BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1942.

I.—ALIPHATIC.

New methods of preparative organic chemistry. XIII. Hydrogenations with Raney catalysts. R. Schröter. **XIV. Boron fluoride as catalyst in chemical reactions.** D. Kästner (*Angew. Chem.*, 1941, **54**, 252—260, 296—304). H. W.

Reactive paraffins. (A) E. E. Gilbert. (B) H. C. Brown and M. S. Kharasch (*J. Chem. Educ.*, 1941, **18**, 435—438, 589).—The reactivity of the paraffin hydrocarbons is illustrated by a review of thermal conversions, alkylations, oxidations, halogenations, and nitrations. L. S. T.

Oxidation of hydrocarbons at low temperatures. P. George, E. K. Rideal, and A. Robertson (*Nature*, 1942, **149**, 601—602).—Results of experiments on the uncatalysed and heavy-metal-catalysed oxidation of alkylbenzene and long-chain saturated aliphatic hydrocarbons (C_{15-25}) in the liquid phase at 100—120° support the hypothesis that hydroperoxides (**I**) are primary oxidation intermediates, peroxide yields representing respectively 60—80 and 5% of the O_2 absorbed. The metallic catalyst both starts and stops reaction chains leading to the production of (**I**) and decomposes them, catalysts showing marked specificity. The long-chain alkyl (**I**) decompose almost exclusively to give ketones. A. A. E.

Products of the joint action of sulphur dioxide and chlorine on aliphatic hydrocarbons in ultra-violet light. I. Propane in carbon tetrachloride. F. Asinger, W. Schmidt, and F. Ebeneder. **II. *n*-Butane in carbon tetrachloride.** F. Asinger, F. Ebeneder, and E. Böck (*Ber.*, 1942, **75**, [*B*], 34—41, 42—48).—I. Simultaneous passage of C_3H_8, Cl_2, and SO_2 (2·5 : 1·1 : 1 vol.) into CCl_4 in ultra-violet light at room temp. gives a mixture of equal parts of propane-α- and -β-monosulphonyl chlorides, chloro- and dichloro-propanemonosulphonyl chlorides, with a small amount of more highly chlorinated products of C_3H_8; the non-volatile residue contains $CH_2(CH_2{\cdot}SO_2Cl)_2$, m.p. 48°. The following appear new: *propane-αγ-disulphonamide*, m.p. 173°, and *-disulphonanilide*, m.p. 130°; *α-thiocyanopropane*; *propane-α-sulphonanilide*, a liquid; *propane-β-sulphonamide*, m.p. 65·7°, and *-sulphonanilide*, m.p. 84°.

II. Exposure of a mixture of C_4H_{10}, Cl_2, and SO_2 (2·5 : 1 : 1·1 vol.) to ultra-violet light gives mono-, di-, and chloro-sulphonyl chlorides in the ratio 85 : 10—11 : 3—5 or in the ratio 10 : 85—90 : 3—5 when the vol. ratio is 0·55 : 1 : 1·1. The following appear new: *butane-αδ-disulphonyl chloride*, m.p. 83·5° (corresponding *disulphonamide*, m.p. 182°, and *disulphonanilide*, m.p. 188·5°); *butane-αγ-disulphonyl chloride*, m.p. 41°, and *-disulphonanilide*, m.p. 170°; *butane-α-sulphonyl chloride*, b.p. 93·5°/15 mm., and *-sulphon*cyclo*hexylamide*, m.p. 71·8°; *butane-β-sulphonyl chloride*, b.p. 85°/15 mm., and *-sulphon*cyclo*hexylamide*, m.p. 58°; *αδ-dithiocyanobutane*, a liquid; *butane-αγ-disulphonyl chloride*, m.p. 41°, and *-disulphonanilide*, m.p. 170°; *αγ-dithiocyanobutane*. H. W.

Polymerisation of ethylene and propylene by free alkyl radicals.—See A., 1942, I, 270.

Mechanism of propylene and propane formation during electrolysis of butyric acids.—See A., 1942, I, 273.

Catalytic oxidation of acetylene.—See A., 1942, I, 271.

Acetylenic analogue of neopentyl bromide. Evidence that the hindrance to displacement reactions in neopentyl halides is steric in nature. P. D. Bartlett and L. J. Rosen (*J. Amer. Chem. Soc.*, 1942, **64**, 543—546).—$CMeBu^{\gamma}Cl_2$ [obtained with much $CH_2{:}CBu^{\gamma}Cl$ (**I**), b.p. 97—99°, from $COMeBu^{\gamma}$ by PCl_5 at 0—5°], b.p. 151—152°, gives $CH{:}CBu^{\gamma}$, b.p. 36·4—37·8°/768·3 mm. [also obtained in 80·5% yield from (**I**) by KOH–EtOH at 160—165°], which with MgEtBr–Et_2O and then dry CH_2O gives δδ-*dimethyl-Δ^β-pentin-α-ol* (**II**) (70·5%), b.p. 71·6°/18 mm., 162·4—163·4°/767·6 mm. (p-*bromo-*, m.p. 63—64·5°, and 3 : 5-*dinitro-benzoate*, m.p. 101·5—102°; *α-naphthyl-*, m.p. 163—164°, and *phenyl-urethane*, m.p. 81·5—82·5°), converted by PBr_3–C_5H_5N–Et_2O into δδ-*dimethyl-Δ^β-n-pentinyl bromide* (**III**) (41%), b.p. 50—52·5°/18—20 mm. Hydrogenation (PtO_2) of (**II**) in EtOH gives $Bu^{\gamma}{\cdot}[CH_2]_3{\cdot}OH$, b.p. 74°/22 mm. (α-naphthyl-, m.p. 80—81°, and *phenyl-urethane*, m.p. 51—52°; 3 : 5-*dinitrobenzoate*, m.p. 66—67°), which with PBr_3–Et_2O gives the bromide (**IV**), b.p. 61·5—62°/31 mm. Relative *k* (bimol.) for interaction of the bromides with KI in $COMe_2$ at 25±0·05° are Bu^{α} 465—474, *n*-C_7H_{15} 543—570, CH_2Bu^{γ} 1, $CHMeEt{\cdot}CH_2$ 29, $Bu^{\gamma}{\cdot}[CH_2]_2$ 19—20, (**IV**) 470, allyl 30,300—33,200, $CBu^{\alpha}{:}C{\cdot}CH_2$ 17,700—18,300, and (**III**) 22,300—23,300. The low reactivity of $CH_2Bu^{\gamma}Br$ is thus due to steric causes (indicated by Stuart models) since the effect is not transmitted through unsaturated linkings. R. S. C.

Reaction of halogens and magnesium with alcohols and esters. V. Reaction of iodine and magnesium with alcohols. M. T. Dangjan (*J. Gen. Chem. Russ.*, 1941, **11**, 616—618).—I and Mg react with MeOH, EtOH, $Bu^{\alpha}OH$, and *iso*-$C_5H_{11}{\cdot}OH$ giving the respective alkyl iodides (yields 54·5, 61·2, 80·3, and 60·3%). The poor yields of the first two iodides are due to side reactions, that of the last to decomp. of the final product. G. A. R. K.

Essential oils. II. Occurrence of Δ^γ-hexen-α-ol in natural raspberry oil. H. Bohnsack (*Ber.*, 1942, **75**, [*B*], 72—74).—The oil obtained by extraction of the expressed juice with Et_2O, removal of the latter, and distillation of the residue with steam contains EtOH, $Bu^{\beta}OH$, *iso*-$C_5H_{10}{\cdot}OH$, and Δ^γ-hexen-α-ol, b.p. 65—67°/15 mm. (α-naphthylurethane, m.p. 69—70°; *formate*, b.p. 53—55°/12 mm.; *acetate*, b.p. 66°/16 mm.; iso*butyrate*, b.p. ~80°/14 mm.), oxidised to $H_2C_2O_4$ and $EtCO_2H$ and hydrogenated (PtO_2 in AcOH) to *n*-hexanol (α-naphthylurethane, m.p. 60—61°). H. W.

Decomposition of acetylenic carbinols. A. F. Thompson, jun., and C. Margnetti (*J. Amer. Chem. Soc.*, 1942, **64**, 573—576).—By passage over hot, commercial (*i.e.*, alkaline) Al_2O_3, $CR{:}C{\cdot}CR'(CH_2R''){\cdot}OH$ are smoothly dehydrated to $CR{:}C{\cdot}CR'{:}CHR''$, unless R = H, Ph, or Me in which cases 50—100% of cleavage to $CR{:}CH + COR'{\cdot}CH_2R''$ occurs (cf. Thompson *et al.*, A., 1941, II, 83). The nature of R′ and R″ has little effect. 50—66% aq. KOH effects only the latter decomp., lower concns. being without action; solid KOH or KOH–EtOH causes the decomp. but the ketone formed reacts further. Condensation of CORR′ with $CR''{:}C{\cdot}MgX$ in Et_2O gives *γ-methyl-Δ^δ-n-hexin-γ-ol*, m.p. 132—135°, *γζ-di-*, b.p. 128—130°/35 mm., and *γζζ-tri-methyl-Δ^δ-n-hexin-γ-ol*, b.p. 137—140°/35 mm., *ε-phenyl-γ-methyl-Δ^δ-n-pentin-γ-ol*, b.p. 138—140°/15 mm., *δ-methyl-Δ^β-n-nonin-δ-ol*, b.p. 105—108°/15 mm., *α-phenyl-γ-methyl-Δ^α-n-octin-γ-ol*, b.p. 114—117°/2 mm., *β-methyl-γ-*iso*propyl-Δ^δ-n-nonin-γ-ol*, b.p. 130—133°/15 mm., (?) *γζ-dimethyl-Δ^β-n-octen-Δ^δ-in-ζ-ol*, b.p. 117—120°/15 mm., and (?) *γζ-dimethyl-Δ^β-n-undecen-Δ^δ-in-ζ-ol*, b.p. 115—118°/5 mm. $Pr^{\alpha}CO_2Et$ with $CBu^{\alpha}{:}C{\cdot}MgX$ gives *η-n-propyl-Δ^εθ-tridecadi-in-η-ol*, b.p. 130—132°/2 mm., which over Al_2O_3 gives $CHEt{:}C(C{:}CBu^{\alpha})_2$; *η-phenyl-Δ^εθ-tridecadi-in-η-ol*, b.p. 168—170°/2 mm. (similarly prepared from EtOBz), over Al_2O_3 gives $CBu^{\alpha}{:}CH$ and a resin (formed from $CBu^{\alpha}{:}C{\cdot}COPh$). R. S. C.

Structure and properties of [dehydration and dehydrogenation] catalysts.—See A., 1942, I, 272.

Mechanism of dehydration and dehydrogenation of alcohols of the homologous series $C_nH_{2n+1}{\cdot}OH$ on homogeneous catalysts.—See A., 1942, I, 272.

Alkyl carbonates. III. Condensation with nitriles. Synthesis of α-cyano-esters. V. H. Wallingford, D. M. Jones, and A. H. Homeyer. **IV. Alkylation of malonic esters by alkyl carbonates.** V. H. Wallingford and D. M. Jones. **V. Alkyl carbonates as solvents for metalation and alkylation reactions.** V. H. Wallingford, M. A. Thorpe, and A. H. Homeyer (*J. Amer. Chem. Soc.*, 1942, **64**, 576—578, 578—580, 580—582; cf. A., 1941, II, 349).—III. $CN{\cdot}CHR{\cdot}CO_2R'$ are obtained in good yield by boiling $CH_2R{\cdot}CN$, R'_2CO_3, and NaOEt with continuous removal of EtOH. KOEt, but not $Mg(OEt)_2$ or $Al(OEt)_3$, may be used. Yields increase as R′ increases in mol. wt., *i.e.*, as the b.p. rises. $CHPhEt{\cdot}CN$ does not react and no reaction occurs if R is *sec.* $CH_2{:}CH{\cdot}CH_2{\cdot}CN$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ are too reactive and give tars. *Et α-cyano-phenyl-*, b.p. 125—126°/2—3 mm. (amide, m.p. 148—149°), -p-*iodo-phenyl-*, b.p. 160°/2 mm., and -p-*tolyl-acetate*, b.p. 120—121°/1 mm., are described.

IV. $CRNa(CO_2R')_2$ [prepared from $CHR(CO_2R')_2$ and NaOR″ by removing R″OH by distillation] in boiling R'_2CO_3 at, usually, 125—175° gives $CRR'(CO_2R')_2$ in yields stated below. In general R. should = R″, but for prep. of (**I**) (below) NaOMe can be used. Yields are good if R′ is primary, independently of the mol. wt., but

poor if R′ is *sec.* $CHNa(CO_2R')_2$ cannot be used as it gives $CH(CO_2R')_3$. The K derivatives can be used and, for $CHEt(CO_2Et)_2$, $Mg(OEt)_2$ at 225°. $CH_2R{\cdot}CO_2R'$ can also be used as starting material, since with NaOR′ and R'_2CO_3 it gives $CRNa(CO_2R')_2$. The following are thus prepared: $CEtR(CO_2Et)_2$ in which R = Et [from Pr^aCO_2Et 36%; from $CHEt(CO_2Et)_2$ 54%], Bu^a (from $C_5H_{11}{\cdot}CO_2Et$ 34%), *iso*amyl (from $Pr^\beta{\cdot}[CH_2]_3{\cdot}CO_2Et$ 45%), Pr^β (from $Bu^\beta CO_2Et$ 10%), octyl (25%), CHMeEt (poor), and Ph (30%), m.p. −9° to −7°, b.p. 105°/1 mm.; *$Bu^a{}_2$ ethylbutyl-* (42%), b.p. 117—119°/1 mm., *butyl-*n-*hexadecyl-* (83%), b.p. 265—268°/4 mm., and *benzylbutyl-malonate* (80%), b.p. 172°/3 mm. (derived *acid*, m.p. 105—107°); *$Bu^\beta{}_2$ ethyl*iso*butylmalonate* (45%), b.p. 175°/30 mm. (derived *acid*, m.p. 109—110°); *di*iso*amyl ethyl*iso*amylmalonate* (60%), b.p. 126—129°/1 mm. (derived *acid*, m.p. 120—121°); $(CHMeEt)_2C(CO_2CHMeEt)_2$ (poor yield); impure *di-γ-pentyl ethyl-γ-pentylmalonate* (~20%), b.p. 132—134°/3 mm.; *$(CH_2Ph)_2$ benzyl-ethylmalonate* (53%), b.p. 245—247°/2 mm. (derived *acid*, m.p. 125—127°). Fluorene gives 45% of *Bu 9-butylfluorene-9-carboxylate*, b.p. 175—176°/2 mm. (derived *acid*, m.p. 112—114°). The following are incidentally described: *$Bu^a{}_2$ ethyl-*, b.p. 98—99°/2 mm., n-*hexadecyl-*, b.p. 255—260°/4—5 mm., and *benzyl-malonate*, b.p. 154°/1 mm.; *$Bu^\beta{}_2$*, b.p. 150°/28 mm., *di*iso*amyl*, b.p. 96°/1 mm., *di-γ-pentyl*, b.p. 168—169°/35 mm., and *$(CH_2Ph)_2$ ethylmalonate*, b.p. 190°/2 mm.; *$(CHMeEt)_2$* sec.-*butylmalonate*, b.p. 115°/3 mm.

V. Alkylations of malonic, acetoacetic, β-keto- and α-cyano-acetic esters are well effected by alkyl halides and NaOEt [or KOEt or, in one case, $Mg(OEt)_2$] in boiling Et_2CO_3, when the EtOH formed is removed. Di-*sec.*-alkylmalonates can thus be prepared. During some difficult alkylations exchange of ester groups occurs but may be avoided by suitable choice of alkyl groups. The limiting factor is probably elimination of HHal from the alkyl halide; this is noteworthy with $Bu^\beta Br$ and prohibitive with $Bu^\gamma Cl$ or $Bu^\gamma Br$ which give solely $CMe_2{:}CH_2$ without alkylation. The following are described: *Et_2* n-*butyl*iso*amyl-*, b.p. 91—93°/1·5 mm., n-*butyl-*sec.-*butyl-*, b.p. 114—116°/4·5 mm., sec.-*butyl*iso*amyl-*, b.p. 95—99°/2—2·5 mm., *allyl-*sec.-*butyl-*, b.p. 109—111°/5 mm., sec.-*butyl-*n-*amyl-*, b.p. 89·5—92·5°/1—1·5 mm., *di-*sec.-*butyl-*, b.p. 112—114°/1·5 mm., *allyl-*tert.-*butyl-*, b.p. 94—95·5°/3·5 mm., iso*propyl-*iso-, b.p. 119—121°/10 mm., and -sec.-*butyl-*, b.p. 120—123°/10 mm., n-*propyl-*n-*amyl-*, b.p. 99—101°/2·6 mm., and *benzyl-*n-*hexadecyl-*, b.p. 238—240°/1 mm., *-malonate*; *Bu^a α-benzoyl-*n-*butyrate*, b.p. 116—117°/1 mm.; *Pr^a α-cyano-α-ethyl-*iso*hexoate*, b.p. 64—67°/1 mm., and *β-keto-α-ethyl-*n-*nonoate*, b.p. 103—105°/3·5 mm.; *Et α-cyano-α-p-tolyl-*n-*butyrate*, b.p. 105—110°/2·5—3 mm.; *α-benzyl-*n-*octadeco-2 : 4 : 6-tribromoanilide*, m.p. 85—87°. R. S. C.

Thioglycerol and related compounds of sulphur. B. Sjöberg (*Ber.*, 1942, **75**, [*B*], 13—29).—*α-Monothioglycerol [βγ-dihydroxy-α-thiolpropane]* (**I**), b.p. 95°/9 mm., 112°/3 mm., is obtained by treating γ-hydroxypropylene αβ-oxide (**II**) with $Ba(OH)_2$ and H_2S or from (**II**) and AcSH, whereby the primary product is a mixture of *βγ-dihydroxy-α-acetylthiolpropane*, b.p. 125—135°/1·8 mm., and the β- or γ-monoacetate; this is hydrolysed (HCl–MeOH at 60°) to (**I**). Alternatively, $CH_2Br{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, obtained from $OH{\cdot}CH(CH_2{\cdot}OH)_2$ and HBr and purified through the $:CMe_2$ derivative, is converted by AcCl into the *diacetate*, b.p. 88—90°/1 mm., transformed by AcSK into the *diacetate thioacetate*, b.p. 130—136°/1·8 mm., which is hydrolysed to (**I**). α-Chloro-*βγ-iso*propylidenedioxypropane and aq. KSH at 100° yield *βγ-iso*propylidenedioxy-α-thiolpropane (**II**), b.p. 54—57°/5 mm., and the corresponding *αα′-disulphide*, b.p. 145—153°/3·5 mm. Condensation (P_2O_5–sand) of (**I**) with $COMe_2$ at 0° affords (**II**) and *α-hydroxy-βγ-iso*propylideneoxythiopropane, b.p. 58—60°/0·8 mm., which appears to re-form (**II**) to some extent when kept. $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH$ and NaSH yield *γ-hydroxy-αβ-dithiolpropane* (**III**), b.p. 91·5—92°/1·7 mm., also obtained by means of KSAc. *αβ′-Dibromohydrin γ-acetate*, b.p. 51°/0·3 mm., and KSAc give *γ-acetoxy-αβ-diacetylthiolpropane*, b.p. 125—130°/0·6 mm., hydrolysed (HCl–MeOH) to (**III**). $OH{\cdot}CH(CH_2Cl)_2$ and NaSH in abs. EtOH yield $OH{\cdot}CH(CH_2{\cdot}SH)_2$, b.p. 82°/1·5 mm., purified through the Hg derivative, which softens and blackens at 190—190·5°. $Cl{\cdot}[CH_2]_3{\cdot}OH$ and K_2S_2 in H_2O afford *γγ′-dihydroxydipropyl disulphide*, b.p. 160°/0·8 mm., reduced at a Pb cathode to $OH{\cdot}[CH_2]_3{\cdot}SH$ (**IV**), b.p. 80°/1·2 mm. Propylene αβ-oxide and AcSH at 60—70° give mainly *β-hydroxy-α-acetylthiolpropane*, b.p. 80—100°/12 mm., hydrolysed (HCl–MeOH) to *β-hydroxypropylthiol* (**V**), b.p. 51°/12 mm. (**IV**) and (**V**) afford *CPr_2* derivatives, b.p. 60°/12 mm. and 72°/80 mm., or 141°/761 mm., respectively. (**V**) is transformed by conc. HCl at 100° into *β-chloropropylthiol*, b.p. 125—125·5°/764 mm., which immediately decomposes in H_2O at 0°. H. W.

Characterisation of lactic acid as the benziminazole derivative. R. J. Dimler and K. P. Link (*J. Biol. Chem.*, 1942, **143**, 557—558).—*d-* or *l-*, m.p. 165—177° (hydrochloride, m.p. 213—215°), and *dl-*lactobenziminazole, m.p. 179—181° (hydrochloride, m.p. 211—213°), are prepared. A. T. P.

Acid synthesis. II. Effect of hindrance. Methyl-*tert.*-butyl- and -ethylpropyl-acetic acids. J. G. Aston, J. T. Clarke, K. A. Burgess, and R. B. Greenburg (*J. Amer. Chem. Soc.*, 1942, **64**, 300—302; cf. A., 1941, II, 4).—Conversion of $COR{\cdot}CR'R''Br$ by $NaOR'''$ into $CRR'R''{\cdot}CO_2R'''$ occurs owing to steric hindrance around the Br and is retarded if R is large. $COMe{\cdot}CHMeBr$ and NaOMe in boiling Et_2O give, by normal metathesis, *γ-methoxybutan-β-one* (39·1%), b.p. 87°/740 mm. [with $NHPh{\cdot}NH_2$ in 5% HCl gives $(CMe{:}N{\cdot}NHPh)_2$]. *γ-Bromo-δδ-dimethylpentan-β-one* (prep. from $COMe{\cdot}CH_2Bu^\gamma$ by Br at 0°), b.p. 106°/88 mm., and NaOMe–Et_2O give *Me αββ-trimethyl-*n-*butyrate* (73%), b.p. 95°/150 mm. [derived *acid*, m.p. 53·5°, b.p. 132°/55 mm. (anilide, m.p. 112°)]. $COPr^a{\cdot}CHMeEt$ and Br at 0° give *γ-bromo-γ-methyl-*n-*heptan-δ-one* (45%), b.p. 88°/22 mm., which with NaOMe–Et_2O gives a const.-boiling mixture (75%) of $COPr^a{\cdot}CMeEt{\cdot}OMe$ (gives a small amount of 2 : 4-dinitrophenylhydrazone, m.p. 139—140°) and $CMeEtPr^a{\cdot}CO_2Me$, whence boiling HI yields *α-methyl-α-ethyl-*n-*valeric acid*, b.p. 105°/20 mm. (*chloride*, b.p. ~110°/100 mm.). $COPh{\cdot}CMe_2Br$ and NaOMe–Et_2O give 70% of α-methoxy*iso*butyrophenone, b.p. 88—88·5°/14 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 139—140°), oxidised by $K_2Cr_2O_7$–H_2SO_4 at 75—80° to $COMe_2$ and BzOH. R. S. C.

Second *dl-βζ-*epoxy-Δ^γ-heptene-γ-carboxylic acid. M. Delépine and M. Badoche (*Compt. rend.*, 1941, **213**, 413—416).—Oxidation with $Ba(OH)_2$ and $AgNO_3$ of the dimeride of $CHMe{:}CH{\cdot}CHO$ gives 1% of *dl-βζ-epoxy-Δ^γ-heptene-γ-carboxylic acid*-b, m.p. 93—93·5° [*bromohydrin* ($+H_2O$), m.p. 101—106° (slight decomp.); *amide*, m.p. 168° (slow heating)], hydrogenated (Ni) to the H_2-acid [*anilide*, m.p. 168—169° (slow heating)]. A. Lt.

Complex formation by ascorbic acid with formaldehyde.—See A., 1942, III, 407.

Colour reaction of dehydroascorbic acid. J. H. Roe and C. A. Kuether (*Science*, 1942, **95**, 77).—The red colour formed by the action of H_2SO_4 and the coupled 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$–dehydroascorbic acid compound is suitable for the colorimetric determination of ascorbic acid. High concns. of pentoses, glucose, and fructose may interfere. E. R. R.

