenzyl chloride* (~75%) (X), m.p. 128°; the corresponding 6-*OEt*-, m.p. 123—124°, 6-*OPr*-, m.p. 117—118°, and 6-*OBu*-compound, m.p. 83—85°, are similarly prepared. With CHAcNa·CO_2Et in C_6H_6, (X) gives *Et* 3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylbenzylacetoacetate* (not quite pure), m.p. 52—53°, and thence (0·5N-NaOH) the derived *acid*, m.p. 128° (decomp.), which at slightly >100° yields almost 50% (calc. on ψ-cumoquinol) of (IX), m.p. 81°. With MgMeI (2 mols.) in Et_2O–C_6H_6, (X) gives δ-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenyl*-β-*methyl*-n-*butan*-β-*ol*, m.p. 104—105°, converted by AgOAc into 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_3([CH_2]$_2$·CMe_2·OH):O, m.p. 55°, whence *p*-C_6H_4Me·SO_3Me–AcOH or Zn dust–HBr–AcOH yields 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman. With MgRBr in Et_2O–C_6H_6, (IX) similarly gives α-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenyl*-γ-*methyl*-n-*pentan*-γ-*ol*, m.p. 98·5—99·5°, -n-*heptan*-γ-*ol*, m.p. 88°, and -n-*pentadecan*-γ-*ol*, m.p. 69—71°. *n*-$C_{13}H_{29}$·MgCl yields an oily carbinol, converted by AgOAc and then HBr–AcOH into (VII), which is purified as above, giving an allophanate, m.p. 176° [absorption max. at 280 mμ. (ε 1740) and min. at 250 mμ. (ε 200)]. R. S. C.

Furo-coumarone group. II. 3 : 3′-Dimethyl-6′ : 7′-furo-coumarone. D. B. Limaye and V. V. Nagarkar (*Rasāyanam*, 1943, **1**, 255—257; cf. A., 1941, II, 374).—2 : 4 : 1 : 3-$C_6H_2Ac_2(OH)_2$ (Na H salt) with CH_2Br·CO_2Et gives *Me* 2 : 4-*diacetylresorcinol*-1-*carboxylate* (I), m.p. 168° (*Et*, m.p. 75°, and *Me* ester, m.p. 69°). (I) with NaOAc and Ac_2O gives 4-*acetoxy*-5-*acetyl*-3-*methylcoumarone*, m.p. 108°, which yields 4-*hydroxy*-5-*acetyl*-3-*methylcoumarone* (II), m.p. 70° (*semicarbazone*, m.p. 255°; *benzoate*, m.p. 118°; *Me ether*, m.p. 72)°. (II) (Na salt) with CH_2Br·CO_2Et gives, after hydrolysis, *Me* 5-*acetyl*-3-*methylcoumarone*-4-*carboxylate*, which with NaOAc and Ac_2O yields 3 : 3′-dimethyl-6′ : 7′-furo-coumarone, m.p. 27°. D. G.

Coumarin-γ-pyrone group. IV. 4 : 2′-Dimethyl-3′-acetyl-7 : 8-coumarin-γ-pyrone and 4 : 4′-dimethyl-7 : 8-coumarin-α-pyrone. D. B. Limaye and K. M. Kulkarni (*Rasāyanam*, 1943, **1**, 251—254).—8-Acetyl-4-methylumbelliferone (*acetate*, m.p. 191°) with Ac_2O and NaOAc gives 4 : 4′-*dimethyl*-1′ : 2′-*pyrono*-5′ : 6′-8 : 7-*coumarin*, m.p. 242°, and (main product) 5′-*acetyl*-4 : 6′-*dimethyl*-1′ : 4′-*pyrono*-5′ : 6′ : 8 : 7-*coumarin* (I), m.p. 265°. (I) with aq. NaOH gives 4-*methylumbelliferone*-8-*carboxylic acid* (II), m.p. 263° (decomp.). (II) is also obtained from γ-resorcylic acid (A., 1936, 854) with CH_2Ac·CO_2Et and H_2SO_4. (II) gives a 7-*OMe*-derivative (III), m.p. 246° (decomp.) [Me (IV), m.p. 189°, and Et ester, m.p. 163°]. (III) and (IV) on hydrolysis (NaOH aq.) yield 2-*hydroxy*-4-*methoxy*-3-*carboxy*-β-*methylcinnamic acid*, m.p. 194°, and (IV) with KOH in EtOH gives 2 : 4-*dimethoxy*-3-*carboxy*-β-*methylcinnamic acid*, m.p. 208° (decomp.). D. G.

Constitution of paraldol.—See A., 1944, II, 183.

Plant growth substances. XXXIV. β-Biotin.—See A., 1944, III, 487.

***iso*Thioindigotin.** P. Chovin (*Compt. rend.*, 1942, **215**, 419—420).—1-Hydroxythionaphthen (I) is converted by PhNO or *p*-NO·C_6H_4·NMe_2 into *leuco*iso*thioindigotin*, m.p. 260° (decomp.), which gives only a violet, non-cryst. resin when its oxidation to iso*thioindigotin* (II) is attempted. A similar resin is produced when (I) is treated with S_2Cl_2, $SOCl_2$, or $FeCl_3$. In EtOH at 0° (I) is transformed by SeO_2 into (II), m.p. 224° (decomp.), which is darker in colour than thioindigotin. H. W.

2 : 4-Diarylpyrroles. IV. Formation of acylated 5-amino-2 : 4-diphenylpyrroles from β-benzoyl-α-phenylpropionitrile and some notes on the Leuckart reaction. W. H. Davies and M. A. T. Rogers (*J.C.S.*, 1944, 126—131).—CH_2Bz·CHPh·CN (I) with HCO_2NH_4 gives 2 : 2′ : 4 : 4′-tetraphenylazadipyrromethine (II), but with HCO·NH_2 affords mainly a colourless compound, m.p. 172°, now shown to be a *formyl* derivative of 5-amino-2 : 4-diphenylpyrrole (III) (cf. Rogers, A., 1944, II, 80), which has been synthesised from the parent pyrrole and the mixed anhydride of HCO_2H and AcOH. The mechanism of this reaction and the formation of (II) from (I) and HCO_2NH_4 or HCO·NH_2 are discussed and inter-related. The mechanisms of the Leuckart reaction and of its Ott–Ingersoll modification are shown to involve different intermediates which may, in the case of certain ketones, result in different products. The following derivatives of (III) have been isolated in readily interconvertible isomeric forms: *formyl*, m.p. 172° and 176°, *Ac*, m.p. 171°, 176°, and 192°, *acetyl-formyl*, m.p. 134°, 139°, and 152°, Ac_2, m.p. 186—188°, and Ac_3, m.p. 111—112°. F. R. S.

Electronic resonance of 1-methyl-2-piperidone.—See A., 1944, I, 143.

Nicotinyl chloride. M. Lora Tamayo and A. Vargas (*Anal. Fis. Quim.*, 1942, **38**, 179—183).—Nicotinyl chloride hydrochloride (cf. Späth and Spitzer, A., 1926, 958) is converted by boiling C_5H_5N, or by prolonged exposure over $CaCl_2$ in vac., into the high-melting form of nicotinyl chloride (cf. Meyer, A., 1901, i, 407). The low-melting form of Meyer and Graf (A., 1928, 1379) was not isolated. F. R. G.

Synthesis of hydroxy-derivatives of 2-methylpyridine-3 : 5-dicarboxylic acid esters. E. Ochiai and Y. Ito (*Ber.*, 1941, **74**, [*B*], 1111—1114).—OEt·CH:C(CO_2Et)$_2$ (I) and NH_2·CMe:CH·CO_2Et at 100° (40 hr.) give *Et₂ hydroxy-2-methylpyridine-3 : 5-dicarboxylate*, m.p. 205°, converted by hot 5% KOH–MeOH into an *Et H* ester, m.p. 225°, and then into the *dicarboxylic acid*, m.p. 305°. Decarboxylation of the acid by Cu chromite in quinoline at 300—315° (bath) gives 6-hydroxy-2-methylpyridine, m.p. 158° (picrate, m.p. 149·5—150°), whence the orientation of the products follows. (I), CH_2Ac·CO_2Et, and HCl gas at room temp. give, with partial decarboxylation, *Et 4-hydroxy-2-methylpyridine-3-carboxylate*, m.p. 207°, converted by $POCl_3$ at 150° into *Et 4-chloro-2-methylpyridine-3-carboxylate*, m.p. 64°, which with Zn dust in dil. HCl at 100° gives Et 2-methylpyridine-3-carboxylate (*picrate*, m.p. 146—147°; hydrochloride, decomp. 225°). CHAcNa·CO_2Et, (I), and Na in hot C_6H_6 give *Et₂ 4-hydroxy-2-methylpyridine-3 : 5-dicarboxylate*, m.p. 156—157°, which with NH_3–EtOH (saturated at <0°) at 100° gives the derived *diamide*, decomp. 321°, and *Et 4-hydroxy-(?)5-carboxylamido-2-methylpyridine-(?)3-carboxylate*, m.p. 252°. R. S. C.

