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MARCH, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

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A II—Organic Chemistry.

MARCH, 1944.

I.—ALIPHATIC.

Catalytic isomerisation of saturated hydrocarbons.—See B., 1944, II, 2.

Production of branched-chain alkanes.—See B., 1944, II, 30, 31.

Production of *iso*octane.—See B., 1944, II, 2.

Reaction of unsaturated molecules with sodium platinichloride. A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 761—764).—Na_2PtCl_6 is reduced by CO, butadiene, or C_2H_4, to Na_2PtCl_4. Removal of the excess of Na_2PtCl_6 and then treatment with C_5H_5N gives the *compounds*, $C_5H_5N,H[PtCl_3{\cdot}CO]$, $[PtCl_2(C_4H_6)(C_5H_5N)]$, and $[PtCl_2(C_2H_4)(C_5H_5N)]$, respectively. Little, if any, reaction occurs with NO. R. S. C.

γδ-Diethyl-Δ$^{\gamma}$-hexene and γδ-diethylhexane. Preparation and properties. H. Koch and F. Hilberath (*Ber.*, 1940, **73**, [*B*], 1171—1173).—$CEt_2(CO_2Et)_2$ passes in presence of Na and EtOH under H_2 at 250°/70 atm. into $CHEt_2{\cdot}CO_2Et$, converted by MgEtBr into γδ-diethylhexan-γ-ol. This is dehydrated by $H_2C_2O_4$ at 110° to a mixture of much *γδ-diethyl-Δ$^{\gamma}$-hexene* (**I**) and little -Δ$^{\beta}$-hexene which are readily separated from one another by fractional distillation. (**I**) has b.p. 158·10°/758·0 mm., 157·85°/754 mm., and 158·2° (corr.)/760 mm. Oxidation with $KMnO_4$ or $Pb(OAc)_4$ affects the side-chains exclusively and ozonisation followed by catalytic hydrogenation takes an abnormal course, probably by reason of the inertia of the double linking and the unusual readiness of substitution. For this reason correct I vals. are obtained only by the I–CNS method. The results with ICl (Wijs) or NaBr–Br solution are 25% and 110% high whereas those with ICl in MeOH saturated with $CaCl_2$ are very low. (**I**) is not hydrogenated in abs. EtOH containing PtO_2 at atm. pressure but passes smoothly in presence of Pd–C into *γδ-diethylhexane*, b.p. 160·7°/760 mm.; this gives an uninvestigated cryst. product when irradiated in presence of Br. H. W.

Hydration of olefines.—See B., 1944, II, 3.

Hydroxylation of unsaturated halides.—See B., 1944, II, 3.

Recent developments in nitroparaffins.—See B., 1944, II, 29.

Purification of pentaerythritol.—See B., 1944, II, 31.

Phosphates. III. Phosphatase models. M. Lora Tamayo and F. Segovia (*Anal. fís. quím.*, 1943, **39**, 382—395).—$Mg^{\cdot\cdot}$ accelerates the trans-esterification of Na β-glycerophosphate by MeOH, and the catalysis by $CH_2Bz{\cdot}OH$ of the hydrolysis of Et phenylphosphate (**I**). Hydrolysis of (**I**) is slightly catalysed by $OH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ but Mg is without effect. F. R. G.

Long-chain acids containing a quaternary carbon atom. II. N. Polgar and (Sir) R. Robinson (*J.C.S.*, 1944, 615—619).—*α-Ethyl-α-decyltetradecoic acid* (**I**) has been synthesised by the method of Hudson *et al.* (A., 1942, II, 130) and found to differ from phthioic acid (**II**) (cf. Stenhagen *et al.*, A., 1941, II, 331). It appears probable that the chain in (**II**) must be longer than thought possible heretofore on *X*-ray evidence. Any structure with two long chains of comparable length will probably be found inconsistent with the small area of the compressed films of (**II**). Hence there is probably only one long chain and the smaller apparent length is due to the considerable tilting of the mols. $n\text{-}C_{10}H_{21}{\cdot}CH(CO_2Et)_2$ is transformed into $n\text{-}C_{10}H_{21}{\cdot}C(C_{12}H_{25})(CO_2Et)_2$, which yields α-decyl-*n*-tetradecoic acid (**III**), m.p. 47° (amide, m.p. 112·5°); the Me ester, b.p. 198—200°/0·25 mm., is transformed by CPh_3Na and MeI followed by alkaline hydrolysis into *α-methyl-α-decyl-n-tetradecoic acid* (**III**), m.p. 41° rising to 44·5° in 8 months (corresponding *amide*, m.p. 42°). It could not be resolved into its optical antipodes by quinine, cinchonine, strychnine, or brucine. *α-Ethyl-α-decyl-n-tetradecoic acid*, m.p. 27—28° rising to 31° in a few weeks (*amide*, a viscous oil), is prepared similarly. The Me ester of α-n-*heptyl*-n-*hexadecoic acid*, m.p. 42°, is transformed analogously into *α-methyl-α-n-heptylhexadecoic acid*, m.p. 44° (*amide*, m.p. 30—31°). *α-n*-Heptylnonoic acid, m.p. 26—27°, obtained from $n\text{-}C_7H_{15}Br$ and $CH_2(CO_2Et)_2$, is transformed through the Me ester into *α-methyl-α-heptylnonoic acid*, a viscous liquid, b.p. 171—171·5°/0·2 mm. (*amide*, a very viscous oil, b.p. 181—182°/0·2 mm.). $COMe{\cdot}C_9H_{19}$ and $C_{12}H_{25}{\cdot}MgBr$ afford mainly *methyl*-n-*nonyl*-n-*dodecylcarbinol*, b.p. 200—204°/~0·2 mm. $CH_2(CO_2Et)_2$, *sec.*-$C_{11}H_{23}Br$, Na, and some NaI in boiling EtOH yield Et_2 *sec.*-undecylmalonate, b.p. 180—182°/18 mm., converted into Et_2 sec.-*undecyl*-n-*dodecylmalonate*, b.p. 210—212°/0·16 mm., hydrolysed by boiling KOH–Pr$^{\alpha}$OH and then decarboxylated to *β-methyl-α*-n-*dodecyl-lauric acid*, b.p. 228—230°/0·3 mm. (*amide*, m.p. 102—103°). (**III**) is converted by successive treatments with $SOCl_2$ and CH_2N_2 in Et_2O into the corresponding diazo-ketone, which with a hot suspension of Ag_2O in MeOH yields Me *β-n*-decyl-*β-n*-dodecylpropionate, b.p. 212—214°/0·25 mm., hydrolysed to the *acid*, m.p. 0° rising after several weeks to 26·5° (*amide*, m.p. 55°). β-Methyl-α-*n*-dodecyl-lauric acid is converted through the chloride and diazo-ketone into the Et ester of *γ-methyl-β*-n-*dodecyltridecoic acid*, b.p. 209—210°/0·1 mm. (non-cryst. *amide*). (**IV**) passes through the chloride into the diazo-ketone, m.p. 36°, which gives *Me β-methyl-β-decylpentadecoate*, b.p. 196—197°/0·2 mm.; the *acid*, a viscous liquid, furnishes a non-cryst. *amide*. $(n\text{-}C_{10}H_{21})_2CO$, Zn filings, and $CH_2Br{\cdot}CO_2Et$ in boiling C_6H_6–Et_2O yield an undistillable product, converted by $SOCl_2$ in C_5H_5N followed by H_2O at 0° into *Et β-decyl-Δ$^{\alpha}$-tridecenoate*, b.p. 192—196°/0·4 mm.; this is hydrogenated (Raney Ni) at 40—60°/60 atm. to Et β-decyltridecoate, b.p. 179—181°/0·2 mm., which is reduced (Na–Bu$^{\alpha}$OH–light petroleum) to *γ-decyltridecanol*, b.p. 163—165°/0·15 mm. The corresponding iodide and $CHNa(CO_2Et)_2$ afford Et_2 *γ-decyltridecylmalonate*, b.p. 221—224°/0·45 mm., transformed by Na and MeI followed by hydrolysis and decarboxylation into *α-methyl-δ-decylpentadecoic acid*, which becomes turbid at 0°. H. W.

Purification of maleic anhydride.—See B., 1944, II, 3.

Production of glutaric acid.—See B., 1944, II, 3.

New reaction of ethylene oxide. V. Condensation of ethylene oxide with cyclic β-keto-esters. K. G. Pakendorf and F. F. Matschus (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 441—443).—Et *cyclo*pentanone-2-carboxylate and $(CH_2)_2O$, with piperidine at room temp. for 20 days, give *α-(γ'-carbethoxypropyl)-γ-butyrolactone*, b.p. 172—174°/6 mm. Me 6-methyl*cyclo*hexanone-2-carboxylate similarly gives *α-(δ'-carbomethoxy*-n-*amyl*)*-γ-butyrolactone*, b.p. 175°/6 mm. The mechanism suggested is the alcoholysis of the spirocyclic lactones first formed. S. A. M.

Separation of aldehydes and ketones.—See B., 1944, II, 4.

Stabilisation of unsaturated ketones.—See B., 1944, II, 32.

Manufacture of tertiary amines.—See B., 1944, II, 32.

Rotatory dispersion of α-amino-acids. J. W. Patterson and W. R. Brode (*Arch. Biochem.*, 1943, **2**, 247—257).—Measurements of the rotatory dispersion for λ 4400 to 6600 mμ. of 14 NH_2-acids, their hydrochlorides, and Na salts are employed to determine configuration. Simple rules are given for assigning configuration to α-NH_2-acids which are based on examination of rotatory dispersion curves. W. McC.

Complexes of zinc and glycine.—See A., 1944, I, 67.

Organic catalysts for the elimination of carbon monoxide from formamide. III. Catalysts with phenolic hydroxyl as active group. T. Enkvist [with A. Kurkela] (*Ber.*, 1940, **73**, [*B*], 1253—1258; cf. A., 1940, II, 71).—In presence of alkali, compounds with phenolic OH accelerate the elimination of CO from $HCO{\cdot}NH_2$ more markedly than the corresponding catalysts with alcoholic OH. PhOH is nearly as potent as the most efficient catalysts (sucrose; $OH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$) with alcoholic OH. The catalytic effect of phenols can be increased by suitable substituents, the position of which frequently has a very decisive influence. In *o*- and *p*-cresol Me is weakly activating, scarcely so in *m*-cresol, and restrictive in orcinol. C_5H_{11} and Pr$^{\beta}$ do not activate. In *o*- and *p*-positions Ph activates slightly but a second C_6 nucleus as in $C_{10}H_8$ has no noticeable effect. Cl is indifferent or inactivating. NH_2 is at most slightly inactivating, strongly inactivating, or indifferent accordingly as it is in the *o*-, *m*-, or *p*-position. NMe_2 and NEt_2 are distinctly inactivating in the *m*-position. OMe and $\cdot CH(OH){\cdot}CH_2{\cdot}NHMe$ are indifferent. NO_2, NO, $N_2{\cdot}SO_3H$, $\cdot CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, and $\cdot CH{:}NPh$ are inactivating, as also is the substitution of

C_5H_5N for C_6H_6. CO_2H is usually inactivating but can be indifferent. In the cases investigated ·CO·NHPh is inactivating. OH in *ortho-* or *vic*-position causes strong activation [*o*-$C_6H_4(OH)_2$; 3 : 4 : 1-$(OH)_2C_6H_3$·CO_2H; adrenaline, 1 : 2 : 3-$C_6H_3(OH)_3$]; in the *p*-position (quinol) activation is less pronounced, whereas in the *m*-position (resorcinol; orcinol), *sym.* [1 : 3 : 5-$C_6H_3(OH)_3$] and *as.* [1 : 2 : 4-$C_6H_3(OH)_3$] positions there is slight or marked inactivation increasing to complete inhibition with 1 : 3 : 5-$C_6H_3(OH)_3$. In the following points the catalysts do not appear to conform with Langenbeck's rules (A., 1940, I, 326). With different substituents there appears to be no definite position causative of activation or inactivation. One and the same substituent can be activating or inactivating according to its position; this is true in particular for OH and less so for Me. Not only all substituents of the second order (CO_2H, NO_2, NO, SO_3H) but also certain typical members of the first order (NH_2, Cl) are inactivating. The reactions are discussed.

H. W.

Properties of urea, biuret, and triuret. R. C. Haworth and F. G. Mann (*J.C.S.*, 1944, 603—606).—Biuret (I) (38%), m.p. 190°, and triuret, $CO(NH{\cdot}CO{\cdot}NH_2)_2$ (15%), m.p. 231—232°, are best prepared from $CO(NH_2)_2$ (II) and $SOCl_2$. Under controlled conditions (II) and SO_2Cl_2 give the *substance*, $C_4H_{16}O_7N_8S$, but on heating cyanuric acid (III) with $ClSO_3H$ (0·5 mol.) it gives (I), with 1·0 mol. it gives (III) or $NH_2{\cdot}SO_3H$ according to conditions. The properties of (II) are the converse of those of $CS(NH_2)_2$ (IV) in that H_2O cannot be abstracted from (II), but H_2S is readily eliminated from (IV), whilst NH_3 is readily lost from (II) but not from (IV). (I) may exist as a resonance hybrid between the normal form and several zwitterion forms, or may be partly or fully enolised. The peculiarities of (I) are discussed. (III) with $CaCl_2$ and NH_3 gives (?) *Ca cyanurate trihydrate.*

H. M. C.

Co-ordination number of bivalent lead.—See A., 1944, I, 68.

Preparation of thioamides.—See B., 1944, II, 4.

***ψ*-Halogens. XXXV. Solid and liquid thiocyanic acid.** L. Birckenbach and E. Büchner [with K. Kraus and, in part, E. Kayser] (*Ber.*, 1940, **73**, [*B*], 1153—1168).—HCNS cannot be prepared by the action of HCl or HF on an alkali thiocyanate but is obtained pure from KCNS and $KHSO_4$ by a modification of the method of Rück *et al.* (A., 1912, i, 954). The vapours condense in liquid air to colourless, enamel-like *thiocyanic acid* (I), m.p. −110° (vac.) (lit. m.p. 5°). When cautiously warmed it melts to a completely colourless, transparent, mobile liquid which solidifies at −110° to colourless (I), which again gives a colourless molten mass if the temp. of warming is $\gg$ −100°. The solidifying point is determined at −110° from the cooling curve. Slow warming of (I) causes formation of individual crystals at ~−90° and between −90° and −85° solidification to a *polymer* (II) although it is sometimes possible by very careful warming and avoidance of all agitation to keep small quantities of substance as liquid up to −50° or over. Generally at −55° to −50° (II) undergoes decomp. with (in vac.) formation of a *substance* (III) of ivory or pale yellow colour which darkens towards 0°. If a good vac. is maintained during slow warming the product can be kept for days in a vac. at room temp. If the amount is not too great, this can be almost completely depolymerised in a high vac., volatilisation being accompanied by absorption of much heat. This behaviour combined with analytical results (determinations of mol. wt. are impossible) allies (III) with cyanuric acid and causes it to be regarded as a trimeride "thiocyanuric acid." (I), (II), and (III) can be kept pure only in a vac. since even in the cold they evolve HCNS vapour which decomposes in the warmer parts of the apparatus and thus induces impurities. In the rectification of larger amounts of substance between −110° and −40° these parts must be cooled in CO_2–Et_2O at −50° to −40°. If (III) is allowed to warm to room temp. in a closed vessel filled or not filled with dry air but without pumping off the gas it darkens slowly to dark brown or red and at 3° a rapid change occurs with considerable evolution of heat, foaming, and formation of a paste (IV); this is accompanied by slight decomp. into HCN and S (this temp. has been incorrectly regarded as the m.p.). The non-volatility, apparently amorphous state, and sparing solubility of (IV) cause it to be regarded as a hexameride although attempted determinations of mol. wt. were unsuccessful. The heating curve of (I) shows breaks at −110°, −92° (between −92° and −89°), at −50° to −49°, and at 0° becoming more pronounced at 3°. Measurements of v.p. give similar results but give the impression that a homogeneous system is not under investigation. The structure H·NCS is assigned provisionally to (I).

H. W.

Production of nitriles.—See B., 1944, III, 33.

System hydrocyanic acid–diethyl ether. L. Birckenbach and E. Büchner (*Ber.*, 1940, **73**, [*B*], 1168—1171).—The m.p. diagram of mixtures of HCN and Et_2O proves the formation of an additive *compound* (1 : 1), m.p. −87°. Its stability is small. It does not exist in the vapour phase. HCN and Et_2O give a eutectic mixture at −121·5° to −121·6°.

H. W.

II.—SUGARS AND GLUCOSIDES.