Carbohydrate characterisation. III. Identification of hexuronic or saccharic acids as benziminazole derivatives. R. Lohmar, R. J. Dimler, S. Moore, and K. P. Link (*J. Biol. Chem.*, 1942, **143**, 551—556; cf. A., 1940, II, 244).—A method for identifying naturally occurring hexuronic acids as dibenziminazole derivatives of the corresponding saccharic acids is described. Thus, *d*-glucuronic, *d*-mannuronic, and *d*-galacturonic acid are oxidised to the respective dibasic acid, which with *o*-$C_6H_4(NH_2)_2$–HCl–H_3PO_4–$(OH{\cdot}[CH_2]_2)_2O$ at ~135° afford d-*saccharo-*, m.p. 238°, $[\alpha]_D^{25}$ +60·3° in aq. citric acid [*dihydrochloride*, m.p. 257—258° (decomp.); *picrate*, m.p. 211° (decomp.)], d-*mannosaccharo-*, m.p. 250°, $[\alpha]_D^{25}$ −1·3° in H_2O [*dihydrochloride*, m.p. 256—257° (decomp.); *picrate*, m.p. 241° (decomp.); *tetra-acetate*, m.p. 255—256°, $[\alpha]_D^{25}$ −11·9° in $CHCl_3$], and *mucic acid-dibenziminazole*, m.p. 298°, $[\alpha]_D^{25}$ 0·0° in aq. citric acid [*dihydrochloride*, m.p. 318° (decomp.); *picrate*, m.p. 250° (decomp.)], respectively. A. T. P.

Photochemical reaction between bromine and choral.—See A., 1942, I, 273.

Dimeric *dl*-glyceraldehyde αγ-diphosphate. E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1942, **143**, 563—564).—Dimeric *dl*-glyceraldehyde and $(OPh)_2POCl$–C_5H_5N give, after hydrogenation (PtO_2–MeOH at room temp.) of the resulting *Ph_3* ester, m.p. 108—109°, dimeric *glyceraldehyde αγ-diphosphate* [*Ba* ($+2H_2O$) and *Ca* ($+2H_2O$) salt], which is probably an intermediate in sugar metabolism. A. T. P.

Reaction of keten diethyl acetal with αβ-unsaturated carbonyl compounds.—See A., 1942, II, 227.

Intramolecular condensations in polymerides. F. T. Wall (*J. Amer. Chem. Soc.*, 1942, **64**, 269—273).—Mathematical. The fractions of O remaining in infinitely long "head to tail," random, and "head to head–tail to tail" polymerides after complete intramol. aldol condensations have been calc. statistically. The results for pure polymerides (*e.g.*, of $COMe{\cdot}CH{:}CH_2$) have been extended to co-polymerides. W. R. A.

Action of sodium on hexamethylacetone. P. G. Stevens and J. H. Mowat (*J. Amer. Chem. Soc.*, 1942, **64**, 554—556).—Results recorded below differ from those of Favorsky *et al.* (A., 1934, 758), possibly for steric reasons. With Na–Et_2O–N_2 at > room temp. $COBu^\gamma{}_2$ gives $CHBu^\gamma{}_2{\cdot}OH$ and 5% of *ββεε-tetramethyl-γδ-di-*tert.-*butyl-*n-*hexane-γδ-diol* (**I**), m.p. 116—117°, b.p. ~200°/13 mm., and a mixture (C 77·2, H 13·6%), b.p. 125—126°/14 mm., 68°/0·8 mm. (*tetrabromide*, m.p. 75—78·5°). (**I**) is stable to $Pb(OAc)_4$–C_6H_6 at 25° and 100° and to boiling $KMnO_4$–C_5H_5N, contains 2 active H, has normal mol. wt. in camphor and *cyclo*hexane but not in C_6H_6 at 5°, does not absorb O_2 or give free radicals, and in conc. H_2SO_4 at −20° (later 25°) gives an unsaturated (Br; $KMnO_4$) oil, b.p. 41—120°/25 mm. (no insol. bromide). R. S. C.

Application of 2-nitroindane-1 : 3-dione to the isolation and identification of organic bases. G. Wanag and A. Dombrowski (*Ber.*, 1942, **75**, [*B*], 82—86; cf. A., 1937, II, 199).—2-Nitroindane-1 : 3-dione (**I**) (modified prep. described) in ~5·7% solution in H_2O gives non-hygroscopic, anhyd. ppts. with the following: NH_2Me, m.p. 203—205°; NH_2Et, m.p. 202—203°; NH_2Pr^a, m.p. 184—185°;

NH_2Pr^{β}, m.p. 205°; NH_2Bu^{α}, m.p. 147°; NH_2Bu^{β}, m.p. 178°; n-$C_5H_{11}\cdot NH_2$, m.p. 158°; iso-$C_5H_{11}\cdot NH_2$, m.p. 162°; iso-$C_6H_{13}\cdot NH_2$, m.p. 155°; n-$C_7H_{15}\cdot NH_2$, m.p. 149—150°; $CH_2Ph\cdot CHMe\cdot NH_2$, m.p. 193°; *cyclo*hexylamine, m.p. 213°; $CH_2(NH_2)_2$ (1 : 2), m.p. 229°; $(CH_2\cdot NH_2)_2$ (1 : 2), m.p. 204—205°; *propylenediamine* (1 : 2), m.p. 206°; *diaminopropanol*, m.p. 195°; $NHBu^{\beta}\cdot CH_2Ph$, m.p. 220°; *mesidine*, m.p. 162°; *ψ*-cumidine, m.p. 162°; s-m-*toluylenediamine*, m.p. 166°; 1 : 2-, m.p. 179°, and 1 : 8-$C_{10}H_6(NH_2)_2$ (1 : 2), m.p. 216°; *naphthidine*, m.p. 195°; 1-$C_{10}H_7\cdot NHMe$, m.p. 196—199°; 2-$C_{10}H_7\cdot NHMe$, m.p. 177°; o-, m.p. 182°, m-, m.p. 192°, and p-, m.p. 188°, -$C_6H_4Cl\cdot NH_2$; o-, m.p. 203—205°, and m-, m.p. 210°, -$NH_2\cdot C_6H_4\cdot OH$; o-, m.p. 198°, m-, m.p. 205°, and p-, m.p. 203°, -$NH_2\cdot C_6H_4\cdot OMe$; o-, m.p. 206°, m-, m.p. 210°, and p-, m.p. 190°, -$NH_2\cdot C_6H_4\cdot OEt$; o-*dianisidine*, m.p. 226°; 2 : 4 : 1-$(NH_2)_2C_6H_3\cdot OH$, (1 : 2), m.p. 198—200°; p-$C_6H_4Ac\cdot NH_2$, m.p. 199°; p-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$, m.p. 214°; m-, m.p. 182°, and p-, m.p. 175°, -$NO_2\cdot C_6H_4\cdot NH_2$; o-, m.p. 189°, m-, m.p. 212°, and p-, m.p. 213°, -$NH_2\cdot C_6H_4\cdot CO_2H$; o-$NH_2\cdot C_6H_4\cdot CO_2Et$, m.p. 197°; 4-*methylquinoline*, m.p. 197—198°; iso*quinoline*, m.p. 187°; 2 : 6-*diaminopyridine* (1 : 2), m.p. 235°; 2-*aminothiazole*, m.p. 208°; *pyrrolidine*, m.p. 215°; *aziminobenzene*, m.p. 178°; *benziminazole*, m.p. 228°. Except where otherwise stated the ratio base : (I) = 1 : 1. Limiting concns. are recorded at which (I) gives ppts. with the above mentioned bases and also with putrescine, cadaverine, histamine, mescaline, $COPh\cdot CH_2\cdot NH_2$, spermine, 1 : 3 : 5-$C_6H_3(NH_2)_3$, 1 : 2 : 4 : 6-$C_6H_2Me(NH_2)_3$, 1 : 2 : 4 : 6-$C_6H_2Cl(NH_2)_3$, tetra-aminoditolylmethane, 1 : 4-, 1 : 5-, and 2 : 7-$C_{10}H_6(NH_2)_2$, o-$C_6H_4(NHMe)_2$, o-$NHAc\cdot C_6H_4\cdot NH_2$, o-$C_6H_4(CO)_2N\cdot C_6H_4\cdot NH_2$-o, p-$NH_2\cdot C_6H_4\cdot N_2Ph$, chrysoidine, methylene- and ethylene-dianiline, piperazine, nitron, narcotine, 3 : 5-dimethylpyrazole, and $NHPh\cdot NH_2$. H. W.

Ethanolamine 3 : 5-di-iodosalicylate, m.p. 199—200° (corr.; decomp.).—See A., 1942, III, 463.

Chromatographic separation of mixtures of amino-acids. J. Wachtel and H. G. Cassidy (*Science*, 1942, **95**, 233; cf. A., 1942, II, 44).—Quant. separations of mixtures of *l*-tyrosine (I) and *dl*-leucine (II), of *dl*-phenylalanine (III) and (II), and partial separations of mixtures of (I) and (III) and of glycine and phenylalanine, are effected by a modified Tswett chromatographic method in which the adsorbent is a commercial C (Darco G-60) mixed with filter pulp. E. R. R.

Preparation of glycine. W. C. Tobie and G. B. Ayres (*J. Amer. Chem. Soc.*, 1942, **64**, 725).—Prep. of glycine (Orten *et al.*, A., 1931, 1042) is improved to give 80% yield. R. S. C.

Complex calcium and copper salts of trilon *A* and *B*. P. Pfeiffer and W. Offermann (*Ber.*, 1942, **75**, [*B*], 1—12).—$NH(CH_2\cdot CO_2Na)_2,6H_2O$ (I) has m.p. 71—72°. $N(CH_2\cdot CO_2H)_3$ (II) is converted by NaOH into $N(CH_2\cdot CO_2Na)_3$ (trilon *A*), (III), but by an excess of KOH into the K_2 H salt (IV). (I) and alkali-free $Cu(OH)_2$ in boiling H_2O afford the *salt*, $C_8H_{10}O_8N_2Na_2Cu,10H_2O$, m.p. 117° (decomp.) after softening at 70°, which is somewhat more stable than the Cu compound of glycine. Similarly (III) yields the complex salt, $C_{12}H_{12}O_{12}N_2Na_4Cu,4H_2O$, which is of the same order of stability; the corresponding Cu salt (+$7H_2O$ and +$1H_2O$), decomp. ~222°, is described. $[CH_2\cdot N(CH_2\cdot CO_2Na)_2]_2$ (trilon *B*) (V) gives the *salt*, $C_{10}H_{12}O_8N_2Na_2Cu,4H_2O$ (VI), and the corresponding *Cu* salt (+$4H_2O$). Polarographic measurements show that Cu is retained in (VI) with remarkable firmness, thus explaining the use of (V) for removal of traces of Cu from fabrics. The stability of (VI) is ascribed to the presence of an ethylenic bridge. $(NH_2\cdot CH_2\cdot CO_2)_2Ca$ appears to be a normal Ca salt and gives an immediate ppt. with $(NH_4)_2C_2O_4$. Attempts to prepare a complex Ca salt of $NH(CH_2\cdot CO_2H)_2$ were unsuccessful. (IV) and $CaCO_3$ in boiling H_2O afford the complex *salt*, $C_{12}H_{12}O_{12}N_2K_4Ca,4H_2O$, which does not give an immediate ppt. with $(NH_4)_2C_2O_4$ or with Na stearate or soap solution; it is very easily decomposed by acids. The *salt*, $C_{12}H_{12}O_{12}N_2Ca_3$ (+$4H_2O$ and anhyd.), is described. $[CH_2(N\cdot CH_2\cdot CO_2H)_2]_2$ is transformed by suitable quantities of KOH and $CaCO_3$ in boiling H_2O into the *salt*, $C_{10}H_{12}O_8N_2K_2Ca,4H_2O$, in which Ca is in such firm complex union that no turbidity is given with Na stearate or soap after many hr. A similar complex *Mg* salt (+$5H_2O$) is described. An explanation of the ability of (III) and (V) to soften H_2O is thus afforded. H. W.

Reaction of allylacetone and dry ammonium cyanide. A. V. Ipatov (*J. Gen. Chem. Russ.*, 1941, **11**, 605—607).—Allylacetone and NH_4CN in EtOH–HCl afford an unsaturated *NH_2-acid*, $C_7H_{13}O_2N$ (I), m.p. 231—234° (decomp.) [*picrate*, m.p. 175—177° (decomp.); *Bz* derivative, m.p. 125—127° (decomp.)], probably methylallylaminopropionic acid. G. A. R. K.

Polycondensation of peptide esters. I. Polyglycine esters. E. Pacsu and E. J. Wilson, jun. **II. Protein models. Preparation of tripeptide methyl esters.** E. J. Wilson, jun., and E. Pacsu (*J. Org. Chem.*, 1942, **7**, 117—125, 126—135).—I. Heating of the esters of simple peptides and the NH_2-acids may lead to intramol. removal of one mol. of EtOH from 1 mol. of acid ester, giving a diradical, ·NH·CHR·CO·, two of which combine in inverted position to give the corresponding diketopiperazine. The ester of a dipeptide may lose 1 EtOH intramolecularly and the corresponding diketopiperazine is formed by ring-closure of the resulting ·NH·CHR·CO·NH·CHR·CO· diradical. This cyclisation is very rapid in the case of glycylglycine ester, the dry crystals of which change into diketopiperazine even at room temp. in 10 days. A tripeptide ester may pass into a hexapeptide ester; an example is the intermol. elimination of one mol. of EtOH from 2 mols. of the tripeptide ester and union of the resulting $NH_2\cdot[CHR\cdot CO\cdot NH]_2\cdot CHR\cdot CO\cdot$ and $\cdot NH\cdot[CHR\cdot CO\cdot NH]_2\cdot CHR\cdot CO\cdot R'$ radicals. Tetrapeptide esters do not condense. Instead of cyclisation to give the simplest model of a "cyclol 6" postulated by the Wrinch theory, hexaglycylglycine Me ester, when heated, undergoes the type of condensation characteristic for the tripeptide esters in a series of successive reactions yielding 12-, 24-, 48- and 96-peptide esters of glycine (I). The course of the reaction has been followed by determining OMe in samples withdrawn at certain intervals of time. Similarly, the condensation reactions of the tripeptide and dodecapeptide esters of (I) proceed according to 3×2^n where n is an integer, giving 96 as the final stage of condensation. Analysis of the condensation products indicates that neither "cyclol 6" nor (probably) nonapeptide is formed when triglycylglycine Me ester is heated. The polypeptides obtained resemble denatured proteins and give strong biuret reactions. An improved prep. of diglycylglycine Me ester (II) is given. The prep. of pentaglycylglycine Me ester from (II) is described.

II. The action between NH_3 and α-bromo-propionyl- and -*iso*hexoyl-glycylglycine, α-bromopropionyl-leucylglycine, and chloroacetyl-leucylalanine is much more rapid than in Fischer's experiments and considerably improved yields are obtained in shorter times since the change is accompanied by elimination of HBr, formation of a corresponding OH-acid, and splitting of the peptide linking. Treatment of alanylglycyl-, leucylglycyl-, and alanylleucyl-glycine and glycyl-leucylalanine with MeOH–HCl under the conditions customary in esterification gives $NH_2\cdot CH_2\cdot CO_2Me,HCl$ and the hydrochlorides of the Me esters of alanylglycine, leucylglycine, alanyl-leucine, and leucylalanine. The tripeptide esters can be obtained, however, by using freshly prepared, saturated HCl–MeOH to insure rapid esterification and immediately pptg. the solutions with dry Et_2O or evaporating them at once in a vac. Thus are obtained dl-*alanylglycylglycine Me ester* (III), m.p. 86—88° [*hydrochloride*, m.p. 157—160° (corr.)]; dl-*leucylglycylglycine Me ester* (IV), m.p. 70° [*hydrochloride*, m.p. 227—228° (corr.; decomp.)]; *glycyl*-dl-*leucyl*-dl-*alanine Me ester*, m.p. 192—105° (*hydrochloride*). When heated, (III) and (IV) undergo condensation in a series of successive reactions apparently according to 3×2^n. The course of the reaction is followed by determination of OMe. Quant. analyses of the condensation products of (III) indicate that "cyclol 6" is not formed in the reaction. A definite conclusion could not be reached as to the formation or non-formation of a nonapeptide ester. The substances are sol. in H_2O and all give strong biuret reactions. H. W.

Biogenesis of pantothenic acid. R. Kuhn and T. Wieland (*Ber.*, 1942, **75**, [*B*], 121—123).—The suggested scheme is:

$$NH_2\cdot CHPr^{\beta}\cdot CO_2H \rightarrow Pr^{\beta}CO\cdot CO_2H\ (I) \rightarrow$$

$$(+CH_2O)\ OH\cdot CH_2\cdot CMe_2\cdot CO\cdot CO_2H \rightarrow \begin{matrix} CO — CO \\ CMe_2\cdot CH_2 \end{matrix}\!\!>O \rightarrow$$

$$OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CO_2H \rightleftharpoons \begin{matrix} OH\cdot CH — CO \\ CMe_2\cdot CH_2 \end{matrix}\!\!>O +$$

$$NH_2\cdot[CH_2]_2\cdot CO_2H \rightarrow OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CO\cdot NH\cdot[CH_2]_2\cdot CO_2H.$$

(I) condenses with CH_2O in presence of K_2CO_3 to *α-keto-ββ-dimethyl-γ-butyrolactone* (II), m.p. 60°, hydrogenated to *dl*-α-hydroxy-ββ-dimethyl-γ-butyrolactone; the corresponding acid gives a sparingly sol. quinine salt, m.p. 183—184°. Addition of (II) to a fermenting mixture of yeast "M," glucose, and NaH_2PO_4 leads to (−)-α-hydroxy-ββ-dimethyl-γ-butyrolactone, m.p. 84—85°, $[\alpha]_D^{22}$ −50·5° in H_2O. H. W.

Analogues of pantothenic acid. I. Attempted preparation of growth promoters. II. Preparation of growth inhibitors. J. W. Barnett and F. A. Robinson (*Biochem. J.*, 1942, **36**, 357—363, 364—367; see also A., 1942, III, 621).—I. ββ-Dimethyl-γ-butyrolactone and $NH_2\cdot[CH_2]_2\cdot CO_2Na$ (I) in boiling abs. MeOH, with subsequent addition to Et_2O or $COMe_2$, give (impure) *Na deoxypantothenate* [*β-γ'-hydroxy-β'β'-dimethylbutyramidopropionate*]. Similarly, *β-hydroxy-γγ-dimethyl-δ-valerolactone* (+H_2O) (II), m.p. 126—126·5° [from $CH_2Br\cdot CO_2Et$, $OH\cdot CH_2\cdot CMe_2\cdot CHO$ (III), and Zn in C_6H_6 with subsequent hyrolysis (EtOH–KOH)], and (I) afford *Na homopanthothenate* [*β-β'δ'-dihydroxy-γ'γ'-dimethylvaleramidopropionate*], whilst *γγ-dimethyl-δ-Δ^{α}-pentenolactone*, m.p. 115° [formed with another lactone from (III) and $CH_2(CO_2H)_2$ in Ac_2O–AcOH at 140°], and (I) give *Na dehydrohomopantothenate* [*β-δ'-hydroxy-γ'γ'-dimethyl-$\Delta^{\alpha'}$-pentenoamidopropionate*]. γ-Butyrolactone or γ-valerolactone and (I) afford *Na bisnordeoxypantothenate* [*β-γ'-hydroxybutyramidopropionate*] or iso*nordeoxypantothenate* [*β-γ'-hydroxyvaleramidopropionate*], respectively, and with EtOH–$NHPh\cdot NH_2$ give the corresponding *phenylhydrazide*, m.p. 94—94·5° or 83—85°, respectively. Analogous compounds are prepared from α-hydroxy-ββ-dimethyl-γ-butyrolactone (IV) and the Ca salts of lysine, leucine, valine, and taurine.

II. (IV) and $NH_2\cdot[CH_2]_2\cdot SO_3Na$ (V) at 120° alone or in boiling

MeOH give "pantoyltaurine" [Na β-α′γ′-dihydroxy-β′β′-dimethylbutyramidoethanesulphonate]. Pantoyltauramide is prepared from (IV) and $NH_2·[CH_2]_2·SO_2·NH_2$ at 120°. (II) and (V) at 120° afford "*homopantoyltaurine*" [*Na β-β′δ′-dihydroxy-γ′γ′-dimethylvaleramidoethanesulphonate*]. H. B.

Complex compounds of diguanide with tervalent metals. X. Hydroxo-aquo cobaltic bisdiguanidine and its salts. P. Rây and S. P. Ghosh (*J. Indian Chem. Soc.*, 1942, **19**, 1—8).—Co bisdiguanidine in aq. NH_3, when oxidised with air and treated with H_2SO_4, gives *diaminocobaltic bisguanidinium* sulphate ($+12H_2O$), and on further treatment affords *hydroxoaquocobaltic bisdiguanidinium sulphate* ($+2·5H_2O$), which on addition of the appropriate reagent yields the *chloride* ($+H_2O$), *hydroxide* ($+H_2O$) [converted by heating into diol-tetrakisdiguanidine dicobalt), *nitrate, sulphite, dithionate* ($+H_2O$), and *thiosulphate* ($+H_2O$). When excess of $Na_2S_2O_3$ is added to the chloride, *thiosulphato-tetrakisdiguanidinium dithiosulphatodicobalt* ($+2H_2O$) is obtained. F. R. S.

II.—SUGARS AND GLUCOSIDES.

Sugar of cozymase.—See A., 1942, III, 641.

***l*-Sorbose. III. Further methyl derivatives of *l*-sorbose.** H. H. Schlubach and P. Olters (*Annalen*, 1942, **550**, 140—145; cf. A., 1940, II, 36).—β-Methyl-*l*-sorboside and TlOEt–EtOH, followed by MeI–Et_2O, afford *tetramethyl-β-methyl-l-sorboside*, b.p. 51°/0·01 mm., $[\alpha]_D^{20}$ +69·8° in $CHCl_3$, converted by dil. HCl at 90° into 1 : 3 : 4 : 5-*tetramethyl-l-sorbose*, b.p. 64°/0·08 mm., $[\alpha]_D^{20}$ −14·6° in $CHCl_3$. 2 : 3-*iso*Propylidene-1 : 4 : 6-trimethyl-*l*-sorbose, b.p. 135—137°/11 mm., $[\alpha]_D^{20}$ +29·6° in $CHCl_3$, and aq. AcOH yield 1 : 4 : 6-trimethyl-*l*-sorbose, which with MeOH–HCl, followed by aq. Me_2SO_4–NaOH–$COMe_2$, affords 1 : 2 : 3 : 4 : 6-*pentamethyl-l-sorbose*, b.p. 56° 0·01 mm., $[\alpha]_D^{20}$ −39·4° in $CHCl_3$, and thence (dil. HCl at 90°) 1 : 3 : 4 : 6-*tetramethyl-l-sorbose*, b.p. 64°/0·01 mm., $[\alpha]_D^{20}$ +29·7° in $CHCl_3$. A. T. P.

Preparation and rearrangement of phenylglucosides. (Miss) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 690—694).—Prep. of α- (I) (64%), m.p. 115°, [α] +168·7° in $CHCl_3$, and β-phenyl-*D*-glucoside tetra-acetate (II) (85%), m.p. 125—126°, [α] −22·5° in $CHCl_3$, is improved. (II) is rearranged to (I) by $ZnCl_2$–PhOH at 120—125°/vac. Glucose α-penta-acetate, p-$NO_2·C_6H_4·OH$, and $ZnCl_2$ at 125° give α- (60%), m.p. 113°, [α] +200° in $CHCl_3$, and β-*p*-nitrophenyl-*D*-glucoside tetra-acetate (18%), m.p. 174—175°, [α] −41° in $CHCl_3$ [46 and 28%, respectively, from the β-penta-acetate], and thence α-, m.p. 216°, [α] +215° in H_2O, and β-*p*-nitrophenyl-*D*-glucoside, m.p. 164°, [α] −103·0° in H_2O. β-, $+H_2O$, m.p. 132°, [α] −83·0° in H_2O, and anhyd., m.p. 152°, [α] −106° in H_2O [tetra-acetate, m.p. 150—152°, [α] +45° in $CHCl_3$), and α-o-*nitrophenyl*-D-*glucoside*, m.p. 186—188°, [α] +206° in H_2O [tetra-acetate, m.p. 110° (lit. 95°), [α] +167° (lit. 124°) in $CHCl_3$], β-*p*-acetophenyl-*D*-glucoside tetra-acetate, m.p. 172—173°, [α] −28·6° in $CHCl_3$, α- (new), m.p. 145°, [α] +189° in H_2O (*triacetate*, m.p. 64—65°, [α] +135° in $CHCl_3$), and β-phenyl-*D*-xyloside, m.p. 179°, [α] −49·4° in H_2O (triacetate, m.p. 148°, [α] −50·5° in $CHCl_3$), are described. With $ZnCl_2$ and PhOH in 19 : 1 AcOH–H_2O at 120—125° various α-methylglucoside acetates give good yields of α-phenylglucosides (and some of the β-isomerides). [α] are $[\alpha]_D^{20}$. R. S. C.