Salts of pyridine-2 : 6-dicarboxylic acid.—See B., 1944, III, 101.

Two new syntheses of quinoline from benzene and glycerol. L. Bert (*Compt. rend.*, 1942, **215**, 415—417).—C_6H_6 is condensed with CH_2Cl·CH:CHCl [obtained by dehydration of OH·CH(CH_2Cl)$_2$] directly (Friedel–Crafts) or indirectly through MgPhBr to CH_2Ph·CH:CHCl, which when added gradually to a deficiency of H_2SO_4–HNO_3 at −10° gives a mixture (I) of *o*- and *p*-NO_2·C_6H_4·CH:CH·CHCl. This when heated with an alcohol ROH (usually R = Me, Et, or Bu^a) and excess of KOH affords a mixture (II) of *o*- and *p*-NO_2·C_6H_4·CH:CH·CH_2·OR converted into *o*- (III) and *p*-NO_2·C_6H_4·CHO, separable from one another by distillation with steam or through their compounds with $NaHSO_3$. Alternatively (I) is nitrated by fuming HNO_3–Ac_2O mainly to (III), which is reduced ($FeSO_4$–NH_3) to *o*-$NH_2C_6H_4$·CHO and thence transformed into quinoline (IV) according to Friedländer. (I) is readily reduced (Fe + HCl) to the corresponding amines, which are easy to separate from one another. The *o*-compound is converted by excess of KOH and boiling ROH (R is any radical) into *o*-NH_2·C_6H_4·CH:CH·CH_2·OR, transformed by HCl under pressure into *o*-CH_2Cl·CH:CH·C_6H_4·NH_2,HCl. This with aq.-alcoholic $(CH_2)_6N_4$ passes into CHO·CH:CH·C_6H_4·NH_2,HCl, readily converted into (IV). Experimental details are not given. H. W.

Reaction product from hydrazine and 4-chloroquinaldine. E. Koenigs and J. Freund (*Ber.*, 1941, **74**, [*B*], 1085—1088).—$SnCl_2$ in conc. HCl at 100° reduces 3-nitro-4-amino- to 3 : 4-*diamino-2-methylquinoline*, m.p. 226—227° (*hydrochloride*, +H_2O, m.p. 317—318°; picrate, m.p. 227—228°), which with HNO_2 gives a triazole derivative (*hydrochloride*, m.p. 316°; picrate, darkens >220°, decomp. 252°). Passing HCl gas into 4-chloro-3-nitro-2-methylquinoline and $SnCl_2$ in AcOH gives exothermally 3-amino-2-methylquinoline, m.p. 160—161° (lit., 159—160°) (gives 3-chloro-2-methylquinoline by a diazo-reaction), and a small amount of 4-chloro-3-amino-2-methylquinoline (*hydrochloride*, m.p. 150° after sintering; picrate, darkens from 200°, decomp. ~220°), which is the sole product of reduction by Fe(OH)$_2$–aq. NH_3–MeOH at 90°. The structure of the product from N_2H_4 and 4-chloro-2-methylquinoline remains obscure (cf. A., 1935, 989). R. S. C.

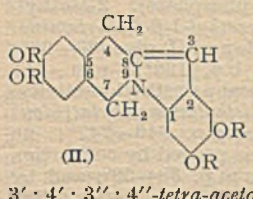
Heterocyclic ketones. II. Alkylation. E. I. Elkina and M. M. Schemjakin. **III. Chlorination by means of oxalyl chloride.** M. M. Schemjakin and E. I. Elkina (*J. Gen. Chem. Russ.*, 1943, **13**, 164—168, 169—174).—II. The K_2 salt of 6-hydroxynicotinic acid with Pr^{a}I in Pr^{a}OH (1 hr. at 180°) yields a mixture of N-*propyl-2-pyridone-5-carboxylic acid* (I), m.p. 141—142°, 6-n-*propoxynicotinic acid*, m.p. 116—117°, and the *Pr^a* ester of (I), b.p. 147—149°/4 mm.

III. *N*-Methyl-2-quinolone and (COCl)$_2$ in Et_2O yield 2 : 2-*dichloro-1-methyl-1 : 2-dihydroquinoline*, whilst with (I) the product is 2 : 2-*dichloro-1-propyl-1 : 2-dihydropyridine-5-carboxylic acid*; these Cl_2-derivatives rapidly decompose on exposure to the atm. 1-Hydroxy-7 : 8-dimethoxy-3-acetyl*iso*quinoline and (COCl)$_2$ in Et_2O give 1-*chloro-7 : 8-dimethoxy-3-acetyl*isoquinoline, m.p. 145—146°, whilst with PCl_5 the product is 1-*chloro-7 : 8-dimethoxy-3-α-chlorovinyl*isoquinoline, m.p. 116—117°. 2-Pyridone and (COCl)$_2$ yield a *substance*, $C_{10}H_{10}ON_2Cl_2$, m.p. 137—138°. R. T.