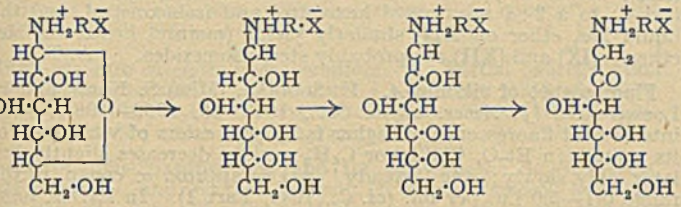
Calcium chloride compounds of *D*-α-glucoheptose (*D*-glycero-*D*-guloaldoheptose). H. S. Isbell and H. L. Frush (*J. Res. Nat. Bur. Stand.*, 1943, **3**, 163—168).—In support of the concept that sugars having like configurations for the atoms comprising the pyranose ring have like properties, it has been found that *D*-glycero-*D*-guloaldoheptose (I) (formerly *D*-α-glucoheptose) resembles *D*-gulose in that it forms cryst. compounds with $CaCl_2$ and that the equilibrium which exists in aq. solutions is shifted markedly by changes in [$CaCl_2$], addition of which shifts the equilibrium towards the unknown α-pyranose modification. The equilibrium optical rotation of (I) in 4% aq. solution in presence of $CaCl_2$ varies according to $[\alpha]_D^{20} = -20{\cdot}2 + 3{\cdot}54m - 0{\cdot}067m^2$, where m = g. of $CaCl_2$ in 100 mols. of solution. The cryst. *compound*, $(I),CaCl_2,2H_2O$, mutarotates in 4% aq. solution in accordance with $[\alpha]_D^{20} = -6{\cdot}5 \times 10^{-0{\cdot}0072t} - 9{\cdot}3°$.

H. W.

The cardiac glucosides. W. E. Bouman (*Pharm. Tijds. Nederl.-Indië*, 1941, **18**, 39—48, 65—75, 97—104, 130—137, 177—187).—A review.

***N*-Glycosides. II. Amadori transformations.** F. Weygand (*Ber.*, 1940, **73**, [*B*], 1259—1278; cf. A., 1940, II, 69).—Glycosides of primary aromatic amines are readily obtained by heating 1 mol. of sugar with 1·1—1·4 mols. of amine and 2—4 mols. of H_2O. Only those derived from glucose are converted into *iso*amines when melted or heated in MeOH or EtOH. Surprisingly, pure *p*-phenetidine-*d*-glucoside (I) is not isomerised in EtOH. Apparently identical experiments in which glucose, *p*-OEt·C_6H_4·NH_2, and H_2O are heated at 100° lead sometimes to (I) and sometimes to *d-iso*glucose-*p*-phenetylamine (II) so that it is doubtful if (II) is formed through (I). Addition to the mixture of increasing amounts of HCl leads to the isolation of (II) (the glucosides of *p*-toluidine, *p*-OMe·C_6H_4·NH_2, and *o*-4-xylidine behave similarly) in very greatly improved yield, small amounts of acid increasing both the rate of glucoside formation and isomerisation. Larger amounts of acid rapidly cause darkening. The prep. of piperidine-*d*-glucoside, m.p. 129—130°, and sulphanilamide-*d*-glucoside, m.p. 207—208°, from the sugar, amide, H_2O, and a little HCl is described. The prep. of the following under varied conditions is described: *d-iso*glucose-*p*-tolylamine (III), m.p. 153—154°, from glucose or mannose; *d-iso*glucose-*p*-phenetylamine, m.p. 154°; d-iso*glucose*-p-*anisylamine*, m.p. 140—141°, and *d-iso*glucose-3 : 4-dimethylphenylamine, m.p. 161—162°. (III) is reduced by Na–Hg in H_2O to *p*-tolyl-*d*-mannamine, m.p. 195—196°. In acid solution in which they form salts the catalytic hydrogenation (PtO_2) of the *iso*sugaramines affects preferentially the aromatic nucleus and the CO group of the side-chain remains intact. In neutral solution the results are variable whereas in alkaline solution reduction occurs generally in the side-chain, whereby 1 mol. of the *iso*amine absorbs exactly 1 H_2. A method of determining *iso*amine in solution is thus afforded. The following are thus produced: 3 : 4-dimethylphenyl-*d*-mannamine, m.p. 185—186°, $[\alpha]_D^{20}$ +21·4° in C_5H_5N; p-*anisyl*-d-*mannamine*, m.p. 191—192°, $[\alpha]_D^{20}$ +27·8°. Xylose, *p*-toluidine, H_2O, and AcOH at 75° rapidly yield *p*-toluidine-*d*-xyloside, further converted into *d-iso*xylose-*p*-tolylamine, which could not be obtained cryst. It is converted into d-*lyxose*-p-*tolylamine*, m.p. 156—158°, $[\alpha]_D^{19}$ +26°, when hydrogenated (PtO_2) in EtOH containing the acid used in the isomerisation or in alkaline solution at 20° or 4° but not at 58°. Non-cryst. *l-iso*arabinose-*p*-tolylamine is obtained from *l*-arabinose (IV), *p*-toluidine, H_2O, and AcOH and identified by hydrogenation to the expected epimerides, l-*arabinose*-p-*tolylamine* (V), m.p. 178—179°, $[\alpha]_D^{19}$ −7·1°, and l-*ribose*-p-*tolylamine*, m.p. 140—141°, $[\alpha]_D^{19}$ +31° in C_5H_5N. (V) is obtained also by reduction of *p*-toluidine-*l*-arabinoside (Ni in aq. MeOH; H_2 at 90°/50 atm.). (IV), *o*-4-xylidine, H_2O, and HCl afford *l-iso*arabinose-3 : 4-dimethylphenylamine, hydrogenated (PtO_2 in EtOH containing acid at 10°) to *l*-arabinose-3 : 4-dimethylphenylamine, m.p. 138—139°, $[\alpha]_D^{22}$ −12·3°, in neutral solution to l-*ribose*-3 : 4-*dimethylphenylamine*, m.p. 143°, $[\alpha]_D^{20}$ +30° in C_5H_5N, also obtained in alkaline solution. *d*-Arabinose is converted into *d-iso*arabinose-3 : 4-dimethylphenylamine, hydrogenated in alkaline solution at 20° to d-*ribose*-3 : 4-*dimethylphenylamine*, m.p. 142°, $[\alpha]_D^{22}$ −31·4°, identical with the substance obtained from *o*-4-xylidine-*d*-riboside. Under the new conditions *p*-toluidine-*l*-rhamnoside is isomerised to l-*rhamnose*-p-*tolylamine*, m.p. 183—184°, $[\alpha]_D^{20}$ −19·7° in C_5H_5N. Aniline-*d*-glucoside in presence of H_2O or a little acid is isomerised to the non-cryst. *d-iso*glucosephenylamine, which strongly reduces cold, alkaline solutions of *o*-$C_6H_4(NO_2)_2$ and is hydrogenated in alkaline solution to *d*-mannosephenylamine, m.p. 175—176°, showing that the Amadori isomerisation, impossible under the older conditions, has actually occurred. *d-iso*Glucose-*p*-tolylamine is obtained by Amadori isomerisation not only from *p*-toluidine-*d*-glucoside but also from *p*-toluidine-*d*-mannoside. In cases in which the *iso*amines can be obtained from two epimeric glycosides it is proposed to name the *iso*-compound from the sugar which is commonest in nature or in the case of the rare sugars from that with which isomerisation is first effected. The successful isomerisation of *p*-tolu-

idine-*d*-galactoside is shown by the subsequent hydrogenation to d-*galactose*-p-*tolylamine*, m.p. 180—181°, $[\alpha]_D^{21}$ −13·6° in C_5H_5N. The mechanism of the Amadori isomerisation is formulated thus (R = C_6H_4Me):



If isolation of the glucosides of primary amines is desired it is generally necessary to work without addition of acid although if the Amadori isomerisation occurs slowly acids or H salts may be added if the reaction is interrupted sufficiently soon. A suitable division of the glycosides is sketched. For the prep. of *N*-polyhydroxylalkyl derivatives by hydrogenation (at 80—100°/high pressure) of *N*-glycosides complete absence of acid is necessary if the hydrogenation product is to be free from epimeric compounds. The formation of (*d*-arabo)tetrahydroxybutylquinoxaline from *o*-$C_6H_4(NH_2)_2$ and *d*-glucose in slightly acid solution is readily explained if the incidence of an Amadori isomerisation is admitted. In the biogenesis of lactoflavin it is possible that the ribityl residue in a preliminary stage enters the flavin mol. by an Amadori isomerisation from either an *N*-*d*-riboside or *N*-*d*-arabinoside. The CO group at $C_{(2)}$ must be reduced to CH·OH with formation of the *d*-ribityl configuration. H. W.

***N*-Glycosides. III. Steric course of the hydrogenation of *iso*-glucosamines. Rules of rotation with 9-polyhydroxyalkylflavines and *N*-polyhydroxyalkylbenzenes.** F. Weygand (*Ber.*, 1940, **73**, [*B*], 1278—1283).—In acid solution, only *l*-arabinose-3 : 4-dimethylphenylamine is isolated by the hydrogenation of *l-iso*arabinose-3 : 4-dimethylphenylamine whereas at 20° in presence of EtOH–alkali the only isolable product is the *l*-ribamine derivative. It is not impossible that the epimerides are formed in small proportion. Hydrogenation of *iso*glycosamines in alkaline solution, *i.e.*, in the enolic form, is an addition of H_2 at an ethylenic linking which occurs in the *cis*- or *trans*-position according to the rate of hydrogenation and to the catalyst employed. Since the ethylenic compound can occur in a maleinoid and fumaroid form varying proportions of epimeric compounds are to be expected according to the form which is present and the mode of addition. The sense of rotation of the 9-polyhydroxyalkylflavines for the *D* line depends solely on the configuration at $C_{(\beta)}$. If in Fischer's projection ('CH_2·OH group below; ·CH_2·N: group above) the OH at $C_{(\beta)}$ of the polyhydroxyalkyl chain projects to the right, the rotation in 0·1N-NaOH is negative and conversely. Similarly for *N*-polyhydroxyalkylbenzenes if in Fischer's projection ('CH_2·OH group below; ·CH_2·NHR group above) the OH at $C_{(\beta)}$ of the polyhydroxyalkyl chain projects towards the right, the rotation in C_5H_5N is negative and conversely. H. W.

Karakin, glucoside of *Corynocarpus lævigata*, and hiptagenic acid. C. L. Carter (*J.S.C.I.*, 1943, **62**, 238—240).—Karakin, a constituent of karaka nuts, closely resembles hiptagin in chemical properties, but from lack of a specimen of hiptagin the exact relationship cannot be established. Their common hydrolytic product, hiptagenic acid, is believed to be the oxime of aldehydroglyceric acid, OH·N:CH·CH(OH)·CO_2H. A second hydrolytic product of karakin is aminoglucose or aminomannose.

Amylolytic degradation of starch. W. N. Haworth, H. Kitchen, and S. Peat (*J.C.S.*, 1944, 619—625).—It is shown that β-amylase (I) hydrolyses the amylopectin component of starch with the formation of maltose and a limit dextrin, dextrin-*A* or α-amylodextrin (II) (40 wt.-% of original starch). End-group assay shows (II) to have an apparent unit chain length of 11—12 glucose units. (II) is not susceptible of further attack by (I) until it has been "sensitised" by contact with salivary amylase. The action of (I) then continues until a second resting stage is reached, viz., dextrin-*B* (III) [38% of (II), 7—8 glucose units]. (III) is not further hydrolysed by (I), nor sensitised by saliva, but is hydrolysed by salivary amylase to dextrin-*C* (IV) [67% of (III); 5—6 glucose units] and maltose. (IV) is slowly hydrolysed by pancreatic amylase to dextrin-*D* (V) [80% of (IV); 4—5 glucose units] and a sugar. Properties of (II)—(V) are given. The mechanism of amylolysis is explicable on the basis of the simple laminated formulation of the structure of starch of Haworth *et al.* (A., 1937, II, 232) if it be assumed (i) that the impediment to the action of (I) is represented by the polymeric link which unites the unit chains; (ii) that the polymeric links are ruptured by an enzymic constituent of saliva and of malt α-amylase; and (iii) that the unit chains so liberated immediately recombine with the formation of new polymeric (1 : 6-α-glucosidic) links with a different orientation of position on the respective chains. It is not necessary to postulate a complex, highly ramified structure for amylopectin, such as that proposed by Meyer (A., 1940, II, 268), to explain the facts of amylolysis. H. M. C.

III.—HOMOCYCLIC.

Cracking of *cyclo*hexane; thermal and catalytic decomposition at high pressures.—See B., 1944, II, 1.

Preparation and absorption spectra of five pure carotenoid pigments. F. P. Zscheile, J. W. White, jun., B. W. Beadle, and J. R. Roach (*Plant Physiol.*, 1942, **17**, 331—346).—Methods of purifying α- and β-carotene, cryptoxanthol, luteol, and zeaxanthol are described, absorption spectra in the range 3800—5300 A. are determined. A. G. P.

Catalytic alkylation of aromatic hydrocarbons.—See B., 1944, II, 4.

Production of benzylsulphonyl chlorides.—See B., 1944, II, 33.

Mechanism of inhibition of styrene polymerisation.—See A., 1944, I, 66.

Mechanism of addition polymerisation. Kinetics and elementary steps of polyreactions. Rate theory and some physical and chemical properties of high polymers.—See A., 1944, I, 65.

Exchange reactions of lithium phenyl. IV. Production of diphenyl from fluorobenzene and lithium phenyl. G. Wittig, G. Pieper, and G. Fuhrmann (*Ber.*, 1940, **73**, [*B*], 1193—1197).—Under identical conditions LiPh reacts with PhI, PhBr, PhCl, and PhF in Et_2O to the extent of 5, 7, 5, and 75%, respectively. The greatly superior reactivity of PhF is due to the strongly electronegative nature of F which polarises the *o*-CH linking more strongly than the other halogens and thus facilitates replacement of H by Li. Entry of the metal polarises the C–F linking and thus increases the reactivity of F. Evidence in favour of this view is found in the production of *o*-C_6H_4Ph·CPh_2·OH (converted by AcOH into 9 : 9-diphenylfluorene) by the action of $COPh_2$ on the product from PhF and LiPh. F appears superior to OMe in polarising action. In practice the change appears somewhat more complex and a scheme is discussed according to which it is impossible to obtain diphenyls in 100% yield from halogenobenzenes and LiPh or other metallic phenyl. With *o*- and *p*-$C_6H_4Br_2$ the production of diphenyls $C_6H_4Br_2$ + LiPh → LiBr + C_6H_4PhBr is overshadowed by halogen–metal interchange, C_6H_4Br·Br + LiPh → Li·C_6H_4Br + PhBr. In the reactions of PhF further evidence is found in favour of the view that alkali-org. compounds are intermediates in the elimination of HHal from AlkHal and alcoholic alkali, EtBr → K·$[CH_2]_2$·Br → CH_2:CH_2 + Br, and in displacements of the ethylenic linking, CH_2Ph·CH:CH_2 → CHPhK·CH:CH_2 → CHPh:CH·CH_2K → CHPh:CHMe. H. W.

Polymerisation of 1 : 2-dihydronaphthalene and polymer.—See B., 1944, II, 4.

Preparation of 1- and 2-methylnaphthalenes from tar oil fractions. II. 1-Methylnaphthalene.—See B., 1944, II, 1.

Preparation of 2 : 3-dinitronaphthalene and 3-nitro-2-naphthylamine. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1944, 635—636).—3 : 1-NO_2·$C_{10}H_6$·NHAc is nitrated (HNO_3) to 2 : 3-*dinitro*-1-*naphthylamine*, m.p. 160—161°, deaminated to 2 : 3-$C_{10}H_6(NO_2)_2$, m.p. 159°. This is reduced to 3-*nitro*-2-*naphthylamine*, m.p. 86·5° (*Ac* derivative, m.p. 191·5—192·5°), by hydrated Na_2S. NN′-*Di*-p-*toluenesulphonyl*-1 : 4-*naphthylenediamine*, m.p. 249—250°, could not be nitrated and 2 : 3 : 1 : 4-$(NO_2)_2C_6H_2(NH_2)_2$ could not be deaminated. H. M. C.

Derivatives of sulphanilamide.—See B., 1944, III, 16, 17.

Complex formation and rearrangement of *p*-hydroxylaminobenzenesulphonamide. H. Burton and N. Walker (*J.C.S.*, 1943, 656—657; cf. A., 1941, II, 220).—Confirmatory evidence is given that *p*-OH·NH·C_6H_4·SO_2·NH_2 (I), m.p. 140°, and *p*-NH_2·C_6H_4·CO_2·NH_2 (II) form a 2 : 1 complex (III), m.p. 161·5° (cf. Sevag, A., 1943, II, 158). (II) can be isolated after removal of (I) [as azoxybenzene-4 : 4′-disulphonamide (IV)] by air oxidation of (III) in dil. aq. NH_3 at room temp. After acetylating (III) by Ac_2O at room temp., the respective Ac derivatives of (I) and (II) are isolable (from MeOH). (III) is prepared from its components in H_2O. (I) and 5% aq. HCl or H_2SO_4 (in CO_2) at 100° (bath) give (IV) and *p*-NH_2·C_6H_4·OH (V); (III) similarly yields (IV), (V), and (II). A. T. P.