Polysaccharide produced by the crown-gall organism. F. C. McIntire, W. H. Peterson, and A. J. Riker (*J. Biol. Chem.*, 1942, **143**, 491—496).—The apparently homogeneous *polysaccharide* (I), $[\alpha]_D^{25}$ −9° to −10° in H_2O, gives a triacetate, $[\alpha]_D^{25}$ +56° to +58·5° in $CHCl_3$. Hydrolysis of (I) yields only *d*(+)-glucose. A shift in rotation during hydrolysis indicates a predominance of β-linkings, and rate of hydrolysis and shape of hydrolysis curve suggest that the inner ring structures are exclusively pyranoside. Mol. wt. of (I) is 3600±200, corresponding with ~22 anhydroglucose units per mol. A. T. P.

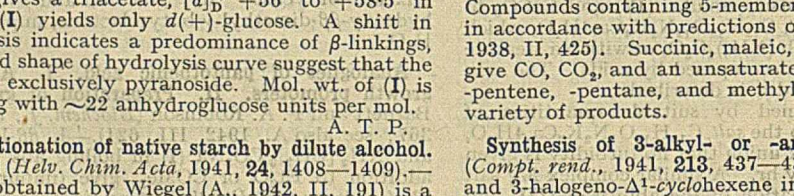
Starch. XVIII. Fractionation of native starch by dilute alcohol. K. H. Meyer and M. Fuld (*Helv. Chim. Acta*, 1941, **24**, 1408—1409).—The "cryst. amylose" obtained by Wiegel (A., 1942, II, 191) is a mixture of amylose and amylopectin. H. W.

Starch. XX. Viscosity of mucilage of starch. K. H. Meyer and M. Fuld. **XXI. Amylolytic enzymes of yeast. XXII. Action of phosphorylase of potato.** K. H. Meyer and P. Bernfeld (*Helv. Chim. Acta*, 1942, **25**, 391—398, 399—403, 404—405).—XX. Measurements of η of mucilages of various starches and of the solutions of the corresponding amyloses obtained after removing the grains by centrifuging support the view of Katz that the principal cause of η is the hydrodynamic effect produced by the suspended swollen grains. The conclusion is corroborated by the observation that η is diminished by the addition of any substance (NaCl, glucose, etc.) which diminishes the vol. occupied by the grains; this phenomenon is most marked with potato starch (I). The unique position of (I) is not due to chemical constitution, unusually high mol. wt., or outstanding size of grain but must be sought in the texture of the grain.

XXI. Details are given of the isolation from yeast of a phosphorylase (II) and amyloglucosidase (III) which hydrolyses starch (IV) and glycogen (V). (II) is capable of degrading (IV), (V), and residual dextrin (VI) which retains its action towards I. After a preliminary treatment by (II), (VI) is hydrolysed by β-amylase to a *dextrin II* which gives a colour with I. (II) appears to attack the non-aldehydic extremities of the chains. (III) degrades (VI) but the reaction with I is very persistent; it is not identical with α- or β-amylase.

XXII. Unlike yeast phosphorylase, the enzyme of potato has no action on (VI) in presence of PO_4'''. H. W.

(A) Probable structure of a crystalline substance derived from starches oxidised by periodate. (B) Reaction between periodate-oxidised starch and methanol containing hydrogen chloride. J. H. Michell and C. B. Purves (*J. Amer. Chem. Soc.*, 1942, **64**, 585—588, 589—593).—(A) When maize starch is oxidised by $Na_3H_2IO_6$ and, after hydrolysis by 10% HCl–MeOH, the $(CHO)_2$ and *d*-erythrose (I) are removed, the residual lævorotatory syrup (*A*) yields a *substance* (II), $C_{10}H_{12}O_5(OMe)_3·OH$ (2%), m.p. 148—148·5°, $[\alpha]_D^{20}$ −4·3° in H_2O [*acetate*, m.p. 120—120·5°, $[\alpha]_D^{21}$ −7·3° in dioxan, reconverted into (II) by 0·1N-$Ba(OMe)_2$]. The p-*toluenesulphonate*, m.p. 87—88°, of (II) does not react with KI, indicating absence of primary OH. In boiling 10% HCl–MeOH, (I) gives 82·5% of $[CH(OMe)_2]_2$ but no erythrose could be isolated. Hydrolysis and simultaneous HIO_3-oxidation of (II) is compatible with (II) being derived from 1 mol. of $(CHO)_2$ and 2 mols. of (I). (II) is thus probably



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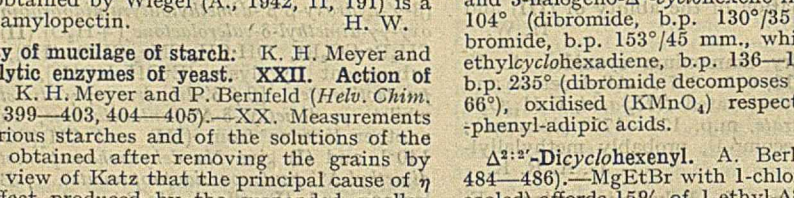
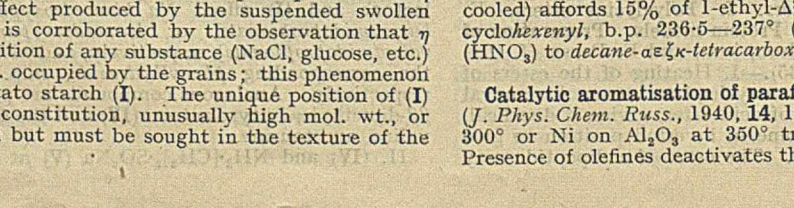


(B) The non-cryst. portion of *A* yields a syrup (III) (24%), b.p. 195—205°/3 mm., $[\alpha]_D$ −53·6° in H_2O, and a fraction (IV) (18%), b.p. 116—119·5°/3 mm. (IV) yields a substance (V*a* or *b*), $C_6H_7O_3(OMe)_3$, m.p. 97—98°, $[\alpha]_D$ −59·1° in H_2O, and a syrup, b.p. 117—118°/4 mm., $[\alpha]_D$ −91·7° in H_2O. In boiling 10% HCl–MeOH,



(V*a*.) (V*b*.)

oxycellulose or (III) gives a syrup resembling (IV). It is concluded that methanolysis of oxidised starch probably proceeds by random fission of acetal linkings and formation of new hemiacetal linkings leading to dioxans, but other structures are possible. M.p. are corr. R. S. C.

III.—HOMOCYCLIC.

Dehydration of *cyclo*propylmethylvinylcarbinol. A. P. Golovtschanskaja (*J. Gen. Chem. Russ.*, 1941, **11**, 608—615).—Acetyl-*cyclo*propane and C_2H_2 in presence of powdered KOH and Et_2O at 0° afford cyclo*propylmethylacetylenylcarbinol* (I) (60—70%), b.p. 145—146°, and a fraction of b.p. 127—133°/6 mm., probably a mixture of glycols $C_{12}H_{18}O_2$, of which one is a solid, m.p. 85—86°. Electrolytic reduction of (I) affords 60—70% of cyclo*propylmethylvinylcarbinol* (II), b.p. 139°/751 mm. (II) when passed over anhyd. $MgSO_4$ at 240—250° gives 14—18% of β-cyclo*propylbutadiene* (III), oxidised by $KMnO_4$ to *cyclo*propanecarboxylic acid and $H_2C_2O_4$. (III) condenses with $(CH·CO)_2O$ to a *product*, m.p. 83—84°, and is polymerised by Na to a solid and a syrupy liquid. G. A. R. K.

Thermal decomposition of five-membered rings. F. O. Rice and (Miss) M. T. Murphy (*J. Amer. Chem. Soc.*, 1942, **64**, 896—899).—Compounds containing 5-membered rings are thermally decomposed in accordance with predictions of the principle of least motion (A., 1938, II, 425). Succinic, maleic, citraconic, and itaconic anhydrides give CO, CO_2, and an unsaturated hydrocarbon. *cyclo*-Pentadiene, -pentene, -pentane, and methyl*cyclo*pentane yield a considerable variety of products. W. R. A.

Synthesis of 3-alkyl- or -aryl-Δ¹-*cyclo*hexenes. A. Berlande (*Compt. rend.*, 1941, **213**, 437—439).—Alkyl or aryl halide with Mg and 3-halogeno-Δ¹-*cyclo*hexene in Et_2O at 0° yields 3-methyl-, b.p. 104° (dibromide, b.p. 130°/35 mm.), 3-ethyl-, b.p. 131·5° (dibromide, b.p. 153°/45 mm., which with hot EtOH–NaOEt yields ethyl*cyclo*hexadiene, b.p. 136—137°), and 3-phenyl-Δ¹-*cyclo*hexene, b.p. 235° (dibromide decomposes when distilled, giving a diene, m.p. 66°), oxidised ($KMnO_4$) respectively to α-methyl-, -ethyl-, and -phenyl-adipic acids. A. Li.

Δ²:²′-Di*cyclo*hexenyl. A. Berlande (*Compt. rend.*, 1941, **213**, 484—486).—MgEtBr with 1-chloro-Δ²-*cyclo*hexene in dry Et_2O (ice-cooled) affords 15% of 1-ethyl-Δ²-*cyclo*hexene and 75% of Δ²:²′-di*cyclo*hexenyl, b.p. 236·5—237° (127°/30 mm.), which is oxidised (HNO_3) to *decane-αεζκ-tetracarboxylic acid*, m.p. 192—193° (decomp.). W. C. J. R.

Catalytic aromatisation of paraffin hydrocarbons. B. A. Kazanski (*J. Phys. Chem. Russ.*, 1940, **14**, 1330—1336).—Platinised C at 270—300° or Ni on Al_2O_3 at 350° transforms $Bu\beta_2$ into *p*-xylene etc. Presence of olefines deactivates the Pt on C. When 1 c.c. per hr. of

a paraffin mixture (C_7H_{16}—$C_{10}H_{22}$) is passed over 10 c.c. of an oxide catalyst, aromatisation takes place at 425—500°. The activity of Cr_2O_3 increases from "commercial" to "pptd. by NH_3 from aq. $Cr(NO_3)_3$" to "pptd. from aq. $Cr(NO_3)_3$ on ignited Cr_2O_3." The activity of these catalysts gradually decreases, especially if they have been used intermittently; heating in air followed by reduction with H_2 restores the activity. V_2O_5 and ThO_2 are inactive but the mixtures V_2O_5 1, Al_2O_3 10—20, and ThO_2 1, Al_2O_3 10 are efficient catalysts at 500°. ThO_2 may also be deposited on C. J. J. B.

Structure of naphthalene. J. K. Sirkin and M. E. Diatkina (*J. Gen. Chem. Russ.*, 1941, **11**, 626—646).—Theoretical. The reactions of $C_{10}H_8$ are discussed in the light of the theory of resonance between the different canonical structures. G. A. R. K.

Reactions of tetraphenyl*cyclo*pentadienone. Condensation with cyclic 1 : 3-diene systems. O. Grummitt, R. S. Klopper, and C. W. Blenkhorn (*J. Amer. Chem. Soc.*, 1942, **64**, 604—607).—Tetraphenyl-*cyclo*pentadienone [tetracyclone] (**I**) and *cyclo*pentadiene (**II**) in boiling C_6H_6 give 4 : 7-endo*carbonyl*-4 : 5 : 6 : 7-*tetraphenyl*-8 : 9-*dihydroindene* (**III**) (60%), m.p. 197—198° (*dibromide*, m.p. 222—223°). Under no conditions do 2 mols. of (**I**) condense with 1 mol. of (**II**) (cf. Dilthey *et al.*, A., 1935, 967). Thermal decomp. of (**III**) is complicated by dissociation into (**I**) and (**II**). Hydrogenation (PtO_2; C_6H_6–EtOH) of (**III**) gives 4 : 7-endo*carbonyl*-4 : 5 : 6 : 7-*tetraphenyl*-2 : 3 : 8 : 9-*tetrahydroindene*, m.p. 209—211°, which in boiling *p*-cymene (**IV**) gives CO and 4 : 5 : 6 : 7-*tetraphenyl*-(?2 : 3 : 8 : 9-)*tetrahydroindene*, m.p. 174—175°. Dehydrogenation, best by Se in boiling (**IV**), gives 4 : 5 : 6 : 7-*tetraphenylhydrindene*, m.p. 225—226°, oxidised by CrO_3–AcOH at 100° to 3 : 4 : 5 : 6 : 1 : 2-$C_6Ph_4(CO)_2O$ and some BzOH. (**I**) does not condense with furan, pyrrole, 1-methylpyrrole, or thiophen. R. S. C.

1 : 2-Diphenyl-3 : 4-dihydronaphthalene. (Miss) H. M. Crawford (*J. Amer. Chem. Soc.*, 1942, **64**, 727—728).—1 : 2-Diphenyl-3 : 4-dihydronaphthalene is dimorphic, the form of m.p. 76·5—77·5° slowly changing to that of m.p. 91·5—93·5° (cf. following abstract and A., 1939, II, 206). Prep. of the carbinol, m.p. 98·5—99°, was repeated. R. S. C.

Polyphenylnaphthalenes. I. 1 : 2-Diphenylnaphthalene. F. Bergmann, H. E. Eschinazi, and D. Schapiro. **II. 1 : 2 : 3-Triphenylnaphthalene.** F. Bergmann, D. Schapiro, and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1942, **64**, 557—558, 559—561).—I. CH_2Bz·CHPh·CN and boiling HCl–EtOH give *Et γ-keto-αγ-diphenyl-n-butyrate*, b.p. 200—205°/1 mm., which with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ gives a stable Al complex (which in CCl_4 gives a substance, m.p. 190°), decomposed by conc. H_2SO_4 to *αγ-diphenyl-γ-butyrolactone* (95%), m.p. 109—110°, b.p. 195—198°/0·5 mm. With red P in boiling HI this gives Ph·$[CH_2]_2$·CHPh·CO_2H (95%), m.p. 75°, b.p. 190°/1 mm., cyclised (Friedel–Crafts but not by P_2O_5–C_6H_6 and in poor yield by H_2SO_4–AcOH) to 1-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene (90%), m.p. 82°. With MgPhBr this gives an oily carbinol, dehydrated by $KHSO_4$ at 160° to 1 : 2-diphenyl-3 : 4-dihydronaphthalene (57%), m.p. 94—95°, b.p. 210—215°/0·5 mm. Dehydrogenation (Se; 280—290°) gives 1 : 2-$C_{10}H_6Ph_2$ (**I**) (80%), m.p. 114° (*picrate*, m.p. 148°), and Li–Et_2O gives 1 : 2-*diphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 183—184°/1·5 mm. [dehydrogenated by Se at ∢320° to (**I**)].

II. Prep. of, successively, CH_2Ph·COPh, CHPh:CPh·COPh, CHPh:CPh·CHPh·OH [by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$], and CHPh:CPh·CHPh·OMe (**II**) (by H_2SO_4–MeOH) is improved. With Na and later CO_2 in Et_2O at 0°, (**II**) gives *αβγ-triphenyl-*Δ^{β}*-n-butenoic acid* (**III**) (63%), m.p. 132—135° (does not react with Br; *Me*, m.p. 107°, and *Et* ester, m.p. 59°, b.p. 190—193°/0·3 mm.), CHPh:CPh·CH_2Ph, m.p. 62°, b.p. 185—188°/0·03 mm. (gives a Br-adduct, which in ligroin yields 1 : 2-diphenylindene), and a neutral resin, b.p. 225—230°/0·03 mm. In conc. H_2SO_4, (**III**) gives exothermally 2 : 3-*diphenylhydrindene-1-carboxylic acid*, m.p. 161° (*Me* ester, m.p. 116—117°), and with H_2–Pd in dioxan gives with difficulty H·$[CHPh]_3$·CO_2H (100%), m.p. 158° (*Me* ester, m.p. 158°; Na salt, m.p. 278—280°; *amide*, m.p. 168—169°), unchanged by conc. H_2SO_4 but with PCl_5–C_6H_6 giving a solid chloride, which with $AlCl_3$ in C_6H_6 at 0° gives 1-keto-2 : 3-diphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 146—147°, b.p. 205—207°/0·02 mm. MgPhBr at 100° then gives a carbinol, dehydrated by $KHSO_4$ at 160° to 1 : 2 : 3-*triphenyl*-3 : 4-*dihydronaphthalene* (52%), m.p. 176°, b.p. 215°/0·5 mm., which with Se at 280—300° gives 1 : 2 : 3-$C_{10}H_5Ph_3$ (70%), m.p. 153—154° (no picrate). R. S. C.

Molecular dissymmetry due to symmetrically placed hydrogen and deuterium. III. Attempted resolution of 4 : 4′-dibromo-2 : 3 : 5 : 6-tetradeuterobenzhydrylamine. Determination of deuterium in organic compounds. G. R. Clemo and G. A. Swan (*J.C.S.*, 1942, 370—374; cf. A., 1940, II, 40).—$(p\text{-}C_6H_4Br)_2CO$ and HCO·NH_2 at 175° yield *form*-4 : 4′-*dibromobenzylhydrylamide*, m.p. 159°, converted by KOH–MeOH into 4 : 4′-*dibromobenzyhydrylamine*, m.p. 76° (*hydrochloride*; *d*-H tartrate, m.p. 210—211°, $[\alpha]_D^{18}$ +9·5° in MeOH; *d*-bromocamphorsulphonate, m.p. 260—262°, $[\alpha]_D^{18}$ +46·4° in MeOH). C_6D_5Br and *p*-C_6H_4Br·COCl–$AlCl_3$–CS_2 give 4 : 4′-*dibromo*-2 : 3 : 5 : 6-*tetradeuterobenzophenone*, m.p. 172—173°, whence (as above) *form*-4 : 4′-*dibromo*-2 : 3 : 5 : 6-*tetradeuterobenzhydrylamide*, m.p. 158—159°, and 4 : 4′-*dibromo*-2 : 3 : 5 : 6-*tetradeuterobenzhydrylamine* (**I**), m.p. 75—76°. Attempted resolution of (**I**) through the *d*-H tartrate, m.p. 210—212°, $[\alpha]_D^{18}$ +9·3° in MeOH, or the *d*-bromocamphorsulphonate, m.p. 260—262°, $[\alpha]_D^{18}$ +45·9° in MeOH, was unsuccessful. The Harteck method (cf. A., 1938, I, 157) for determination of D is developed for the estimation of relative proportions of H and D in org. compounds. A. T. P.

Characterisation of carboxylic acids as ureides by means of carbodiimides. XII. Methiodides and methosulphates of *pp′*-tetramethyldiaminodiphenylcarbodi-imides. F. Zetzsche and G. Baum (*Ber.*, 1942, **75**, [*B*], 100—105; cf. A., 1940, II, 274).—C(:N·C_6H_4·NMe_2-*p*)$_2$ (**I**) and MeI in C_6H_6 yield the *monomethiodide* (**II**), m.p. 163—167°, converted by cold, saturated $H_2C_2O_4$ into pp′-*tetramethyldiaminodiphenylcarbamide methiodide*, decomp. 223—227°, and by H_2S in MeOH into the corresponding *thiocarbamide methiodide*, m.p. 190—192°. With 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2$·OH, (**II**) gives a mixed *picrate-methopicrate*, m.p. 205—207° (decomp.) after softening at 180°. BzOH in $CHCl_3$ at room temp. and CHPh:CH·CO_2H in $COMe_2$ transform (**II**) into the *benz-*, m.p. 120—125°, and *cinnam-ureide*, m.p. 135—140°, respectively. (**I**) and MeI in $CHCl_3$ at room temp. and subsequently at 50° give the *dimethiodide*, m.p. 175—180° (decomp.) (softens at 150°), which evolves CO + CO_2 with $H_2C_2O_4$ and CO with HCO_2H. It is rapidly transformed by boiling H_2O into pp′-*tetramethyldiaminodiphenylcarbamide dimethiodide*, m.p. 206° (decomp.) (softens at 195°) (corresponding *dimethopicrate*, decomp. 189—196° after softening at 188°). The *thiocarbamide dimethiodide* decomposes at 185—187°. (**I**) and Me_2SO_4 in warm C_6H_6 afford the *monomethosulphate*, m.p. 155—158° (softens at 145°), from which are derived the *monomethosulphates* (+H_2O), m.p. 175—181° (softens at 170°), and (anhyd.) decomp. 188—190°, of the corresponding carbamide and thiocarbamide, respectively. Me_2SO_4 and (**I**) in $CHCl_3$ at room temp. yield the *dimethosulphate* of (**I**), rapidly converted by boiling H_2O into pp′-*tetramethyldiaminodiphenylcarbamide dimethosulphate*, m.p. 194—198° (corresponding *dipicrate*, m.p. 211°). H. W.

Phenylthiocarbamides. Triad –N·C·S–. XI. Oxidation of phenylthiocarbamide with copper sulphate, cupric chloride, copper nitrate, ferric chloride, and iodine. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1942, **19**, 25—29).—$CuSO_4$ and $CuCl_2$ are reduced by NHPh·CS·NH_2 (**I**) in acid media producing Hector's base (**II**); the reaction is independent of temp., concn., and dilution of the medium. Secondary reactions are the production of complexes (*A*) of (**I**) with Cu^I salts, the constitution of (*A*) being largely dependent on temp. $FeCl_3$ is reduced and gives (**II**) but no (*A*); $Cu(NO_3)_2$ and I similarly afford (**II**). F. R. S.

Complex compounds of diguanide with bivalent metals. III. Copper and nickel phenyldiguanidines and their different modifications. P. Rây and K. Chakravarty (*J. Indian Chem. Soc.*, 1941, **18**, 609—622).—Cu and Ni phenyldiguanidine, the hydrates and salts exist in α- and β-forms which are regarded as *cis–trans* isomerides, but may be dimorphs. Conditions for inter-conversion are described; the following are new: *α-Cu*, m.p. 155° (decomp.), *α-Ni* (+0·5H_2O), decomp. 255°, and *γ-Ni phenyldiguanidine* (+0·5H_2O) (considered to be a mixture of α- and β-), decomp. 263°; *α-Cu phenyldiguanidinium hydroxide, chloride*, m.p. 170° (decomp.) (*hexahydrate*, effervesces at 100°, resolidifying later with m.p. 210°), *bromide* (+2H_2O), *iodide* (+2H_2O), *nitrate, sulphate* (+4H_2O), *nitrite* (+H_2O), and *dithionate*; *β-Cu phenyldiguanidinium hydroxide, bromide* (+2H_2O), *iodide* (+2H_2O), *nitrate* (+H_2O), *nitrite*, and *dithionate* (+H_2O); *Cu phenyldiguanidinium sulphite, thiosulphate* (+2H_2O), *thiocyanate* (+H_2O), *chlorate, bromate*, and *iodate*; *Ni phenyldiguanidinium bromide* (+2H_2O), *iodide* (+H_2O), *dithionate, thiosulphate, nitrate* (+H_2O), *sulphite* (+H_2O), *chlorate, bromate, iodate* (+2H_2O), *thiocyanate*, and *nitrite* (+H_2O). F. R. G.

Interpretation of the Sandmeyer reaction. II. Corrections. H. H. Hodgson, S. Birtwell, and T. Walker (*J.C.S.*, 1942, 376—377; cf. A., 1942, II, 52). A. T. P.

Aralkylphenols.—See B., 1942, II, 253.

Branched-chain alkylphenylphenols.—See A., 1942, II, 253.

***N*-Dichlorocarbamates.**—See A., 1942, II, 217.

Stilbœstrol and related compounds.—See B., 1942, III, 171.

Molten alkali and benzenesulphonic acids. H. E. Fierz-David and G. Stamm (*Helv. Chim. Acta*, 1942, **25**, 364—370).—Only traces of *m*-$C_6H_4(OH)_2$ (**I**) in addition to PhOH are obtained by fusion of *m*-$C_6H_4(SO_3Na)_2$ with alkali under pressure; at 400° CO_2 is formed in 46% yield. In the "baking apparatus" at temp. up to 350° and with a 100% excess of alkali, pure (**I**) is obtained in 80% yield. With molten alkali *p*-$C_6H_4(SO_3Na)_2$ gives up to 5% of (**I**), very small yields of which are derived from *p*-OH·C_6H_4·SO_3H or *p*-C_6H_4Cl·SO_3H. At 280° *p*-C_6H_4Cl·OH is converted by alkali into PhOH with some $(C_6H_4$·OH$)_2$ and HCO_2H. Baking appears to be inefficient for the conversion of $C_{10}H_7$·SO_3H and 2 : 6-OH·$C_{10}H_6$·SO_3H into the OH-compounds. H. W.