Syntheses by means of sodamide. O. Eisleb (*Ber.*, 1941, **74**, [*B*], 1433—1450).—*tert.* Halogenoalkyl-amines or -amides do not react with $NaNH_2$ or $NaNH_2$–NH_3 at 100°. $NaNH_2$ is thus a very effective reagent for introducing aminoalkyl groups into substances which contain H replaceable by Na. Further, use of NR([CH_2]$_2$·Cl)$_2$ and substances containing activated CH_2 leads to di-condensation with formation of 4-substituted piperidine derivatives. X([CH_2]$_2$·Cl)$_2$ (X = S or O) react similarly. The best technique is to add $NaNH_2$, ground in a warm, dry mortar, gradually to the reactants in PhMe, usually at 40—60°, raised later to ~100°; condensations below are thus effected, successive temp. being noted in parentheses. NEt_2·[CH_2]$_2$·Cl (I) and COPh·CH_2Ph give (45—50°, b.p.) *γ-diethylamino-α-phenyl-n-butyrophenone* (80%), b.p. 192—193°/4 mm., the hydrochloride, m.p. 148°, of which has spasmolytic activity. CH_2Ph·SO_2Ph and (I) give (50—55°, 90—95°) *Ph γ-diethylamino-α-phenyl-n-propyl sulphone*, m.p. 39—40°, b.p. 210°/3 mm. (hydrochloride, m.p. 139—140°, neutral in H_2O). CH_2Ph_2 and (I) give (b.p.) only 14% of *γγ-diphenyl-n-propyldiethylamine*, b.p. 170—175°/4 mm., the hydrochloride, m.p. 143—144°, of which has local anæsthetic and spasmolytic activity. Indene and (I) give (in C_6H_6; 40—50°, 80°) 3-*β-diethylaminoethylindene*, b.p. 140°/4 mm., the hydrochloride, m.p. 156—159°, of which has local anæsthetic activity. Fluorene and (I) give (60°; 100°) 9-*β-diethylaminoethylfluorene*, b.p. 192—210°/4 mm., the hydrochloride, m.p. 217—218°, of which is weakly acid in H_2O and has local anæsthetic activity. $NHPh_2$ and (I) give (60°, 90—100°) NN-*diphenyl-N'N'-diethylethylenediamine* (81%; <40% in absence of $NaNH_2$), b.p. 173—174°/4 mm., the monohydrochloride, m.p. 169—170°, and N'-methobromide, m.p. 173°, of which have local anæsthetic activity. Pyrrole and (I) give (in C_6H_6; 40—50°, 80°) 1-*β-diethylaminoethylpyrrole* (~66%), b.p. 223—225°/760 mm., 80°/4 mm. (hydrochloride, m.p. 113—114°, has no pharmacological action; ethylethosulphate, m.p. 131—132°). Pyrrole does not react with (I) in presence of NaOEt–EtOH, but tetraiodopyrrole at 30—35° and then 40° thus gives 2 : 3 : 4 : 5-tetraiodo-1-β-diethylaminoethylpyrrole, sinters 114°, m.p. 120° (decomp.) (hydrochloride; nitrate; phosphate). 2-Methylindole and (I) (in C_6H_6; 40—50°, 80°) give 2-*methyl-1-β-diethylaminoethylindole* (80%), b.p. 156°/4 mm. Carbazole and (I) give (85—90°; 100°) 9-*β-diethylaminoethylcarbazole* (94%), b.p. 196°/3 mm., the phosphate, m.p. 151—155°, of which has local anæsthetic activity. Acridone and (I) give (120—130°) 10-*β-diethylaminoethylacridone* (97%), m.p. 112—113° (hydrochloride, decomp. 246—247°; no oxime or hydrazone), the structure of which is proved by conversion by Na–EtOH into 10-β-diethylaminoethyl-, m.p. 58—59°, and by MgPhBr into 5-hydroxy-5-phenyl-10-β-diethylaminoethyl-acridan, m.p. 151—153° (and the derived acridinium chloride hydrochloride). CH_2Ph·CN and (I) give (in C_6H_6; <40°, 75—80°) *γ-diethylamino-α-phenyl-n-butyronitrile* (~60%), b.p. 132°/3 mm. *n*-C_6H_{13}·CHPh·CN and (I) give *α-phenyl-α-β'-diethylaminoethyl-n-octonitrile* (>75%), b.p. 180—185°/4 mm. CH_2Ph·CHPh·CN and 1-β-chloroethylpiperidine give (45—50°, 95—105°) *γ-piperidino-α-phenyl-α-benzyl-n-butyronitrile*, m.p. 93°, b.p. 203°/3 mm. (hydrochloride, m.p. 215°), and another base, b.p. 200—210°/3 mm. $MeSO_2$·NEt_2 and (I) give (80°, 100—105°) *γ-diethylaminopropanesulphondiethylamide*, b.p. 185°/20 mm. (hydrochloride, m.p. 120—121°). NR([CH_2]$_2$·Cl)$_2$,HCl are prepared from NR([CH_2]$_2$·OH)$_2$ by $SOCl_2$ and are stable, but the free bases are unstable and are prepared therefrom *in situ* just before use. CH_2Ph·CN and NMe([CH_2]$_2$·Cl)$_2$ (II), b.p. 71°/9 mm., give (30—40°, b.p.) 4-*phenyl-1-methylpiperidine-4-nitrile* (III) (66%), m.p. 53°, b.p. 148°/4·5 mm. (hydrochloride, m.p. 221—222°, sublimes at 6 mm.), hydrolysed by KOH–MeOH–H_2O at 160—170° to the 4-carboxylic acid (IV), +H_2O, m.p. 299° (decomp.) [neutral in H_2O; chloride hydrochloride, m.p. indefinite, >150° (decomp.)], which at 340° slowly gives 4-*phenyl-1-methylpiperidine*, b.p. 255—260°/760 mm., 130°/15 mm. (hydrochloride, m.p. 196—197°; picrate, decomp. 236—237°; picrolonate, m.p. 221°). Treating (III) with 80% (wt.) H_2SO_4 at 130—150° and then gradually adding EtOH at 103—108° (temp. in liquid) gives the *Et* ester (~95%), m.p. 30°, b.p. 155°/5 mm. (*hydrochloride*, m.p. 187—188°; picrate, m.p. 189—190°; H_2 citrate, decomp. >206°), of (IV). p-*Toluenesulphondi-β-hydroxyethylamide* {prep. from *p*-C_6H_4Me·SO_2Cl and NH([CH_2]$_2$·OH)$_2$ in 2N-Na_2CO_3 at 65—70° and then 95°}, m.p. 100—101°, with $SOCl_2$ at 90—95° and then 130° yields p-*toluenesulphondi-β-chloroethylamide*, m.p. 48—49°, which with CH_2Ph·CN gives (40—45°, b.p.) p-*toluenesulphon-4-phenylpiperidide-4'-nitrile* (37%), m.p. 200—201°, converted by 75% H_2SO_4 at 140—150° and then EtOH at 110° as above into *Et 4-phenylpiperidide-4-carboxylate* (~85%), m.p. 36—37°, b.p. 155°/3·5 mm. [hydrochloride (V), m.p. 133—134°; picrate, m.p. 157—158°]. CH_2Ph·N([CH_2]$_2$·Cl)$_2$, b.p. ~126—127°/1 mm. (hydrochloride, m.p. 149°), and CH_2Ph·CN give (35—50°, b.p.) 4-*phenyl-1-benzylpiperidine-4-nitrile*, m.p. 75—76° (hydrochloride, m.p. 259—260°), and thence (70% H_2SO_4) the 4-carboxylic acid, decomp. 288° (*Et* ester, m.p. 73—74°); the derived Et ester hydrochloride, decomp. 235—238°, with H_2–Pd-black in EtOH at 40—50° gives (V). O([CH_2]$_2$·Cl)$_2$ and CH_2Ph·CN give (40—50°, 100°) 4-*phenyltetrahydropyran-4-nitrile* (49%), m.p. 49—50°, b.p. 147—148°/5 mm., hydrolysed by 66% H_2SO_4 at 100° to the 4-carboxylamide, m.p. 216—218° (which has sedative action), and by hot KOH–MeOH to the 4-*carboxylic acid*, m.p. 129—130° [chloride, m.p. 53—54°, b.p. 140°/3 mm.; *β-diethylaminoethyl* ester, an oil (hydrochloride, m.p. 181°, spasmolytic)]. CH_2Ph·CN and S([CH_2]$_2$·Cl)$_2$ give (40—45°, b.p.) 4-*phenylpentamethylene sulphide-4-nitrile* (47%), m.p. 56—57°, b.p. 175°/6 mm., and thence by 80% H_2SO_4 at 72° the 4-carboxylamide (VI), m.p. 158—159°, and 4-*carboxylic acid* (better obtained by KOH–MeOH at 190—200°), m.p. 157—158° (1 : 1-dioxide, m.p. 215°); the 1 : 1-dioxide, m.p. 237—238°, of (VI) has sedative action. 1-Methyloxindole and (II) give (35—45°, b.p.) 1 : 1'-*dimethylpiperid-*

ine-4-spiro-3′-*oxindole* (51%), m.p. 104—106° (hydrochloride, m.p. 245—246°). Fluorene and (II) give (100—105°, 140°) 1-*methylpiperidine*-4-spiro-9′-*fluorene*, m.p. 113·5—114·5° (hydrochloride, m.p. 274—275°, has local anæsthetic action; phosphate, m.p. 244—246°). $MeSO_2{\cdot}NEt_2$ and (II) give (80°, 100—105°) 1-*methylpiperidine*-4-*sulphondiethylamide*, m.p. 32°, b.p. 138°/3 mm. (hydrochloride, m.p. 183—185°). $PhMeSO_2$ and (II) give (90—95°, 105—110°) 1-*methyl*-4-*piperidyl Ph sulphone*, m.p. 115°, b.p. 182—192°/3 mm. (hydrochloride, m.p. 228—229°). $CH_2Ph{\cdot}SO_2Ph$ and (II) give (45—50°, 95—100°) 4-*phenyl*-1-*methyl*-4-*piperidyl Ph sulphone*, m.p. 165° [hydrochloride, m.p. 251° (decomp.)]. Attempts to alkylate $CH_2Ph{\cdot}CO{\cdot}NR_2$ (R = Et or Ph) failed, as did attempts to prepare piperidine derivatives from $CH_2Ph{\cdot}COPh$ or CH_2Ph_2 by (II).
R. S. C.