Derivatives of *p*-aminobenzenesulphonanilide.—See B., 1944, II, 4.

Preparation and properties of certain poly-sulphanilamide compounds. F. G. Mann and J. Watson (*J.C.S.*, 1943, 606—609).—*p*-NHAc·C_6H_4·SO_2Cl (I) and 10% aq. NaOH, added successively in very small quantities to aq. $C(CH_2$·$NH_2)_4$ at 45—50°, at great dilution, give *tetra*-(p-*acetamidobenzenesulphonamidomethyl*)*methane*, m.p. 304—306°, hydrolysed by boiling dil. HCl to the $(NH_2)_4$-derivative, m.p. 243·5—244°. Similarly, $N([CH_2]_2$·$NH_2)_3$ affords *tri*-(β-p-*acetamidobenzenesulphonamidoethyl*)*amine*, m.p. 198·5—200·5° (softens at 115°), and thence *tri*-(β-*sulphanilamidoethyl*)*amine*, m.p. 178·5—180° (decomp.). The analogous sulphonamido-derivative

from $N([CH_2]_3\cdot NH_2)_3$ could not be prepared. $OH\cdot CH(CH_2\cdot NH_2)_2$ gives, through the *Ac*$_2$ derivative, m.p. 232·5—233·5°, *βγ-di(sulphanilamido)iso**propyl alcohol***, m.p. 177—179°. $NH_2\cdot CH(CH_2\cdot NH_2)_2$ yields *αβγ-tri(sulphanilamido)**propane***, m.p. 234·5—236° (decomp.) (softens at 220°) (*Ac*$_3$ derivative, m.p. 218·5—220·5°). NN′-*Di*-(p-*acetamidobenzenesulphonyl*)-NN′-*di*-(*β*-p-*acetamidobenzenesulphonamidoethyl*)*ethylenediamine*, m.p. 290·5—291·5°, and thence the (NH_2)$_4$-derivative, m.p. 208—209°, are obtained from $(CH_2\cdot NH\cdot[CH_2]_2\cdot NH_2)_2$ and (I) in C_5H_5N. No antimalarial activity is noted with the compounds. A. T. P.

***p*-Substituted benzenesulphonyldiguanides.**—See B., 1944, II, 5.

Mechanism of the diazo-coupling reaction. II. Further evidence in favour of the polarisation theory. H. H. Hodgson and E. Marsden (*J. Soc. Dyers and Col.*, 1944, **60**, 16—19; cf. A., 1943, II, 8).—Examples are discussed of the decomp. of unstable equilibrium mixtures of diazonium and their isomeric diazo-compounds, whereby reactions of both types of compound could be simultaneously compared. Evidence is given supporting the theory developed previously (*loc. cit.*). A. T. P.

Separation of phenols and alkylated products thereof.—See B., 1944, II, 5.

Synthesis of 5-hydroxyindane. (Miss) K. Paranjape, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1943, **12**, **A**, Part 3, 66—67).—Addition of Et *cyclo*pentylideneacetate and HCO_2Et to Na in Et_2O at 0° and then at room temp. gives unstable Et 2-formyl-*cyclo*pentylideneacetate (*semicarbazone*, m.p. 201°), converted by $CH_2(CO_2H)_2$ in C_5H_5N containing a little piperidine at 100° followed by hydrolysis into cyclo*pentylideneacetic*-2-*β-acrylic acid*, m.p. 62°, in 80% yield. This is converted by heating at 150° with $Ba(OH)_2$ followed by distillation at 180°/80 mm. into 5-*keto*-$\Delta^{4:5\cdot6:7}$-*dihydroindane*, b.p. 105°/20 mm., 140°/80 mm. (*semicarbazone*, m.p. 161°), more conveniently obtained by condensation of 2-formyl*cyclo*pentanone with $COMe_2$ and NaOEt in EtOH. It is converted by long contact with fuming HCl in a sealed tube at room temp. into 5-hydroxyindane, m.p. 55° (benzoate, m.p. 106—107°). H. W.

Halogenated 2 : 2′-dihydroxydiphenylmethanes.—See B., 1944, II, 33.

Dienœstrol. G. I. Hobday and W. F. Short (*J.C.S.*, 1943, 609—612).—*α-Chloro-α*-p-*anisyl*-Δ^{α}-*propene*, m.p. 43°, is obtained from anethole dichloride (I) and boiling EtOH–NaOEt, or from *p*-$OMe\cdot C_6H_4\cdot COEt$ (II) and PCl_5 at −5°, followed by aq. KOH–EtOH at room temp. *β-Chloro-α*-p-*anisyl*-Δ^{α}-*propene* (III), b.p. 135—136°/10 mm., is prepared from (I) and C_5H_5N at 100° (bath) or from anisylacetone and PCl_5. Crude (III) and boiling KOH–MeOH give *α*-p-*anisyl*-Δ^{α}-*propinene* (IV), b.p. 115—117°/9 mm. The structure of (III) is shown by ozonolysis in $CHCl_3$ to anisaldehyde (60%), and by the isolation of *β-p*-anisyl-*α*-methylacrylic acid (V) and a little *αδ*-di-*p*-anisyl-*βγ*-dimethyl-$\Delta^{\beta\gamma}$-butadiene, m.p. 162°, from the products of the successive action of Mg and CO_2 in Et_2O. Anethole dibromide (VI) and $NPhMe_2$ give *β*-(N-*methylanilino*)*anethole*, m.p. 116°; (IV) is also probably formed. *αβ*-Dibromo-*β-p*-anisyl*iso*butyric acid and dil. aq. NaOH afford *β-bromo-α*-p-*anisyl*-Δ^{α}-*propene* (VII), b.p. 130—132°/6 mm. (not the *α*-Br-derivative, as stated by Balaban *et al.*, B.P. 547,027; B., 1942, III, 246), also obtained from (VI) and boiling 1·7N-KOH–EtOH. (VII) gives a Grignard reagent, which when carbonated at −10° yields (V). (VII) and Mg give *αδ*-di-*p*-anisyl-*βγ*-dimethyl-$\Delta^{\beta\gamma}$-butadiene, m.p. 163° [ozonolysis products anisaldehyde (73%) and some Ac_2], reduced (H_2–Pd–C–$COMe_2$) to some *αδ-di*-p-*anisyl-βγ-dimethylbutane*, m.p. 68—69°; the latter is also obtained from *β*-chloro-*α-p*-anisylpropane and Mg in boiling Et_2O. *γδ*-Di-*p*-hydroxyphenylhexane-*γδ*-diol, m.p. 204—206°, gives a *dibenzoate*, m.p. 235—236°, and *di*-p-*toluenesulphonate*, m.p. 205°. *γδ-Di*-p-*anisylhexane-γδ-diol*, m.p. 194° [Ac_2O–AcCl give mainly *γγ*-di-*p*-anisylhexan-*δ*-one (see below)], is also obtained from (II)–$HgCl_2$–Et_2O–Mg–C_6H_6, or by electrolysis of (II) in aq. NaOH–EtOH, or from propionoin and SeO_2 (distil slowly), and treatment of the resulting dipropionyl with *p*-$OMe\cdot C_6H_4\cdot MgBr$. A second *form* (VIII) (*iso*pinacol), m.p. 94—95°, of *γδ*-di-*p*-hydroxyphenylhexane-*γδ*-diol is obtained as by-product on electrolytic reduction of *p*-$OH\cdot C_6H_4\cdot COEt$, or by electrolytic reduction of p-*benzoyloxypropiophenone*, m.p. 117°, in aq. NaOH–dioxan. Benzoylation of (VIII) yields probably its dibenzoate, readily converted into *γγ-di*-p-*benzoyloxyphenylhexan-δ-one*, m.p. 178°. (VIII) and warm AcOH or mineral acid give *γγ-di*-p-*hydroxyphenylhexan-δ-one*, m.p. 136°, which does not form CO-derivatives, but affords a diacetate, m.p. 91—92°, and a liquid Me_2 ether reducible by Na–$C_5H_{11}\cdot OH$ to stilbœstrol Me_2 ether; with KOH at 200°, it (or its diacetate) gives (probably) *αα*-di-*p*-hydroxyphenylpropane, m.p. 134° (Me_2 ether, m.p. 44°). (IV) and HBr–C_6H_6 at 0° (whence *α*-bromo-*α-p*-anisyl-Δ^{α}-propene; cf. Balaban, *loc. cit.*), followed by Mg and then $CuCl_2$, afford anethole, (?) (IV), and a resin; demethylation (MgMeI) of the last gives a little dienœstrol (IX), m.p. 230—233° [$(CH_2Ph)_2$ *ether*, m.p. 205°; *di*-p-*toluenesulphonate*, m.p. 168°; *dibenzoate*, m.p. 224°]. Some *Me*$_1$ *ether* (X), m.p. 142°, is obtained from (IX) and CH_2N_2 at room temp., whereas Me_2SO_4 (4 mols.) in N-NaOH yields (X) (73%) and the *Me*$_2$ *ether* (XI), m.p. 130—131°, also prepared [29% of (X) + 30% of (XI)] using MeI in boiling KOH–EtOH. Ozonolysis of (XI) in AcOH gives anisil (16%), converted into 2 : 3-*di*-p-*anisylquinoxaline*, m.p. 149—150°. (X) or (XI) is demethylated to (IX) by MgMeI, but gives an isomeride, iso*dienœstrol* (XII), m.p. 189°, with EtOH–KOH at 220°. (XII) is reduced (Pd–C) to a 2 : 1 mixture of hexœstrol and *iso*hexœstrol, and the liquid Me_2 ether of (XII) similarly yields (mainly) hexœstrol Me_2 ether. (IX) and (XII) are probably stereoisomerides. A. T. P.

Fluorescence of vitamin-*A*. H. Sobotka, (Miss) S. Kann, and E. Loewenstein (*J. Amer. Chem. Soc.*, 1943, **65**, 1959—1961).—The intensity of fluorescence of higher fatty acid esters of vitamin-*A* or its acetate in Et_2O, $CHCl_3$, or C_6H_6 rapidly decreases slightly but later only slowly; the "steady" val. is approx. ∝ concn. in the range 0·1—5·0 i.u. per ml. (cf. C., 1944, Part 1). In EtOH, however, there is a rapid great initial increase, followed by a slightly slower, but still rapid, decrease, finally to extinction. The highest val. obtained is increased by increasing the intensity of illumination. Cessation of illumination during the decrease gives after its resumption the same val. and the same rate of subsequent decline. The rate of decline is lowered by flushing with CO_2 or N_2. Vitamin-A_2 esters show the same phenomena, but cryst. -*A* itself shows only an immediate decline. Adding C_6H_6 to -*A* esters in MeOH, EtOH, or $Bu^{\beta}OH$ is without effect until with 65—70% of C_6H_6 a sudden complete change to the non-polar solvent behaviour occurs. R. S. C.

Conversion of lutein in a boric acid–naphthalene melt. I. L. Zechmeister and J. W. Sease (*J. Amer. Chem. Soc.*, 1943, **65**, 1951—1955).—Chromatography of lutein (prep. from *Tagetes* extract described) which has been heated at 140° in $C_{10}H_8$–H_3BO_3 yields *deoxylutein*-I (3—4%), m.p. 149° (corr.; in CO_2; block) [acetate, m.p. 139° (corr.)], -II (10%), m.p. 156·5—158° (corr.) after softening [acetate, softens 139°, m.p. 141° (corr.)], and -III (3—4%), m.p. 162° (corr.) after softening. All are $C_{40}H_{56}O$ ($+H_2$), have no vitamin-*A* activity (rats), contain 11 C:C and an esterifiable OH, resemble cryptoxanthin on partition, and undergo isomerisation by I, developing *cis*-peaks. Photomicrographs are given. -II and -III are brownish-orange, -I is redder. Absorption spectra of -II and -III are similar, showing several peaks, but -I shows only one peak (at 494 mμ.). Only 10 C:C are conjugated in -II and -III. Structural possibilities are discussed. R. S. C.

*cyclo***Alkanyl peroxides.**—See B., 1944, II, 34.

Chlorination product of benzyl thiocyanate. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1943, **16**, **B**, No. 12, 3 pp.).—Slow (2—3 hr.) chlorination of $CH_2Ph\cdot CNS$ in H_2O suspension at 0° gives *benzylsulphinyl cyanide* (I), m.p. 81—82°; $CH_2Ph\cdot SO_2H$ (II) (identified by reaction with $CH_2{:}CH\cdot CO_2H$ to $CH_2Ph\cdot SO_2\cdot[CH_2]_2\cdot CO_2H$) is formed in small amount only, by hydrolysis of (I) (cf. Johnson *et al.*, A., 1939, II, 498). (I) is rapidly hydrolysed to (II) by dil. NaOH. M. H. M. A.

Mercapturic acids. I. Synthesis of phenyl-*l*-cysteine and *l*-phenylmercapturic acid. S. H. Zbarsky and L. Young (*J. Biol. Chem.*, 1943, **151**, 211—215).—Treatment of *l*-cystine in 1·5N-H_2SO_4 at 100° with Zn dust with occasional additions of mossy Zn and of the filtrate with an aq. suspension of Cu_2O leads to cysteine Cu^{I} mercaptide, converted by $PhN_2\cdot HSO_4$ into phenyl-*l*-cysteine (I), decomp. 170—172°, $[\alpha]_D^{25}$ +11° in 0·1N-NaOH; (I) is also obtained by debromination (Na–Hg at room temp.) of *p*-bromophenyl-*l*-cysteine. *l*-Phenylmercapturic acid, m.p. 142°, $[\alpha]_D^{27}$ −23° in EtOH, is obtained by decomp. the product of the interaction of PhN_2Cl and acetylcysteine with Cu powder, by treatment of (I) with Ac_2O and N-NaOH at 0°, and by debromination of *p*-bromophenylmercapturic acid by Na–Hg. H. W.

Mechanism of chemical reactions. VII. Significance of molecular compounds in catalytic hydrogenations. III. Hydrogenation of mandelic acid and mandelic esters. K. Kindler and D. Kwok (*Annalen*, 1943, **554**, 9—15; cf. A., 1934, 879; 1935, 1362).—Catalytic hydrogenation (Pd sponge) of $OH\cdot CHPh\cdot CO_2H$ (I) in AcOH containing H_2SO_4 proceeds rapidly at room temp., giving $CH_2Ph\cdot CO_2H$ in 90% yield. In absence of H_2SO_4 hydrogenation occurs very slowly or not at all and ceases after absorption of ~15% of the theoretical quantity of the gas. The action is ascribed in part to the formation of mol. compounds $HX\cdots OH\cdot CHPh\cdot C(OH){:}O\cdots HX$ in which the asterisked atoms are so extensively saturated that the reductive removal of the greatly loosened alcoholic OH proceeds more readily than in (I), and in part to the production of esters $CHPhX\cdot CO_2H$ in which X is more readily removable than the OH of (I). $HClO_4$ has the same effect. Similarly $OH\cdot CHPh\cdot CO_2Et$ (II) is not hydrogenated in AcOH alone but in presence of H_2SO_4 or $HClO_4$ gives $CH_2Ph\cdot CO_2Et$ in ~85% yield. At 100°, (II) rapidly absorbs H_2 even in absence of H_2SO_4 or $HClO_4$; reaction ceases after absorption of 4 H_2 with production of Et *cyclo*hexylacetate (III); if the change is interrupted after absorption of 1 H_2 the products are $CH_2Ph\cdot CO_2Et$ (~90%) with traces of (III), the OH being reduced more rapidly than the ring. This difference in reactivity is much less when OAlk or Alk is substituted in the

nucleus. Thus Et *p*-ethylmandelate is converted by partial hydrogenation at 100° into a difficultly separable mixture of unchanged material, Et 4-ethyl*cyclo*hexylacetate, and a little *p*-$C_6H_4Et{\cdot}CH_2{\cdot}CO_2Et$. The rate of hydrogenation of (I) in presence of H_2SO_4 or $HClO_4$ diminishes with diminished concn. of mineral acid and also with increasing H_2O content of the mixture. $ZnCl_2$–HCl can replace H_2SO_4 or $HClO_4$. H. W.

High-pressure catalytic hydrogenation. I. Partial hydrogenation of diphenylacetic acid. A. Sandoval L. (*Ciencia*, 1943, **4**, 107—108).—$OAc{\cdot}CPh_2{\cdot}CO_2Me$ is hydrogenated (Raney Ni) to $CHPh_2{\cdot}CO_2Me$ and thence to Me *cyclo*hexylphenylacetate. F. R. G.