Reaction between quinones and metallic enolates. XV. Structure of the chloromethylation product of trimethylquinol diacetate. L. I. Smith and R. B. Carlin (*J. Amer. Chem. Soc.*, 1942, **64**, 524—527).—The product obtained from 2 : 3 : 5 : 1 : 4-$C_6HMe_3(OAc)_2$, CH_2O, and HCl depends on the conditions, particularly the temp. At 0° it is mainly a substance, m.p. 228—229°, and at 15—20° mainly a substance, m.p. 167—168°. At 30° it is 6-*hydroxy*-3-*acetoxy*-2 : 4 : 5-*trimethylbenzyl chloride* (I) (89%), m.p. 150—151°, previously (A., 1939, II, 416) believed to be the 3 : 6-$(OAc)_2$-compound (II) (see below). The structure of (I) is shown by a positive Folin reaction, ready interaction with $AgNO_3$–MeOH, insolubility in aq. NaOH, by synthesis of (impure) 3 : 6 : 2 : 4 : 5 : 1-$(OH)_2C_6Me_3{\cdot}CH_2Cl$ (III), m.p. 114—115° (decomp.) (positive Folin test), and prep. of (II), m.p. 165° (negative Folin reaction; very slow interaction with $AgNO_3$–MeOH), from (I) or (III) by Ac_2O and a drop of H_2SO_4. Duroquinol is obtained from (III) by Zn dust in AcOH and duroquinone from (II) by $CHAcNa{\cdot}CO_2Et$–EtOH–H_2 followed by aq. $Cu(OAc)_2$ on the product. With $CHNa(CO_2Et)_2$ (IV) (1 mol.) in Et_2O at room temp. (2 hr.), (I) gives *Et*$_2$ 6-*hydroxy*-3-*acetoxy*-2 : 4 : 5-*trimethylbenzylmalonate* (V) (30%), m.p. 81—82° (positive Folin test), but on longer interaction or with slightly >1 mol. of (IV) gives Et 6-acetoxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin-3-carboxylate (VI), m.p. 117—118°. (V) is accompanied by varying amounts (≯50%) of *Et*$_2$ *di*-(6-*hydroxy*-3-*acetoxy*-2 : 4 : 5-*trimethylbenzyl*)*malonate*, m.p. 175° (positive Folin test). (VI) is also obtained from (V) by NaOH–Et_2O or from (I) and (IV) in Et_2O. R. S. C.

Bromination of 1 : 5-dihydroxy- and 1 : 5-diacetoxy-naphthalene, 5-methoxy-1-naphthol, and 1 : 5-dimethoxynaphthalene. A. H. Carter, E. Race, and F. M. Rowe (*J.C.S.*, 1942, 236—239).—1 : 5-$C_{10}H_6(OH)_2$ and Br–AcOH at 80° yield 2 : 6 : 1 : 5-$C_{10}H_4Br_2(OH)_2$, m.p. 224° (decomp.) (cf. Wheeler *et al.*, A., 1931, 215), converted by Me_2SO_4–aq. NaOH at 60° into the Me_2 ether, m.p. 160°, and 5 : 2 : 6 : 1-OMe·$C_{10}H_4Br_2$·OH, m.p. 150°. 1 : 5-$C_{10}H_6(OAc)_2$ similarly gives 2 : 4-*dibromo*-5-*acetoxy*-1-*naphthol* (I), m.p. 175° [the 1 : 5-*diacetate*, m.p. 131°, is stated by Willstätter *et al.* (A., 1928, 408) to be 4 : 8 : 1 : 5-$C_{10}H_4Br_2(OAc)_2$], hydrolysed by cold 0·4% aq. NaOH to 2 : 4 : 1 : 5-$C_{10}H_4Br_2(OH)_2$ (II), m.p. 153°. (I) and CH_2N_2–MeOH–Et_2O at −15° yield 2 : 4-*dibromo*-5-*acetoxy*-1-*methoxynaphthalene*, m.p. 121°, and thence (10% aq. NaOH) 6 : 8-*dibromo*-5-*methoxy*-1-*naphthol* (III), m.p. 112°. (II) and CH_2N_2 yield 2 : 4-*dibromo*-1 : 5-*dimethoxynaphthalene*, m.p. 88°. 5 : 1-OMe·$C_{10}H_6$·OH and Br–CCl_4 at 70° afford 2-*bromo*- (IV), m.p. 95°, or 2 : 8-*dibromo*-5-*methoxy*-1-*naphthol* (V), m.p. 130° (*acetate*, m.p. 133°); (V)–Me_2SO_4–aq. NaOH at 30° give 2 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene*, m.p. 84°. 1 : 5-$C_{10}H_6(OMe)_2$ and Br–CCl_4 at 70° yield 4 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene*, m.p. 187°. 2 : 6 : 1 : 5-$C_{10}H_4Br_2(OH)_2$ and CrO_3–AcOH at 85° give 2 : 6-dibromo-5-hydroxy-, m.p. 202°, and thence 6-bromo-2-anilino-5-hydroxy-1 : 4-naphthaquinone, m.p. 249°. 5 : 2 : 6 : 1-OMe·$C_{10}H_4Br_2$·OH, (I), (IV), or (V) is oxidised by CrO_3–AcOH to 2 : 6-*dibromo*-5-*methoxy*-, m.p. 177°, 2-*bromo*-5-*acetoxy*-, m.p. 158°, 2-*bromo*-5-*methoxy*-, m.p. 134°, or 2 : 8-*dibromo*-5-*methoxy*-1 : 4-*naphthaquinone*, m.p. 199°, respectively. (V) or (III) with aq. $KMnO_4$–NaOH, followed by H_2O_2, yields 5-*bromo*-, m.p. 212° (*phthalanil*, m.p. 232°), or 3 : 5-*dibromo*-6-*methoxyphthalic anhydride*, m.p. 140° (*phthalanil*, m.p. 191°), respectively. A. T. P.

Xenyl aryloxyalkyl ethers.—See B., 1942, II, 254.

Duroquinol alkyl ethers.—See B., 1942, II, 254.

Method of preparing mono-ethers of methylene glycol. M. L. Gupta, R. Kaushal, and S. S. Deshapande (*J. Indian Chem. Soc.*, 1941, **18**, 638—640).—$CH_2Cl{\cdot}OAc$ with $CH_2Ph{\cdot}ONa$ in boiling C_6H_6 gives *benzyloxymethyl acetate*, b.p. 152—155°/29 mm., hydrolysed with 10% KOH in EtOH to *formaldehyde monobenzyl acetal*, b.p. 75—77°/4 mm. (*phenylurethane*, m.p. 75°). $CH_2Cl{\cdot}OMe$ with $CH_2Ph{\cdot}ONa$ yields *formaldehyde Me benzyl acetal*, b.p. 84—87°/8 mm., together with a compound, b.p. 165—167°/8 mm. F. R. G.

Phenol–formaldehyde resins. VIII. Mode of formation of phenolic aldehydes during the hardening of phenolic alcohols. K. Hultzsch (*Ber.*, 1942, **75**, [*B*], 106—114).—Further evidence is presented in favour of the view that quinonemethides are intermediates in the conversion of phenolic alcohols into aldehydes etc., and that the change does not necessarily take place through polymeric forms. Trimeric 2 : 3 : 5 : 1-O:$C_6H_2Me_2$:CH_2 [3 : 5-dimethyl-*o*-benzoquinonemethide] at 250° gives very small amounts of 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CHO, mesitol, 2 : 3 : 5 : 1-$(OH{\cdot}C_6H_2Me_2{\cdot}CH_2)_2$, and a dark resin. At 230° dimeric 3-methyl-5-*tert.*-butyl-*o*-benzoquinonemethide gives similarly the expected aldehyde, phenol, and C_2H_6 derivative. Analogous results are obtained with 5-*cyclo*hexyl-3-methyl-*o*-benzoquinonemethide. Attempts to resinify di-2-acetoxy-3-methyl-5-*tert.*-butylbenzyl ether were unsuccessful. 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2{\cdot}CH_2{\cdot}OH$ (I) is unchanged by HCl in Et_2O at room temp. or PhMe at the b.p. and is converted by HCl in AcOH into 2 : 3 : 5 : 1-OAc·$C_6H_2Cl_2{\cdot}CH_2{\cdot}OH$, m.p. 115°. At 205°, (I) affords (?) trimeric 3 : 5-*dichloro*-*o*-*benzoquinonemethide* (+$3C_6H_6$), m.p. 278—280° (decomp.) after darkening at 260°. H. W.

Preparation of 1- and 2-indanol and their derivatives from indene. W. F. Whitmore and A. I. Gebhart (*J. Amer. Chem. Soc.*, 1942, **64**, 912—917).—Indene bromohydrin (I) in aq. MeOH–KOH in dioxan at room temp. gives indene oxide (100%), reduced by H_2–Raney Ni to 2-indanol (65%), also obtained directly from (I) by H_2–Raney Ni in KOH–EtOH. With boiling Ac_2O–NaOAc, (I) gives the glycol diacetate. BzCl–C_5H_5N–dioxan at 0°—room temp. converts (I) into the *benzoate*, m.p. 104°, which with 0·5N-KOH–EtOH at room temp. gives KBr, EtOBz, and indene glycol. Addition of chloroindane (II) to NaOAc–AcOH–H_2O at 98° gives mainly 1-indanyl acetate (III) (86%) and 1-indanol (IV) (14%), whence boiling N-KOH–EtOH yields (IV), *forms*, m.p. 40·5° (unstable) and 52·5°. (IV) is also obtained from indan-1-one or (I) by H_2–Raney Ni–H_2PtCl_6–NaOH [or –$Mg(OH)_2$] in EtOH. With boiling HCl–EtOH–H_2O, (IV) gives 1-*indanyl Et ether* (V), b.p. 78—80°/2 mm., reaction proceeding by way of (II), which also gives (V) when boiled with $CaCO_3$–EtOH. With conc. HCl in boiling dioxan, (IV) gives *di*-1-*indanyl ether*, *forms*, m.p. 68° and 74°, also obtained from (IV), (II), and $CaCO_3$ in dioxan. 1-*Indanyl benzoate*, m.p. 63°, p-*nitrobenzoate*, m.p. 75°, and α-*naphthylurethane*, *forms*, m.p. 137° and 145°, and 2-*indanyl benzoate*, m.p. 63°, p-*nitrobenzoate*, m.p. 139°, and α-*naphthylurethane*, m.p. 191°, are described. M.p. are on a Dennis-Shelton bar. R. S. C.

Organic osmium compounds. II. R. Criegee, B. Marchand, and H. Wannowius (*Annalen*, 1942, **550**, 99—133; cf. A., 1936, 603).—OsO_4 and MeOH–KOH (or –CsOH) yield K_2 (I) (or Cs_2) *tetramethylosmiate*, $Os(OMe)_4(OK)_2$, converted by warm AcOH into *K* (or *Cs*) *triacetylosmiate*, $OsO(OAc)_3OK$ (+2AcOH, lost at 60°/0·5 mm.). EtOH–C_5H_5N and OsO_4 in *cyclo*hexane at room temp. for 2—3 days give the *complex* (II), $OsO_3,2C_5H_5N$; in absence of EtOH at 0°, the *complex*, OsO_4,C_5H_5N, results. *trans-cyclo*Hexane-1 : 2-diol and (I) in KOH–MeOH yield K_2 *di*-(trans-cyclo*hexane*-1 : 2-*diol*)*osmiate*, $C_{12}H_{20}O_6K_2Os$, and thence (dil. H_2SO_4 in CH_2Cl_2) *di*-(trans-cyclo*hexane*-1 : 2-*diol*)*osmiate*, $C_{12}H_{20}O_5Os$; K_2 *di*-(trans-cyclo*heptane*-1 : 2-*diol*)*osmiate*, *di*-(cis- and trans-cyclo*heptane*-1 : 2-*diol*)-, and *diethylene glycol-osmiate* are also prepared. $\Delta^{1:3}$-*cyclo*Pentadiene and Et_2O–OsO_4 afford cyclo*pentenediolosmiate*, $C_5H_6O_4Os$ (type *A*), and α-pinene yields *pinene glycolosmiate*, $C_{10}H_{16}O_4Os$, decomp. 169°. Similar *monoesters* are obtained from CMe_2:CMe_2, CHPh:CH·COPh, CMe_2:CH·COMe, *cyclo*pentene, 1 : 2-dimethyl*cyclo*hexene, camphene, limonene, Δ^1-dihydronaphthalene, cholesterol, and ergosterol. $\Delta^{1\ 3}$-*cyclo*Hexadiene, *cyclo*heptene, or phenanthrene and OsO_4 in C_5H_5N–Et_2O or –C_6H_6 afford Δ^3-cyclo*hexene*-1 : 2-*diolosmiate* (+$2C_5H_5N$), cyclo*heptanediolosmiate* (+$2C_5H_5N$), or 9 : 10-*dihydrophenanthrene*-9 : 10-*diolosmiate* (+$2C_5H_5N$), respectively. Similar *esters* (all +$2C_5H_5N$) are obtained from C_2H_4, CMe_2:CMe_2, *cyclo*pentadiene, di*cyclo*pentadiene, *cyclo*hexene, CPh_2:CPh_2, $(CPh_2{:}CH{\cdot})_2$, camphene, stilbene, limonene, cholestenone, cholesterol, ergosterol, Δ^1-dihydronaphthalene, di(diphenylene)-ethylene, and CHPh:CH·COPh; tolan gives the *ester*, $C_{14}H_{10}O_8Os_2,4C_5H_5N$. Some of the esters are also prepared from the corresponding diol and (II); other *esters* (+$2C_5H_5N$) are obtained from (II) and *cis-cyclo*pentanediol, *cis*- and *trans-cyclo*hexane- and -*cyclo*heptane-diol, *cis*-hydrindenediol, *cis*-acenaphthenediol, *cis*-dimethyl- and -diphenyl-acenaphthenediol, *cis*-diphenyldihydrophenanthrenediol, and *o*-$C_6H_4(OH)_2$. Similar *esters* (all + 1 mol. of 2 : 2′-dipyridyl) are prepared from *cyclo*hexene, *cyclo*hexadiene, limonene, α-pinene, Δ^1- and Δ^2-dihydronaphthalene, sorbaldehyde, CMe_2:CH·COMe, CHPh:CH·COPh, and cholestenone. Stilbene, limonene, or C_2H_2 and OsO_4 in Et_2O–quinoline give the *adducts*, $C_{14}H_{12},OsO_4,2C_9H_7N$, or $C_{10}H_{16},OsO_4,2C_9H_7N$, or $C_2H_2,2OsO_4,4C_9H_7N$, respectively. The esters (or their C_5H_5N compounds) from *cyclo*pentadiene or *cyclo*hexadiene are hydrolysed by aq. K_2CO_3 or KOH (usually in presence of mannitol), and thence hydrogenated (PtO_2) to *cis-cyclo*-pentane- or -hexane-1 : 2-diol. respectively. Phenanthrene–OsO_4–$2C_5H_5N$ and aq. KOH–mannitol afford cis-9 : 10-*dihydrophenanthrene*-9 : 10-*diol*, m.p. 178—179° (corr.) [*di*-*acetate*, m.p. 109° (corr.)]. The adduct ergosterol–OsO_4–$2C_5H_5N$ and aq. KOH–mannitol give ergostadiene-3 : 5 : 6-triol (*cis*-configuration), m.p. 244°, converted by $Pb(OAc)_4$ into the ketoaldehyde, m.p. 155—157° (cf. Heilbron *et al.*, A., 1933, 500). A. T. P.

$$\begin{matrix} >C{\cdot}O \\ >C{\cdot}O \end{matrix}\!\!>OsO_2$$
(*A*.)

Condensation of *o*-, *m*-, and *p*-nitrobenzaldehydes with malonic acid in presence of organic bases. D. S. Mittal (*J. Indian Chem. Soc.*, 1942, **19**, 47—48).—The nitrocinnamic acids are obtained in 75—90% yields from 1 mol. of aldehyde, 1 mol. of $CH_2(CO_2H)_2$, and 0·15 mol. of C_5H_5N, piperidine, or quinoline at 100° (bath). F. R. S.

Condensation of aldehydes with malonic acid in presence of organic bases. XIV. Condensation of 2 : 4-dinitrobenzaldehyde; influence of nitro-groups. K. C. Pandya, P. I. Ittyerah, and (Miss) R. K. Pandya (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 78—82).—Under mild conditions reaction between 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CHO$ and $CH_2(CO_2H)_2$ does not appear to occur and traces of C_5H_5N, piperidine (I), and lutidine bring little advantage. Higher temp. and longer periods of heating and use of a mixture of C_5H_5N and (I) invariably lead to decomp., charring, and resinification. The best

yields (50%) of 2 : 4 : 1-$(NO_2)_2C_6H_3$·CH:CH·CO_6H, m.p. 179°, are secured by heating the reactants with C_5H_5N for 4 hr. at 100° (bath) and for a further 4 hr. at 105—110° (bath). The cause of the diminished activity of CHO by two NO_2-groups at $C_{(2)}$ and $C_{(4)}$ is unexplained. H. W.

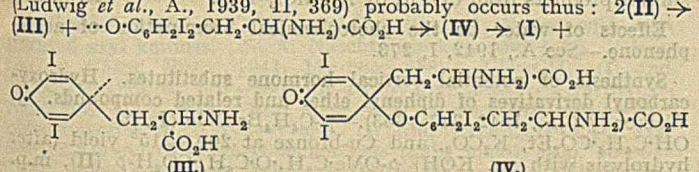
Unsymmetrical cyanostilbenes. J. B. Niederl and A. Ziering (*J. Amer. Chem. Soc.*, 1942, **64**, 885—886).—RCHO, NHAc·CH_2·CO_2H, and NaOAc give azlactones (30—40%), R (here and below) = *p*-OMe·C_6H_4, m.p. 114°, 3 : 4-$(OMe)_2C_6H_3$, m.p. 167°, and 3 : 4-CH_2O_2:C_6H_3, m.p. 181°, hydrolysed by boiling aq. NaOH to CHR:C(NHAc)·CO_2H, m.p. 216°, 208°, and 219°, respectively, and then by boiling aq. acid to CH_2R·CO·CO_2H (~90%), m.p. 184°, 185°, and 213°, respectively. The oximes, m.p. 159°, 164°, and 170°, respectively, thereof in Ac_2O give CH_2R·CN (50—70%), b.p. 120°/4 mm., 183°/16 mm., and 160°/10 mm., respectively, which with R'CHO in warm 95% EtOH–NaOEt give, usually, excellent yields of CN·CR:CHR'. *α-Cyano-4-methoxy-*, m.p. 94°, *-3 : 4-*, m.p. 87°, *-4 : 2'-*, m.p. 98°, and *-4 : 4'-dimethoxy-*, m.p. 108°, and *-3 : 4-methylenedioxy-*, m.p. 125°, *2'-*, m.p. 129°, and *4'-chloro-α-cyano-4-methoxy-*, m.p. 110°, *2'-*, m.p. 113°, and *4'-chloro-α-cyano-3 : 4-dimethoxy-*, m.p. 115°, *2'-*, m.p. 135°, and *4'-chloro-α-cyano-3 : 4-methylenedioxy-*, m.p. 130°, *3'-nitro-α-cyano-4-methoxy-*, m.p. 159°, *-3 : 4-dimethoxy-*, m.p. 166°, and *-3 : 4-methylenedioxy-*, m.p. 195°, *α-cyano-4-methoxy-4'-methyl-*, m.p. 97°, *α-cyano-3 : 4-dimethoxy-4'-methyl-*, m.p. 112°, *α-cyano-3 : 4-methylenedioxy-4'-methyl-*, m.p. 122°, *α-cyano-4 : 3' : 4'-*, m.p. 105°, *-3 : 4 : 2'-*, m.p. 87°, and *-3 : 4 : 4'-trimethoxy-*, m.p. 129°, *α-cyano-3 : 4 : 3' : 4'-tetramethoxy-*, m.p. 155°, *α-cyano-4-methoxy-3' : 4'-methylenedioxy-*, m.p. 129°, and *-2'-*, m.p. 102°, and *-4'-methoxy-3 : 4-methylenedioxy-*, m.p. 129°, *α-cyano-3 : 4-dimethoxy-3' : 4'-methylenedioxy-*, m.p. 150°, and *-3' : 4'-dimethoxy-3 : 4-methylenedioxy-*, m.p. 144°, *α-cyano-3 : 4 : 3' : 4'-bismethylenedioxy-*, m.p. 185°, and *α-cyano-4'-dimethylamino-4-methoxy-*, m.p. 149°, *-3 : 4-dimethoxy-*, m.p. 121°, and *-3 : 4-methylenedioxy-*, m.p. 169°; *-stilbene* are described. These have feeble œstrogenic properties. R. S. C.

Nitration of *p*-iodophenylacetic acid. S. N. Slater (*New Zealand J. Sci. Tech.*, 1941, **23**, **B**, 15—16).—*p*-C_6H_4I·CH_2·CO_2H and KNO_3 added to conc. H_2SO_4–AcOH give ~85% of 3 : 4 : 1-NO_2·C_6H_3I·CH_2·CO_2H, m.p. 122—123° (also formed, less well, using H_2SO_4–HNO_3), oxidised ($KMnO_4$) to 3 : 4 : 1-NO_2·C_6H_3I·CO_2H. M. H. M. A.

Synthetic anthelmintics. II. γ-Substituted butyrolactones. III. γγ-Disubstituted butyrolactones. J. J. Trivedi and K. S. Nargund (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 99—101, 102—105).—II. *β-o-Anisoylpropionic acid*, m.p. 98° (*Ag* salt; *Me*, b.p. 160°/3 mm., and *Et*, b.p. 170°/7 mm., ester), obtained from the OH-acid, Me_2SO_4, and 10% NaOH, is reduced (Na–abs. EtOH at 100°) and then lactonised by boiling 15% H_2SO_4 to *γ-o-anisylbutyrolactone*, b.p. 170°/16 mm. Similarly, *β-3-methoxy-p-toluoylpropionic acid*, m.p. 126° (sol. Ca and insol. Ba and Zn salts; *Me*, b.p. 190—192°/14 mm., and *Et*, m.p. 76°, ester), is converted into *γ-3-methoxy-p-tolylbutyrolactone*, b.p. 197—198°/9 mm., hydrolysed to *γ-hydroxy-γ-3-methoxy-p-tolylbutyric acid*, m.p. 114°. *γ-3 : 4-*, m.p. 120—121°, and *γ-2 : 5-*, m.p. 94—95°, *-dimethoxyphenylbutyrolactone* are described.

III. The requisite keto-ester is treated with the appropriate Grignard reagent; the product is hydrolysed and, after removal of neutral impurities, lactonised by hot 15% H_2SO_4. Thus are obtained: *γ-phenylvalerolactone*, b.p. 145—147°/5 mm.; *γ-hydroxy-γ-phenylvaleric acid*, m.p. 106°; *γ-phenylhexolactone*, b.p. 160°/16 mm.; *γ-hydroxy-γ-phenyl-n-hexoic acid*, m.p. 102—103°; *γ-phenylheptolactone*, b.p. 145—150°/20 mm.; *γ-phenyloctolactone*, b.p. 173—174°/10 mm.; *γγ-diphenylbutyrolactone*, m.p. 90—91°; *γ-hydroxy-γγ-diphenylbutyric acid*, m.p. 141°; *γ-p-anisylvalerolactone*, b.p. 215—220°/42 mm.; *γ-hydroxy-γ-p-anisylvaleric acid*, m.p. 120°; *γ-p-anisyl-hexolactone*, b.p. 180—185°/5 mm. (corresponding *γ-OH-acid*, m.p. 123°), *-heptolactone*, b.p. 215—217°/20 mm., *-δ-methylhexolactone*, b.p. 190°/12 mm., *-octolactone*, b.p. 220—225°/15 mm., *-ε-methylheptolactone*, b.p. 200—205°/22 mm., *-ζ-methyloctolactone*, b.p. 205—210°/15 mm., and *-decolactone*, b.p. 215—220°/7 mm. *Et β-p-anisoylpropionate* has m.p. 57°. H. W.