Synthesis of nitrogenous hetero-rings. XXIV. Synthesis of dibenzindolizine derivatives. I. Synthesis of 4′ : 5′ : 4′′ : 5′′-tetramethoxy-3 : 4 : 7 : 8-tetrahydro-1 : 2 : 5 : 6-dibenzindolizine. S. Sugasawa and K. Kodama (*Ber.*, 1941, **74**, [*B*], 1237—1241).—6 : 7 : 3′ : 4′-Tetramethoxy-3-benzyl-3 : 4-dihydro*iso*quinoline methylmethosulphate and H_2–PtO_2 in EtOH give 6 : 7 : 3′ : 4′-*tetramethoxy*-3-*benzyl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 99°, converted by HI (*d* 1·7) at 150° into the corresponding $(OH)_4$-compound (*tetra-acetate*, m.p. 133—135°), the hydriodide of which with KOAc, then chloranil in EtOH, and finally HCl gives 3′ : 4′ : 3′′ : 4′′-tetrahydroxy-9-methyl-3 : 4 : 7 : 8-tetrahydroindolizinium chloride (I) (cf. Robinson *et al.*, A., 1932, 527). Me_2SO_4–33% KOH–H_2 and then KI converts (I) into the *Me₄ ether iodide*, decomp. 248—249°, which at 215—220° (the crude salt decomposes) gives 3 : 4′ : 3′′ : 4′′-*tetramethoxy*-3 : 4 : 7 : 8-*tetrahydro*-, m.p. 146—147° (decomp.), dehydrogenated by Pt-black and air in boiling EtOH to 3′ : 4′ : 3′′ : 4′′-*tetramethoxy*-4 : 7-*dihydro*-1 : 2 : 5 : 6-*dibenzindolizine* [(II) R = Me], m.p. 193—194° (purple-red Ehrlich reaction). With boiling Ac_2O and a few drops of C_5H_5N, (I) gives 3′ : 4′ : 3′′ : 4′′-*tetra-acetoxy*-4 : 7-*dihydro*-1 : 2 : 5 : 6-*dibenzindolizine* [(II) R = Ac], m.p. 198—200°, unaffected by air–Pt-black in EtOH.
R. S. C.



(II.)

***p*-Nitrophenylmethylpyrazolone.** T. Iseki, T. Sugiura, S. Yasunaga, and M. Nakasima (*Ber.*, 1941, **74**, [*B*], 1420—1424).—Picrolonic acid (I) and conc. HNO_3 (*d* 1·45) give 4 : 4-*dinitro*-1-p-*nitrophenyl*-3-*methyl*-5-*pyrazolone* (II) (almost 100%), m.p. 204°, which is unstable. In NaOH, (II) gives CO_2 and as.-*dinitroacetone*-p-*nitrophenylhydrazone*, m.p. 147°. In MeOH, (II) gives *nitropyrazole-blue* [*di*-(5-*keto*-1-p-*nitrophenyl*-3-*methyl*-4-*pyrazolidene*)] (III) (96%), decomp. 255°, which is also obtained from 1-*p*-nitrophenyl-3-methyl-5-pyrazolone by $NHPh{\cdot}NH_2$ and then $FeCl_3$. Heating (I) at 124—125° (10 min.) gives 4 : 4-*dihydroxy*-1-p-*nitrophenyl*-3-*methyl*-5-*pyrazolone* (IV), yellow, m.p. 185° [obtained as a by-product (1·7%) during the above prep. of (III)], with small amounts of (III) and an orange-red substance, m.p. 199—200°. With $NHPh{\cdot}NH_2$, (IV) in boiling AcOH gives 1-p-*nitrophenyl*-3-*methyl*-4 : 5-*diketopyrazoline*-4-*phenylhydrazone*, m.p. 242°, and, when repeatedly crystallised from MeOH, gives 4-*hydroxy*-5-*methoxy*-1-p-*nitrophenyl*-3-*methyl*-5-*pyrazolone*, m.p. 192—193° (red in alkali). (IV) gives a red colour in dil. NaOH and hydrolysis occurs yielding α*β*-*diketo*-n-*butyric acid*-*β*-p-*nitrophenylhydrazone* (90%), m.p. 175—176°. R. S. C.

Pyridyl and pyrazole acetamides.—See B., 1944, II, 101.

Action of nitric acid on ethyl *iso*dehydroacetate.—See A., 1944, II, 179.

***p*-Nitrobenz-*β*-4-iminazylethylamide.**—See B., 1944, III, 101.

Action of phosphorus pentasulphide on barbituric acids. H. C. Carrington (*J.C.S.*, 1944, 124—126).—When barbituric acids containing two hydrocarbon residues in the 5-position react with P_2S_5, one, two, or three of the O of the barbituric acid ring may be replaced by S according to the reaction conditions and the nature of the substituents (cf. Henze *et al.*, A., 1943, II, 339). 5 : 5-Diethylbarbituric acid, P_2S_5, and K_2S in xylene give 5 : 5-*diethyl*-2 : 4-*di*-, m.p. 205—206°, and -2 : 4 : 6-*tri*-*thiobarbituric acid* (I), m.p. 192—193°, also obtained from the -2-thio-acid. Aq. NH_3 and (I) afford 6-*imino*-5 : 5-*diethyl*-2 : 4-*dithiobarbituric acid*, decomp. at 230°, whilst (I) with Me_2SO_4–NaOH gives the 6-*methylthio-acid*, m.p. 130°. The following are also described: 5-*ethyl*-5-n-*propyl*-2 : 4-*di*-, m.p. 180°, and -2 : 4 : 6-*tri*-, m.p. 177°, -5-iso*propyl*-2 : 4-*di*-, m.p. 173°, 5 : 5-*di*-n-*propyl*-2 : 4-*di*-, m.p. 189°, and -2 : 4 : 6-*tri*-, m.p. 205—206°, 5-*ethyl*-5-n-*butyl*-2 : 4-*di*-, m.p. 127°, 5-*ethyl*-5-iso*butyl*-2 : 4-*di*-, m.p. 190°, and -2 : 4 : 6-*tri*-, m.p. 143°, 5-*ethyl*-5-*β*-*methylbutyl*-2 : 4-*di*-, m.p. 158°, 5 : 5-*di*-n-*butyl*-2 : 4-*di*-, m.p. 125°, and -2 : 4 : 6-*tri*-, m.p. 164°, 5-*phenyl*-5-*ethyl*-2 : 4-*di*-, m.p. 246°, and -2 : 4 : 6-*tri*-, m.p. 162—164°, and 5-*benzyl*-5-*ethyl*-2-*mono*-, m.p. 180°, and -2 : 4-*di*-*thiobarbituric acid*, m.p. 160°. F. R. S.

Thiobarbituric acids.—See B., 1944, III, 101.

Formation of pyrimidine rings. Z. Földi and A. Salamon (*Ber.*, 1941, **74**, [*B*], 1125—1128).—$NH_2{\cdot}CMe{:}N{\cdot}CH{:}C(CN){\cdot}CO_2Et$ (I) with HCl–EtOH at 0° gives the imino-ether and thence by hot NaOEt–EtOH Et 4-amino-2-methylpyrimidine-5-carboxylate (II), m.p. 122°, converted by aq. NH_3 (*d* 0·91) at room temp. into the derived amide, m.p. 260—261° (*hydrochloride*), and by 2·5% NaOH at 90° into the derived *acid*, m.p. 275° (*hydrazide*, m.p. 220°). If (I) is freed from traces of alkali by AcOH and then heated in boiling H_2O, (II) is formed, and the picrate, m.p. 170—175°, of (II) is obtained when the picrate, m.p. 140—144°, of (I) is melted. The effect of alkali on the direction of ring-closure is noted (cf. Todd *et al.*, A., 1937, 216). R. S. C.