α-Chlorodiphenylacetic acid and its derivatives. S. A. Setlur, A. N. Kothare, and V. V. Nadkarny (*J. Univ. Bombay*, 1943, **12**, A, Part 3, 68—70).—$CPh_2Cl{\cdot}CO_2H$ (I) is converted by the requisite NaOAlk into *α-methoxy-*, m.p. 100°, and *α-ethoxy-*, m.p. 114°, *-diphenylacetic acid*. With $(NH_4)_2CO_3$ and conc. aq. NH_3 at 100° (I) gives a small proportion of *α-aminodiphenylacetic acid*, m.p. 245°, but much $OH{\cdot}CPh_2{\cdot}CO_2H$ is produced. With the respective amine in C_6H_6 at 100° (I) yields *α-benzylamino-*, m.p. 211° (decomp.), *α-o-toluidino-*, m.p. 150° (decomp.), *α-m-toluidino-*, m.p. 165° (decomp.), *α-m-nitroanilino-*, *α-o-carboxyanilino-*, m.p. 193° (decomp.), and *α-piperidino-*, m.p. 180° (decomp.), *-diphenylacetic acid*. Almost all the anilinodiphenylacetic acids are rapidly hydrolysed by conc. H_2SO_4, which gives a blood-red colour [as with (I)] on warming or keeping for some time. H. W.

Synthetic anthelmintics. VII, VIII. Compounds related to desmotroposantonin. (Miss) K. Paranjape, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1943, **12**, A, Part 3, 60—63).—VII. 1-Keto-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (I), $CHMeBr{\cdot}CO_2Et$, and Zn turnings in boiling PhMe yield *Et α-1-hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*1-*naphthylpropionate*, b.p. 185°/25 mm., converted by P_2O_5 in C_6H_6 at 100° into *Et α-7-methoxy-*3 : 4-*dihydro-*1-*naphthylpropionate*, b.p. 175°/25 mm. The corresponding *acid*, b.p. 215°/25 mm., is transformed by the protracted action of 60% H_2SO_4 at room temp. into *α-2-hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*1-*naphthylpropionolactone*, b.p. 210°/25 mm., demethylated (HBr in AcOH) to *α-*2 : 7-*dihydroxy-*1 : 2 : 3 : 4-*tetrahydro-*1-*naphthylpropionolactone*, b.p. 240°/25 mm.

VIII. (I), $Me_2C_2O_4$, and MeOH–NaOMe give *Me* 1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylglyoxylate*, m.p. 57° (semicarbazone, m.p. 225°), which at 150—180° followed by distillation affords *Me* 1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydronaphthalene-*2-*carboxylate*, b.p. 205°/70 mm., m.p. 57·5° (violet colour with $FeCl_3$). This with Na and $CH_2Br{\cdot}CO_2Et$ gives *Et* 1-*keto-*2-*carbomethoxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetate*, m.p. 61°, which could not be hydrolysed under any conditions. (I) and Br in CS_2 afford 2-*bromo-*1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydronaphthalene* (II), m.p. 48°. (I) is converted by successive treatments with $NaNH_2$ in boiling Et_2O and $CH_2Br{\cdot}CO_2Et$ followed by hydrolysis into 1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetic acid* (III), m.p. 88°. (II) and $CHNa(CO_2Et)_2$ in boiling C_6H_6 afford Et_2 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthylmalonate, which on acid hydrolysis yields (III) and is reduced by $Al(OPr^{\beta})_3$ in boiling $Pr^{\beta}OH$ and then hydrolysed to 1-*hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetic acid*, m.p. 88°; this is converted at 100° into the corresponding *lactone*, m.p. 76°, demethylated to 1 : 7-*dihydroxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetolactone*, m.p. 101°. (II) and $CMeNa(CO_2Et)_2$ in C_6H_6 afford Et_2 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthylmethylmalonate, which gives *α-*1-*keto-*, m.p. 91°, and *α-*1-*hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylpropionic acid*, m.p. 77°; the corresponding *lactone*, m.p. 83°, is demethylated to *α-*1 : 7-*dihydroxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylpropionolactone*, m.p. 112°. H. W.

Electrolytic reduction of *p*-nitro- to *p*-amino-benzoic acid. P. H. Ravenscroft, R. W. Lewis, and O. W. Brown (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 2, 11—17).—*p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ (I) is reduced to *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (II) in yields of 98—98·5% using, *e.g.*, a Sn cathode, a catholyte consisting of 500 c.c. of 14·1 wt.-% HCl, 5 g. of (I), 3—5 g. of $SnCl_2,2H_2O$, and a c.d. of 8 amp. per sq. dm. at 70°. Temp., acid concn., and c.d. must be controlled so that $Sn^{\cdot\cdot}$ ions remain in solution until sufficient current to reduce (I) has passed. With a Pb cathode at 70°, a c.d. of 6 amp. per sq. dm., a catholyte consisting of 500 c.c. of 8·7 wt.-% HCl, and 5 g. of (I) 94—95% yields of (II) were obtained. (II) was separated by neutralisation of its hydrochloride with NaOH to the isoelectric point. H. Sch.

Electrolytic reduction of aromatic trinitro-compounds to triamines by use of a carrier catalyst. R. W. Lewis and O. W. Brown (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 1, 1—9).—A $SnCl_2$ carrier-catalyst was employed in the electrolytic reduction of 1 : 2 : 4 : 6-$C_6H_3R(NO_2)_3$ (I) (R = CO_2H, OH, Me) to the $C_6H_3R(NH_2)_3$ (II). The method has several advantages over the method using a Pb cathode. The best conditions for complete reduction to (II) are: a Sn cathode, a catholyte (total vol. 500 c.c.) of 1 : 1 (vol.) HCl containing respectively 3·95, 4·43, or 4·47 g. of $SnCl_2,2H_2O$, and (usually) 5 g. of (I), a c.d. of 7—8 amp. per sq. dm., and a temp. of 35°. Yields and current efficiencies under these conditions are 93—97%. To obtain high yields of (II) temp., acid concn. of the catholyte, and c.d. must be controlled so that the $Sn^{\cdot\cdot}$ ions remain in solution until sufficient current to reduce (I) has passed. The $Sn^{\cdot\cdot}$ ions are mainly responsible for the reduction. H. Sch.

Electrolytic reduction of cinnamic acid. New preparative method for *βγ*-diphenyladipic acid. C. L. Wilson and K. B. Wilson (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 4, 25—35; cf. B., 1943, II, 276).—Reduction of $CHPh{:}CH{\cdot}CO_2H$ (I) at a Hg cathode in aq. H_2SO_4 in presence of a H_2O-sol. org. solvent (*e.g.*, EtOH) gives <10% of $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$, ~45% (55% under most favourable conditions) of a ~1 : 1 mixture of *meso-* (II) (Me_2 ester, m.p. 166—168°) and *dl-* (III) -$(CHPh{\cdot}CH_2{\cdot}CO_2H)_2$, and ~45% of a partly reduced polymer (IV) which seems to be formed by union of 2 or more mols. of (I) with reduction of some of the CO_2H groups. The yield of (II) + (III) is not materially altered when (I) is replaced by its Et ester, and is highest when $OH{\cdot}[CH_2]_2{\cdot}OEt$ and $NMe_2{\cdot}CHO$ are added to the catholyte. (IV), readily separated by its solubility in cold C_6H_6, is a viscous liquid, equiv. ~300 [*i.e.*, 1 CO_2H to 2 mols. of (I)]. With 85% H_2SO_4 at 100°, (II) and (III) give the known *trans-* and *cis-*diketohexahydrochrysene, respectively. Similar reduction of *o*-$C_6H_4Cl{\cdot}CH{:}CH{\cdot}CO_2H$ gives *βγ-di-o-chlorophenyladipic acid*, forms, m.p. 301—307° and 197—200°. *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$ affords *dianisyladipic acids*, m.p. 257—258° and 178—180°. Reduction of *o*-$CN{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$ in presence of 30% H_2SO_4 gives (probably) *di(cyanophenyl)adipic acid*, m.p. 310—314° (decomp.), and (probably) *β-o-carbamylphenylpropionic acid* (V), m.p. 173—174°. In 25% H_2SO_4 only (V), m.p. 176—178°, is formed. 10% NaOH converts (V) at 100° into *β-o*-carboxyphenylpropionic acid. The viscous reduction product of *m*-$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$ gives after methylation mixed di-*m*-anisyladipic acids (form, m.p. 247—250°, isolable). H. Sch.

Addition of maleic anhydrides to substituted styrenes. M. Lora Tamayo (*Anal. fís. quím.*, 1943, **39**, 209—214).—Differences between the adduct of $(CH{\cdot}CO)_2O$ and anethole previously obtained (A., 1941, II, 134) and that of Hudson and Robinson (A., 1942, II, 53) are attributed to differences in experimental conditions. F. R. G.

Condensation of *n*-alkylsuccinic anhydrides with anisole. S. U. Mehta, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1943, **12**, A, Part 3, 64—65).—Anhyd. $AlCl_3$ is added gradually to a mixture of the *n*-alkylsuccinic anhydride and PhOMe in $PhNO_2$ at >40°; after 4 hr. at room temp. the mixture is decomposed with ice and HCl. Thus are obtained: *α-p*-methoxyphenacyl-propionic acid, m.p. 141° (*Me*, b.p. 173—180°/18 mm., and *Et*, b.p. 190°/30 mm., ester), *-butyric acid*, m.p. 108—109° (*semicarbazone*, m.p. 155°; *Me* ester, m.p. 56—57°), *-valeric acid*, m.p. 88—89° (*semicarbazone*, m.p. 145°), *-heptoic acid*, m.p. 80° (*semicarbazone*, m.p. 135°; *Me* ester, m.p. 41—42°), *-octoic acid*, m.p. 92° (*semicarbazone*, m.p. 142°), *-hexadecoic acid*, m.p. 99—100° (does not form a semicarbazone; *Me* ester, m.p. 45°), and *-octadecoic acid*, m.p. 85—86° (*semicarbazone*, m.p. 170—171°; *Me*, m.p. 38—39°, and *Et*, m.p. 41—42°, ester). H. W.

Preparation of derivatives of 2 : 2-dialkyl*cyclo*hexanone. A. J. Birch (*J.C.S.*, 1943, 661—662; cf. Johnson, A., 1943, II, 330).—2-Methyl*cyclo*hexanone, piperonal (I), and EtOH–NaOEt at room temp. for 4 days afford 6-*piperonylidene-*2-*methyl*cyclo*hexanone*, m.p. 74—75°, converted by $NaNH_2$ in boiling PhMe, followed by MeI, into 6-*piperonylidene-*2 : 2-*dimethyl*cyclo*hexanone*, m.p. 67° [also obtained from 2 : 2-dimethyl*cyclo*hexanone and $NaNH_2$ in boiling C_6H_6 followed by (I)], or by $NaNH_2$–C_6H_6, then EtI, into 6-*piperonylidene-*2-*methyl-*2-*ethyl*cyclo*hexanone*, m.p. 60—61°. A. T. P.

Condensation of ethylene oxide with cyclic β-keto-esters.—See A., 1944, II, 70.

Ionone. I. Cleavage of ethyl ionylideneacetate. H. Sobotka, (Miss) E. Bloch, and D. Glick (*J. Amer. Chem. Soc.*, 1943, **65**, 1961—1963).—*α-* and *β-*Ionone give, by the method of Karrer *et al.* (A., 1932, 852; 1933, 605), probably the same Et ionylideneacetate, b.p. 155°/1 mm., which, by distillation of the derived Ba salt with $(HCO_2)_2Ba$ and SiO_2 or soft glass at 150°/2 mm., gives *α-*ionone (2 : 4-dinitrophenyl-, m.p. 143°, and *p*-chlorobenzoyl-hydrazone, m.p. 214—215°; phenylsemicarbazone, m.p. 183—184°) (cf. Heilbron *et al.*, A., 1935, 978; 1936, 983). *β-*Ionone-2 : 4-dinitrophenyl-, m.p. 125—127°, and *-p*-chlorobenzoyl-hydrazone, m.p. 218—219°, and -phenylsemicarbazone, m.p. 160—162°, are described. R. S. C.

Electrolytic production of benzoquinone and quinol.—See B., 1944, II, 6.

IV.—STEROLS AND STEROID SAPOGENINS.

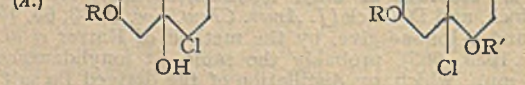
Water-soluble derivatives of vitamin-*D*.—See B., 1944, III, 19.

Minor sterols of yeast. XII. Hydrogenation of sterols. H. Wieland and W. Benend [with, in part, F. Rath] (*Annalen*, 1943, **554**, 1—8).—Further evidence is adduced in favour of the view that

catalytic hydrogenation of poly-unsaturated sterols occurs in such a manner that the saturation of reactive double linkings is accompanied by a displacement of the inert double linking also present. This retains its passive character and is displaced from $\Delta^{7:8}$, $\Delta^{8:9}$, or $\Delta^{9:11}$ to $\Delta^{8:14}$. *iso*Dehydrocholesterol is hydrogenated (Pt in AcOH) to α-cholestenol, m.p. 119—120° (acetate, m.p. 77—78°), also obtained in presence of Pd–C in EtOAc, whereas with Pt in EtOAc the product is δ-cholestenol, m.p. 120°, $[\alpha]_D^{20}$ +11° (acetate, m.p. 107—108°, $[\alpha]_D^{20}$ +12·5°). 7-Dehydrocholesteryl benzoate is hydrogenated (Pt in EtOAc) to γ-cholestenyl benzoate, m.p. 157°, clear at 176°. Ergosteryl benzoate (**I**) is hydrogenated (PtO_2 in EtOAc) to γ-ergostenyl benzoate (**II**), m.p. 179°, $[\alpha]_D^{20}$ ±0°, hydrolysed (KOH–MeOH) to γ-ergostenol (**III**), m.p. 148°, $[\alpha]_D^{20}$ ±0° [acetate, m.p. 160°, also obtained (m.p. 158°) by hydrogenation (Pt in EtOAc) of γ-ergosteryl acetate]; under somewhat different conditions (**I**) is converted (PtO_2 in EtOAc) into γ-dihydroergosteryl benzoate (**IV**), m.p. 193—195°, $[\alpha]_D^{20}$ −8° in $CHCl_3$, hydrolysed to γ-dihydroergosterol (**V**), m.p. 173—175°, $[\alpha]_D^{20}$ −21° in $CHCl_3$ (acetate, m.p. 180—181°, $[\alpha]_D$ −21° in $CHCl_3$. (**V**) is hydrogenated (Pt in EtOAc) to (**III**), m.p. 145—146°, also obtained by use of Na in EtOH; similarly (**IV**) is hydrogenated to (**II**). The transition of ascosterol into fæcosterol appears exceptional. H. W.

Sterol group. XLV. Investigation of the homogeneity of sitosterol by oxidation with the Oppenauer reagent. D. H. R. Barton and E. R. H. Jones (*J.C.S.*, 1943, 599—602; cf. A., 1942, II, 286).—Oppenauer oxidation, followed by chromatographic analysis of the ketones, is of great val. for examining the homogeneity of sitosterols, and in particular for determining the approx. proportion of sitostanol. It provides a convenient criterion of purity and may be generally applicable in the steroid series. Tall-öl sitosterol (**I**), m.p. 137—138°, after oxidation (Oppenauer) and chromatographic analysis (large columns; adsorbent : adsorbate : : 100 : 1) thus affords 66% of sitostenones, mainly Δ^4-β-sitostenone (**II**), new m.p. 88° [oxime, m.p. 175·5°; semicarbazone, m.p. 250° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 253° (decomp.)], and a little of a closely-related sitostenone, m.p. 86°; 3·2% of unidentified ketone (**III**) (mainly αβ-unsaturated), m.p. ~115°, and 3·8% of unoxidised (**I**) are also isolated. Similar treatment of sitosterol (**IV**), m.p. 137—138°, from wheat-germ oil gives sitostenones (69·5%) [mainly (**II**)], triacontane (0·3%) [also isolable from (**IV**)], (**III**) (1·8%), and recovered (**IV**) (1·5%). The small amount of sitostanol present in (**I**) and (**IV**) is oxidised to sitostanone, m.p. 157° [2 : 4-*dinitrophenylhydrazone*, m.p. 223° (decomp.)] [2·5% or 5·9% from (**I**) or (**IV**), respectively]. A. T. P.