Oxidation of 3 : 5-di-iodotyrosine to thyroxine. T. B. Johnson and L. B. Tewkesbury, jun. (*Proc. Nat. Acad. Sci.*, 1942, **28**, 73—77).—The production of thyroxine (**I**) from 3 : 5-di-iodotyrosine (**II**) (Ludwig *et al.*, A., 1939, II, 369) probably occurs thus: 2(**II**) → (**III**) + ···O·$C_6H_2I_2$·CH_2·CH(NH_2)·CO_2H → (**IV**) → (**I**) +



(**III.**) (**IV.**)

CH_2:C(NH_2)·CO_2H → NH:CMe·CO_2H → NH_3 + $AcCO_2H$. R. S. C.

Preparation of *p*-alkyl-substituted benzoic acids. A. Zaki and H. Fahim (*J.C.S.*, 1942, 307—308).—PhAlk-*n* and AcCl–$AlCl_3$ in light petroleum at 0°—room temp., and then at 100° (bath), afford the *p*-C_6H_4Alk·COMe, oxidised (NaOBr) to *p*-C_6H_4Alk·CO_2H. *p-n-*Butyl-, b.p. 268—270°/766 mm. (*oxime*, m.p. 43—44°; *semicarbazone*, m.p. 182—183°; p-*nitrophenylhydrazone*, m.p. 151—152°), *p-n-*amyl-, b.p. 145°/11 mm. (*oxime*, m.p. 62—63°; *semicarbazone*, m.p. 180—181°; p-*nitrophenylhydrazone*, 149—150°), *p-n-*hexyl-, b.p. 158°/12 mm. (*oxime*, m.p. 45—46°; *semicarbazone*, m.p. 178°; p-*nitrophenylhydrazone*, m.p. 135°), *p-n-*heptyl-, b.p. 160—163°/7 mm. (*oxime*, m.p. 41—42°; *semicarbazone*, m.p. 176°; p-*nitrophenylhydrazone*, m.p. 140°), and *p-n-*octyl-acetophenone, b.p. 165—168°/4 mm. [oxime, m.p. 52—53° (lit. 43°); *semicarbazone*, m.p. 174°; p-*nitrophenylhydrazone*, m.p. 127°], afford p-n-*butyl-*, m.p. 101°, *-amyl-*, m.p. 88°, *-hexyl-*, m.p. 97°, *-heptyl-*, m.p. 101·5°, or *p-n-*octylbenzoic acid, m.p. 99—100° (lit. 139°), respectively. A. T. P.

Substituted amides of mesitoic acid. R. G. Kadesch (*J. Amer. Chem. Soc.*, 1942, **64**, 726).—*Mesit-ethyl-*, m.p. 114·5—115·5°, *-isopropyl-*, m.p. 113·5—115°, *-benzyl-*, m.p. 137·5—138·5°, and *-α-phenylethyl-amide*, m.p. 130—131°, *-o-*, m.p. 124—125·5°, *-m-*, m.p. 110—111·5°, and *-p-toluidide*, m.p. 173—174°, *-p-anisidide*, m.p. 185°, *-p-phenetidide*, m.p. 171—172°, *-o-tert.-butylanilide*, m.p. 150·5—152°, *-β-naphthalide*, m.p. 165—166·5°, *-piperidide*, m.p. 75·5—77°, and *-morpholide*, m.p. 70—71·5°, are prepared from the chloride and amine in C_6H_6. R. S. C.

Preparation of 3 : 5-dinitrobenzoic acid and 3 : 5-dinitrobenzoyl chloride. Acylation of amino-acids by 3 : 5-dinitrobenzoyl chloride and other acid chlorides. B. C. Saunders, G. J. Stacey, and (in part) I. G. E. Wilding (*Biochem. J.*, 1942, **36**, 368—375; cf. Town, A., 1941, II, 213).—Prep. of 3 : 5 : 1-$(NO_2)_2C_6H_3$·CO_2H and 3 : 5 : 1-$(NO_2)_2C_6H_3$·COCl (**I**), new m.p. 69·5°, is improved. Reaction between various ArCOCl and a slight excess of N-NaOH shows that (**I**) and *p-* and *m*-NO_2·C_6H_4·COCl (**II**) are completely hydrolysed within 2 min.; $AlkSO_2Cl$ are similarly very reactive whilst $ArSO_2Cl$ are not. The relative merits of (**I**) and other chlorides as acylating agents for NH_2-acids are discussed. With NH_2Ph in EtOAc, (**I**) and BzCl give 95 and 78%, respectively of NH_2Ph,HCl (not formed using *p*-C_6H_4Me·SO_2Cl or $MeSO_2Cl$) after 2 min. The following are prepared in N-NaOH: dl-*α-3 : 5-dinitrobenzamido-n-valeric*, m.p. 227·5—228·5° (decomp.), *-n-hexoic* m.p. 203·5—204°, and *-α-methyl-n-butyric acid*, m.p. 186°; 3 : 5-dinitrobenzoylglycine, new m.p. 179·5°; *Me* o-*3' : 5'-dinitrobenzoyloxybenzoate*, m.p. 107·5°; *m-*nitrobenzoylglycine, new m.p. 166° [from (**II**)]; 3 : 5-*dinitrobenzenesulphonylglycine*, m.p. 191—192°; methanesulphonyl-glycine, m.p. 172—173°, and *-anthranilic acid*, m.p. 190·5—191·5°; *Ph*, m.p. 59·5°, and p-NO_2·C_6H_4, m.p. 93—93·5°, *methanesulphonate*; *α-toluenesulphonylglycine*, m.p. 152° *Na* 3 : 5-*dinitrobenzene-* and *α-toluene-sulphonate*. *dl*-OH·CHPh·CO_2H does not react with (**I**) in N-NaOH. 3 : 5-Dinitrobenzoyl derivatives of some NH_2-acids may exist in different forms (cf. *loc. cit.*). H. B.

Separated auxo-enoid systems. XV. Colour of *p*-nitro- and 3 : 5-dinitro-benzoates of phenols containing an additional auxo-group. V. A. Izmailski and A. V. Belotzvetov (*J. Gen. Chem. Russ.*, 1941, **11**, 650—660).—The colour of *p*-nitro- and 3 : 5-dinitro-benzoates of a series of phenols is explained by assuming an intra- or, more probably, an inter-mol. interaction (complex formation) between a nitro-enoid and an auxo-enoid system, as in the corresponding arylamides (A., 1937, II, 239). The *p*-nitrobenzoates are coloured only if the phenol contains a powerful auxochrome (*e.g.*, NMe_2) *para* to OH, but OMe or NHAc in this position is sufficient to cause colour in the dinitrobenzoates. Di-esters of quinol are colourless. The following are described: p-*anisyl*, m.p. 115·2—115·8°, *p*-NMe_2·C_6H_4, m.p. 176—177°, p-*acetamidophenyl* (**I**), m.p. 216·2—216·8°, and p-*hydroxyphenyl*, m.p. 192—193·5°, p-*nitrobenzoates*; p-*anisyl*, m.p. 166—166·5°, p-*dimethylaminophenyl*, m.p. 206·5—207°, p-*acetamidophenyl* (**II**), m.p. 212·5—213·2°, and p-*hydroxyphenyl*, m.p. 169—170·5°, 3 : 5-*dinitrobenzoates*. *Quinol di-3 : 5-dinitrobenzoate* has m.p. 329—330°. p-p'-*Nitrobenzamidophenyl acetate*, m.p. 234·5—235·5°, is not identical with (**I**) and is hydrolysed to *p-p'*-nitrobenzamidophenol; the corresponding 3 : 5-*dinitrobenzoyl* compound differs from (**II**) and is hydrolysed to *N*-3 : 5-dinitrobenzoyl-*p*-aminophenol. G. A. R. K.

Rearrangement of 3 : 5-dichloro-*O*-crotylsalicylic acid and related compounds. D. S. Tarbell and J. W. Wilson (*J. Amer. Chem. Soc.*, 1942, **64**, 607—612).—2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CO_2Me (**I**) with CHMe:CH·CH_2Br (**II**) and K_2CO_3 in boiling COMeEt and later KOH–MeOH–H_2O gives 3 : 5-*dichloro-2-crotyloxybenzoic acid* (**III**) (>58%), m.p. 121·5—122·5°, oxidised by aq. $KMnO_4$ to (?) an anhydride, decomp. 257—259°, of 2 : 4-*dichloro-6-carboxyphenoxyacetic acid* (**IV**) (53%), m.p. (from 3N-HCl) 210—211°, and converted at 130—131° in CO_2 into 2 : 4-dichloro-6-α-methylallylphenol (**V**) (58%), b.p. 95—98°/5 mm. (*phenylurethane*, m.p. 103—104°), 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CO_2H (20%), and a fraction (5%), b.p. ~150°/5 mm. CH_2Br·CO_2Et, (**I**), and NaOMe–MeOH give a diester, m.p. 57—59°, hydrolysed by 30% KOH–MeOH to (**IV**). Hydrogenation (PtO_2) of (**V**) in EtOH gives 2 : 4-dichloro-6-*sec.*-butylphenol (**VI**), b.p. 142°/22 mm. (*phenyl-*, m.p. 114—115°, and *α-naphthyl-urethane*, m.p. 151—153°), also obtained thus: 2 : 4 : 1-$C_6H_3Cl_2$·OH → (Ac_2O–C_5H_5N) -$C_6H_3Cl_2$·OAc, b.p. 133—134°/22 mm. → ($AlCl_3$; 135—145°) 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·COMe, m.p. 94—96° → ($MgEtBr$–Et_2O) *β-3 : 5-dichloro-2-hydroxyphenylbutan-β-ol* (68%), m.p. 108—109° →

(heat + trace of I) ? 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CMe:CHMe (86%), b.p. 140—142°/25 mm. → (H_2–Pt) (VI). At ~175—180° *o*-CH_2:CH·CH_2·O·C_6H_4·CO_2H gives 3 : 2 : 1-CH_2:CH·CH_2·C_6H_3(OH)·CO_2H (64%) and *o*-allylphenol (23%). 2 : 3 : 5 : 1-CH_2:CH·CH_2·O·$C_6H_2Cl_2$·CO_2H rearranges more slowly than does (III) and in $NPhMe_2$ at 150° gives (I) (23%) and 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CO_2H (13%). 2 : 4 : 1-$C_6H_3Cl_2$·O·CH_2·CH:CHMe [prep. from the phenol, (II), and K_2CO_3 in COMeEt], b.p. 90—103°/3 mm., rearranges more readily than does the allyl ether, b.p. 98—99°/2 mm. M.p. are corr. R. S. C.

Preparation and properties of *p*-thiolbenzoic acid. D. Bramley and N. H. Chamberlain (*J.C.S.*, 1942, 376).—A temp. of 90—100° is maintained during reduction (method: Smiles *et al.*, *J.C.S.*, 1922, **121**, 2024) of *p*-SO_2Cl·C_6H_4·CO_2H to give nearly pure *p*-SH·C_6H_4·CO_2H. A. T. P.

Alkyl carbonates. III—V.—See A., 1942, II, 246.

Substituted succinic acids. I. R. H. Siddiqui and Salah-ud-din (*J. Indian Chem. Soc.*, 1941, **18**, 635—637).—*o*-C_6H_4Cl·CHO, CN·CH_2·CO_2·Et, and piperidine yield *o*-C_6H_4Cl·CH:C(CN)·CO_2Et, m.p. 225°, which with KCN in EtOH and hydrolysis with HCl gives *o*-chlorophenylsuccinic acid, m.p. 177° (anhydride, m.p. 119—120°; *monoanilide*, m.p. 168°). Similarly prepared, *Et α-cyano-β*-p- (I), m.p. 84°, and *-β*-o-*anisylacrylate* (II), m.p. 77°, give respectively *p*-, m.p. 206° and *o*-anisylsuccinic acid, m.p. 182°. CHPh:C(CN)·CO_2Et (III), m.p. 54°, was prepared similarly and converted into CO_2H·CHPh·CH_2·CO_2H. The *compounds*, m.p. 73°, 85°, and 69°, formed by addition of HCN to (I), (II), and (III), respectively, contain more N than is required for the CN·CHAr·CH(CN)·CO_2Et. F. R. G.

Alkyl*cyclo*pentanones. IV. Synthesis of α-1-carboxy-3-methyl-*cyclo*pentyl- and α-1-carboxy*cyclo*pentyl-β-phenylpropionic and α-1-carboxy*cyclo*pentylpropionic acids. R. D. Desai and G. S. Sahariya (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 93—96).—Successive treatments of CN·CHNa·CO_2Et suspended in EtOH with 3-methyl-*cyclo*pentanone cyanohydrin and CH_2PhCl give *Et α-cyano-α*-1-*cyano*-3-*methyl*cyclo*pentyl-β-phenylpropionate*, b.p. 252—254°/30 mm., hydrolysed by H_2SO_4 to *α*-1-*carboxy*-3-*methyl*cyclo*pentyl-β-phenylpropionic acid*, m.p. 112°, which gives a non-cryst. anhydride, sparingly sol. Pb and Cu salts, and freely sol. Ca and Ba salts. *cyclo*Pentanone cyanohydrin under similar conditions gives *Et α-cyano-α*-1-*cyano*cyclo*pentyl-β-phenylpropionate*, b.p. 220—225°/15 mm., m.p. 70°, hydrolysed (aq. H_2SO_4) to *α*-1-*carboxy*cyclo*pentyl-β-phenylpropionic acid*, m.p. 145° (*anhydride*, m.p. 115°; *anilic acid*, m.p. 159—160°). Et *cyclo*pentylidenecyanoacetate, CH_2PhCl, and NaOEt in hot EtOH yield *Et α-cyano-α*-Δ^1-cyclo*pentenyl-β-phenylpropionate*, b.p. 234—235°/16 mm., hydrolysed to *α*-Δ^1-cyclo*pentenyl-β-phenylpropionic acid*, m.p. 156—157°. Et sodio-1-cyano*cyclo*pentylcyanoacetate is methylated (MeI) to the *-α-cyanopropionate*, b.p. 152—154°/10 mm., hydrolysed to *α*-1-*carboxy*cyclo*pentylpropionic acid*, m.p. 140° (insol. Pb and sol. Cu, Ca, and Ba salts; non-cryst. anhydride; *anilic*, m.p. 170°, and p-*toluidinic acid*, m.p. 167°). H. W.

*cyclo*Hexane series. V. Isomeric α-1-carboxy-4- and -3-methyl-*cyclo*hexyl-β-phenylpropionic acids. R. D. Desai, R. F. Hunter, and G. S. Sanariya (*Proc. Indian Acad. Sci.*, 1941, **14, A**, 516—520; cf. A., 1936, 1251; 1940, II, 130).—Successive treatments of CN·CHNa·CO_2Et in EtOH with 1-hydroxy-1-cyano-4-methyl*cyclo*hexane at room temp. and CH_2PhCl at room temp. and then at 100° yield *Et α-cyano-α*-1-*cyano*-4-*methyl*cyclo*hexyl-β-phenylpropionate* (I), b.p. 230—234°/6 mm., m.p. 84—92°, and some *α*-1-*cyano*-4-*methyl*cyclo*hexyl-β-phenylpropionitrile* (II), m.p. 143°. (I) is hydrolysed by H_2SO_4 to a mixture of *α*-1-*carboxy*-4-*methyl*cyclo*hexyl-β-phenylpropionic acids* (*A*), m.p. 183° (decomp.) [*anhydride*, m.p. 115°; *anilic acid* (+0·5H_2O), m.p. 165° *imide*, m.p. 181°], and (*B*), m.p. 195° [also obtained from (II)] [*anhydride*, m.p. 109°; *anilic acid* (+0·5H_2O), m.p. 175°]. Similarly, *Et α-cyano-α*-1-*cyano*-3-*methyl*-cyclo*hexyl-β-phenylpropionate*, b.p. 237—239°/8 mm., m.p. 95—105°, is hydrolysed to a mixture of *α*-1-*carboxy*-3-*methyl*cyclo*hexyl-β-phenylpropionic acids* (*C*), m.p. 184° (*anhydride*, m.p. 102°; *anilic acid*, m.p. 152°; *imide*, m.p. 165—166°), and (*D*), m.p. 178° (*anhydride*, m.p. 130°, *anilic acid*, m.p. 170°). The results can be interpreted on the uniplanar form of the *cyclo*hexane ring. H. W.

Diethyl 1 : 4-dihydroxy-2 : 3-naphthalate. A. H. Homeyer and V. H. Wallingford (*J. Amer. Chem. Soc.*, 1942, **64**, 798—801).—1 : 4 : 2 : 3-$(OH)_2C_{10}H_4(CO_2Et)_2$ (I) [prep. from *o*-$C_6H_4(CO_2Et)_2$, $(CH_2·CO_2Et)_2$, and NaOEt in 48% yield] with MeI–NaOEt–EtOH gives *Et_2 1-hydroxy-4-methoxy-* (II), m.p. 80—81°, and then or directly [with some impure Et_2 2 : 3-dimethyl-2 : 3-dihydro-1 : 4-naphthaquinone-2 : 3-dicarboxylate (*A*), b.p. 175—180°/3 mm., hydrolysed (EtOH–NaOH–N_2) to 2 : 3 : 1 : 4-$C_{10}H_4Me_2(OH)_2$] *Et_2 1 : 4-dimethoxy-naphthalene-2 : 3-dicarboxylate* (III), m.p. 48—49°. In warm NaOH–EtOH–H_2O, (III) gives 1 : 4-*dimethoxynaphthalene-2 : 3-dicarboxylic acid*, which at ∢120° loses H_2O to give the *anhydride*, m.p. 203—204°. When boiled in aq. NaOH and then kept at 70°, (II) gives 4-*hydroxy*-1-*methoxy*-2-*naphthoic acid*, m.p. 217—218°, converted by CH_2N_2 (4 mols.) in MeOH–Et_2O into *Me* 1 : 4-*dimethoxy*-2-*naphthoate* (IV), m.p. 57—59°. When kept in aq. NaOH containing a little $Na_2S_2O_4$, (I) loses CO_2 and gives 1 : 4 : 2-$(OH)_2C_{10}H_5$·CO_2H, m.p. ~200° (decomp.) (lit. 186°) [with Ac_2O–NaOAc yields 1 : 5-$C_{10}H_6(OAc)_2$]. In boiling HCl–MeOH this gives 1 : 4 : 2-OH·$C_{10}H_5$(OMe)·CO_2H (V), m.p. 196—198° (decomp.) (lit. 178°, 180°), and -OH·$C_{10}H_5$(OMe)·CO_2Me (VI), m.p. 137—138° (lit. 134°). CH_2N_2 (4 mols.) in MeOH–Et_2O converts (V) into (VI), but MeI–NaOMe or a large excess of CH_2N_2 gives some (IV). The vitamin-*K* activity of (*A*) approx. equals that of 2-methyl-1 : 4-naphthaquinone; the other products are inactive. R. S. C.

Chemistry and biochemistry of plant substances. VIII. Galloyl-ellagic acid. L. Reichel and A. Schwab (*Annalen*, 1942, **550**, 152—159).—Ellagic acid (in aq. NaOH and H_2) shaken with tricarbomethoxygalloyl chloride in cold $COMe_2$ gives *tetra(tricarbomethoxygalloyl)ellagic acid*, m.p. 182—185°, converted (N-NH_3 at room temp. in H_2, then aq. H_2SO_4) into *tetragalloylellagic acid* (+11H_2O), dedecomp. ~300—320°. Tetracarbethoxyellagic acid, new m.p. 247°, and boiling aq. NaOH–dioxan (5 min.) give the *Na_2* salt and thence (warm 2N-H_2SO_4) *dicarbethoxyellagic acid*, decomp. 350—380°, *dicarbethoxybis(tricarbomethoxygalloyl)ellagic acid*, m.p. 106—110°, and *digalloylellagic acid* (+7H_2O), decomp. 300—310°. A. T. P.

Preparation of 4-nitrosalicylaldehyde. J. R. Segesser and M. Calvin (*J. Amer. Chem. Soc.*, 1942, **64**, 825—826).—Addition of Br to an illuminated (W lamp) solution of 4 : 1 : 2-NO_2·C_6H_3Me·OAc in CCl_4 gives successively *4-nitro-2-acetoxy-benzyl bromide*, m.p. 82°, and *-benzylidene dibromide* (I), m.p. 77—78°. In conc. H_2SO_4 at 50° and then 100°, (I) gives *4-nitrosalicylaldehyde* (II), m.p. 133—134° (2 : 4-dinitrophenyl-, decomp. ~323°, and phenyl-hydrazone, m.p. 168—169°). *m*-NO_2·C_6H_4·OH with NPhMe·CHO–$POCl_3$ gives a H_2O-sol. green compound and by the Reimer–Tiemann reaction a little CH(O·C_6H_4·NO_2-*m*)$_3$ which cannot be rearranged. R. S. C.

Synthesis of compounds related to mould metabolic products. I. 3 : 5-Dihydroxy-2-formylbenzoic acid and 3 : 5-dihydroxyphthalic acid. J. H. Birkinshaw and A. Bracken (*J.C.S.*, 1942, 368—370).—3 : 5 : 1-$(SO_3K)_2C_6H_3$·CO_2H and KOH at 360° afford 3 : 5 : 1-$(OH)_2C_6H_3$·CO_2H. 3 : 5 : 1-$(OH)_2C_6H_3$·CO_2Me and $Zn(CN)_2$–$AlCl_3$–HCl–Et_2O give *Me* 3 : 5-*dihydroxy*-2-*formylbenzoate* (I), m.p. 163·5° [2 : 4-*dinitrophenylhydrazone*, m.p. 293° (decomp.) or 297° (decomp.) (pre-heated to 288°)], hydrolysed [15% aq. NaOH at room temp. (3 days)] to the *acid*, m.p. 233° (decomp.) [2 : 4-*dinitrophenylhydrazone*, m.p. 301° (decomp.)]. KOH and (I) at 180—190° give 3 : 5 : 1 : 2-$(OH)_2C_6H_2(CO_2H)_2$. A. T. P.

Dialdehydes of phloroglucinol and its homologues. W. Gruber (*Ber.*, 1942, **75**, [*B*], 29—33).—Treatment of 1 : 3 : 5-$C_6H_3(OH)_3$ with $Zn(CN)_2$ and HCl in abs. Et_2O and of the product with saturated aq. $NaHCO_3$ gives *phloroglucinoldialdehyde* (1·5% yield), m.p. 221—224° (vac.; decomp.), identified by reduction (Clemmensen) to 2 : 4 : 1 : 3 : 5-$C_6HMe_2(OH)_3$, m.p. 160—161°. 2 : 1 : 3 : 5-$C_6H_2Me_2(OH)_2$, anhyd. HCN, and HCl in abs. Et_2O yield an aldimide mixture, hydrolysed by $NaHCO_3$ which removes C-*methylphloroglucinoldialdehyde*, m.p. 225—227° (vac.; decomp.) when rapidly heated [*bisphenylhydrazone*, m.p. 230—232° (vac.; decomp.)], reduced to *trimethylphloroglucinol*, m.p. 187—189°. The use is described of anhyd. HCN in the prep. of C-*ethylphloroglucinoldialdehyde*, m.p. 176—178° (vac.; decomp.) [*bisphenylhydrazone*, m.p. 230—232° (vac.; decomp.); reduced to *dimethylethylphloroglucinol*, m.p. 135—136°], and iso*amylphloroglucinoldialdehyde*, m.p. 176—177° (reduced to *dimethyl*iso*amylphloroglucinol*), and, mainly, the non-cryst. monoaldehyde [*phenylhydrazone*, m.p. 204—206° (decomp.; vac.)]. H. W.

Action of an aluminium–aluminium chloride catalyst in Friedel–Crafts reactions. Benzoylation. O. Grummitt and E. N. Case (*J. Amer. Chem. Soc.*, 1942, **64**, 878—880).—1 : 0·55 : 0·57 (mol.) C_6H_6–BzCl–$AlCl_3$ in CS_2 give 62% of $COPh_2$, also if Al (0·54) is added. Reactants in the ratio 1 : 0·179 : 0·182 (no solvent) give 90% of $COPh_2$, greatly reduced (46, 18, and 9% at 25—30°, 50°, and 80°, respectively) by presence of Al which leads also to C_2Ph_4, *p*-COPh·C_6H_4·$CHPh_2$, and resins. These products are formed by reduction (Al + HCl → H_2) of $COPh_2$ to $(CPh_2·OH)_2$ and decomp thereof by way of epoxytetraphenylethane and CPh_3·COPh. Thi. mechanism is confirmed by (i) evolution of H_2 during the Al–AlCs reaction, (ii) stability of $COPh_2$ to Al–$AlCl_3$, and (iii) formation l_3 similar products from $COPh_2$ by Al–$AlCl_3$–HCl. R. S. C.of

Effects of water on the photochemical bromination of acetophenone.—See A., 1942, I, 273.