Ethyl esters of 2-keto- and 2-thio-1 : 2 : 3 : 4-tetrahydro-5-pyrimidinecarboxylic acids. D. W. McKinstry and (Miss) E. H. Reading (*J. Franklin Inst.*, 1944, **237**, 203—205).—$CO(NH_2)_2$ (1 mol.), $CH_2Ac{\cdot}CO_2Et$ (1·5 mols.), and a substituted PhCHO (1 mol.) boiled in EtOH (modified Biginelli condensation) give Et 2-*keto*-4-*R*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylates*, R depending on the aryl substituent. R = 2-*chlorophenyl*, m.p. 214°, 5-*chloro*-2-*hydroxyphenyl*, m.p. 203°, 3 : 4-*diethoxyphenyl*, m.p. 165°, 4-*dimethylaminophenyl*, m.p. 231°, 4-*diethylaminophenyl*, m.p. 199°. With $CS(NH_2)_2$ the following *Et* 2-*thion*-4-*R*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylates* are obtained: R = 3 : 4-*dimethoxyphenyl*, m.p. 231°, 3 : 4-*diethoxyphenyl*, m.p. 125°, 4-*dimethylaminophenyl*, m.p. 197°, and 4-*diethylaminophenyl*, m.p. 200°.
D. G.

Pyrazine–water azeotrope.—See A., 1944, I, 150.

Reactions of *NN′*-diacetyltetrahydro-4 : 4′-dipyridyl. B. Emmert and A. Wolpert (*Ber.*, 1941, **74**, [*B*], 1015—1018).—Di-1-acetyl-1 : 4-dihydro-4-pyridyl (I) (modified prep.; cf. Dimroth *et al.*, A., 1922, i, 48) in Ac_2O–CO_2 at 100° gives C_5H_5N, 4-ethylpyridine (II), and a little di-4-pyridyl, but in boiling MeOH–CO_2 gives C_5H_5N, (II), and 4-acetylpyridine [oxime, m.p. 157·5—158° (lit., 142°)]. With NH_2OH in boiling MeOH–CO_2 (I) gives 1-*acetyl*-4-α-*oximinoethyl*-1 : 4-*dihydropyridine*, m.p. 121—122° (rapid heating), and some C_5H_5N. In presence of Pd-black in EtOH, (I) absorbs ~4 H_2 to yield *di*-1-*acetyl*-4-*piperidyl*, m.p. 174°. Reaction mechanisms are discussed. R. S. C.

Pyridylquinolines etc.—See B., 1944, II, 102.

Synthesis of dimethoxyquinazolones. V. M. Rodionov and A. M. Fedorova (*J. Gen. Chem. Russ.*, 1943, **13**, 249—252).—2-Amino-3 : 4-dimethoxybenzoic acid, heated with Ac_2O, yields 6-*keto*-3′ : 4′-*dimethoxy*-2-*methylbenzo*-2 : 1-4 : 5-*oxazine* (I), m.p. 165—168°, converted by recrystallising from AcOH into 2-*acetamido*-3 : 4-*dimethoxybenzoic acid*, m.p. 194—195°, and by aq. NH_3 into 7 : 8-*dimethoxy*-2-*methyl*-4-*quinazolone* (*hydrochloride*, m.p. 226—228°). 6-Amino-2 : 3-dimethoxybenzoic acid similarly yields 6-keto-3′ : 4′-dimethoxy-2-methylbenzo-1 : 2-4 : 5-oxazine, but this reacts differently with aq. NH_3, giving 2-acetamido-5 : 6-dimethoxybenzamide. *β*-Amino-ε-diethylaminopentane and (I) (2—3 hr. at 120—130°) afford 7 : 8-*dimethoxy*-2-*methyl*-3-(δ-*diethylamino*-α-*methylbutyl*)-4-*quinazolone* (*trihydrochloride*, m.p. 171—173°). R. T.

***iso*Oxindigo.** P. Chovin (*Compt. rend.*, 1942, **215**, 466—468).—Condensation of *o*-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ with *o*-$OH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ by PBr_3 gives an orange substance (I), converted by KOH–EtOH followed by HCl into a yellow *compound* (II), $C_{16}H_8O_3$, m.p. 305°. The constitution of the two isomerides cannot be elucidated by considerations of colour. (I) gives a difficultly purified ozonide (III), transformed by hydrolysis or pyrolysis into *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ and *o*-$OH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ or its lactone, whereas (II) affords a colourless *substance*, $C_{16}H_8O_6$, m.p. 269°, which behaves like (III) when pyrolysed. Improvement in the yield of (I) by the substitution of the lactones for the acids indicates for it the *iso*indigoid structure and this view is strengthened by the exclusive formation of (I) in 50% yield from 2-coumaranone. (II) is thus probably the dibenzonaphthyrone. H. W.

Action of oxidising agents on 5-keto-3-thion-6-benzyl-1 : 2 : 4-triazine. E. Cattelain (*Compt. rend.*, 1942, **215**, 257—259).—5-Keto-3-thion-6-benzyl-1 : 2 : 4-triazine (I) is converted by I in neutral solution into *di*-5-*keto*-6-*benzyl*-1 : 2 : 4-*triazinyl* 3 : 3′-*disulphide*, m.p. 173°, which does not reduce Nessler's reagent or Cu^{II} salts but is transformed into (I) by $(NH_4)_2S$ or $NaHSO_3$. It gives a green Cu^{II} (II) and a yellow Cu^{I} (III) salt, both insol. in H_2O. When freshly prepared it liberates I from KI in acid solution. In presence of phenolphthalein it can be titrated as a di-acid. It is converted by Na–Hg into α-*thiosemicarbazido*-*β*-*phenylpropionic acid*. With excess of I in alkaline solution (I) gives 3 : 5-*diketo*-6-*benzyl*-1 : 2 : 4-*triazine*. (I) is transformed by $CuSO_4$ according to the relative proportions into a mixture of the Cu compound of (I) and (III), a mixture of (II) and (III), or exclusively (III). H. W.

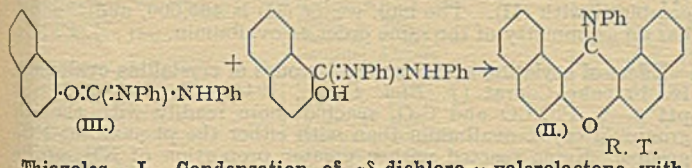
Invert soaps. VII. Tetrazolium salts. R. Kuhn and D. Jerchel [with, in parts, E. F. Möller, M. von Czernucki-Hrebeljanowitsch, and R. Brill] (*Ber.*, 1941, **74**, [*B*], 941—948).—$NHPh{\cdot}N{:}CH{\cdot}CO_2Et$, m.p. 133° (lit., 131°), is best obtained by exothermal interaction of $NHPh{\cdot}NH_2$ with $CO_2Et{\cdot}CH(OH){\cdot}OEt$. Formazans, $NR{:}N{\cdot}CR{:}N{\cdot}NHR''$, are obtained by treating $CHR{:}N{\cdot}NHR''$ with RN_2Cl and NaOAc in EtOH; they are tautomeric with $NR''{:}N{\cdot}CR{:}N{\cdot}NHR$ (cf. von Pechmann, A., 1894, i, 456; Busch

et al., A., 1931, 1156), since the pairs, R = Ph, R″ = p-NO_2·C_6H_4 or vice versa, and R = Ph, R″ = p-C_6H_4Br or vice versa (R′ = n-$C_{11}H_{23}$ in both cases), are identical when prepared from any possible set of components. Formazans are best (72—83%) oxidised to tetrazolium salts by $Pb(OAc)_4$. Thus are prepared: *C*-carbethoxy-*NN′*-diphenylformazan, m.p. 110° (lit., 114·5°); *NN′-diphenyl*-C-n-*hexyl*- (I), m.p. 76°, and -C-n-*undecyl*-, m.p. 61°, *-formazan*; N-*phenyl*-N′-p-*nitrophenyl*- (II), m.p. 108—109°, -N′-p-*bromophenyl*-, m.p. 53°, and -N′-α-*naphthyl*-, m.p. 60°, -C-n-*undecylformazan*; 2 : 3-*diphenyl*-5-*methyl*-, decomp. 271°, -5-n-*hexyl*- (III), decomp. 220°, and -5-n-*undecyl*- (IV), m.p. 141°, *-tetrazolium chloride*; 2 : 3 : 5-triphenyl-, decomp. 263° (lit., m.p. 243°), and 5-carboxy-2 : 3-diphenyl-, decomp. 198—200° (lit., 195—198°), -tetrazolium chloride; 2-*phenyl*-3-p-*bromophenyl*- (V), m.p. ~60°, and -3-α-*naphthyl*- (VI), a glass, -5-n-*undecyltetrazolium chloride*. M.p. are taken on a microscope stage. Absorption spectra (detailed) of (I) and (III) differ greatly. (II) gives a deep green $Cu^{II}_{0\cdot5}$ derivative, m.p. 131°, indicating that the tautomerism of formazans depends on chelation. The tetrazolium salts ppt. egg-albumin at pH > the isoelectric point. Drop nos. of 1% solutions are (III) 46·4 and (IV) 75·7. Bacteriostatic properties of (IV)—(VI) against lactic acid bacteria approx. equal those of n-$C_{12}H_{25}$·NMe_2Br·CH_2Ph; those against *Staph.*, paratyphus, *B. coli*, diphtheria and Friedländer bacilli are ≪ those of benztriazolium salts (A., 1942, II, 112).