β-Cholesterol oxide. R. A. Baxter and F. S. Spring (*J.C.S.*, 1943, 613—615).—Oxidation [BzO_2H or o-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ (cf. Chakravorty *et al.*, A., 1943, II, 58)] of cholesteryl benzoate gives a mixture of the α-benzoate oxide, m.p. 168—169°, and "αβ-cholesteryl benzoate oxide" (**I**), m.p. 150—151°, $[\alpha]_D^{20}$ +3·6° (all vals. in $CHCl_3$) (previously described as the β-derivative; A., 1939, II, 477). (**I**) is hydrolysed to "αβ-cholesterol oxide" (**II**), m.p. 107—108°, $[\alpha]_D^{21}$ −15° (previously described by many investigators as the β-oxide), and the suggestion of Hattori (*J. Pharm. Soc. Japan*, 1940, **60**, 334) that it is a 1 : 1 mixed crystal of α-cholesterol oxide (**III**) and β-cholesterol oxide (**IV**) is confirmed; (**IV**), m.p. 131—132°, $[\alpha]_D^{18\cdot5}$ +11·5° [acetate (**V**), m.p. 111°, $[\alpha]_D^{18}$ ±0°; *benzoate* (**VI**), m.p. 172—173°, $[\alpha]_D^{22}$ +16°], identical with the (**IV**), m.p. 136°, of Hattori, is isolated from the mother-liquors of (**II**). (**II**) can be prepared from equal parts of (**III**) and (**IV**) in MeOH. Vals. of [α] indicate that (**I**) is a 1 : 2 mixed crystal of the α-benzoate oxide and (**VI**). Fission of (**III**) and its derivatives with HCl affords solely chlorohydrins of type *A*. Fission of (**II**) and its derivatives is more complicated. (**II**) or (**I**) and BzCl–C_5H_5N at 100° (bath) give



5-chloro-3 : 6-dibenzoyloxycholestane, m.p. 183—184° (type *B*; R = R′ = Bz); with (**II**), some 6-chloro-5-hydroxy-3-benzoyloxycholestane (*A*; R = Bz) is also formed. In contrast to the results of Chakravorty *et al.* (*loc. cit.*), αβ-cholesteryl acetate oxide (**VII**) affords 5-*chloro*-6-*benzoyloxy*-3-*acetoxycholestane* (**VIII**), m.p. 176°, $[\alpha]_D^{22}$ −75·8°, and a little 6-chloro-5-hydroxy-3-acetoxycholestane (**IX**), m.p. 186—187°. (**VII**) and HCl in $CHCl_3$ affords 5-chloro-6-hydroxy-3-acetoxycholestane (**X**), new m.p. 190—191° (cf. Hattori) (*B*: R = Ac, R′ = H), and (**IX**), whereas interaction with HCl–EtOH gives 5-chloro-3 : 6-dihydroxycholestane, m.p. 171°, $[\alpha]_D^{19}$ −22·5° (*B*; R = R′ = H), the latter being formed also from (**II**) and HCl in $CHCl_3$ or EtOH. Fission of (**IV**) and its derivatives affords chlorohydrins of type *B* in ~90% yield. With BzCl–C_5H_5N, (**VI**) gives 5-chloro-3 : 6-dibenzoylcholestane, and (**V**) yields (**VIII**). With HCl in $CHCl_3$, (**V**) gives (**X**). A. T. P.

Œstradiol derivatives.—See B., 1944, III, 17.

Steroid ketones.—See B., 1944, III, 17, 18.

Sterol group. XLVI. Isolation of a new form of Δ^4-cholestenone. D. H. R. Barton and E. R. H. Jones (*J.C.S.*, 1943, 602—603; cf., A., 1942, II, 286).—Oppenauer oxidation of cholesterol and careful chromatographic analysis of the product gives Δ^4-cholestenone in two interconvertible forms, m.p. 88° and 82°, both $[\alpha]_D^{20}$ +92·2° in $CHCl_3$ (cf. lit.), which afford the same semicarbazone and 2 : 4-dinitrophenylhydrazone. Vals. of [α] and light-absorption intensities of both forms are slightly > those previously recorded. A. T. P.

VI.—HETEROCYCLIC.

Derivatives of furfuraldehyde; determination of their physicochemical constants. H. Paillard and R. Szasz (*Helv. Chim. Acta*, 1943, **26**, 1856—1861).—Appreciable amounts of tetrahydrofurfuraldehyde (**I**) are not obtained from tetrahydrofurfuryl alcohol (**II**) by catalytic dehydrogenation (Bouveault) at 270—450°, by oxidation by air in xylene containing quinoline, m-$C_6H_4(NO_2)_2$, or finely-divided Cu, by SeO_2 or N_2O_4, by CrO_3, by O_3, or by electrolytic oxidation. Treatment of tetrahydrofurfuryl chloride, b.p. 149—150°/720 mm., with $Pb(NO_3)_2$ or hydrolysis of tetrahydrofurfurylidene chloride does not afford (**I**). (**II**) is converted by Na and the requisite alkyl halide into *tetrahydrofurfuryl* iso*butyl*, b.p. 65—67°/8 mm., n-*amyl*, b.p. 89—91°/12 mm., n-*heptyl*, b.p. 122—124°/12 mm., n-*octyl*, b.p. 139—142°/12 mm., *phenyl*-n-*propyl*, b.p. 165—167°/12 mm., and *cinnamyl*, b.p. 182—183°/13 mm., *ether*. (**II**), Na, and PrβBr afford propylene whilst resins are derived from NaOPrβ and tetrahydrofurfuryl bromide. *d*, *n*, surface tension, parachor, and dielectric const. are recorded for the ethers. H. W.

Condensation of phenols with αβ-unsaturated aldehydes. E. Adler and S. Tingstam (*Arkiv Kemi, Min., Geol.*, 1943, **16**, **B**, No. 18, 7 pp.).—Addition of CH_2:CH·CHO (1 mol.) slowly (15 hr.) to o-4-xylenol (**I**) in glacial AcOH at 5° in presence of a trace of HCl yields an alkali-insol. compound, m.p. 185° (not investigated further), and 1-(2′ : 4′-*dimethylphenoxy*)-2 : 4 : 6-*trimethyl*-1 : 2-*dihydrobenzfuran* (**II**), m.p. 89°. The constitution of (**II**) follows from its insolubility in alkali, stability to Ac_2O–C_5H_5N, Br, and $KMnO_4$, and its conversion on Zn-dust distillation into (**I**) and 2 : 4 : 6-trimethylbenzfuran (**III**). (**II**) with hot conc. HBr–AcOH yields (**I**), much resin, and traces of (probably) (**III**). M. H. M. A.

Synthesis of cantharidin. (Miss) K. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Current Sci.*, 1943, **12**, 256—257).—CMeAcNa·CO_2Et and I afford Et_2 αα′-diacetyl-αα′-dimethylsuccinate, which is brominated and then converted by mol. Ag into Et_2 3 : 6-diketo-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylate (**I**). Clemmensen reduction of (**I**) followed by hydrolysis affords deoxycantharidin. Reduction of (**I**) by $Al(OPr^{\beta})_3$ followed by etherification and hydrolysis by H_2SO_4 yields cantharidin, m.p. 217°, identical with a sample obtained from *Mylabris pustulata* (cf. Woodward *et al.*, A., 1942, II, 142). No experimental details are given. H. W.

Steric isomerides of α-tocopherol. P. Karrer and H. Rentschler (*Helv. Chim. Acta*, 1943, **26**, 1750—1758).—(−)-Phytyl bromide and trimethylquinol (**I**) afford [$C_{(2)}$-dl, $C^*_{(\delta)}C^*_{(\theta)}$-l]-α-*tocopherol* (**II**), which is sterically homogeneous at $C_{(\delta)}$ and possibly at $C_{(\theta)}$ but racemic at $C_{(2)}$. It gives an *allophanate*, m.p. 192°, and a non-cryst. *acetate*. Attempted resolution of (**II**) by means of 3-bromo-*d*-camphor-7′-sulphonyl chloride does not give decisive results. The compound obtained from (**I**) and natural *d*-phytol is possibly optically homogeneous with respect to $C_{(\delta)}$ and $C_{(\theta)}$ and racemic with respect to $C_{(2)}$, and hence is designated [$C^*_{(2)}dl$, $C^*_{(\delta)}C^*_{(\theta)}$-*d*]-α-tocopherol. (**II**) and the product from (**I**) and synthetic *dl*-phytol is racemic with respect to all three asymmetric C and hence is termed [$C^*_{(2)}dl$, $C^*_{(\delta)}C^*_{(\theta)}$-*dl*]-α-tocopherol (**III**). Optical activity cannot be detected in (**I**) and (**II**) or its acetate and no differences are observed in the m.p. of the allophanates, dinitrobenzoates, and p-nitrophenylurethanes of (**I**), (**II**), and (**III**). The physiological activities of (**I**), (**II**), (**III**), and natural α-tocopherol (**IV**) are identical within the limits of experimental error. The sole marked difference between the physical properties of (**IV**) and (**I**), (**II**), and (**III**) is the m.p. of the allophanate (161—162° and 172—173° respectively). Reply is made to John (A., 1942, II, 421). H. W.

Halogenated 1 : 3-dioxans.—See B., 1944, II, 6.

Dioxan derivatives.—See B., 1944, II, 35.

Ethyl 4-phenyl-1-methylpiperidine-4-carboxylate.—See B., 1944, II, 35.

2 : 4-Diarylpyrroles. I. Synthesis of 2 : 4-diarylpyrroles and 2 : 2′ : 4 : 4′-tetra-arylazadipyrromethines. II. Methines. III. 3-Amino-2 : 4-diphenylpyrrole. M. A. T. Rogers (*J.C.S.*, 1943, 590—596, 596—597, 598—599).—I. γ-Nitro-β-phenylbutyrophenone with HCO_2NH_4 at 180—190° gives some 2 : 4-*diphenylpyrrole* (**I**), m.p. 178—179°, and 2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine* (**II**), m.p. 287—288°, a deep blue substance containing a new chromo-

phoric system. Compounds similarly prepared are: 2 : 2′-*diphenyl*-4 : 4′-*di*-(m-*nitrophenyl*)-, m.p. 330°, from *γ-nitro*-β-(m-*nitrophenyl*)-*butyrophenone*, m.p. 74—77°; -(m-*hydroxyphenyl*)-, m.p. 304—306°, from *γ-nitro*-β-(m-*hydroxyphenyl*)*butyrophenone*, m.p. 96—98°; -(p-*dimethylaminophenyl*)-, m.p. 276—278° (*dimethiodide*), from *γ-nitro*-β-(p-*dimethylaminophenyl*)*butyrophenone*, m.p. 114—115° (*oxime*, m.p. 121—123°); -(3 : 4-*methylenedioxyphenyl*)-, m.p. 258—259°; and -(p-*acetamidophenyl*)-, m.p. ~370°, from β-*benzoyl*-α-(p-*acetamidophenyl*)*propionitrile*, m.p. 163—164·5°; 4 : 4′-*diphenyl*-2 : 2′-*di*-p-*anisyl*-, m.p. 239—242°, from *γ-nitro*-β-*phenyl*-p-*methoxybutyrophenone*, m.p. 92—93°; 2 : 2′-*diphenyl*-4 : 4′-*di*-p-*anisyl*-, m.p. 288—290°, from *γ-nitro*-β-p-*anisylbutyrophenone*, m.p. 66°; and 2 : 2′ : 4 : 4′-*tetra*-p-*anisyl*-*azapyrromethine*, m.p. 281—282°. Metal complexes of certain of the compounds are described, *e.g.*, *Cu*, *Co*, *Ni*, and *Zn bis*-(2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine*). Se-dehydrogenation of 2 : 4-diphenylpyrrolidine affords (I). Reduction (H_2–Ni) of β-*p*-anisoyl-α-phenylpropionitrile yields 4-*phenyl*-2-p-*anisyl*-*pyrroline*, b.p. 235—250°, m.p. 74—75° (*picrate*, m.p. 180—181°), dehydrogenated (Se) to the *-pyrrole*, m.p. 205—207°. 2-*Phenyl*-4-p-*anisyl*-*pyrroline*, b.p. 232—238°/7 mm., s.p. 27° (*picrate*, m.p. 156—158°), and *-pyrrole* (III), m.p. 197—199°, are similarly obtained. Nitrosation (HCl–$NaNO_2$) of (I) leads to 5-*nitroso*-2 : 4-*diphenylpyrrole* (IV), m.p. 139—140° [*hydrochloride*, m.p. 190° (decomp.); *picrate*, m.p. 188° (decomp.)], which is reduced (H_2–PtO_2) to the 5-NH_2-compound, m.p. 155—156° (*Ac* derivative, m.p. 171—172°). 5-*Nitroso*-2-*phenyl*-4-p-*anisyl*- (V) [*base*, m.p. 176—177° (decomp.)], and -4-*phenyl*-2-p-*anisyl*-*pyrrole hydrochloride* (+MeOH), decomp. 170°, are similarly prepared. Condensation of (I) and (IV) in AcOH–Ac_2O leads to (II), and 2 : 2′ : 4-*triphenyl*-4′-p-*anisylazadipyrromethine*, m.p. 256—257°, is obtained from (IV) and (III) or (I) and (V). Degradation of (II) by 55% HI gives (I); the solution of (II) in moist dioxan, C_5H_5N, or OH·$[CH_2]_2$·OEt is reduced by $NaHSO_3$ to a nearly colourless leuco-compound, readily reoxidised to (II) by air. *γ-Nitro*-β-*phenyl*-*hexophenone*, m.p. 156—158°, and *-butyrophenoneoxime*, m.p. 108—110°, are also described.

II. CH(OEt)$_3$ and (I) in AcOH give 2 : 2′ : 4 : 4′-*tetraphenyldipyrromethine* (VI), m.p. 284—286° (*Cu bis*-complex, 2 methine = 1 Cu). HCO·NPhMe, $POCl_3$, and (I) yield 2 : 4-*diphenylpyrrole*-5-*aldehyde*, m.p. 187—188° [*oxime*, m.p. 202° (slow decomp.); p-*nitrophenylhydrazone*, m.p. 241—242°], which gives α-(2 : 4-*dinitrophenyl*)-β-(2 : 4-*diphenyl*-5-*pyrrolyl*)*ethylene*, m.p. 254—255°, with 1 : 2 : 4-$C_6H_3Me(NO_2)_2$]; condensed with (I) it affords (VI) and is reduced (Ni–H_2) to the -5-*carbinol*, m.p. ~170° (decomp.). 2-*Phenyl*-4-p-*anisylpyrrole*-5-*aldehyde*, m.p. 158—159° (*oxime*, m.p. 196—198°, mixture of *syn*- and *anti*-forms), similarly prepared, with (III) yields 2 : 2′ : 4-*triphenyl*-4′-p-*anisyldipyrromethine*, m.p. 240—247°. $CPhCl_3$ and (I) in AcOH give 2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine*, m.p. 268—270°, the *Cu* complex of which contains 1 methine = 1 Cu.

III. The blue compound obtained by Gabriel (cf. A., 1908, i, 464) from 3-amino-2 : 4-diphenylpyrrole (VII) and PhCHO in air is shown to be 3 : 3′-*dibenzylideneamino*-2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine*. Benzoylation of (VII) affords the 3-NHBz-compound (VIII) and a red compound, 3 : 3′-*dibenzamido*-2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine*, m.p. 345° (decomp.), also obtained from (VIII) and $CPhCl_3$. F. R. S.

2-Halogeno-5-sulphanilamidopyridines.—See B., 1944, III, 18.

Pyridine derivatives.—See B., 1943, III; 303; 1944, II, 6.

Nitration of isatin. W. C. Sumpier and W. F. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 1802—1803).—By the methods of Baeyer (A., 1879, 938), Rupe *et al.* (A., 1924, i, 764), or Calvery *et al.* (A., 1926, 187), isatin gives the 5-NO_2-derivative (85%), m.p. 254—255° [phenylhydrazone, m.p. 295° (lit., 284°, 286°)], the structure of which is proved by oxidation by H_2O_2–NaOH–H_2O to 5 : 2 : 1-NO_2·$C_6H_3(NH_2)$·CO_2H (86%), m.p. 278° (decomp.) (Ac derivative, m.p. 221°) (cf. Rupe *et al.*, A., 1926, 843). R. S. C.