Synthesis of potential cortical hormone substitutes. Hydroxycarbonyl derivatives of diphenyl ether and related compounds. J. Walker (*J.C.S.*, 1942, 347—353).—*p*-C_6H_4Br·OMe (I), *p*-OH·C_6H_4·CO_2Et, K_2CO_3, and Cu-bronze at 200—215° yield (after hydrolysis with aq. KOH) *p*-OMe·C_6H_4·O·C_6H_4·CO_2H-*p* (II), m.p. 176—177°, converted by boiling HBr–AcOH into 4-4′-*hydroxyphenoxybenzoic acid*, m.p. 192—193° (*Et* ester, m.p. 112—113°), and thence (Ac_2O–N-NaOH at 0°) into the 4′-*OAc-acid* (III), m.p. 149—150°. $SOCl_2$–$CHCl_3$ and (III) give the chloride, which with CH_2N_2–Et_2O at room temp. yields *ω-diazo*-4-(4′-*acetoxyphenoxy*)*acetophenone* (IV), m.p. 118—119·5°, and thence (AcOH) the *ω-OAc*-compound (V), m.p. 117·5—118°. (IV) and 2N-H_2SO_4–dioxan at

50°, then N-HCl–EtOH, give *ω-hydroxy-4-(4′-hydroxyphenoxy)-acetophenone*, m.p. 171—172·5°, also obtained from (V) with aq. EtOH–HCl. 3 : 4 : 1-OMe·C_6H_3(ONa)·CO_2Et, (I), and Cu-bronze–Cu$(OAc)_2$ at 240°, then MeOH–KOH, yield 4-(4′-*methoxyphenoxy)-3-methoxybenzoic acid*, m.p. 170—171°, and thence (AcOH–HBr) *3-hydroxy-4-(4′-hydroxyphenoxy)benzoic acid*, m.p. 204—205° (*Et* ester, m.p. 128—129°). The corresponding 3 : 4-(*OAc*)$_2$-*acid* (VI), m.p. 173—174°, gives *ω* : 3-*diacetoxy-4-(4′-acetoxyphenoxy)acetophenone*, b.p. ~255°/1·6 mm., converted by Cu$(OAc)_2$–CH_2O–aq.NH_3, followed by picric acid, into the *picrate* (+1·5H_2O), effervesces at 128—130°, resolidifies and melts at 183—184°, of 2 : 4′-dihydroxy-4-4″-iminazolyldiphenyl ether. The chloride of (III) and CHNaAc·CO_2Et–C_6H_6 (reflux, then room temp.) give a Na derivative, converted by aq. NH_3–NH_4Cl into the intermediate *β*-keto-ester (*phenylpyrazolone*, m.p. 128·5—130°) and thence (10% aq. H_2SO_4) 4-(4′-*hydroxyphenoxy)acetophenone*, (VII), m.p. 155—156°. The chloride of (VI) similarly yields 3-*hydroxy-4-(4′-hydroxyphenoxy)-acetophenone* (VIII), m.p. 149—150·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 234°). *p*-OMe·C_6H_4·OPh (IX) and AcCl–$AlCl_3$–CS_2 at room temp. afford 4-(4′-*methoxyphenoxy)acetophenone*, m.p. 60—61° (2 : 4-*dinitrophenylhydrazone*, m.p. 171°) [also obtained from (VII) and aq. Me_2SO_4–KOH], oxidised (NaOCl) to (II). 2 : 5 : 1-OMe·C_6H_3Br·CO_2Et and NaOPh–Cu-bronze–Cu$(OAc)_2$ at 230° afford *Et 5-phenoxy-2-methoxybenzoate*, m.p. 63° (free *acid*, m.p. 108·5—110°). 4-(4′-Methoxyphenoxy)cinnamic acid, new m.p. 176—177° (*Me* ester, m.p. 129—130°), is hydrogenated (Pd–$SrCO_3$–EtOAc) to *Me β*-4-(4′-*methoxyphenoxy)phenylpropionate*, m.p. 55—56°, converted by boiling HBr–AcOH into *β*-4-(4′-*hydroxyphenoxy)phenylpropionic acid*, m.p. 161° (*Et* ester, m.p. 76—77°). NPhMe·CHO, (IX), and $POCl_3$ at 100° (bath) give only a little *p*-OMe·C_6H_4·O·C_6H_4·CHO-*p* (semicarbazone, new m.p. 215°). (V), (VII), and (VIII) show no progesterone activity. A. T. P.

Condensation of succinic anhydride with resorcinol and orcinol. Further case of γ-substitution in orcinol. R. D. Desai and (Mrs.) V. H. Shroff (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 97—98).—*m*-$C_6H_4(OH)_2$ is converted by $AlCl_3$ and $(CH_2{\cdot}CO)_2O$ (I) in $PhNO_2$ at room temp. and then at 100° into *β*-2 : 4-*dihydroxybenzoylpropionic acid*, m.p. 199—200° [p-*nitrophenylhydrazone*, m.p. 194° (decomp.)], oxidised by NaOBr to *β*-resorcylic acid. Similarly orcinol affords *β*-3 : 5-*dihydroxy*-p-*toluoylpropionic acid*, m.p. 207° [p-*nitrophenylhydrazone*, m.p. 203—204° (decomp.)], oxidised to *p*-orsellinic acid. Resacetophenone, (II), 1 : 3 : 5-$C_6H_3(OH)_3$, Me *β*-resorcylate (III), and *α*-$C_{10}H_7$·OH could not be condensed with (I) in presence of anhyd. $AlCl_3$ or $ZnCl_2$ in $PhNO_2$ or $C_2H_2Cl_4$. (II) or (III) does not condense with $CO_2Et{\cdot}[CH_2]_2{\cdot}COCl$ in presence of $AlCl_3$ or $ZnCl_2$. H. W.

Action of benzoyl chloride on ethyl β-diethylaminocrotonate. W. M. Lauer and N. H. Cromwell (*J. Amer. Chem. Soc.*, 1942, **64**, 612—614).—NEt_2·CMe:CH·CO_2Et and BzCl in Et_2O at 0° give mixed hydrochlorides, whence are obtained by hydrolysis in H_2O at room temp. *Et β-diethylamino-αγ-dibenzoylcrotonate* [*β-diethylamino-δ-hydroxy-α-benzoyl-δ-phenyl-*$\Delta^{\alpha\gamma}$*-pentadienoate*] (I), m.p. 76·5—77·5° (*hydrochloride*, m.p. 125—126°, obtained by HCl–Et_2O), and, by treatment of the filtrate with aq. NH_3 (?) *Et δ-amino-β-diethylamino-benzoyl-δ-phenyl-*$\Delta^{\alpha\gamma}$*-pentadienoate*, m.p. 129—131°. In boiling 1·4% H_2SO_4 or AcOH, (I) gives 4-*diethylamino-3-benzoyl-6-phenyl-2-pyrone* (II), m.p. 126—127°, also obtained by treating dehydrobenzoylacetic acid (III) successively with PCl_5–$POCl_3$ and $NHEt_2$. In 15% aq. NaOH, (I) gives a Na salt, but in 1% NaOH gives slowly (II) and some BzOH. NPr^{α}_2·CMe:CH·CO_2Et and BzCl–Et_2O give *Et β-di-*n*-propylamino-αγ-dibenzoylcrotonate*, m.p. 71—72°, hydrolysed by boiling AcOH to 4-*di-*n*-propylamino-3-benzoyl-6-phenyl-2-pyrone*, m.p. 147—147·5°, also obtained (cf. above) from (III). R. S. C.

Condensation of maleic anhydride with naphthyl methyl ethers. K. P. Dave, K. U. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 122—123).—Condensation of *α*-$C_{10}H_7$·OMe with (CH·CO)$_2$O (I) in $PhNO_2$ gives an 88% yield of *β*-4-*methoxy*-1-*naphthoylacrylic acid*, m.p. 192—193° (resinous Me and Et ester; *dibromide*, m.p. 160°), oxidised ($KMnO_4$) to 4 : 1-OMe·$C_{10}H_6$·CO_2H, m.p. 230°. Under similar conditions *β*-$C_{10}H_7$·OMe and (I) give a product, m.p. 105—120°, consisting mainly of 2-methoxy-1-naphthoylacrylic acid since it gives a large proportion of 2 : 1-OMe·$C_{10}H_6$·CO_2H when oxidised. H. W.

Conjugated systems. XVI. Condensation of dienes with unsaturated aryl ketones. N. A. Naschtschinskaja and A. A. Petrov (*J. Gen. Chem. Russ.*, 1941, **11**, 665—668).—$(CH_2{:}CH)_2$ (I) and CHPh:CH·COMe at 170—180° for 10 hr. give 2-*acetyl-1-phenyl-*Δ^4-cyclo*hexene* (47% yield), m.p. 62·2—62·7° (*oxime*, m.p. 94·5—95°; semicarbazone, m.p. 175—175°). (I) and CHPh:CH·COPh (II) afford 2-*benzoyl-1-phenyl-*Δ^4-cyclo*hexene* (82% yield), m.p. 100·4—101·5° (*dibromide*, m.p. 120·2—121·2°). (I) and CO(CH:CHPh)$_2$ give 2 : 2′-*diphenyl-*$\Delta^{4:4'}$*-octahydrobenzophenone*, m.p. 163·5—164·7° (*tetrabromide*, m.p. 235—236°). Isoprene and (II) give 2-*benzoyl-1-phenyl-5-methyl-*Δ^4-cyclo*hexene* (56·6% yield) (*dibromide*, m.p. 111·5—112°, and a higher bromide, m.p. 153—154·5°). G. A. R. K.

Conjugated systems. XV. Condensation of alkoxybutadienes with acraldehyde. Synthesis of 4-ketohexahydrobenzaldehyde and derivatives. A. A. Petrov (*J. Gen. Chem. Russ.*, 1941, **11**, 661—664).—*β*-Methoxybutadiene and CH_2:CH·CHO (containing 0·7% of quinol) at 120—140° for 6 hr. give 65% of 4-*methoxy-*Δ^3*-tetrahydrobenzaldehyde* (I), b.p. 92—92·5°/10 mm.; *β*-ethoxybutadiene similarly affords (50%) 4-*ethoxy-*Δ^3*-tetrahydrobenzaldehyde*, b.p. 101·5—102°/10 mm. (I) is partly polymerised on keeping for a year; the remainder undergoes hydrolysis by atm. H_2O to 4-*ketohexahydrobenzaldehyde* (II), b.p. 113—113·5°/10 mm., also rapidly produced on shaking (I) with dil. H_2SO_4; it is miscible with H_2O, not volatile in steam, and polymerises to a solid on keeping (disemicarbazone, m.p. 199°; *p*-nitrophenylhydrazone). (II) is oxidised by $KMnO_4$ to 4-keto*cyclo*hexane-1-carboxylic acid. G. A. R. K.

Reactions of perinaphthane derivatives. L. F. Fieser and L. W. Newton (*J. Amer. Chem. Soc.*, 1942, **64**, 917—921).—Perinaphthen-7-one (I) (A., 1938, II, 356) with $Na_2S_2O_4$ gives a red vat, with NH_2OH,HCl in abs. EtOH gives an *oxime*, sinters at 165°, m.p. 166·8—167·3° (cf. lit.), and with $NaHSO_3$ in aq. EtOH and then NH_2Ph gives the *salt*, $C_{10}H_6$<CH(SO$_3$H,NH$_2$Ph)/CO>CH_2, m.p. 173·2—174·6° (decomp.), which regenerates (I) in boiling, dil. HCl. (I) does not undergo the Michael, Diels–Alder, or Friedel–Crafts (C_6H_6–$AlCl_3$) reaction, but with BzCl–$AlCl_3$–$ZnCl_2$ at 130—140° gives 8-*benzoylperinaphthen-7-one* (II) (>38%), m.p. 167·9—168·4° (red vat; proof of structure by synthesis below), and small amounts of an *isomeride*, m.p. 304—307°, and a *substance*, m.p. 274—275° (decomp.). Perinaphthan-7-ol is best (80%) obtained by hydrogenation of (I) in presence of old Raney Ni, but fresh catalyst gives also much phenol; dehydration by Tschugaev's method or by PCl_5–$POCl_3$ and later C_5H_5N failed. With MgMeI–Et_2O and later aq. NH_4Cl, (I) gives 7-*methylperinaphthan-7-ol* (67%), m.p. 74·6—76·1°, dehydrated by boiling HCl–abs. EtOH to 7-*methylperinaphthene*, m.p. 59·5—60·3° [purified by Al_2O_3; picrate, m.p. 174·5° (decomp.)], stable in N_2 (becomes green) but not in air. (I) is more stable than is 1 : 2 : 4-O:$C_{10}H_5$Me:O to H_2O_2–Na_2CO_3–EtOH–H_2O, but after rather long boiling gives 8 : 9-*epoxyperinaphthan-7-one* (58%), sinters at 116°, m.p. 117—117·4°, which in conc. H_2SO_4 gives 8-*hydroxyperinaphthen-7-one* [*perinaphthane*-7 : 8-*dione*] (III) (98·5%), m.p. 184·4—185° (*acetate*, m.p. 183·5—185·5°; *benzoate*, sinters at 159°, m.p. 163·5—165·6°). Br–AcOH at 100° converts (I) into the 8-*Br*-derivative, m.p. 152—152·4°, which could not be converted into (III). Perinaphthen-7-one-8-carboxylic acid (IV) (prep. from 2 : 3-OH·$C_{10}H_6$·CO_2H, glycerol, NO_2·C_6H_4·SO_3Na, H_2SO_4, and H_2O modified; 18·7% yield), sinters at 275°, m.p. 284·5—285° (gas), when heated at 3—5 mm. gives (I) and with PCl_5–C_6H_6 gives the acid *chloride*, sinters at 207°, m.p. 209—211°, which with C_6H_6–$AlCl_3$ yields (II) (40%). $(CH_2{:}CMe)_2$ and (IV) in boiling AcOH give 9 : 10-*dimethyl-*(? 8 : 11-)*di-* (V), m.p. 188·6—189·4°, and *-7a* : 8 : 11 : 11*a-tetra-hydrobenzanthr-7-one*, m.p. 124·7—125·2°, or after prolonged boiling 9 : 10-*dimethylbenzanthr-7-one*, m.p. 188·6—189·4°, also obtained from (V) by Pd–C at 300° and oxidised by CrO_3–AcOH to 2 : 3-*dimethylanthraquinone-5-carboxylic acid*, m.p. 313—314° (decomp. from ~310°; uncorr.) [*compound* with Ac_2O, m.p. 215—217° (loss of solvent), resolidifies, remelts at 312—316° (uncorr.)], which with Cu-bronze in quinoline at 170° gives 2 : 3-dimethylanthraquinone. M.p. are corr. R. S. C.

Preparation of 2-iodo-p-benzoquinone. H. H. Hodgson and D. E. Nicholson (*J.C.S.*, 1942, 375—376).—1 : 3 : 4-OH·C_6H_3I·NH_2 and aq. $Fe_2(SO_4)_3$ give 2-*iodo*-p-*benzoquinone*, m.p. 62°. A. T. P.

Sulphonation. VII. Sulphonation of 1 : 2-benzanthraquinone with sulphuric acid. J. S. Joffe and N. M. Fedorova (*J. Gen. Chem. Russ.*, 1941, **11**, 619—625).—1 : 2-Benzanthraquinone with 96% H_2SO_4 at 150—160° for 5—6 hr. affords 1 : 2-*benzanthraquinone-2′-sulphonic acid* (I), isolated as the K salt (80% yield), apparently the sole product formed (cf. Sempronj, A., 1939, II, 514). Mild fusion of (I) with KOH gives 2′-*hydroxy*-1 : 2-*benzanthraquinone* (II), m.p. 248—250° [*acetate* (III), m.p. 253—255°], forming blue solutions in alkali. A by-product is 2 : 7-OH·$C_{10}H_6$·CO_2H, m.p. 268—269° (acetate, m.p. 209°), also formed when (I) or (II) is fused with KOH under drastic conditions [when no 2 : 8-OH·$C_{10}H_6$·CO_2H is formed, so that fission always takes place between CO and the *α*- and not the *β*-C atom (cf. *loc. cit.*)]. Reduction of (I) with Zn dust and aq. NH_3 gives 1 : 2-*benzanthracene-2′-sulphonic acid*, forming 2′-*hydroxy*-1 : 2-*benzanthracene* (IV), m.p. 178—179° [*acetate* (V), m.p. 152—153°], on alkaline fusion. (IV) couples with ArN_2Cl to form azo-dyes (*e.g.*, dye, m.p. 248—249°, with 2 : 4 : 1-$C_6H_3Cl_2$·N_2Cl). (V) is oxidised (CrO_3) to (III). G. A. R. K.

Perylene and its derivatives. LV. Supposed 1 : 12-furano-2 : 3 : 10 : 11-dibenzoperylene-4 : 9-quinone of E. Clar. A. Zinke, E. Ziegler, and H. Gottschall [with, in part, K. Lercher] (*Ber.*, 1942, **75**, [*B*], 148—151).—The alkali-insol. product obtained by Clar (A., 1932, 731) by the oxidation of his dibenzoperylene is 2 : 3 : 8 : 9-*dibenzoperylene*-4 : 10-*quinone* (I), m.p. 367° after becoming discoloured at 360°. It is converted (aq. NaOH–$Na_2S_2O_4$, then Et_2O–*p*-C_6H_4Br·COCl) into 4 : 10-*di-*p-*bromobenzoyloxy*-2 : 3 : 8 : 9-*dibenzoperylene*, m.p. 344°, and chlorinated by Cl_2 in dry $PhNO_2$ at 100° to a *substance*, $C_{28}H_{12}O_2Cl_6$, decomp. ~300° after darkening at 220°, converted by boiling $PhNO_2$–C_5H_5N into the *compound*, $C_{28}H_{10}O_2Cl_4$,

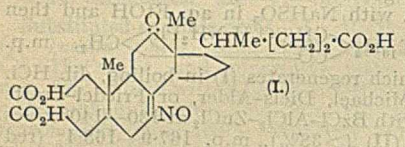
m.p. >350°. (I) is oxidised by CrO_3 in boiling AcOH to (?) an *acid*, $C_{27}H_{14}O_5$, m.p. 300—302°. H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

***sym.*-Dicholesteryl pyrophosphate dihydrate.** T. Wagner-Jauregg and T. Lennartz (*Ber.*, 1942, **75**, [*B*], 178—179).—Dicholesteryl H_2 pyrophosphate dihydrate (**I**) is converted by K in boiling PhMe into the K_1 salt, m.p. 186—189° (darkens at 180°). The Na_4 salt and boiling AcOH yield the Na_1 salt, m.p. 178—180°. (**I**) contains 4 active H (Zerevitinov). H. W.

3-Acyloxybisnorcholanic acids.—See B., 1942, III, 171.

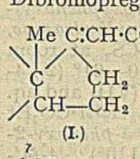
Pernitrosodeoxybilianic acid. M. Schenck (*Ber.*, 1942, **75**, [*B*], 198—202).—Treatment of the NO-acid (**I**) with 23% aq. $NaNO_2$ in AcOH gives the enol-nitrate, $C_{24}H_{33}O_{10}N$, decomp. 125°, also obtained from *iso*bilianic acid dioxime. Deoxybilianic acid oxime and HNO_2 afford the *pernitroso-acid*, $C_{24}H_{36}O_8N_2$, decomp. 110°, which does not give a colour with $NHPh_2$–H_2SO_4. It evolves N_2O when treated with conc. H_2SO_4 or, particularly easily, with NaOH. H. W.



Total synthesis of a stereoisomeride of the sex hormone, œstrone. W. E. Bachmann, S. Kushner, and A. C. Stevenson (*J. Amer. Chem. Soc.*, 1942, **64**, 974—981).—$[CH_2]_3(CO)_2O$ [prep. from $CO_2Me·[CH_2]_2·CH(CO_2Et)_2$ by boiling 18% HCl and later AcCl], m.p. 52—55°, b.p. 165—170°/20 mm., with EtOH gives the Et H ester and thence $(SOCl_2)$ $CO_2Et·[CH_2]_3·COCl$, which with *m*-$OMe·C_6H_4·[CH_2]_2·CH(CO_2Et)_2$ (modified prep.), b.p. 195—200°/0·6—0·8 mm., in C_6H_6 at, first, room temp. and then the b.p. gives Et δ-keto-εε-dicarbethoxy-η-*m*-anisyl-*n*-octoate (52%), b.p. 210—220°/0·05 mm., converted by 100% H_3PO_4 at 42° and then KOH–MeOH–H_2O into γ-2:2-*dicarboxy*-6-*methoxy*-1:2:3:4-*tetrahydro*-1-*naphthylidene*-n-*butyric acid* (**I**), m.p. 180·5—182° (gas; bath preheated at 175°). This is decarboxylated and rearranged in boiling H_2O to γ-2-*carboxy*-6-*methoxy*-3:4-*dihydro*-1-*naphthyl*-n-*butyric acid* (**II**) (52%), m.p. 189—190° (decomp.), the structure of which is proved by conversion by boiling HCl–AcOH–H_2O–N_2 or of its Me_2 ester (**III**) (prep. by CH_2N_2) by NaOMe–C_6H_6–N_2 into 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene (**IV**), m.p. 76—77·5°, also obtained similarly (both methods) from (**I**) and from *m*-$OMe·C_6H_4·[CH_2]_3·CO·[CH_2]_3·CO_2Me$ by boiling NaOMe–C_6H_6 (gives 2-β-*m*-anisylethyl*cyclo*hexane-1:3-dione, m.p. 150—152°) and then H_3PO_4 at 100° (cf. Robinson *et al.*, A., 1935, 1499; Hewett, A., 1936, 326). Ring-closure of (**III**) and methylation (MeI–MeOH–C_6H_6) of the crude Na derivative gives *Me* 1-*keto*-7-*methoxy*-2-*methyl*-1:2:3:4:9:10-*hexahydrophenanthrene*-2-*carboxylate* (**V**), m.p. 98—100°, which affords (Reformatsky) *Me* 1-*hydroxy*-2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1:2:3:4:9:10-*hexahydro*-1-*phenanthrylacetate* (**VI**) (69%), m.p. 112—113°, converted by hot KOH–MeOH–H_2O into the known (*loc. cit.*) 2-Me derivative of (**IV**) [also obtained similarly from (**V**)]. With dry HCl–C_6H_6 at 15° or warm HCO_2H–C_6H_6, (**VI**) gives *Me* 2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1:2:3:4:9:10-*hexahydro*-1-*phenanthrylideneacetate*, m.p. 136·5—138°, isomerised by Pd–C at 300° to the known Me 1:2:3:4-tetrahydro-1-phenanthrylacetate and hydrogenated (Pd–C; EtOH) to mixed stereoisomeric 1:2:3:4:9:10:11:12-H_8-esters. Half hydrolysis (NaOH–MeOH–H_2O–N_2), lengthening of the chain (Arndt–Eistert), ring-closure (NaOMe–C_6H_6–N_2) to mixed 16-carbomethoxyœstrone Me ethers, hydrolysis and decarboxylation (HCl–AcOH–H_2O–N_2) to mixed œstrone Me ethers (distilled at 180°/0·05 mm.), and finally demethylation (48% aq. HBr–AcOH) gives mixed œstrones (**VII**), solid. In MeOH these deposit *œstrone*-a (**VIII**), m.p. 214—214·5°, sublimes at 200°/0·05 mm. (*benzoate*, m.p. 175—176° after slight softening), the Na salt of which with Me_2SO_4 in H_2O gives the Me ether, dimorphic, m.p. 81·5—82° and 101·5—102·5°, converted by, successively, MgMeI, $KHSO_4$, and Pd–C at 300° into 7-methoxy-3′:3′-dimethyl-1:2-*cyclo*pentanophenanthrene, m.p. 162—163·5°, identical with that obtained from equilenin Me ether. Hydrogenation (Pd–C; AcOH) of (**II**) gives γ-2-*carboxy*-6-*methoxy*-1:2:3:4-*tetrahydro*-1-*naphthyl*-n-*butyric acid*, m.p. 156—157·5°, the Me_2 ester of which, when cyclised as above and then boiled in HCl–AcOH–H_2O–N_2, gives the known 1-keto-7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene (**IX**), m.p. 107—108°, or, when cyclised and then methylated as above, yields the oily 2-carbomethoxy-2-methyl and thence (KOH–MeOH–H_2O) the 2-Me derivative of (**IX**). Reduction of (**II**) by 2% Na–Hg in H_2O gives an acid, whence cyclisation etc. gives mixed ketones including some (**IX**). The absorption spectrum of (**VIII**) very closely resembles that of œstrone (**X**). Doses of (**X**), (**VII**), and (**VIII**) for equal œstrogenic activity are 1:50:250. (**VIII**) is a *dl*-form of a stereoisomeride of (**X**). R. S. C.