R. S. C.

Identity of "euglenarhodone" with astacene.—See A., 1944, III, 444.

Internal rearrangements in the aromatic series. III. Arylation and alkylation of aryl substituted carbamides. G. I. Gerschzon (*J. Gen. Chem. Russ.*, 1943, **13**, 136—144).—β-$C_{10}H_7$·OH (I) with NHPh·CO·NPhEt or NHPh·CO_2Me at 240—250° for 4 hr. yields 2 : 3 : 5 : 6-di-2′ : 1′-naphtha-1 : 4-pyrone 4-anil (II). (I) and NHPh·CO·NH_2 (6 hr. at 245°) give 2-$C_{10}H_7$·NHPh, in 54% yield. $CO(NPhEt)_2$ does not react with (I), even at 300°. The process of formation of (II) is, on the basis of the above results, and of those of Dziewonski *et al.* (cf. A., 1933, 833), presented as: (I) + $CO(NHPh)_2$ → NHPh·C(O·$C_{10}H_7$):NPh (III). Part of (III) undergoes intramol. rearrangement to the anil of 1-phenylcarbamyl-2-naphthol, which condenses with (III) as follows:



R. T.

Thiazoles. I. Condensation of αδ-dichloro-γ-valerolactone with thioamides. H. Beyer (*Ber.*, 1941, **74**, [*B*], 1100—1104).—δ-Chloro-α-acetyl-γ-valerolactone (I) and SO_2Cl_2 (1 mol.) at 0° (exothermally) and then 100° give *αδ-dichloro-α-acetyl-γ-valerolactone* (I), b.p. 130—131°/0·3 mm., which in dil. HCl at 100° gives CH_2Cl·CH(OH)·CH_2·CHCl·COMe (II), which spontaneously yields mostly 4-*chloro*-5-*methyl*-2-*chloromethyl*-2 : 3-*dihydrofuran*. When (I) is heated with $CS(NH_2)_2$ in 4N-HCl at 100°, the intermediate (II) condenses to yield, with loss of HCl, 2-*amino*-4-*methyl*-5-*βγ-epoxy-n-propylthiazole*, sinters 145°, m.p. 150—152° (clear at 153°) (*picrate*, sinters 172°, m.p. 175—176°) (and some dihydrofuran derivative, b.p. 70—75°/0·1 mm.), which, when made acid to Congo-red by HCl in MeOH, yields 2-*amino*-4-*methyl*-5-*γ-chloro-β-hydroxy-n-propylthiazole*, m.p. 144—146° (*picrate*, sinters 185°, m.p. 190—192°). With MeCS·NH_2 or PhCS·NH_2, (I) in 4N-HCl at 100° similarly yields 2 : 4-dimethyl-5-*βγ*-epoxy-*n*-propylthiazole (*picrate*, m.p. 136—137°) and 2-phenyl-4-methyl-5-γ-chloro-β-hydroxy-*n*-propylthiazole (*hydrochloride*, m.p. 198—199° (decomp.)], respectively. R. S. C.

Benzthiazole. E. Ochiai and T. Nishizawa (*Ber.*, 1941, **74**, [*B*], 1407—1415).—Although cyclic S is generally equiv. to cyclic CH:CH, the reactivity of the C_6H_4 ring of benzthiazole differs from that of the C_6H_4 ring of quinoline. 6-Hydroxy-2-methylbenzthiazole (I) with CH_2:CH·CH_2Br and K_2CO_3 in boiling abs. EtOH gives the *allyl ether* (II) (85%), b.p. 130—140° (bath)/0·03 mm. (*picrate*, m.p. 152°), which at 240—250° (10 min.) gives a mixture (~20 : 1) of 6-*hydroxy*-2-*methyl*-7- (III), m.p. 133—135°, resolidifies, remelts 141° (*picrate*, m.p. 125—126°), and -5-*allylbenzthiazole* (IV), m.p. 188° (*picrate*, decomp. 216—219°), with 4% of unchanged (II). (III) and (IV) give allyl ethers, b.p. ~180° (bath)/0·1 mm. (*picrates*, m.p. 115—116° and 161—163°, respectively), converted at 235—250° into 6-*hydroxy*-2-*methyl*-5 : 7-*diallylbenzthiazole* (V), m.p. 148°, the allyl ether (*picrate*, m.p. 92°) of which is stable at 240°. PhN_2Cl does not couple with (I) in aq. AcOH but in NaOH gives the *PhN_2*-derivative (82%), m.p. 119°. p-NO_2·C_6H_4·N_2Cl (VI) and (I) in aq. AcOH or NaOH give the *p-NO_2·C_6H_4·N_2*-derivative (90—95%), m.p. 224—225°. PhN_2Cl does not couple with (III) in acid or alkali, but (VI) in alkali (not acid) gives a little 6-*hydroxy*-5-p-*nitrobenzeneazo*-2-*methyl*-7-*allylbenzthiazole*, m.p. 203°. (IV) couples with (VI) in acid or alkali giving 6-*hydroxy*-7-p-*nitrobenzeneazo*-2-*methyl*-5-*allylbenzthiazole*, m.p. 147°. (V) and (VI) do not react in acid or alkali.

R. S. C.

Constitution of the so-called carbothialdines and the preparation of some homologous compounds. A. D. Ainley, W. H. Davies, H. Gudgeon, J. C. Harland, and W. A. Sexton (*J.C.S.*, 1944, 147—152).—Consideration of methods of formation leads to structure $S<^{CHR'\cdot NH}_{CS\text{——}NR}>CHR'$ [(I), R = H, R′ = Me] for "carbothialdine" (or "thiuram carbomethyl") and to (I) (R = Me, R′ = H) for "dimethylformocarbothialdine" which is identical with "2 : 4-dimethyl-2-methylenecarbothialdine" Absorption spectra are in accord with the proposed formulæ and the names should be 2-thio-4 : 6- and -3 : 5-dimethyltetrahydro-1 : 3 : 5-thiadiazine, respectively. NH_3Ph, CS_2, and H_2O with aq. NH_2Me give 2-*thio*-3-*phenyl*-5-*methyltetrahydro*-1 : 3 : 5-*thiadiazine*, m.p. 148°. By treatment of the Ba salt of the aryldithiocarbamic acid with the sulphate of the aliphatic amine, followed by CH_2O, the following have been prepared: 2-*thio*-3-α-*naphthyl*-, m.p. 159—160°, -3-(p-*chlorophenyl*)-, m.p. 139—140°, -3-(p-*anisyl*)-, m.p. 160—161°, -3-(p-*hydroxyphenyl*)-, m.p. 163—164°, 3-(3′-*chloro*-4′-*hydroxyphenyl*)-, m.p. 146°, and -3-(p-*dimethylaminophenyl*)-5-*methyltetrahydro*-, m.p. 168—169°; and 2-*thio*-3-*phenyl*-5-(β-*diethylamino*)-, m.p. 103—104° (with some *OH·CH_2* derivative of 2-anilino-4 : 5-dihydrothiazole, m.p. 165°), and -5-(β-*hydroxyethyl*)-*tetrahydro*-1 : 3 : 5-*thiadiazine*, m.p. 136°; and p-*diethylaminophenylammonium* p-*diethylaminophenyldithiocarbamate*, m.p. 97—99°. F. R. S.

VII.—ALKALOIDS.

Hydrazides of dihydro-lysergic and -*iso*lysergic acids.—See B., 1944, III, 102.