Benzoylated derivatives of indigotin. VII. H. de Diesbach, G. Rey-Bellet, and T. S. Klang (*Helv. Chim. Acta*, 1943, **26**, 1869—1885).—2-*o*-Carboxyphenylquinoline-4-carboxylic acid is reduced (Na–Hg) in alkaline solution to the *lactam* (I), m.p. 239°, of 2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (*Me* ester, m.p. 175°), decarboxylated to 2-*o*-*carboxyphenyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 140°, and oxidised by CrO_3 in AcOH to the *lactam* (II), m.p. 168°, of 4-keto-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline (*phenylhydrazone*, m.p. 222°; *CHPh* derivative, m.p. 228°; unstable 3-*Br*-compound, m.p. 257°). This is converted into the *lactam* (III), m.p. 267°, of 4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline by heating with Se, SeO_2, or S, by treatment with PCl_5, and by bromination in $CHCl_3$ followed by removal of a mol. of HBr by boiling with C_5H_5N. This compound is not identical with that obtained by Hope *et al.* (A., 1933, 1060) by degradation of Höchst-yellow R, thus disproving the constitution assigned to this dye and also to Höchst-yellow U. Alternatively (III) is obtained by condensing *o*-NH_2·C_6H_4·COMe with *o*-$C_6H_4(CO)_2O$ to *o*-*phthaloylamidoacetophenone*, m.p. 135°, which is heated with P_2O_5 at 160°. (III) is transformed by alkali into 4-*keto*-2-*o*-*carboxyphenyl*-1 : 4-*dihydroquinoline*, m.p. 263° (recyclisation) (*Me* ester, m.p. 314°). (III) is converted by Br in boiling $CHCl_3$ into a *perbromide*, also formed in AcOH, in which it passes on prolonged treatment into the *lactam*, m.p. 233°, of 3-bromo-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline. (III) is converted by P_2S_5 in boiling C_6H_6 into the *lactam*, m.p. 253—254°, of 4-thio-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline, which with excess of NHPh·NH_2 in boiling C_5H_5N affords a *phenylhydrazone*, $C_{22}H_{15}ON_3$, m.p. 224—225°; Hope's degradation product does not react with P_2S_5. (I) is converted by Br in AcOH at 100° into the *lactam*, m.p. 257°, of *x*-bromo-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, oxidised by $KMnO_4$ in alkaline solution to *o*-$C_6H_4(CO_2H)_2$ and oxidised by CrO_3 in AcOH to the *lactam* (IV), m.p. 202°, of *x*-bromo-4-keto-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline (phenylhydrazone, m.p. 247—248°; *CHPh* derivative, m.p. 231—232°). (IV) is converted by Br in hot $CHCl_3$ followed by C_5H_5N into the *lactam*, m.p. 261°, of *x*-bromo-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydropyridine, showing that Br is not attached to $C_{(2)}$ of the quinoline nucleus; in AcOH this gives a perbromide which gradually passes into the *lactam*, m.p. 272°, of *x* : 3-dibromo-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline. (I) is converted by short ebullition with HNO_3 (*d* 1·4) into the *lactam*, m.p. 260° (decomp.), of *x*-nitro-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, oxidised by CrO_3 in AcOH to the (?) *lactam*, m.p. 309—310°, of *x*-nitro-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline and a substance which gives a *phenylhydrazone*, $C_{22}H_{18}O_3N_4$, m.p. 264°. (II) and boiling HNO_3 (*d* 1·4) yield the *lactam*, m.p. 253°, of 3-nitro-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline. (II) is converted by boiling KOH–MeOH into a (?) *polymeride*, m.p. 310°. With *o*-NO_2·C_6H_4·CHO and a little piperidine at 170° (II) gives the *o-nitrobenzylidene* derivative, m.p. 262°, which could not be satisfactorily reduced by Zn, Sn, or $SnCl_2$ in acid solution or by Zn–Hg. Condensation with *o*-NHAc·C_6H_4·CHO leads to the *o-acetamidobenzylidene* compound, m.p. 283°, hydrolysed and decyclised by boiling conc. HCl to the *compound*, $C_{23}H_{18}O_3N_2,H_2O$, m.p. 185°. With *o*-NH_2·C_6H_4·CO_2H at 170° (II) gives a polymerised *product*, $C_{32}H_{16}O_3N_2$, m.p. >360°, analogous to the product, $C_{32}H_{20}O_2N_2$, m.p. 375°, obtained from (I) and S at 375°. H. W.

Steric factors in quaternary salt formation. W. G. Brown and S. Fried (*J. Amer. Chem. Soc.*, 1943, **65**, 1841—1845).—Methiodides and ethiodides of *N*-methyl-indoline and -tetrahydroquinoline at 45° are formed much faster than those of *N*-methyltetrahydrohomo*iso*-quinoline. Hindrance thus occurs when the two rings are not planar. Similarly, with monocyclic bases there is hindrance when the groups attached to the C_6H_6 ring cannot assume co-planarity with it; thus, the relative effects of substituents reported by Evans *et al.* (A., 1939, I, 527) are the same as their effectiveness in preventing free rotation in the Ph_2 series; also formation of *o*-$C_6H_4Bu^{\gamma}$·NMe_3I is very slow. Attack of the RI occurs at the free electrons and is easier if these are exposed. Relative rates of formation of methiodides of 2 : 6 : 1-$C_6H_3Me_2$·NMe_2, 4 : 3 : 1-NO_2·C_6H_3Me·NMe_2, m.p. 83°, 2-*nitro*-NN-*dimethyl*-m-5-*xylidine* (Me = 1; prep. from the Br-compound by $NHMe_2$ at 100—120°), m.p. 111°, are inconclusive: *E* and log *PZ* are also recorded. R. S. C.

Aminoacridines: some partition and surface phenomena. A. Albert, R. Goldacre, and E. Heymann (*J.C.S.*, 1943, 651—654).—The results obtained from measurements of oil–H_2O partition coeffs. and air–H_2O surface activities of a no. of aminoacridines suggest that marked oleophilic and surface-active properties are unnecessary for, and if present in high degree are inimical to, the development of good antiseptic properties in this series. The following are described: 2-*chloro*-5-*amino*-7-*methoxyacridine*, m.p. 271°, and the *hydrochlorides* of 5-*butyl*-, m.p. 189—190°, -cyclo*hexyl*-, m.p. 271°, *-heptyl-* (+H_2O), m.p. 106°, *-dodecyl-* (+H_2O), m.p. 92°, and *-hexadecyl-aminoacridine* (+H_2O), m.p. 99—100°. F. R. S.

***N*-Substituted 6-chloro-9-amino-2-methoxyacridines.** J. H. Burckhalter, E. M. Jones, W. F. Holcomb, and L. A. Sweet (*J. Amer. Chem. Soc.*, 1943, **65**, 2012—2015).—CH_2:CH·CN and the appropriate amine at the b.p. or 100°/>1 atm. give β-*di*-n- (90%), b.p. 104—105°/10 mm., and -iso-*propyl*- (12%), b.p. 100—102°/13 mm., and β-*di*-n- (96%), b.p. 127—131°/11 mm., and -iso-*butyl*- (51%), b.p. 116—117°/10 mm., β-n-*amyl*- (88%), b.p. 112—113°/10 mm., β-*di*-n-*octyl*- (80%), b.p. 180—182°/2 mm., β-*di*-β′-*ethyl*-n-*hexyl*- (65%), b.p. 163—164°/2 mm., β-ethyl-β′-hydroxyethyl- (72%), b.p. 133—134°/7 mm. (*picrate*, m.p. 72—74°), and β-*N*-β′-hydroxyethyl-*N*-*n*-butyl- (61%), b.p. 147—148°/7 mm. (*picrate*, m.p. 62—63°), *-propionitrile*. The following are recorded: γ-di-*n*-, b.p. 91—93°/15 mm. (*dipicrate*, m.p. 180—181°), and -*iso*-propyl-, b.p. 98—99°/15 mm. [*dipicrate*, m.p. 211—213° (decomp.)], γ-di-*n*-, b.p. 121—123°/16 mm. (*dipicrate*, m.p. 182—184°), and -*iso*-butyl-, b.p. 104—108°/10 mm. [*dipicrate*, m.p. 190—192° (decomp.)], γ-*n*-amyl-, b.p. 102—103°/15 mm. (*dipicrate*, m.p. 173—174°), γ-ethyl-β′-hydroxyethyl-, b.p. 130—131°/15 mm., and γ-*N*-β′-hydroxyethyl-*N*-*n*-butyl-*n*-propylamine, b.p. 147—148°/15 mm. *o*-$C_6H_4(CO)_2N$·$[CH_2]_2$·Br and *p*-NH_2·C_6H_4·NMe_2 at 120—130° give N-γ-p-*diethylaminoanilino*-n-*propylphthalimide*, m.p. 106—107°, converted by 85% N_2H_4,H_2O in boiling EtOH into *p*-NEt_2·C_6H_4·NH·$[CH_2]_3$·NH_2, an oil. 6 : 9-Dichloro-2-methoxyacridine and the appropriate diamine, some-

times with K_2CO_3, in PhOH at 100° give 6-chloro-9-γ-di-*n*- (45%) [*dihydrochloride*, $+H_2O$, m.p. 228—229° (decomp.)], and -*iso*-propyl- (62%) [*dihydrochloride*, $+H_2O$, m.p. 227—230° (decomp.)], -9-γ-di-*n*- (50%) (*dihydrochloride*, $+H_2O$, m.p. 200—201°), and -*iso*-butyl- (73%) [*dihydrochloride*, $+H_2O$, m.p. 219—221° (decomp.)], -9-γ-n-*amyl*- (65%), m.p. 90—91°, -9-γ-di-*n*-amyl- (63%) (*dihydrochloride*, $+H_2O$, m.p. 165—166°), -9-γ-ethyl-β′-hydroxyethyl- (65%) [*dihydrochloride*, $+H_2O$, m.p. 246—247° (decomp.)], -9-γ-*N*-β′-hydroxyethyl-*N*-*n*-butyl- (53%) (*dihydrochloride*, $+H_2O$, m.p. 180—182°), -9-γ-*p*-diethylaminoanilino- (79%) [*dihydrochloride*, m.p. 185° (decomp.)], -9-γ-β′-diethylaminoethoxy- (40%) [*dihydrochloride*, $+H_2O$, m.p. 221—222° (decomp.)], -9-γ-2′-*amino*-4′-*pyrimidylamino*- (75%), m.p. 221—222°, -9-γ-6′-methoxy-8′-quinolylamino- (76%) [*dihydrochloride*, $+H_2O$, m.p. 241—242° (decomp.)], -9-γ-6′-*chloro*-2′-*methoxy*-9′-*acridylamino*- (72%), m.p. 189—190° (decomp.), and -9-γ-6′-*chloro*-2′-*methoxy*-9′-*acridylamino*-ββ-*dimethyl*- (60%), $+H_2O$, m.p. 112—113°, -*propylamino*-2-*methoxyacridine*, 6-chloro-9-β-hydroxyethyl- (55%), m.p. 201—202° (lit., 191—192°), -9-β-chloroethyl- (64%) [*hydrochloride*, m.p. 265° (decomp.)], -9-*carboxymethyl*- (58%), m.p. 248° (decomp.), -9-3′-*pyridyl*- (57%), $+H_2O$ (lost at 150°), m.p. 202—203° (decomp.), -9-ζ-2′-*amino*-4′-*pyridylamino*-n-*hexyl*- (80%), m.p. 217—220° (decomp.), -9-δ-6′-methoxy-8′-quinolylamino-*n*-butyl- (48%) (*dihydrochloride*, $+H_2O$, m.p. 231—233°), -9-ε-6′-methoxy-8′-quinolylamino-*n*-amyl- (55%) [*hydrochloride*, $+H_2O$, m.p. 135—138° (decomp.)], -*amino*-2-*methoxyacridine*, and 6-*chloro*-9-*anilino*- (65%), m.p. 199—201°, -9-p-*dimethylaminoanilino*- (66%), m.p. 187—188°, -9-p-*diethylaminoanilino*- (48%), m.p. 127—129° (decomp.), and -9-p-*anisidino*- (79%), m.p. 177—179°, -2-*methoxyacridine*. R. S. C.

Attempts to prepare optically active tervalent nitrogen compounds. II. 1 : 9-(2′ : 3′ : 4′ : 5′-Tetrahydrophenylene)carbazole. R. W. G. Preston and S. H. Tucker (*J.C.S.*, 1943, 659—661).—9-Aminocarbazole (*picrate*, m.p. 136—138°) and *cyclo*hexanone give *cyclo*hexanonediphenylenehydrazone (cf. Manjunath, A., 1927, 978), which with dry HCl in tetralin affords 1 : 9-(2′ : 3′ : 4′ : 5′-*tetrahydrophenylene*)*carbazole*, m.p. 99—100° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 164—166°; *picrate*, m.p. 159—160°], dehydrogenated (S) to 1 : 9-phenylenecarbazole, m.p. 136·5—138·5°. This compound is synthesised by diazotisation (in H_2SO_4–AcOH) of 1-*amino*-, m.p. 96—98°, obtained by reduction (Na_2S–EtOH) of 1-*nitro*-9-*phenylcarbazole*, m.p. 130—132°, which is prepared from 1-nitrocarbazole, PhI, K_2CO_3, and Cu. 3-*Nitro*-9-*phenylcarbazole*, m.p. 140—142°, and the *diphenylenehydrazones* of $AcCO_2H$, m.p. 157—160° (decomp.) [lit., 148—150° (decomp.)], $AcCO_2Me$, m.p. 89—90°, $CH_2Ac{\cdot}CO_2Et$, m.p. 113°, Et oxaloacetate, m.p. 85—87°, and $COMe_2$, m.p. 78—81°, are described. F. R. S.

4-Amino-2-methyl-5-β-bromoethylpyrimidine hydrobromide. J. M. Slobodin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 237—238).—In the compound $C_6H_{10}N_3Br_3$ all 3 Br are titrated with $AgNO_3$, so that the bond $CH_2{\cdot}Br$ must be nearly dissociated. J. J. B.

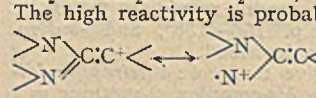
Sulphonamidopyrimidines.—See B., 1944, III, 18.

Pharmacological properties of simple compounds of histamine with amino-acids. M. Rocha e Silva (*J. Pharm. Exp. Ther.*, 1943, **77**, 198—205).—See A., 1944, III, 211. The following are described: *acetyldehydrophenylalanyl*- [α-*acetamidocinnamyl*-], m.p. 134—137°, *acetyl*-dl-*phenylalanyl*-, m.p. 95—100°, *benzoyl*-l-*tyrosyl*-, m.p. 140—146°, *carbobenzyloxy*-l-*tyrosyl*-, m.p. 147°, *carbobenzyloxy*-l-*leucylhistamine*, m.p. 113—117°.

Preparation of sulphanilamidoindazoles. C. E. Kwartler and P. Lucas (*J. Amer. Chem. Soc.*, 1943, **65**, 1804—1806).—6-Amino-, m.p. 209—210°, is rapidly obtained from 6-nitro-indazole by H_2–Raney Ni in MeOH at 50°/30 atm. *o*-$CN{\cdot}C_6H_4{\cdot}N_2Cl$ and $SnCl_2$–conc. HCl give 3-aminoindazole. *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ with the appropriate aminoindazole in $COMe_2$ or C_5H_5N gives 3-, m.p. 253—255°, 5-, m.p. 250—252°, 6-, m.p. 245—246°, and -7-N⁴-*acetylsulphanilamidoindazole*, m.p. 258—260°, hydrolysed by aq. acid or alkali or 20% HCl–EtOH to 3-, m.p. 225—226°, 5- (**I**), m.p. 247—248°, 6- (**II**), m.p. 195—196°, and 7-*sulphanilamidoindazole*, m.p. 254—256°, respectively. These have bacteriostatic action; some are bactericidal and show promise against *Streptococcus hæmolyticus* and *Pneumococcus* in mice. (**I**) and (**II**) are, respectively, 2 and 3—4 times as effective as *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ against *Streptococcus*. R. S. C.