Sterols. CXL. 17-Bromo- and 17:21-dibromo-*allo*pregnan-20-one. R. E. Marker, H. M. Crooks, jun., R. B. Wagner, A. C. Shabica, E. M. Jones, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 822—824).—*allo*Pregnan-20-one (**I**) with Br in AcOH + a little HBr at room temp. gives 17-*bromo*- (**II**), m.p. 127—129°, and then at 40° 17:21-*dibromo*-allo*pregnan*-20-*one* (**III**), m.p. 128—130°. (**I**) is regenerated from (**II**) by Zn powder or Fe filings in AcOH at 100° or by H_2–Pd–$BaSO_4$–C_5H_5N–MeOH at 2 atm., and from (**III**) by Zn– or Fe–AcOH or HCO_2H–HCO_2K at 130°. In boiling C_5H_5N, (**II**) gives Δ^{16}-allo*pregnen*-20-*one*, m.p. 156—158°, hydrogenated (Pd–$BaSO_4$) in EtOH–dioxan to (**I**). With hot KOH–MeOH, (**III**) gives $\Delta^{17:20}$-allo*pregnenoic* 21-*acid*, m.g. 242—244°, converted by O_3 into $CHCl_3$ into *androstan*-17-*one*, m.p. 117—119°, isolated as *semicarbazone*, m.p. 284—285° (decomp.). R. S. C.

Sterols. CXXXVIII. Conversion of pregnan-3(β)-ol-20-one into ætiocholan-3(β)-ol-17-one. R. E. Marker, H. M. Crooks, jun., and R. B. Wagner (*J. Amer. Chem. Soc.*, 1942, **64**, 817—818).—17:21-Dibromopregnan-3(β)-ol-20-one in boiling KOH–MeOH–H_2O gives 3(β)-*hydroxy*-$\Delta^{17:20}$-*pregnenoic* 21-*acid* (**I**), m.p. 257—258° (decomp.) [*acetate* (**II**), +H_2O, m.p. 209—212°, and (?) its mixed *anhydride* with AcOH, m.p. 234°], reduced by H_2–PtO_2 in AcOH at 3 atm. to 3(β)-*hydroxypregnanoic* 21-*acid*, m.p. 219—221°. (**II**) with O_3–$CHCl_3$ or CrO_3–AcOH at 50—55° gives (after hydrolysis) ætiocholan-3(β)-ol-17-one (isolated as semicarbazone and obtained therefrom by boiling H_2SO_4–H_2O–EtOH). R. S. C.



Separation of pregnenolone esters.—See B., 1942, III, 172.

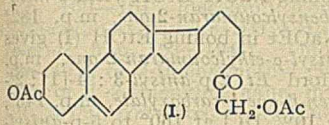
Constituents of the adrenal cortex and related substances. LV. *allo*Pregnane-3(β):17(α):21-triol-20-one and attempts to prepare other 17(α)-hydroxypregnane derivatives with dihydroxyacetone grouping. D. A. Prins and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 300—322).—Δ^{20}-*allo*Pregnene-3(β):17(α)-diol diacetate and Et_2O–OsO_4 give a mixture of Os esters, converted by agitation with aq. $HClO_3$ in Et_2O into a difficultly separable mixture (*A*) of substances which is partly acetylated (Ac_2O–C_5H_5N at room temp.) and then subjected to chromatography, thereby giving the well-cryst. allo*pregnane*-3(β):17(α):20(α):21-*tetraol* 3:17:21-*triacetate* (**I**), m.p. 120—121°, $[\alpha]_D^{15}$ −31·5°±4°, $[\alpha]_{5461}^{15}$ −38·5° ±4° in $COMe_2$, and allo*pregnane*-3(β):17(α):21-*triol*-20-*one triacetate* (**II**), m.p. 178—180° (softens at 173°), $[\alpha]_D^{15}$ −12·8°±5°, $[\alpha]_{5461}^{15}$ −18·9°±5° in $COMe_2$. In one experiment a small amount of allo*pregnane*-3(β):17(α):21-*triol*-20-*one* 3:21-*diacetate* (**III**), m.p. 158—161°, $[\alpha]_D^{19}$ −55·7°±2°, $[\alpha]_{5461}^{19}$ −66·7°±2° in $COMe_2$, was isolated; the production of this is due to acyl migration. Attempted separation of (*A*) by crystallisation from Et_2O gave an allo*pregnanetetraol diacetate*, m.p. 160—162°, $[\alpha]_D^{18}$ −18·6°±2°, $[\alpha]_{5461}^{18}$ −26°±2° in $COMe_2$, oxidised (CrO_3) to androstan-3(β)-ol-17-one acetate. An allo*pregnanetetraol tetra-acetate*, m.p. 252—256°, $[\alpha]_D^{18}$ −28·0°±5°, $[\alpha]_{5461}^{18}$ −33·7°±6° in $COMe_2$, which is not derived from (**I**), is described. (**I**) is oxidised by CrO_3 to (**II**) and is distinguished from (**IV**) (below) only by this method. (**I**) is converted by energetic hydrolysis followed by re-acetylation into *allo*pregnane-3(β):17(α):20(α):21-tetraol 3:20:21-triacetate (**IV**), m.p. 119—121°. (**II**) is hydrolysed ($KHCO_3$ in MeOH at room temp.) to a mixture which is re-acetylated to (**II**) and degraded by HIO_4 in aq. MeOH at room temp. followed by hydrolysis to 3(β):17(α)-dihydroxyætio*allo*cholanic acid (**V**). Successive hydrogenation (Raney Ni under pressure), energetic hydrolysis, and re-acetylation of (**II**) affords (**IV**). Ac at $C_{(17)}$ in (**II**) cannot be simply removed without disturbing the mol. structure of the residue. Δ^{20}-*allo*Pregnene-3(β):17(α)-diol 3-monoacetate is similarly converted by the successive actions of OsO_4 and $HClO_3$ in Et_2O into a mixture from which, after acetylation, (**III**), m.p. 160—162°, is isolated in 6% yield. It is hydrolysed ($KHCO_3$ in aq. MeOH) at 20° to a mixture of the free OH-ketone (**VI**) and its 3-*monoacetate*, m.p. 195—197°, $[\alpha]_D^{19}$ −42·9°±3° in $COMe_2$; crude (**VI**) is oxidised by HIO_3 to (**V**). $\Delta^{4:20}$-Pregnadien-17(α)-ol-3-one (**VII**) and boiling C_5H_5N–Ac_2O give the *acetate* (**VIII**), m.p. 120—122°, $[\alpha]_D^{15}$ +82·7°±3° in $COMe_2$, also obtained by the oxidation [$Al(OBu^{\gamma})_3$, $COMe_2$, C_6H_6] of $\Delta^{5:20}$-*pregnadiene*-3(β):17(α)-*diol* 17-*monoacetate*, m.p. 172—174° (from the diacetate and aq. MeOH–$KHCO_3$). (**VIII**) is treated successively with OsO_4 and $HClO_3$, partly acetylated, and oxidised to a product from which Δ^4-pregnene-17(α):21-diol-3:20-dione diacetate could not be isolated. Similar treatment of (**VII**) leads to two substances, m.p. 149—151°, $[\alpha]_D^{19}$ +13·4°±2° in $COMe_2$, and m.p. 265—268°, $[\alpha]_D^{14}$ +58·4°±4° in dioxan, the structures of which are not elucidated. H. W.

Glucosides of deoxycorticosterone.—See A., 1942, II, 219.

Steroids and sex hormones. LXXVI. Preparation of a digitaloid aglucone by oxidation of methyl 3(β)-acetoxy-$\Delta^{20:22}$-nor*allo*cholenate by selenium dioxide. L. Ruzicka, P. A. Plattner, and J. Pataki (*Helv. Chim. Acta*, 1942, **25**, 425—435).—Pregnenolone acetate, Zn, and $CH_2Br·CO_2Et$ in C_6H_6 give (after hydrolysis) 3(β):20-*dihydroxy*-Δ^5-*norcholenic acid*, m.p. 204—206°, $[\alpha]_D^{17}$ −47·1°±2° in EtOH [*Me* ester, m.p. 131—133°, $[\alpha]_D^{17}$ −55·8°±1° in $CHCl_3$, and its 3-*acetate* (**I**), m.p. 146—147°, $[\alpha]_D^{17}$ −58·8°±2° in $CHCl_3$]. (**I**) is converted slowly by boiling Ac_2O or more rapidly by $KHSO_4$ at 180—190°/high vac. into *Me* 3(β)-*acetoxy*-$\Delta^{5:6\text{-}20:22}$-*norcholadienate*, m.p. 147—149°, $[\alpha]_D^{17}$ −54·4°±1° in $CHCl_3$, hydrolysed by boiling KOH–MeOH to

3(β)-*hydroxy*-$\Delta^{5:6\text{-}20:22}$-*norcholadienic acid*, m.p. 262—265°, $[\alpha]_D^{14}$ −49·8°±2° in dioxan (*Me* ester, m.p. 139—142°, $[\alpha]_D^{14\cdot8}$ −50·2°±1° in $CHCl_3$). Hydrogenation (PtO_2 in AcOH) of (I) gives *Me* 20-*hydroxy*-3(β)-*acetoxynor*allo*cholanate* (II), m.p. 180—181°, $[\alpha]_D^{17}$ +3·5°±1° in $CHCl_3$, hydrolysed to 3(β) : 20-*dihydroxynor*allo*cholanic acid*, m.p. 201—202°, $[\alpha]_D^{15}$ +9·2°±1° in EtOH (*Me* ester, m.p. 163—165·5°, $[\alpha]_D^{15}$ +6°±1° in $CHCl_3$). Boiling Ac_2O slowly transforms (II) into *Me* 3(β)-*acetoxy*-$\Delta^{20:22}$-*nor*allo*cholenate* (III), m.p. 161—163°, $[\alpha]_D^{18}$ +6·3°±0·5° in $CHCl_3$, whence 3(β)-*hydroxy*-$\Delta^{20:22}$-*nor*allo*cholenic acid*, m.p. 237—239°, $[\alpha]_D^{18}$ +0·5°±1° in EtOH (*Me* ester, m.p. 148—150° after softening at 131°, $[\alpha]_D^{17}$ +10·9°±1° in $CHCl_3$). (III) is oxidised by SeO_2 to 21-hydroxy-3(β)-acetoxy-$\Delta^{20:22}$-nor*allo*cholenolactone, m.p. 192—196°, $[\alpha]_D^{15}$ −0·7°±2° in $CHCl_3$. M.p. are corr. (vac.). H. W.

Steroids and sex hormones. LXXVII. Homologue of the digitaloid aglucone ; β′-[3(β)-hydroxy-Δ^5-23-norcholenyl]-$\Delta^{\alpha'\beta'}$-butenolide. L. Ruzicka, P. A. Plattner, and H. Heusser (*Helv. Chim. Acta*, 1942, **25**, 435—438).—3(β)-Hydroxy-Δ^5-cholenic acid, m.p. 236—237°, $[\alpha]_D$ −39·4° in C_5H_5N, is converted into its acetate, and thence into the acid chloride and diazo-ketone, which with AcOH at 95° gives

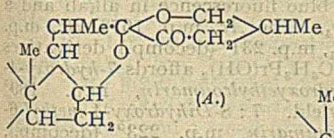


(I.)

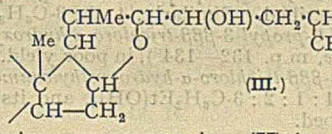
Δ^5-24-*keto*-3(β) : 25-*diacetoxy*-25-*homocholene* (I), m.p. 125·5—126°, $[\alpha]_D$ −45·06° in $CHCl_3$. Zn and $CH_2Br\cdot CO_2Et$ convert (I) into essentially β′-hydroxy-β′-[3(β)-hydroxy-Δ^5-23-norcholenyl]-γ′-butanolide, transformed by Ac_2O at 153° (bath) into β′-[3(β)-*acetoxy*-Δ^5-23-*norcholenyl*]-$\Delta^{\alpha'\beta'}$-*butenolide*, m.p. 204—205°, $[\alpha]_D$ −40·55° in $CHCl_3$, hydrolysed to the 3(β)-*OH*-derivative, m.p. 229—230°, $[\alpha]_D$ −42·52° in $CHCl_3$. M.p. are corr. (vac.). H. W.

Sterols. CXXXVI. Sapogenins. LVII. Structure of the side-chain of chlorogenin. R. E. Marker, D. L. Turner, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 809—812).—The structure of chlorogenin is confirmed and differs from that of β-chlorogenin (I) only in the configuration of the OH at $C_{(6)}$. Zn–Hg in conc., aq. HCl + EtOH reduces chlorogenone to deoxychlorogenin (= deoxytigogenin) (II) and a carbinol, converted by PBr_3 and then H_2–PtO_2 in abs. EtOH into cholestane. With, successively, Ac_2O at 200°, boiling KOH–MeOH, CrO_3–AcOH at 30°, and KOH–MeOH–H_2O, (II) gives Δ^{16}-*allo*pregnen-20-one and thence *allo*pregnan-20-one. Ac_2O at 200° and then KOH converts (I) into *ψ-β-chlorogenin* (III), m.p. 180—182°, reconverted into (I) by boiling conc. aq. HCl–MeOH and oxidised by CrO_3–AcOH at 25° to $CO_2H\cdot CHMe\cdot[CH_2]_2\cdot CO_2H$ and Δ^{16}-*allo*pregnane-3 : 6 : 20-trione (IV) and thence (H_2–PtO_2–AcOH ; 45 lb.) *allo*pregnane-3(β) : 6(β) : 20(β)-triol (V). Acetylation of (III) prior to oxidation as above gives, after hydrolysis, Δ^{16}-allo*pregnene*-3(β) : 6(β)-*diol*-20-*one*, m.p. 214—216° (*diacetate*, m.p. 233—235°), oxidised by CrO_3 to (IV) and hydrogenated to (V). R. S. C.

Sterols. CXXXVII. Sapogenins. LVIII. Oxidation products of sarsasapogenin : ketosarsasapogenin. R. E. Marker and A. C. Shabica (*J. Amer. Chem. Soc.*, 1942, **64**, 813—816).—23-Ketosarsasapogenin (I), m.p. 225—226° [best purified by way of the *acetate* (II), m.p. 172—173° ; cf. A., 1939, II, 31, 510], contains the grouping (*A*). The *semicarbazone*, m.p. 291—293° (decomp.), of (I)



(*A*.)



(III.)

with NaOEt–EtOH at 180° gives sarsasapogenin. (II) is reduced by H_2–PtO_2 in abs. EtOH at 2 atm. to (after hydrolysis) 23-*hydroxydihydro*- (III), m.p. 219—221°, by Na–EtOH to 23-*hydroxy*- (*A* with CH·OH for CO), m.p. 234—236°, and by Zn–Hg–HCl to tetrahydrosarsapogenin. With $K_2S_2O_8$–K_2SO_4–H_2SO_4–AcOH at 25° (16 days) and later KOH–EtOH, (I) gives pregnane-3(β) : 16 : 20-triol, m.p. 221—222°, and the OH-lactone (IV), $C_{22}H_{34}O_3$. With CrO_3–AcOH at 60°, and later aq. NaOH, (II) gives (IV) and some of the CO-acid, $C_{22}H_{34}O_4$, but no sarsasapogenoic acid. R. S. C.

Sterols. CXXXIX. Sapogenins. LIX. Bio-reduction of 4-dehydrotigogenone. R. E. Marker, E. L. Wittbecker, R. B. Wagner, and D. L. Turner (*J. Amer. Chem. Soc.*, 1942, **64**, 818—822 ; cf. A., 1936, 1386).—Smilagenone is reduced (H_2, PtO_2, EtOH or Na, EtOH) to epi*smilagenin* (epi-iso*sarsasapogenin*) (I), m.p. 217—220° (*acetate*, m.p. 158—159°), and is regenerated therefrom by CrO_3–AcOH at 25°. Hydrogenation (PtO_2) of (I) in AcOH at 70—75°/3 atm. gives dihydro*epi*sarsasapogenin, dimorphic, m.p. 134—136° and 180—182°. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Inactivation in the camphene series. J. J. Ritter and G. Vlases, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 583—585).—ω-Hydroxymethylcamphene, b.p. 120—125°/10 mm., $[\alpha]_D^{20}$ +24·0° (acetate, b.p. 130—138°/20 mm., $[\alpha]_D^{20}$ +18·9°), with PCl_3 in light petroleum gives the CH_2Cl derivative (71%), b.p. 109—111°/15 mm., $[\alpha]_D^{20}$ +18·5°, which with MgRHal in Et_2O gives *ω-β-phenylethyl*- (I) (81%), b.p. 138—140°/5 mm., $[\alpha]_D^{25}$ +0·66° (*hydrochloride*, m.p. 58—60° ; *hydrobromide*, an oil, dissociates when distilled ; Br adduct), *ω-n-propyl*- (34%), b.p. 104—106°/45 mm., $[\alpha]_D^{20}$ +16·4° (*hydrochloride* ; Br adduct), *ω-n-hexyl*- (II) (51%), b.p. 124°/15 mm., $[\alpha]_D^{20}$ +17·8° [*hydrochloride* (III) ; Br adduct], and *ω-cyclohexylmethyl-camphene* (45%), b.p. 133°/4 mm., $[\alpha]_D^{20}$ +16·5° (*hydrochloride* ; Br adduct). In boiling NH_2Ph, (III) gives probably a mainly racemised (II), $[\alpha]_D^{20}$ +0·20°. With NH_2Ph,HBr in boiling NH_2Ph, (I) is probably only racemised (product, $[\alpha]_D^{25}$ +0·10°). In $CCl_3\cdot CO_2H$ at 40° (several days), (II) gives an ester, hydrolysed to *amyl*iso*borneol*, m.p. 63—64°, b.p. 105—120°/1 mm. Failure to yield an active position isomeride rebuts the theory of Lipp *et al.* (A., 1932, 398). The racemisation probably occurs by 1 : 6 pinacol change. R. S. C.

Sesquiterpenes. LI. Constitution of cedrenene. L. Ruzicka, P. A. Plattner, and G. W. Kusserow (*Helv. Chim. Acta*, 1942, **25**, 85—95).—The cedrene fraction of cedar-wood oil is converted by moist O_2 into cedrenol, m.p. 103·5—104°, dehydrated by boiling Ac_2O to cedrenene (I), b.p. 122°/11 mm. Under mild conditions (I) does not react with $(CH\cdot CO)_2O$, whilst at higher temp. insol. heteropolymerides result. With $(CO_2Me)_2$ at 180°, (I) gives ~25% of polymerides and ~35% of the normal *adduct*, $C_{12}H_{28}O_4$, m.p. 132—132·5°, $[\alpha]_D$ +83° in MeOH. This distils unchanged under room pressure. It is hydrolysed to an *acid*, $C_{10}H_{24}O_4$, m.p. 230°, and hydrogenated (PtO_2 in AcOH) to the *compound*, $C_{21}H_{32}O_4$, m.p. 123·5—125°, $[\alpha]_D$ −62° in MeOH, which is saturated towards $C(NO_2)_4$. (I) in freshly distilled $CHCl_3$ under CO_2 is quantitatively converted by Br into the dibromide, m.p. 90—91°, converted by boiling KOH–MeOH into the *substance*, $C_{16}H_{25}OBr$, m.p. 149—150° ; a Br-free product could not be obtained by prolonged action of KOH–MeOH, KOH–60% dioxan, or of NaOAc in boiling AcOH, C_5H_5N, or 2 : 6-dimethylpyridine. (I) is oxidised by $KMnO_4$ in aq. $COMe_2$ to norcedrenedicarboxylic acid (II), m.p. 212·5—213°, $[\alpha]_D$ −39° in $CHCl_3$; this with boiling Ac_2O gives the *anhydride*, m.p. 128—128·5°, $[\alpha]_D$ +50° in $CHCl_3$, hydrolysed by aq. dioxan to (II). Cedrenedicarboxylic acid is similarly transformed into its *anhydride*, m.p. 79—82°. M.p. are corr. H. W.

Triterpenes. LXIII. Oxidation of betulin diacetate with monoperphthalic acid and selenium dioxide. L. Ruzicka, M. Brenner, and E. Rey (*Helv. Chim. Acta*, 1942, **25**, 161—170).—The experience gained in the oxidation of lupeol has been applied to that of betulin. Betulin diacetate (I) is converted by *o*-$CO_2H\cdot C_6H_4\cdot CO_3H$ in $CHCl_3$ into its *oxide* (II), m.p. 198—205° after softening at 190°, which gives no yellow colour with $C(NO_2)_4$ and (absorption spectrum) does not contain CHO. (II) is isomerised by boiling EtOH or aq. dioxan into diacetoxylupanal (III), m.p. 248—253° (softens at 230°), and by boiling KOH–MeOH into *dihydroxylupanal*, m.p. 263—272° (*oxime*, m.p. ~230°). Oxidation of (II) with CrO_3 gives the mixture of stereoisomeric diacetoxylupanic acids (characterised as esters) identical with the products obtained similarly from (I) ; the neutral by-products include diacetoxynorlupanone and (III). (I) is oxidised by SeO_2 in boiling AcOH or Ac_2O or in C_6H_6 at 160° to *diacetoxylupenal* (IV), m.p. 249—251°, $[\alpha]_D$ +8·4° in $CHCl_3$, which gives a pale yellow colour with $C(NO_2)_4$. Hydrolysis (N-KOH–EtOH) of (IV) affords *dihydroxylupenal*, m.p. 254°, $[\alpha]_D$ −2·5° in $CHCl_3$ [*oxime* (V), m.p. 201°]. Boiling Ac_2O and (V) afford *diacetoxylupenonitrile*, m.p. 234°, $[\alpha]_D$ +14·7° in $CHCl_3$, which does not give a yellow colour with $C(NO_2)_4$ and is hydrogenated (Pd–$CaCO_3$ in EtOH–dioxan) to *diacetoxylupanonitrile*, m.p. 275°, $[\alpha]_D$ +12° in $CHCl_3$. (IV) is hydrogenated (PtO_2 in AcOH) to trihydroxylupan diacetate, converted by Ac_2O–C_5H_5N at room temp. into *triacetoxylupan*, m.p. 140—141°, $[\alpha]_D$ −1·2° in $CHCl_3$, and oxidised by CrO_3 to (+)-diacetoxylupanic acid, identified as the Me ester, m.p. 234—235°, $[\alpha]_D$ +17·0° in $CHCl_3$. M.p. are corr. (vac.). H. W.

Triterpenes. LXIV. Degradation of betulin diacetate by ozone. L. Ruzicka and E. Rey (*Helv. Chim. Acta*, 1942, **25**, 171—179).—Treatment of betulin diacetate in $CHCl_3$–EtOAc with 3—4% O_3 and decomp. of the ozonide with boiling N-KOH–MeOH gives almost equal amounts of acid and neutral products. The former with CH_2N_2 give *Me dihydroxybisnorlupanate* (I), m.p. 268°, $[\alpha]_D$ −5·7° in $CHCl_3$ (*diacetate*, m.p. 226—227°, $[\alpha]_D$ −13·7° in $CHCl_3$), hydrolysed by alkali to the *acid*, m.p. 312°, $[\alpha]_D$ −2·4° in dioxan. The latter yields diacetoxynorlupanone (II), m.p. 190—191°, $[\alpha]_D$ −11·3° in $CHCl_3$, converted by Br–KOH followed by CH_2N_2 into (I). (I) is transformed by an excess of MgPhBr in Et_2O–C_6H_6 into *triacetoxydiphenylbisnorlupan*, m.p. 235—237°, $[\alpha]_D$ −24·8° in $CHCl_3$, which gives no colour with $C(NO_2)_4$. With MgMeI in Et_2O–PhOMe (II) affords *diacetoxy*iso*lupene* (iso*betulin diacetate*), m.p. 210°, $[\alpha]_D$ +15° in $CHCl_3$. Chromatographic purification of dicarboxylic acid *A*, obtained by the oxidation of betulin monoacetate with CrO_3, leads to a product, $C_{32}H_{50}O_6$, m.p. 310°, $[\alpha]_D$ −44·5° in $CHCl_3$ (Me_2 ester, m.p. 182°, $[\alpha]_D$ −44·2° in $CHCl_3$) ; acids *A* and *E* are therefore stereoisomeric hydroxylupandicarboxylic acids. H. W.