Chemical study of *Fritillaria raddeana*, RGL. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 159—163).—The dry bulbs contain carbohydrates 60·5 (monosaccharides 2·4, disaccharides 6·2, starch 41·3, cellulose 7·8, and hemicellulose 2·8%), resins 4, and an alkaloid *raddeanine* (I), $C_{21}H_{35}O_2N$, m.p. 255—257°, 0·7%. The carbohydrates may be utilised as fodder, or as a nutrient medium for yeast. The *perchlorate*, m.p. 204—205°, *hydrochloride*, m.p. 167—168°, *aurochloride*, m.p. 130—132°, *methiodide*, m.p. 248—250°, and *Bz* derivative, m.p. 235—236°, of (I) are described. (I) is not affected by treatment with KOH–EtOH (5 hr. at the b.p.).

R. T.

Aconite alkaloids. XIII. Isolation of pimanthrene from dehydrogenation products of staphisine. XIV. Oxidation of the hydrocarbon from dehydrogenation of atisine. L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1944, **152**, 645—650, 651—657; cf. A., 1943, II, 210).—XIII. Commercial abietic acid (probably contains some *d*-pimaric acid) is dehydrogenated by Se at 340° (in N_2) for 2 hr. to give, after chromatographic separation, retene and some pimanthrene, m.p. 84—85° (picrate, m.p. 131—133°), identical with the product, m.p. 78—81°, obtained by dehydrogenating staphisine (I) (cf. A., 1942, II, 40). The main hydrocarbon, $C_{19}H_{20}$, from (I) is probably a methylretene with the second Me in position 2, 3, or 4. It is oxidised by CrO_3–AcOH at 100° (bath) to a quinone, m.p. 213—216°, further oxidised by $KMnO_4$ to (probably) a *hydroxy-iso*propylphthalic *acid* (II), $C_{11}H_{12}O_5$, melts with effervescence at ~170°, resolidifies and melts at ~290—294°. (II) is not found in the $KMnO_4$ oxidation products of retenequinone, but in addition to hydroxy*iso*propyldiphenyltricarboxylic acid, m.p. ~186—192° (cf. Ruzicka *et al.*, A., 1931, 360), a new acid, $C_{10}H_6O_7$, probably a dicarboxyphenylglyoxylic acid, is isolated as the *Me_3* ester (III), m.p. 149—151°.

XIV. The hydrocarbon, $C_{17}H_{16}$ (probably 1 : 6- or 6 : 1-methylethylphenanthrene), obtained by dehydrogenating atisine is oxidised by CrO_3–AcOH at 100° (bath) for 7 hr. and then at 0° for 24 hr. to a *quinone*, $C_{17}H_{14}O_2$, m.p. 149—151°, further oxidised ($KMnO_4$) to a *diphenyltetracarboxylic acid* (IV), m.p. 340—345°, with decomp. and sublimation and probable anhydride formation (*Me_2* ester, m.p. 149—150°, hydrolysed by aq. NaOH–MeOH to a *Me* ester, m.p. 338—341°). Attempts to oxidise (IV) by fuming HNO_3 and a little $Mn(NO_3)_2$ at 100° (bath) afford only a *monoanhydride*, m.p. 338—340°, of (IV). After separation of (IV) in the above oxidation, the mother-liquors are esterified (CH_2N_2 in $COMe_2$) to yield the Me_3 ester, m.p. 93—98°, of (?) hemimellitic acid, and (after hydrolysis with aq. HCl at 110° in a sealed tube) (?) trimellitic acid, m.p. 220—227°. In addition to the above Et_2O-extracted acid oxidation products, an acid is obtained which yields a Me_3 ester, m.p. 148—149°, identical with (III). A. T. P.

Veratrine alkaloids. XXI. Conversion of rubijervine into *allo*-rubijervine. The sterol ring systems of rubijervine. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1944, **152**, 641—643; cf. A., 1943, II, 246, 313).—Rubijervine (I), like solanidine, possesses the regular steroidal skeleton, with a six-membered ring B. (I) and Cu (in CO_2) at 150—200° for 15 min., then 200—290° for 15 min., at 1 atm., then 290°/0·1 mm. for 1 hr., yield *rubijervone* (II), m.p. 202—204° (slight previous sintering). Its *oxime* melts largely at 160°, resolidifies, and remelts at ~247—254° (depends on rate of heating). (II) and $Al(OPr^{\beta})_3$ yield a product, $C_{27}H_{43}O_2N$, softens to a melt at 218—220°, isomeric with (I) and probably containing *allo-* + *epi-*

allo-rubijervine. This transformation is analogous to that of cholestenone and *allo*cholesterol; the original suggestion that $C_{(5)}$ in (I) carries an ang. Me is improbable. A. T. P.

Comparative study of *Boerhaavia diffusa*, Linn., and the white- and red-flowered varieties of *Trianthema portulacastrum*, Linn. R. N. Chopra, N. R. Chatterjee, and S. Ghosh (*Indian J. Med. Res.*, 1940, **28**, 475—480).—Extraction with EtOH of the three plants used as the drug "Punarnava," yielded KNO_3: *B. diffusa* 0·36%, *T. portulacastrum* (white) 1·7%, *T. portulacastrum* (red) 2·6%. Extraction of the NH_3-alkaline mother-liquors with $CHCl_3$ and pptn. with Et_2O yielded a crude alkaloid, punarnavine, m.p. ~175° (decomp.) (*picrate*, m.p. 118—120°; *chloroplatinate*, m.p. 121—122° (cf. A., 1936, 652). The yield (on dry wt.) of drug was 0·04, 0·02, and 0·05%, respectively. S. E. M.

Alkaloids in *Adenocarpus intermedius*. I. Rivas (*Anal. Fís. Quím.*, 1942, **38**, 197—198).—The leaves contain 1·28% of alkaloids (cf. Santos Ruiz and Albiñana, B., 1942, III, 275). F. R. G.

Alkaloids of the seeds of *Delphinium consolida*, L.—See A., 1944, III, 516.

VIII.—ORGANO-METALLIC COMPOUNDS.

Organo-metallic compounds. I. Silver methyl, ethyl, and *n*-propyl. G. Semerano and L. Riccoboni (*Ber.*, 1941, **74**, [*B*], 1089—1099).—$PbMe_4$ and $AgNO_3$ in EtOH at −80° give AgMe or, if an excess of $AgNO_3$ is used, the compound, $AgMe,AgNO_3$. This is stable at −50°, but decomposes rapidly at −35°, giving Ag and C_2H_6 with traces of CO_2 and CO. $PbEt_4$ and $AgNO_3$ at −80° give a ppt. (AgEt) which decomposes when warmed to give Ag, C_2H_6 53, C_2H_4 10, and C_4H_8 37% with traces of CO. $PbPr^a_4$ and $AgNO_3$ in EtOH at −80° give a similar ppt. ($AgPr^a$), which is less stable, decomp. at ~−60° to give Ag (1 atom) and <1 mol. of (C_3H_8 + C_3H_6) with, presumably, C_6H_{14}. Clearly the decomp. is $AgR \rightarrow Ag + R\cdot$, followed by dimerisation and disproportionation of R· (except for R = Me) and small amounts of reduction by R·. The initial reaction is: $Ag^+ + PbR_4 \rightarrow AgR + PbR_3^+$. AgAlk are not explosive but are thermally less stable than AgAryl. R. S. C.