(A) **Allylic character of 2-α-chloroalkylbenziminazoles.** H. Skolnik, J. G. Miller, and A. R. Day. (B) **Reaction of 2-α-chloroalkylbenziminazoles with potassium iodide in acetone solution.** H. Skolnik, A. R. Day, and J. G. Miller (*J. Amer. Chem. Soc.*, 1943, **65**, 1854—1858, 1858—1862).—(A) 2-α-Chloroalkylbenziminazoles are even more reactive than the usual allyl chloride types (cf. A., 1939, II, 285; 1941, II, 150). 2-Chloromethylbenziminazole (**I**), m.p. (at 1° per min.) 159—160° or (at 2° per min.) >250° (after changing to a yellow solid at 140°; ? polymerisation), with MgPhBr in Et_2O or boiling KCN–EtOH–H_2O gives gums, in boiling H_2O (45 min.) gives 2-hydroxy- (94%), m.p. 170·5—171·5° [also obtained from *o*-$C_6H_4(NH_2)_2$ (**II**) and $OH{\cdot}CH_2{\cdot}CO_2H$], with KI in boiling $COMe_2$ gives 2-*iodo-methylbenziminazole* (31%), m.p. 137—139° (decomp.), and with boiling NaOEt–EtOH gives 1 : 2-4 : 5-*di*-1′ : 2′-*benziminazolopiperazine* (73%), m.p. >300°, but is unchanged by boiling EtOH or $NPhMe_2$– or C_5H_5N–EtOH. 2-*Ethoxymethylbenziminazole*, m.p. 154·5—155°, is obtained (88%) from (**II**) and $OEt{\cdot}CH_2{\cdot}CO_2H$. 2-α-Chloro- (**III**), m.p. 134—135°, in boiling H_2O (10 min.) gives 2-α-hydroxy-ethylbenziminazole (70·6%), m.p. 179—180°, and 2-α-*chloro*- (**IV**), m.p. 144·5—145·5°, gives similarly 2-α-*hydroxy*-n-*propylbenziminazole*, m.p. 220—221° [whence (**IV**) is prepared by $SOCl_2$–$CHCl_3$]; the products are also obtained from (**II**) by $OH{\cdot}CHMe{\cdot}CO_2H$ or $OH{\cdot}CHEt{\cdot}CO_2H$ (prep. from $OH{\cdot}CHEt{\cdot}CN$ by conc. HCl at room temp. and then 60—70°), respectively. 2-α-*Chloroisopropylbenziminazole* (**V**), m.p. 135·5—136·6°, is hydrolysed to the 2-α-*OH*-compound, m.p. 227·5—228° [prepared from (**II**) by $OH{\cdot}CMe_2{\cdot}CO_2H$ and giving (**V**) with $SOCl_2$–$CHCl_3$], by evaporating its solution in $COMe_2$ containing a little H_2O in a stream of air at room temp., and with a little C_5H_5N in boiling EtOH gives 2-α-*ethoxyisopropylbenziminazole* (56%), $+H_2O$ (retained at 130°), m.p. 203·7—204·4°. *o*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$,2HCl (**VI**) and $CH_2Cl{\cdot}CO_2H$ in boiling 2N-HCl give 1-*methyl*-2-*chloro*- (**VII**) (58%), m.p. 94·5—95·5°, which with KCN–$COMe_2$–H_2O gives 1-*methyl*-2-*cyano-methylbenziminazole* (80%), m.p. 239—240°. $OH{\cdot}CHMe{\cdot}CO_2H$ and (**VI**) give 1-*methyl*-2-α-*hydroxy*-, m.p. 59·6—61°, and thence ($SOCl_2$–$CHCl_3$) 1-*methyl*-2-α-*chloro-ethylbenziminazole* (**VIII**), m.p. 64—65°. M.p. are corr.

(B) Interaction of 2-α-chloroalkylbenziminazoles with KI in $COMe_2$ proceeds to conclusion as a bimol. reaction. *k* is measured at 25° by the method of Conant *et al.* (A., 1924, i, 273), but not by other methods. It is const. for given concns. but increases greatly as the concn. of the Cl-compound decreases. Relative *k* vals. are (**I**) < (**III**) < (**IV**) < (**VIII**) < (**V**) < (**VII**); all are $\gg k$ for $CH_2{:}CH{\cdot}CH_2Cl$ or CH_2PhCl, which are similarly affected by concn. The high reactivity is probably caused by resonance of the type,



R. S. C.

Diels–Alder synthesis with 2 : 3-dimethylquinoxaline. Reaction between maleic anhydride and anthranil. A. Schönberg and A. Mostafa (*J.C.S.*, 1943, 654—656).—2 : 3-Dimethylquinoxaline (**I**) and $(CH{\cdot}CO)_2O$ form a 1 : 1 additive *product*, m.p. >305°; *p*-benzoquinone in PhMe gives a 2 : 1 additive *product*, m.p. 190°. Alternative formulæ are suggested for the products. No reaction of this kind is observed between (**I**) and $(CH_2{\cdot}CO)_2O$ or between (**II**) or *p*-benzoquinone and quinoxaline or its derivatives not capable of forming a diene system. *o*-$C_6H_4(NH_2)_2$ and (**II**) give an additive *product*, $C_{14}H_{12}O_6N_2$, m.p. 189—190°, and an additive *product*, m.p. ~150°, (some decomp.), is formed from 1 : 1 mol. proportions of (**II**) and anthranil. F. R. S.

Heterocylic nitrogen compounds. I. Derivatives of 7 : 16-diazanaphthacene. H. H. Hatt and (Miss) E. F. M. Stephenson (*J.C.S.*, 1943, 658—659).—Phthalaz-1 : 4-dione and *o*-$C_6H_4(CH_2Br)_2$ at 215—220° give 6 : 17-*diketo*- 6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene*, m.p. 196·5—197·5°, in 65% yield [also obtained from *o*-$C_6H_4(COCl)_2$ and 1 : 2 : 3 : 4-tetrahydrophthalazine hydrochloride (**I**)], which with NaOEt–EtOH affords the *Na* salt of 2-o-*carboxybenzoyl*-1 : 2 : 3 : 4-*tetrahydrophthalazine* (+2·5H_2O). 3 : 1 : 2-$NO_2{\cdot}C_6H_3(COCl)_2$ and (**I**) in C_5H_5N yield 1-*nitro*-6 : 17-*diketo*-6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene*, m.p. 249—250° (slight decomp.), reduced ($SnCl_2$–HCl) to the 1-NH_2-compound, m.p. 185—187° (decomp.) [*Bz* derivative, m.p. 260—261° (slight decomp.)]. 4 : 1 : 2-$C_6H_3Cl(CO)_2NH$, N_2H_4, and EtOH give 6-*chlorophthalaz*-1 : 4-*dione*, m.p. 348—350° (sealed tube). F. R. S.

Ichthyopterin, the blue-fluorescent substance of fish skin. R. Hüttel and G. Sprengling (*Annalen*, 1943, **554**, 69—82).—The presence of blue or green fluorescence in fish skins appears to be a family property; green or no fluorescence is observed in species without or with slightly developed scales. The intact skin of *Phoxinus laevis*, Ag, is not fluorescent but slight injury induces this phenomenon. If the fish is killed without other damage, fluorescence appears slowly after 1—2 hr. Alcohols, 1% CH_2O, and urethane solution cause almost immediate death with simultaneous appearance of fluorescence. Dil. acids and alkalis induce fluorescence only if the animal is so hurt that it dies within 15 min. The activity of neutral salts depends on the anion; only univalent ions induce fluorescence. The skins of freshly-killed *Leuciscus rutilus*, *Scardinius erythrophthalamus*, and *Blicca björkna* are pre-extracted and preserved by EtOH and then extracted several times with dil. AcOH. The conc. extracts are pptd. with EtOH, and Ca is removed as CaC_2O_4. The remaining solution is treated with $Pb(OAc)_2$ at pH 8—9, the ppt. is decomposed with H_2SO_4, and the fluorescent material is eluted from the $PbSO_4$ by C_5H_5N–H_2O. It is purified first by use of NH_3 and finally through the Na H salt, thereby giving *ichthyopterin* (**I**), probably $C_7H_8O_3N_4$. Spectroscopically (**I**) is similar to but distinct from leucopterin and almost identical with "anhydroleucopterin" (8-deoxyleucopterin) (**II**). Like (**II**) it shows the characteristic "redox" reaction with

fuming HI. Fluorescences of (I) and (II) are identical in colour, in dependence on pH, and, generally, in intensity. However, (I) and (II) are certainly not identical. Very probably (I) is the chromophor of (II) and therefore a derivative of 9-hydroxypteridin. H. W.

Constitution of yeast-ribonucleic acid. VI. Nature of the carbohydrate radicals. J. M. Gulland and G. R. Barker (*J.C.S.*, 1943, 625—628).—Examination of the evidence on which the conclusion that *d*-ribose is the carbohydrate of yeast-nucleic acid (I) and the related nucleotides is based shows it to be unsatisfactory. *d*-Ribose, and *l*-lyxose in small amount, have been identified, by oxidation and conversion into benziminazoles, in the products of hydrolysis of (I), and *d*-ribose has been similarly identified as the carbohydrate of guanylic, adenylic, and cytidylic acids prepared from (I), which is therefore designated correctly as the ribonucleic acid of yeast. d-*Ribobenziminazole*, m.p. 239—240°, $[\alpha]_D^{20}$ −50·4° in 5% aq. citric acid [lit. m.p. ~190° (decomp.), $[\alpha]_D^{20}$ +21·6°], has been prepared from synthetic *d*-ribonic acid. d(−)-*Arabinose*-2 : 4-*dinitrophenylosazone*, m.p. 259—260°, is identical with that obtained from (I). F. R. S.

Chlorophyll *d*, a green pigment of red algæ. W. M. Manning and H. H. Strain (*J. Biol. Chem.*, 1943, **151**, 1—19).—Various species of red algæ contain, in addition to chlorophyll *a* (I), a second green pigment containing Mg, *chlorophyll* d (II). Chlorophyll *b* or *c* is not found in these algæ. (II) is most easily prepared by adsorption of the pigments obtained by the partial extraction of *Sigartina agardhii*. Max. light absorption by (II) occurs at λ longer than that of the max. of (I); in MeOH the max. absorption for (II) is at 696 mμ., and for (I) at 665 mμ. Absorption at long λ by (II) may extend by 30 mμ. the range of light used in photosynthesis. (II) is converted, rapidly when heated or slowly at room temp., into a mixture containing three isomerides in addition to unaltered material. One of these isomerides, *chlorophyll* d′, has an absorption spectrum very similar to that of (II) whereas the other two, iso*chlorophyll* d (III) and iso*chlorophyll* d′, have spectra resembling that of (I). The isomerides are reconvertible into (II). Treatment of (II) with acid removes the Mg and forms a mixture of two interconvertible phæophytins. At −80° treatment with acid produces mainly the labile, yellow-brown *phæophytin* d (IV); at room temp., grey iso*phæophytin* d (V) is the principal product. (IV) is rapidly converted into (V) when it is treated with acid at room temp. (III) yields (V) when treated with acid at room temp. or −80°. (V) is remarkably similar to phæophytin *a* in its absorption spectrum and in its adsorbability on powdered sugar. With Grignard's reagent (V) produces (III) but little or no (I). Neither (II) nor (III) is formed when (IV) is treated with Grignard's reagent. The same final product is formed in each case when (II) and its isomerides are treated successively with alkali and acid. When treated in this manner (I) gives a product distinctly different from that derived from (II). H. W.

Effect of pH changes on the properties of sodium thymonucleate solutions. C. F. Vilbrandt and H. G. Tennent (*J. Amer. Chem. Soc.*, 1943, **65**, 1806—1809).—η of 0·3% Na thymonucleate solution (pH 5·6) containing 1% of NaCl decreases gradually as the pH is changed to 2·6 or 11·6. Subsequent neutralisation raises η, but not to the original val. and the recovery is slow. Sedimentation and diffusion experiments connect these changes with de- and re-polymerisation; the range of mol. wts. after re-polymerisation is ≫ it was originally and some of the newly formed mols. are very large. Isolation of nucleic acids will thus give altered substances unless it is conducted in neutral solution. R. S. C.

Quaternary cetylammonium compounds.—See B., 1943, III, 308.

Interaction of *o*-quinones and *o*-quinoneimines with primary amines. G. McCoy and A. R. Day (*J. Amer. Chem. Soc.*, 1943, **65**, 1956—1959).—Retenequinone (I) with $CH_2R{\cdot}NH_2$ (R = Pr$^\alpha$, $OH{\cdot}CH_2$, or Ph) in EtOH, PhMe, etc. at 75—100° gives 40—80% yields of 2-substituted reteneoxazoles, but with $CHPhMe{\cdot}NH_2$ or NH_2Pr^β gives gums (cf. Bamberger *et al.*, A., 1885, 905; Pschorr, A., 1902, i, 672). Reaction proceeds by way, of successively, (i) the Schiff's base, (ii) 9-alkylideneamino-10-hydroxy-compound, and (iii) 2 : 3-dihydro-oxazole, which is oxidised by unchanged (I). Step (i) is proved by isolation of H_2O when the reaction is effected in PhMe and by evolution of NH_3 when retenequinonemonoimine (II) replaces (I). Step (ii) is proved by formation of PhCHO when a reacting mixture of (I) and $CH_2Ph{\cdot}NH_2$ is treated with HCl and by the fact that 9-amino-10-phenanthrol with Pr$^\alpha$CHO or PhCHO gives 2-*n*-propyl- and 2-phenyl-phenanthroxazole (III), respectively. The final oxidation by (I) is proved by adding *p*-$O{:}C_6H_4{:}O$, which finally appears as quinol and quinhydrone. That yields exceed 100% is due to the ready re-oxidation of retenequinol. Liberation of NH_3 from (II) proves that reaction occurs at the NH. Yields from (II) are > those from (I), because side-reactions due to H_2O are eliminated. Phenanthraquinone and $CH_2Ph{\cdot}NH_2$ in boiling PhMe give (III) (9%), 2-*phenyl*-1-*benzylphenanthriminazole* (IV) (2·7%), m.p. 241—241·5°, and PhCHO, but in boiling AcOH give 48% of *phenanthroxazine*, m.p. >360°, with 14% of (III) and 4% of (IV); NH_2Bu^α gives only gums. Phenanthraquinonemonoimine with $CH_2Ph{\cdot}NH_2$ or NH_2Bu^α in PhMe gives (III) (59%) and 2-propylphenanthroxazole (35%), respectively. 2-*Hydroxymethylreteneoxazole*, m.p. 187·5—189° (*acetate*, m.p. 134·5—136°), is described. R. S. C.

Vitamin-B_1. 4-Methyl-5-β-hydroxyethylthiazole. J. M. Slobodin and E. E. Gelms (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 152—154).—In Buchman's synthesis (A., 1936, 1394) of 4-methyl-5-β-hydroxyethylthiazole some 4-*methyl*-5-α-*hydroxyethylthiazole*, b.p. 121—122·5°/2 mm. (*picrate*, m.p. 91°), is also produced. J. J. B.

2-Amino-4 : 5-trimethylenethiazole.—See B., 1944, II, 35.

Photosynthesis of a fluorescent substance of the thiazole series (vitachrome). P. Karrer and M. C. Sanz (*Helv. Chim. Acta*, 1943, **26**, 1778—1784).—Exposure of crude 4-methyl-5-β-hydroxyethylthiazole (I) in 1% aq. solution at pH 8 to ultra-violet light followed by chromatographic purification leads to the isolation of *vitachrome* (II) in 1—3% yield. (II) does not arise from (I) which has been purified through the picrate and its production is due to the presence in (I) of small amounts of 2-*chloro*-4-*methyl*-5-β-*hydroxyethylthiazole* (III), b.p. 88—92°/0·002—0·003 mm., which does not form a picrate, gives a viscous *acetate*, and is converted by anhyd. KOAc in AcOH followed by hydrolysis with 10% H_2SO_4 into 2-*keto*-4-*methyl*-5-β-*hydroxyethyl*-2 : 3-*dihydrothiazole*, m.p. 132—133°. Fluorescence is observed sooner in the irradiation of crude (I) than in that of (III) but the difference disappears after a few hr. (II) has m.p. 175° (corr.). The crystals have a pale yellow-green fluorescence in ultra-violet light, in which the aq. solution appears a very intense pale blue. (II) gives a cryst. *diacetate* with a very marked, pale blue fluorescence and is probably $\left[C<\begin{matrix}S\text{–}C{\cdot}[CH_2]_2{\cdot}OH\\ \| \\ N{\cdot}CMe\end{matrix}\right]_2$. (II) diffuses very rapidly into the cell, accumulates in the vacuoles, and is frequently fixed by the living cytoplasm. Generally it is the neighbourhood of the cell nucleus which fluoresces most strongly. No harmful effects have been noticed. It appears completely non-toxic to small animals and to pass unchanged through the kidneys. H. W.

Pyrazolones, benzthiazoles, etc.—See B., 1943, II, 400.

Cyanines.—See B., 1944, II, 10.

Photographic sensitisers.—See B., 1944, II, 57, 58.

Miscellaneous heterocyclic compounds.—See B., 1944, II, 7.

VII.—ALKALOIDS.

Ergot alkaloids. IX. Dihydro-derivatives of the natural, lævorotatory ergot alkaloids. A. Stoll and A. Hofmann (*Helv. Chim. Acta*, 1943, **26**, 2070—2081).—Lævorotatory ergot alkaloids (I) are converted into homogeneous H_2-derivatives (II) in good yield by hydrogenation at 60°/35 atm. in dioxan containing Pd sponge. They differ so little from (I) in cryst. form, solvent of crystallisation, and solubility that it may be assumed that hydrogenation does not cause any marked change in the configuration of the mols. With org. and inorg. acids (II) generally give stable, well-cryst. salts. (II) scarcely show the intense blue fluorescence in the ultra-violet which is characteristic of (I) but the dark blue Keller colour reaction is retained. The following are described: *dihydroergotamine*, $C_{33}H_{37}O_5N_5{,}2COMe_2{,}2H_2O$, m.p. 239° (decomp.), $[\alpha]_D^{20}$ −64°, $[\alpha]_{5461}^{20}$ −79° in C_5H_5N [*hydrochloride*, m.p. 220—225° (decomp.); *methanesulphonate*, m.p. 230—235° (decomp.); normal *tartrate*, m.p. 210—215° (decomp.)]; *dihydroergosine*, m.p. 212° (decomp.), $[\alpha]_D^{20}$ −52°, $[\alpha]_{5461}^{20}$ −64° in C_5H_5N; *dihydroergocristine*, m.p. 180° (decomp.) from $COMe_2$, 200° from C_6H_6, $[\alpha]_D^{20}$ −56°, $[\alpha]_{5461}^{20}$ −68° in C_5H_5N; *dihydroergocryptine*, m.p. 235° (decomp.), $[\alpha]_D^{20}$ −41°, $[\alpha]_{5461}^{20}$ −52° in C_5H_5N; *dihydroergocornine*, m.p. 185—187° (decomp.), $[\alpha]_D^{20}$ −48° in C_5H_5N. (II) are far more stable than (I) towards light, oxidising influences, acids, and alkalis. These properties are shared by d(−)-*dihydrolysergic acid* (III), decomp. >300°, darkens at 250°, $[\alpha]_D^{19}$ −122°, $[\alpha]_{5461}^{20}$ −146° in C_5H_5N, obtained from them by alkaline hydrolysis. Fission of (II) by N_2H_4 leads without racemisation or isomerisation to d(−)-*dihydrolysergh ydrazide*, m.p. 247° (decomp.), $[\alpha]_D^{20}$ −123°, $[\alpha]_{5461}^{20}$ −147° in C_5H_5N, hydrolysed by alkali to (III). Saturation of the double linking in (I) causes complete disappearance of the reaction towards the uterus and a great diminution in toxicity but the neurovegetative action is retained and in certain cases is enhanced. M.p. are corr. Diagrams of apparatus and photomicrographs of (II) are given. H. W.

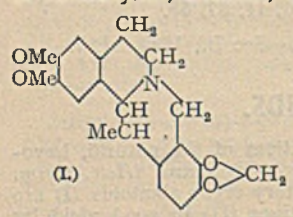
Synthesis in the series of cinchona alkaloids. IV. Homomeroquinine and the partial synthesis of quinotoxine. M. Prostenik and V. Prelog (*Helv. Chim. Acta*, 1943, **26**, 1965—1971).—Technical cinchonine is purified by $Hg(OAc)_2$ and successively treated with 50% H_2SO_4 at 140°, benzoylated in presence of K_2CO_3 and $CHCl_3$, and treated with NH_2OH, thereby giving a mixture of stereoisomeric *N*-benzoylcinchotoxineoximes, m.p. 65—95°. This is transformed by *p*-$C_6H_4Me{\cdot}SO_2Cl$ and NaOH into a mixture of amides,

hydrolysed by alkali to homomeroquinine, isolated as the *Et* ester, b.p. 102—104°/0·1 mm., $[\alpha]_D^{18}$ +42·2° in 96% EtOH [*aurichloride*, m.p. 110·5—112° (decomp.); *N-Bz* derivative (I), b.p. 190—194°/0·1 mm., which rapidly becomes discoloured when kept]. This is hydrolysed by alkali to the free *base*, m.p. 211—212° (decomp.), $[\alpha]_D^{20}$ +50·4° in H_2O [normal *dibenzoyl*-d-*tartrate*, m.p. 186° (decomp.); *reineckate*, m.p. 131·5—132°]. N-*Methylhomomeroquinine Et ester*, b.p. 135—140°/23 mm., $[\alpha]_D^{16.5}$ +30·3° in EtOH, results similarly from *N*-methylcinchotoxincoxime. (I) is condensed with Et quinate by dry NaOEt at 80—90° and the product is hydrolysed to quinotoxine [normal *dibenzoyl*-d-*tartrate*, m.p. 183° (decomp.), $[\alpha]_D^{20}$ −16·0° in EtOH–$CHCl_3$ (1 : 2), identical with the product obtained from quinine; *dipicrolonate*, m.p. 210° (decomp.)], transformed into a mixture of stereoisomeric benzoylquinotoxincoximes, m.p. 65—95°. H. W.

10-Iodohydroquinines. (Miss) A. G. Renfrew, C. L. Butler, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1943, **65**, 2038—2039).—*iso*Quinine and HI (*d* 1·7) at 100° give 10-iodohydroquinine, α-, [α] −218°, and α′-form, anhyd., m.p. 130°, $[\alpha]_D$ −22·3°, and +C_6H_6, [α] −19° (cf. Suszko *et al.*, A., 1936, 490, 870). Rotations in (?) EtOH. R. S. C.

Berberine content of *Coscinium fenestratum* (Colebr.). R. Child and W. R. N. Nathaniel (*Current Sci.*, 1943, **12**, 255—256).—Extraction of the air-dried stems (H_2O, 6·8%) of Ceylonese material with 95% EtOH removes 9·2% of material and from the alcoholic extract berberine is readily pptd. as the H sulphate (yield of crude salt ~4·1%) by a slight excess of H_2SO_4. The residue from the evaporated filtrates is treated with H_2O and then with Et_2O, which removes 4·1% of resin. The aq. extract after being made alkaline with NaOH gives crude alkaloids (0·67%) to Et_2O and after saturation with CO_2 0·2% of crude phenolic alkaloids, thus partly confirming the findings of Varier *et al.* (A., 1944, III, 156). The ash, insol. in 2N-HCl, contains CaO 36·8, K_2O 7·6, and Cl′ 0·33%. The high Ca content is noticeable, corresponding with 1·0% of CaO in the original stems. H. W.

Alkaloids of fumariaceous plants. XXXVI. *Corydalis thalictrifolia*, **Franch. and constitution of a new alkaloid, thalictrifoline. XXXVII.** *Dactylicapnos macrocapnos*, **Hutchinson.** R. H. F. Manske (*Canad. J. Res.*, 1943, **21**, B, 111—116, 117—118).—XXXVI. *C. thalictrifolia*, Franch., contains protopine, *d*-stylopine (partly racemised), *l*-corypalmine, adlumidine, d-*thalictrifoline* (I), m.p. 155°, $[\alpha]^{25}$ +218° in MeOH, dehydrothalictrifoline, isolated as *hydrochloride* (II), m.p. 271°, and alkaloids *F* 59, $C_{19}H_{20}O_3N(OMe)$, m.p. 176°, largely resolidifying and remelting at 192—200°, and *F* 60, $C_{19}H_{18}O_2N(OMe)$, m.p. 123°. (I)



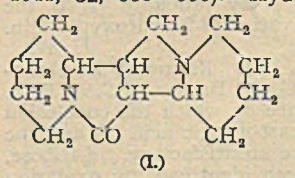
(I.)

with I and NaOAc in hot EtOH yields a quaternary salt, reduced (Zn + HCl) to the hydrochloride of dl-*thalictrifoline*, m.p. 151°, similarly obtained from (II). Oxidation ($KMnO_4$) of (I) yields *m*-hemipinic acid, but no 3 : 4-methylenedioxyphthalic acid. (I) with dil. H_2SO_4 containing phloroglucinol, followed by methylation and racemisation (by oxidation and reduction), yields *meso*corydaline. All m.p. are corr.

XXXVII. *D. macrocapnos*, Hutchinson, contains protopine, *allo*cryptopine, stylopine, and a considerable amount of fumaric acid, but no phenolic bases. A. Li.

Structure of monocrotaline. IX. Proof of the position of the ethylenic linking in retronecine. R. Adams and J. E. Mahan (*J. Amer. Chem. Soc.*, 1943, **65**, 2009—2012).—The structure of retronecine (A., 1943, II, 113) is confirmed. Deoxyretronecine hydrochloride in $SOCl_2$ at the b.p. gives *chloro*iso*heliotridene* (83%), b.p. 59·5—60·5°/4·5 mm., $[\alpha]_D^{32}$ +50·10° (homogeneous) [*picrate*, m.p. 179·5—180° (decomp.)], reduced by $CrCl_2$–HCl (prep. *in situ* described) to iso*heliotridene* (88%), $[CH_2]_3<^{CH\cdot CMe}_{N-CH_2}>CH$, b.p. 73°/30 mm., $[\alpha]_D^{28}$ −45·79° (homogeneous) (*picrate*, m.p. 198·5—199·5°), which with H_2–PtO_2 gives heliotridane and, as hydrochloride in H_2O, with O_3 yields 2-*acetylpyrrolidinoacetic acid hydrochloride* (42%), m.p. 180—181°, $[\alpha]_D^{27}$ −4·40° in MeOH [free acid unstable; 2 : 4-*dinitrophenylhydrazone*, m.p. 199—201° (decomp.), titrates as an NH_2-acid hydrochloride; CHI_3 test positive in H_2O]. This is hydrogenated (PtO_2) in EtOH to 2-α-*hydroxyethylpyrrolidinoacetic acid*, m.p. 186·5—187·5°, $[\alpha]_D^{28}$ −63·47° in H_2O [*hydrochloride* (II), m.p. 147—148°, $[\alpha]_D^{32}$ −54·31° in EtOH; gives the CHI_3 test] [and some of its lactone (III) (see below)], which with CH_2N_2–Et_2O gives the hygroscopic, oily betaine, $^{OH\cdot CHMe}_{[CH_2]_3}>N^+Me\cdot CH_2\cdot CO_2^-$ (*hydrochloride*, softens 170°, m.p. 176—177°). In Ac_2O at 100° (II) gives (III) (*methiodide*, m.p. 242—243°; *picrate*, m.p. 169—170°). M.p. are corr. R. S. C.

Constitution of hydroxypachycarpine. A. P. Orechof, M. I. Kabatschnik, and T. J. Kefeli (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 335—338).—Hydroxypachycarpine (I) is very resistant towards acids and alkalis but is hydrolysed by conc. HCl at 180° for 15 hr. and the product is esterified to *Et pachycarpate* (II), b.p. 162—166°/2 mm., $[\alpha]_D^{14}$ −12·2° in EtOH, which re-forms (I) when hydrolysed by 50% H_2SO_4. The presence of NH in (II) is established by the isolation of a *Bz* derivative, m.p. 121—122°, and a *NO*-compound, m.p. 86—88°. A lactam group is therefore present in (I) and consequently also in hydroxysparteine. The constitution of (I) is established. H. W.



(I.)

VIII.—ORGANO-METALLIC COMPOUNDS.

Mercuric derivatives of acetamido-acids.—See B., 1944, III, 18.

3-Pyridylmercuric chloride.—See B., 1944, III, 18.

Azo-lead dyes. C. G. Stuckwisch (*Iowa State Coll. J. Sci.*, 1943, **18**, 92—94).—Halogen–metal interconversion studies led to the prep. of $PbPh_3$ *p*-, m.p. 172°, and *o*-amino-, m.p. 164—165°, *p*-methylamino-, m.p. 97—98°, *o*-dimethylamino-, m.p. 101°, and *o*-hydroxyphenyl, m.p. 217—218° (decomp.), and Pb *p*-dimethylaminophenyl Et_3, b.p. 130°/1 mm. (no details given). Organo-Pb compounds containing an azo-linking are preferably prepared from PbR compounds and diazotised amines rather than from diazotised Pb amino-aryl compounds. The following were prepared: $PbPh_3$ 4- and 2-(2′-hydroxy-1′-naphthaleneazo)phenyl, 2-hydroxy-3 : 5-di-(*p*-nitrobenzeneazo)phenyl, 2-hydroxy-5-(*p*-chloro-, -bromo-, -iodo-, and -carboxybenzeneazo)phenyl; 4 : 4′-bis-(4′-hydroxy-3′-triphenylplumbophenylazo)diphenyl; $PbPh_3$ 5-(*p*-nitro-, -chloro-, -bromo-, and -carboxybenzeneazo)-2-dimethylaminophenyl; $PbPh_3$ 4-methoxy-3- and 2-methoxy-5-*p*-nitrobenzeneazophenyl. F. R. G.

IX.—PROTEINS.

Rôle of glycine in protein structure. H. Neurath (*J. Amer. Chem. Soc.*, 1943, **65**, 2039—2041).—The absence of side-chains in, and free rotation of, glycine allows closer packing of bulky NH_2-acids, readier orientation of polar side-chains at interfaces, and unusual repeating patterns (*e.g.*, in silk fibroin). Glycine is probably present at least in small amounts in all proteins, difficulties in its detection having often led to its being overlooked. The large space-requirements of proline and hydroxyproline in gelatin (~32%) and elastin (~17%) are compensated by large contents (~25% and 29%, respectively) of glycine. R. S. C.

Hydrolysis of proteins and peptones at high temperatures and catalytic effect of metal ions on rate of hydrolysis. F. Lieben (*J. Biol. Chem.*, 1943, **151**, 117—121).—Complete hydrolysis of casein is effected by heating a 2% solution in 20% H_2SO_4 for 1 hr. at 160°. Similar data are given for other proteins. The importance of a low initial substrate concn. is stressed. Ti and Sn salts catalyse the reaction appreciably; Cu, Mn, and Ni salts are without effect. Peptones proved more resistant than casein or gelatin. E. C. W.

Influence of sugars on formation of sulphydryl groups in heat-denaturation and coagulation of egg-albumin. C. D. Ball, C. R. Hardt, and W. J. Duddles (*J. Biol. Chem.*, 1943, **151**, 163—169).—Hexoses and pentoses inhibited the formation of SH groups (for determination cf. C., 1944, Part 1) and increased the amount of non-coagulable N when ovalbumin (I) was denatured by heat. This inhibiting influence towards coagulation is not increased by longer contact of the sugar with (I) at a pH of either 4·8 or 8·6. (I) coagulated in presence of glucose yields no more reducing substances after partial hydrolysis than (I) coagulated alone. E. C. W.

Amino-acids yielded by β-lactoglobulin. D. Bolling and R. J. Block (*Arch. Biochem.*, 1943, **2**, 93—95).—Cryst. β-lactoglobulin contained N 15·53, S 1·68, cystine 3·5, arginine 3·2, histidine 1·8, lysine 9·9, tyrosine 4·2, tryptophan 1·9, phenylalanine 5·2, threonine 5·8, *iso*leucine 6·4, valine 6—9, and leucine 13—21%. E. R. S.

Dispersion of keratins. I. Dispersion and degradation of keratins by sodium sulphide. C. B. Jones and D. K. Mecham (*Arch. Biochem.*, 1943, **2**, 209—223).—When the keratin (I) (N 15·7—16·1, H_2O 7—10%) of the freshly plucked feathers of hens is treated with Na_2S, max. dispersion and min. degradation are achieved by using 100 ml. of 0·1M-Na_2S at 30° and digesting for ~2 hr. Approx. quant. recovery of the dispersed material is attained by adjusting the pH to 4·2. (I) of the feathers is more readily dispersed and less stable in solution than are (I) of cattle hooves, wool, and hog's hair. W. McC.

INDEX OF AUTHORS' NAMES, A II

MARCH, 1944.

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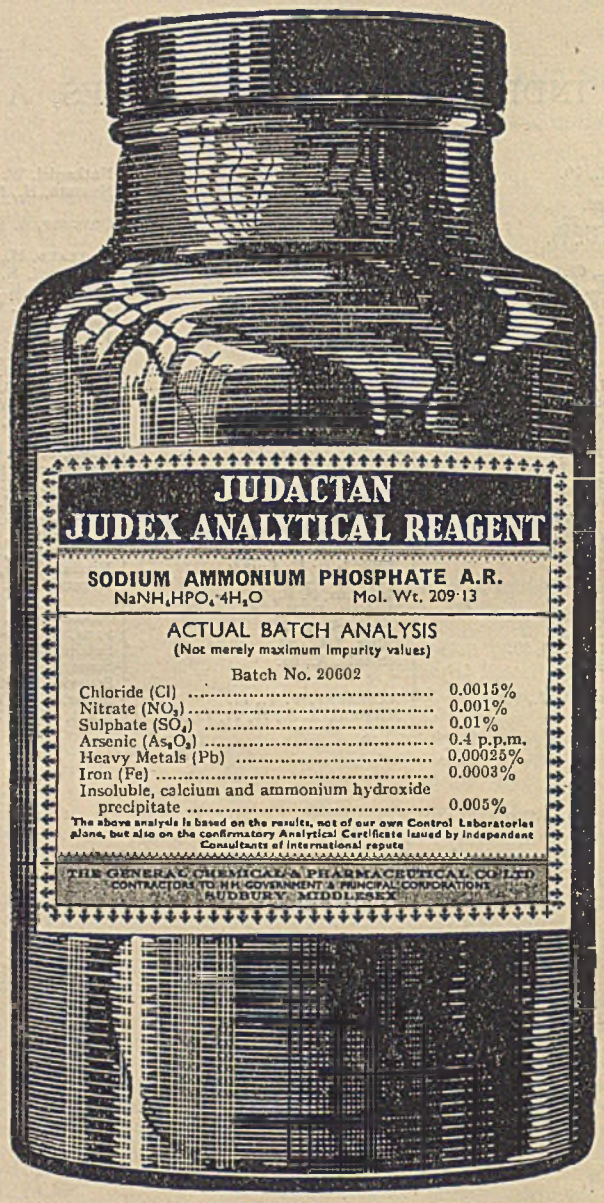
ACTUAL BATCH ANALYSIS



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