Mode of reaction of halogenated hydrocarbons with lithium phenyl [(VI)] and mechanism of the Wurtz–Fittig synthesis. G. Wittig and H. Witt (*Ber.*, 1941, **74**, [*B*], 1474—1491).—Exchange of Li and halogen occurs when sufficient electro-negative groups are present, the Li going to the more anionic component. In the series, *o*-OMe·C_6H_4·Hal, reactivity is I > Br > Cl, F. With aryl-alkyl chlorides exchange occurs only if $CHCl_3$ is absent (cf. below). CH_2PhBr (2 mols.) and LiPh (1 mol.) give $(CH_2Ph)_2$ and PhBr in almost 100% yield; $CHPh_2Br$ (1) and LiPh (1 mol.) give PhBr and $(CHPh_2)_2$ (90%); CPh_2Br_2 (2 mols.) and LiPh (1 mol.) give, by way of Li·CPh_2Br, PhBr (~100%), C_2Ph_4, and tar. CH_2Br_2 (1) and LiPh (1 mol.) give ~25% of PhBr and, by way of CH_2PhBr + LiBr, mainly CH_2PhBr and $(CH_2Ph)_2$. Interaction of $CHBr_3$ or CBr_4 is still more complex, but gives ~40% of PhBr. CCl_4 similarly gives PhCl and an inseparable mixture. $CPhCl_3$ gives very rapidly PhCl (30%) and a tar. CPh_2Cl_2 (1) and LiPh (1 mol.) give more slowly PhCl (30%) and C_2Ph_4. CPh_3Cl (1) and LiPh (1 mol.) give $(CPh_3\cdot O)_2$ and CPh_4, but no PhCl. $CHPh_2Cl$ (1) and LiPh (1 mol.) give $(CHPh_2)_2$ (30%). Exchange of H for Li depends on the "acidifying" nature of the substituent (F > Cl > Br > I > OMe > Ph). Thus, CH_2PhCl (1) and LiPh (1 mol.) give $CHPh_2\cdot CH_2Ph$ (I) (52%) by way of Li·CHPhCl and Li·$CHPh_2$; CH_2Ph_2 does not react with LiPh and is thus not an intermediate. *Benzyl fluoride* (prep. from $CHPhN_2$ by HF–Et_2O; 18% yield), b.p. 60—61°/55 mm., gives CH_2Ph_2 (24%), (I) (27%), and other products. $CHPhCl_2$ reacts rapidly to give a tar, not containing PhCl. Loss of HCl can also occur with unreactive halides, but the factors governing this reaction are not yet clear. CHPh:CHBr (1 mol.) and LiPh (2 mols.) give CHPh:CHLi, whence $COPh_2$ gives OH·CPh_2·C:CPh (II) (54%). CHPh:CHCl (1 mol.) with LiPh (2 mols.) gives, after hydrolysis, CPh:CH (70%) and PhCl, but with 1 mol. of LiPh and then $COPh_2$ gives (II) (32%) and CPh_3·OH (also formed by initial reaction at −30°). Bu^yI and LiPh at 100° (no reaction at room temp.) give CMe_2:CH_2 (60%). Bu^yCl also does not react at room temp. *cyclo*-Hexyl iodide at 100° gives 71% of *cyclo*hexene, but the fluoride is unaffected by LiPh. The "side-reactions" thus revealed for organo-metallic compounds suffice to allow full interpretation of the Wurtz–Fittig reaction on the basis of formation of NaR. R. S. C.

IX.—PROTEINS.

Formula for agar. V. C. Barry and T. Dillon (*Chem. and Ind.*, 1944, 167).—*Gelidium latifolium* is bleached in sunlight, boiled for several hr. with distilled H_2O (which does not become acid), and filtered. The filtrate sets to a stiff jelly which after being twice frozen and thawed gives an agar (I) with 2·59% of ash and S 0·364%. This does not yield glyoxal when left in contact with HIO_4 for 6 months. Since the *l*-galactose (II) units are linked in the chain through $C_{(4)}$ each of them would, if they were ordinary (I) units, contain a pair of adjacent CH·OH groups. The absence of such groups, proved by the stability of (I) to HIO_4, shows that the 3 : 6-anhydro-*l*-galactose isolated from (I) as its 2 : 6-Me_2 derivative (Jones *et al.*, A., 1942, II, 219) is not an artefact produced during methylation but a constituent of (I). Secondly, ≯1% of S (if any) can be present in the mol. of (I) as SO_4 groups attached to $C_{(6)}$ of the (II) units. Thirdly, the mol. of (I) cannot contain as much as one non-reducing end group for every 140 galactose units. This result agrees with the absence of detectable quantities of tetramethylgalactose in the product of hydrolysis of methylated (I) (Percival *et al.*, A., 1943, II, 56). H. W.

Complex affinity of heavy metals for proteins. II. Effect of acidity on flocculation of proteins by silver salts. Binding of silver by proteins and organic nitrogen compounds. W. Haarmann and E. Frühauf-Heilmann (*Biochem. Z.*, 1941, **309**, 13—31).—Proteins differ very greatly in the extent to which they are pptd. from unbuffered solutions by $AgNO_3$, gelatin not being pptd. even by high concns. There are also great variations in the optimum pH for pptn., the val. for serum-albumin, ψ-globulin, and hæmoglobin being 7·5 and that for ovalbumin, casein, and euglobulin 5·0. With gelatin, capability for flocculation increases as pH increases. The Ag-binding power of proteins and NH_2-acids (*e.g.*, alanine, glycine, tyrosine) increases with increase in alkalinity, 2—3 times as much being bound at pH 10 as at pH 7. K_2CrO_4 serves as indicator of the extent of formation of complex Ag–protein and –NH_2-acid compounds. The extent varies greatly with the N compound used. W. McC.

Ferritin and *apo*ferritin in the ultracentrifuge. A. Rothen (*J. Biol. Chem.*, **152**, 1944, 679—693).—Results from the ultracentrifuging of ferritin (I) solution showed that ferritin is a mixture of a colourless, homogeneous protein and a coloured, heterogeneous material. The former proved to be identical with *apo*ferritin (II), a protein already isolated from (I) by removing the Fe. The latter appeared to be a complex of $Fe(OH)_3$ micelles of various sizes combined with (II). The mol. wt. of (II) is 465,000, and the mol. has an asymmetry of the same order as ovalbumin. J. F. M.

Effect of acylating agents on thiol groups of crystalline ovalbumin. H. Fraenkel-Conrat (*J. Biol. Chem.*, 1944, **152**, 385—389).—At pH 5—6, PhNCO and C_3O_2 reacted more readily with the ·SH groups of cryst. ovalbumin than with either the phenolic or NH_2-groups. Keten reacted with a greater proportion of NH_2-groups than of ·SH groups of the native protein. Esters formed by any of the reagents were hydrolysed by alkali at room temp.; reversible acylation of ·SH groups was demonstrated also with cysteine and glutathione. G. D.

Partial hydrolysis products from the action of proteolytic enzymes on casein.—See A., 1944, III, 500.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin. XLVI. Action of glycol chlorohydrin on pine lignin. K. Freudenberg and L. Acker (*Ber.*, 1941, **74**, [*B*], 1400—1406).—Heating pine-wood with Cl·$[CH_2]_2$·OH (I) gives an alkali-sol. lignin (II) with 3% of OH·$[CH_2]_2$·O·$[CH_2]_2$·Cl, *methylene di-β-chloroethyl ether*, b.p. 93—94°/11 mm. [also obtained by heating (I), $(CH_2O)_x$, HCl, and $CaCl_2$], and traces of PhOH and a β-chloroethyl-hexoside [? -glucoside] (*tetra-acetate*, m.p. 105°, $[\alpha]_D^{20}$ +46° in $CHCl_3$). (II) contains ~14% of hexosan and 6% of Cl, due to retained (I); when allowance is made for this, the analysis shows loss of C, undoubtedly connected with a much decreased yield (0·5—1%) of CH_2O obtained by the action of conc. acid. This loss of CH_2O is held to come from CH_2O_2: groups, although various model substances are not thus affected by heating in (I). *Methylene dibenzyl ether*, b.p. 179—182°/11 mm., is described. R. S. C.

Isolation of gliotoxin and fumigacin from culture filtrates of *Aspergillus fumigatus*. A. E. O. Menzel, O. Wintersteiner, and J. C. Hoogerheide (*J. Biol. Chem.*, 1944, **152**, 419—429).—The fumigacin of Waksman *et al.* (cf. A., 1943, III, 770) is a mixture of fumigacin and gliotoxin; the latter contributes most of the antibiotic activity. Fumigacin is identical with helvolic acid, isolated from *A. fumigatus* culture medium by Chain *et al.* (cf. A., 1943, III, 917). The prep. of *fumigacin Me ester*, $C_{30}H_{40-42}O_7$, m.p. 260—261° (*oxime*, m.p. 204—206°; *semicarbazone*, m.p. 225—228°), is described. R. L. E.

Toxic principle of poison ivy and other related plants. D. Wasserman and C. R. Dawson (*J. Chem. Educ.*, 1943, **20**, 448–453).—A review. L. S. T.

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