Triterpenes. XLV. β-Elemonic acid. L. Ruzicka and H. Häusermann (*Helv. Chim. Acta*, 1942, **25**, 439—457).—The mixture

of acids from Manila elemi resin is purified by crystallisation from EtOH and separated by Girard's reagent *T* into α-elemolic acid (**I**) and β-elemonic acid, $C_{30}H_{46}O_3$ (**II**), m.p. 224—225°, $[\alpha]_D$ +47·6° in $CHCl_3$ [Me ester (**III**), m.p. 104—105°, $[\alpha]_D$ +35° in $CHCl_3$]. Hydrogenation (PtO_2 in AcOH–EtOH) of (**II**) gives *dihydro-β-elemolic acid* (**IV**), m.p. 251—252°, $[\alpha]_D$ +15·1° in $CHCl_3$ (*acetate*, m.p. 266—267°, $[\alpha]_D$ +15·6° in $CHCl_3$), which gives a yellow colour with $C(NO_2)_4$. Esterification and acetylation of the compounds contained in the mother-liquors from (**IV**) leads to the isolation of Me acetyldihydro-α-elemolate (**V**), m.p. 139—140°, $[\alpha]_D$ −33·1° in $CHCl_3$. Under similar conditions (**III**) is hydrogenated and subsequently acetylated to *Me acetyldehydro-β-elemolate* (**VI**), m.p. 137—137·5°, $[\alpha]_D$ +14·2° in $CHCl_3$, which gives a marked yellow colour with $C(NO_2)_4$. In presence of Pd–C in AcOH at room temp. (**II**) is hydrogenated to *dihydro-β-elemonic acid* (**VII**), m.p. 245—246°, $[\alpha]_D$ +37·5° in $CHCl_3$ [*oxime*, m.p. 240° (decomp.)], which gives a yellow colour with $C(NO_2)_4$. With Raney Ni as catalyst and H_2 at 125°/70 atm. (**II**) gives (**VII**); acetylation and esterification of the acid residue leads to the isolation of (**VI**) and (**V**). Na and $Bu^{\beta}OH$ reduce (**II**) to *β-elemolic acid*, m.p. 234—235°, $[\alpha]_D$ +9·5° in $CHCl_3$ (*acetate*, m.p. 248—249°, $[\alpha]_D$ +25·6° in $CHCl_3$), hydrogenated (PtO_2 in AcOH) to (**IV**) which is oxidised (CrO_3 in AcOH) to (**VII**). *Acetyldihydro-β-elemolyl chloride*, m.p. 178—179°, from the acid and $SOCl_2$ in *n*-hexane, is reduced (Rosenmund) to *acetyldihydro-β-elemolaldehyde*, m.p. 167—168°, $[\alpha]_D$ +11·5° in $CHCl_3$ (*oxime*, m.p. 93—95°); the *semicarbazone* is reduced (Wolff–Kishner) to *dihydro-β-tritelemol*, m.p. 146—147°, $[\alpha]_D$ ±0° in $CHCl_3$ (*acetate*, m.p. 146°, $[\alpha]_D$ −0·41° in $CHCl_3$; *benzoate*, m.p. 155·5—156°), which gives a marked yellow colour with $C(NO_2)_4$; it is oxidised by CrO_3 in AcOH to *dihydro-β-tritelemone*, $C_{30}H_{50}O$, m.p. 66—67°, $[\alpha]_D$ +32·3° in $CHCl_3$. Reduction (Bouveault–Blanc) of Me β-elemonate affords *β-tritelemidiol*, $C_{30}H_{50}O_2$, m.p. 179—180°, $[\alpha]_D$ −7° in $CHCl_3$. (**II**) or (**III**) is reduced (Wolff–Kishner) to *deoxo-β-elemonic acid*, $C_{30}H_{48}O_2$, m.p. 236—237°, $[\alpha]_D$ +10·45° in $CHCl_3$. A great similarity in structure of (**I**) and (**II**) is thus established but the difference between them cannot consist solely of a difference in the position of the more readily hydrogenated double linking. M.p. are corr. (vac.).

H. W.

Triterpenes. LXVI. Introduction of double linkings and carbonyl groups into the rings C—E of β-amyrin. L. Ruzicka, O. Jeger, and J. Norymberski (*Helv. Chim. Acta*, 1942, **25**, 457—463).—β-Amyrin acetate is oxidised by SeO_2 in dioxan at 200° to β-amyradienedionol acetate, m.p. 239° (converted by N_2H_4,H_2O in EtOH at 200° into the pyridazine derivative, $C_{30}H_{44}ON_2$, m.p. 292—293°), also obtained by the similar oxidation of β-amyradienol 11-acetate (**I**) and δ-amyrin acetate. The latter substance is oxidised by 30% H_2O_2 in boiling AcOH to the corresponding *oxide* (**II**), m.p. 266—267°, which is saturated towards $C(NO_2)_4$, does not react with Ac_2O–C_5H_5N at 80°, and is indifferent towards H_2O–dioxan at 200—210°. (**II**) is transformed by boiling AcOH containing conc. HCl into (**I**). $Pb(OAc)_4$ in AcOH–C_6H_6 oxidises (**I**) to β-amyradienonol acetate, m.p. 258—259°, $[\alpha]_D$ +336° in $CHCl_3$.

H. W.

VI.—HETEROCYCLIC.

Action of benzoyl chloride on ethyl β-diethylaminocrotonate.—See A., 1942, II, 261.

Reaction between quinones and metallic enolates. XVI. Dibromo-*o*-xyloquinone and sodiomalonic ester. L. I. Smith and F. L. Austin (*J. Amer. Chem. Soc.*, 1942, **64**, 524—527; cf. A., 1941, II, 201).—The mode of interact on of CHNa $CO_2Et)_2$ (**I**) with dibromodimethylquinones depends on the relative positions of the Br rather than Br and Me (cf. A., 1937, II, 255; 1941, II, 144). *o*-Xyloquinone is best (61%) obtained from *o*-3-xylenol by successive treatment with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$, $Na_2S_2O_4$, and $Fe_2(SO_4)_3$–aq. H_2SO_4. With Br–$CHCl_3$ at room temp. it gives 4 : 5-*dibromo*-2 : 3-*dimethylbenzoquinone*, m.p. 152·5—153°, reduced by $SnCl_2$–aq. HCl–EtOH to the *quinol*, m.p. 163—164°, and by Zn dust and H_2SO_4 in Ac_2O–AcOH to the *quinol diacetate*, m.p. 203—206°, and with (**I**) in dioxan (not under other conditions) gives successively 5-*bromo*-6-*dicarbethoxymethyl*-, b.p. 115—120°/1 mm., isolated by way of the *quinol* (**II**), m.p. 126—127° [*diacetate* (**III**), m.p. 92—93°], and 5 : 6-*bisdicarbethoxymethyl*-2 : 3-*dimethylbenzoquinone*, m.p. 83—84°. With 75% H_2SO_4 at room temp., (**II**) in $CHCl_3$ gives 3-*bromo*-4-*hydroxy*-2-*carbethoxy*-5 : 6-*dimethylisocoumaranone* (**IV**), m.p. 109—110° [*acetate* (**V**), m.p. 117—118°], converted in boiling AcOH into 3-*bromo*-4-*hydroxy*-5 : 6-*dimethylisocoumaranone* (**VI**), m.p. 155—156° [*acetate*, m.p. 195—197°, also obtained from (**V**) by boiling AcOH], which is obtained also from (**II**) by boiling AcOH containing a trace of Zn and from (**III**) by boiling HCl–AcOH. Me_2SO_4–KOH–MeOH converts (**II**) into 3-*bromo*-2-*carboxy*-1 : 4-*dimethoxy*-5 : 6-*dimethylcoumarone*, m.p. 141—143°, converted by distillation in steam into 3-*bromo*-4-*methoxy*-5 : 6-*dimethylisocoumaranone* (**VII**), m.p. 113—113·5°, which is also (m.p. 108—110°) obtained from (**IV**) by Me_2SO_4–KOH–MeOH, followed by acidification and distillation of the resultant oil in steam. *o*-*Xyloquinol Me₂ ether* (prep. from the quinol by Me_2SO_4–KOH–MeOH), m.p. 78°, is unaffected by morpholine–CH_2O–EtOH at 100°, but with 40% CH_2O–HCl (exothermally and then at 100°) gives 2 : 5-*dimethoxy*-3 : 4-*dimethylbenzyl chloride* (52%), m.p. 67—68°, b.p. 162—163°/25 mm. [and some ? $(CH_2Cl)_2$ compound], which with KCN in EtOH containing a little H_2O at 100° gives the *cyanide* (55%), m.p. 95—96°, and thence by boiling 1 : 1 : 1 H_2SO_4–AcOH–H_2O 2 : 5-*dimethoxy*-3 : 4-*dimethylphenylacetic acid* (44%), m.p. 120—121°. With Br–$CHCl_3$ at room temp. this gives 6-*bromo*-2 : 5-*dimethoxy*-3 : 4-*dimethylphenylacetic acid*, m.p. 154—155°, also obtained from (**VI**) by Me_2SO_4–KOH–MeOH and from (**VII**) by KOH–MeOH. This proves the structure of the products named above.

R. S. C.

New reactions of 1-benzylidenecoumaran-2-ones. II. T. B. Panse, R. C. Shah, and T. S. Wheeler (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 83—85).—Bromination of 2-acetoxy-4-methoxyphenyl *p*-methoxystyryl ketone in CCl_4 leads to 2-*acetoxy*-4-*methoxyphenyl* αβ-*dibromo*-β-p-*anisylethyl ketone*, m.p. 143°, converted by boiling EtOH followed by boiling 10% KOH into 5-*methoxy*-1-p-*anisylidenecoumaran*-2-*one* (**I**), m.p. 134°. This is converted by Br in cold $CHCl_3$ into 1-*bromo*-5-*methoxy*-1-ω-*bromo*-p-*methoxybenzylcoumaran*-2-*one* (**II**), m.p. 161°. When boiled with the requisite alcohol (**II**) affords 1-*bromo*-5-*methoxy*-1-ω : p-*dimethoxybenzyl*-, m.p. 131°, and 1-*bromo*-5-*methyl*-1-p-*methoxy*-ω-*ethoxybenzyl*-, m.p. 139°, -*coumaran*-2-*one*. (**II**) and *cyclo*hexanone in boiling NaOH–EtOH yield 5-*methoxy*-1-p-*methoxy*-ω-2′-*keto*cyclo*hexylbenzylcoumaran*-2-*one*, m.p. 182° (decomp.). With CH_2PhBz and NaOEt in boiling EtOH (**I**) gives 5-*methoxy*-1-*benzoyl*-β-*phenyl*-α-p-*anisyl*-α-*ethylcoumaran*-2-*one*, m.p. 273°. $CH_2Ac{\cdot}CO_2Et$ and (**I**) afford *Et* 2-p-*anisyl*-3 : 4-[1′ : 2′-(5′-*methoxycoumarano*)]-Δ^4-cyclo*hexen*-6-*one*-1-*carboxylate*, m.p. 146°, hydrolysed and decarboxylated by 10% HCl at 160° to 5-p-*anisyl*-3 : 4-[2′ : 1′-(5′-*methoxycoumarano*)]-Δ^2-cyclo*hexen*-1-*one*, m.p. 154° [*semicarbazone*, m.p. 246° (decomp.); *oxime*, m.p. 142°; 2 : 4-*dinitrophenylhydrazone*, m.p. 912°; *Cu* salt, m.p. 215°].

H. W.

Chemistry and biochemistry of plant substances. VII. Formation of hydroxy-chalkones and -flavanones. L. Reichel, W. Burkart, and K. Müller (*Annalen*, 1942, **550**, 146—161; cf. A., 1939, III, 219).—2 : 4 : 1-$(OH)_2C_6H_3{\cdot}COMe$ or 2 : 4 : 6 : 1-$(OH)_3C_6H_2{\cdot}COMe$ and 3 : 4 : 1-$(OH)_2C_6H_3{\cdot}CHO$ in EtOH–aq. NaOH at 60° or in a borate–NaOH buffer (p_H 10·9) at 37° for 30 days (in N_2) give 3 : 4 : 2′ : 4′-tetrahydroxychalkone (butein), m.p. 198°, or 5 : 7 : 3′ : 4′-tetrahydroxyflavanone (eriodictyol), m.p. 267°, respectively. *o*-$OH{\cdot}C_6H_4{\cdot}COMe$ (**I**), 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ (**II**), and aq. NaOH at 37° (p_H 10·65) for 7 days afford 3′ : 4′-*dimethoxyflavanone*, m.p. 125°. (**I**) and piperonal in aq. NaOH (p_H 10·74 at 37° for 15 days) give 2′-*hydroxy*-3 : 4-*methylenedioxychalkone*, m.p. 138°, and 3′ : 4′-*methylenedioxyflavanone*, m.p. 129°. 2 : 4 : 6 : 1-$(OMe)_2C_6H_2(OH){\cdot}COMe$ and PhCHO or (**II**) in aq. NaOH (p_H 11·8) at 37° yield 5 : 7-dimethoxyflavanone, m.p. 145°, or 2-hydroxy-3 : 4 : 4′ : 6′-tetramethoxychalkone, m.p. 151°, respectively.

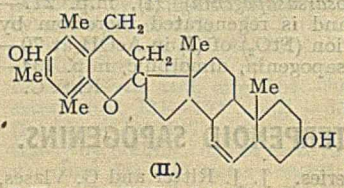
A. T. P.

Condensation of α-substituted acetoacetates with phenols. V. Coumarins from alkylresorcinols, and ethylpyrogallol and ethyl α-β′β′β′-trichloro-α′-hydroxyethylacetoacetate. N. M. Shah and D. R. Kulkarni (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 86—88).—The alkyl group has no retarding influence on the course of the reaction. Gradual addition of $POCl_3$ to a cooled mixture of 4 : 1 : 3-$C_6H_3Et(OH)_2$ and $CCl_3{\cdot}CH(OH){\cdot}CHAc{\cdot}CO_2Et$ gives 7-*hydroxy*-4-*methyl*-6-*ethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin* (**I**), m.p. 211—212° (decomp.), also obtained in poor yield when 80% H_2SO_4 is used as condensing agent. (**I**) gives a blue fluorescence in alkali and a violet fluorescence in conc. H_2SO_4. The *Ac*, m.p. 167°, *Bz*, m.p. 185—186°, Me_2, m.p. 167° and Me_1, m.p. 231° (decomp.), derivatives are described. Similarly, 4 : 1 : 3-$C_6H_3Pr(OH)_2$ affords 7-*hydroxy*-4-*methyl*-6-*propyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 189° (*acetate*, m.p. 132—134°), in poor yield. 7 : 8-*Dihydroxy*-4-*methyl*-6-*ethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 223° (decomp.), from 4 : 1 : 2 : 3-$C_6H_2Et(OH)_3$, and its *acetate*, m.p. 177—178°, are described.

H. W.

Coumarins etc.—See B., 1942, II, 220.

Syntheses of chroman derivatives with tocopherol-like structure. P. Karrer and F. Kehrer (*Helv. Chim. Acta*, 1942, **25**, 29—34).—*cyclo*Hexanone and C_2H_2 in presence of $NaNH_2$ yield 1-*acetylenyl*cyclo*hexan*-1-*ol*, b.p. 80—83°/20 mm., hydrogenated (Pt in EtOH) to 1-*vinyl*cyclo*hexan*-1-*ol*, b.p. 75—77°/10 mm. This is converted by PBr_3 in light petroleum at −15° to 18° into cyclo*hexylidene*-*ethyl bromide*, b.p. 90—93°/20 mm., which with trimethylquinol (**I**) in boiling C_6H_6 containing anhyd. $ZnCl_2$ gives 6-*hydroxy*-2 : 2-*pentamethylene*-5 : 7 : 8-*trimethylchroman*, a viscous, strongly reducing oil (*allophanate*, m.p. 184—186°). Δ^5-3*t* : 17*t*-Dihydroxy-17-vinylandrostene is converted into its *acetate*, m.p. 160—161°, which with PBr_3 in $CHCl_3$ at −15° to room temp. gives 17-β-*bromoethylidene*-Δ^5-3*t*-*acetoxyandrostene*, which does not solidify at −8°; it condenses with (**I**) to spiro-2-[6-*hydroxy*-5 : 7 : 8-*trimethylchroman*]-17′-[3′-*hydroxy*-Δ^{5}′-*androstene*] (**II**), m.p. 226—228°, which reduces alcoholic $AgNO_3$ and can be determined colorimetrically with $FeCl_3$ and 2-dipyridyl. Me pentadecyl ketone, C_2H_2, and $C_5H_{11}{\cdot}OK$ give γ-*hydroxy*-γ-*methyl*-Δ^{α}-*octadecinine*, b.p.



(II.)

129—134°/0·23 mm., m.p. 25°, reduced (H_2–Pt–EtOH) to *γ-hydroxy-γ-methyl-Δ^α^-octadecene*, b.p. 155—159°/0·7 mm., m.p. ~27°. This with PBr_3 in light petroleum at −15° to room temp. yields α-bromo-γ-methyl-Δ^β^-octadecene, condensed with (I) to 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethyl*-2-*pentadecylchroman*, m.p. 68°, which has great reducing power. H. W.

1 : 3-Dioxans.—See B., 1942, II, 255.

5 : 7-Dimethyltocol formate.—See B., 1942, III, 157.

Oreoselone. F. von Bruchhausen and H. Hoffmann (*Ber.*, 1942, **75**, [*B*], 146—147; cf. A., 1931, 1298).—The m.p. of dihydro-oreoselonic acid (I) depends greatly on the rate of heating. (I) can be sublimed at 165°/0·01 mm., or 165°/0·15 mm., without appreciable conversion into the lactone. H. W.

2-Thienylalkylamines. F. F. Blicke and J. H. Burckhalter (*J. Amer. Chem. Soc.*, 1942, **64**, 477—480).—The pressor activity of the 2-thienylalkylamines named below is semiqualitatively equal to that of the corresponding phenylalkylamines. 2-Thienylcarbinol (obtained from MgRI and CH_2O) with PBr_3 gives the bromide, which with $(CH_2)_6N_4$ in boiling $CHCl_3$ yields exothermally an adduct (72%), m.p. 160—161° (decomp.), converted by HCl–abs. EtOH into 2-thienylmethylamine, $NH_2{\cdot}CH_2{\cdot}C_4H_3S$, b.p. 73—75°/11 mm. (*hydrochloride*, m.p. 193—194°). Thiophen, conc. HCl, and 40% CH_2O give 40% of 2-thienylmethyl chloride, b.p. 80—81°/18 mm. [with 38% of di-2-thienylmethane, m.p. 45—47°, b.p. 125—126°/9 mm. (lit. 267°)], converted by NH_2Me–EtOH–H_2O at 60° into 2-*thienylmethylmethylamine* (52%), b.p. 75—80°/14 mm. (*hydrochloride*, m.p. 189—190°). 2-Thienyl Me or Et ketone with $HCO{\cdot}NH_2$ at 180—190° gives form-α-2-thienyl-ethylamide (not isolated) or -n-*propylamide* (I), b.p. 174—178°/12 mm., converted by 30% NaOH at 130° and 100°, respectively, into α-2-*thienyl-ethylamine* (51%), b.p. 83—84°/16 mm. (*hydrochloride*, m.p. 140—142°), and -n-*propylamine*, b.p. 89—91°/13 mm. [*hydrochloride* (II), m.p. 173—175°], respectively. Similar interaction with HCO·NHMe gives α-2-*thienyl-ethyl-* (45%), b.p. 75—76°/10 mm. (*hydrochloride*, m.p. 133—134°), and -n-*propylmethylamine* (27%), b.p. 90—92°/12 mm. (*hydrochloride*, m.p. 121—122°). With HCl–Et_2O, (I) gives a *hydrochloride*, m.p. 234—235° (decomp.), hydrolysed in H_2O, and a little (II). Thiophen with Br–CCl_4 at 0° and later solid NaOH at 100° gives 55% of 2-bromo- (III), b.p. 153—154°, and much 2 : 5-dibromo-thiophen, b.p. 95—98°/16 mm. The Mg derivative (IV) from (III) with $(CH_2)_2O$ in Et_2O at 0° and later C_6H_6 at room temp. gives β-2-thienylethyl alcohol (53%), b.p. 107—109°/14 mm. (*phenylurethane*, m.p. 57—58°), and with propylene oxide in Et_2O gives β-2-thienyl*iso*propyl alcohol (60%), b.p. 106—109°/13 mm. (*phenylurethane*, m.p. 62—63°). With PBr_3 in C_6H_6 or $CHCl_3$, respectively, these give the bromides (*A*), b.p. 98—99°/13 mm. and 98—99°/11 mm., converted by NH_3–EtOH at room temp. into β-2-thienyl-ethylamine (56%), b.p. 88—90°/13 mm. (also obtained from the cyanide by Na–BuOH), and -iso*propylamine*, b.p. 94—96°/15 mm. (*hydrochloride*, m.p. 139—141°), respectively. With NH_2Me–MeOH at 100°, (*A*) give β-2-*thienylethyl-*, b.p. 90—91°/13 mm. (*hydrochloride*, m.p. 154—155°), and β-2-*thienyl*iso*propyl-methylamine*, b.p. 85—88°/14 mm. (*hydrochloride*, m.p. 133—135°). *p*-$C_6H_4Me{\cdot}SO_2{\cdot}[CH_2]_3{\cdot}Cl$ and (IV) in Et_2O at room temp. and later the b.p. give 2-γ-chloro- (61%), b.p. 84—86°/4 mm., converted by NaI in boiling $COMe_2$ into 2-γ-iodo-*n*-propylthiophen, an oil, and thence (as above) γ-2-*thienyl*-n-*propyl-amine* (53%), b.p. 110—112°/19 mm. (*hydrochloride*, m.p. 194—195°), and -*methylamine* (64%), b.p. 112—114°/19 mm. (*hydrochloride*, m.p. 127—128°). Mg β-2-thienylethyl chloride and $(CH_2)_2O$ in Et_2O at room temp. give αβ-*di*-2-*thienylethane* (69%), m.p. 64—65°, b.p. 152—156°/10 mm., and a small fraction, b.p. 100—112°/18 mm. R. S. C.

2 : 3 : 6-Triaminopyridine.—See B., 1942, II, 255.

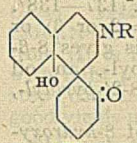
Furoyl- and nicotinoyl-amides.—See B., 1942, II, 272.

Reactions of *N*-dichlorocarbamates. J. Bougault and P. Chabrier (*Compt. rend.*, 1941, **213**, 487—488).—Indole-2-carboxylic acid (I) with $NCl_2{\cdot}OAc$ in AcOH yields 2 : 3 : (5?)-*trichloro*-2 : 3-*epoxy*-2 : 3-*dihydroindole*, m.p. 188°, reduced (Zn dust–AcOH or KI–AcOH) to (5?)-*chloro*-2 : 3-*epoxy*-2 : 3-*dihydroindole*, m.p. 192°. The Me ester of (I) similarly gives *Me* 2 : 3 : (5?)-*trichloro*-3-*hydroxy*-2 : 3-*dihydroindole*-2-*carboxylate*, m.p. 184°, reduced (KI–AcOH) to a *Me dichloro*-3-*hydroxy*-2 : 3-*dihydroindole*-2-*carboxylate*, m.p. 152°. Glycine with $NCl_2{\cdot}CO_2Et$ in H_2O affords $CH_2(NH{\cdot}CO_2Et)_2$, m.p. 130°. W. C. J. R.

Carbazoles.—See B., 1942, III, 172.

Isolation of organic bases.—See A., 1942, II, 248.

Syntheses and reactions of αγ-keto-bases with secondary nitrogen. C. Mannich and O. Hieronimus (*Ber.*, 1942, **75**, [*B*], 49—64).—$CH_2Ph{\cdot}NH_2,HCl$, 40% CH_2O, and *cyclo*hexanone (1 : 1 : 3 mol.) react vigorously when heated together, giving a small proportion of *tert.* base (see later) and, mainly, 2-benzylaminomethyl*cyclo*hexanone (I) [*hydrobromide* (II), m.p. 129°; *oxime*, m.p. 85°; *Bz*, m.p. 134°, and *CO_2Et*-, b.p. 222°/11 mm., derivative] in ~65% yield. (I) is reduced by Na–Hg in well-cooled, dil. HCl to 2-benzylaminomethyl-*cyclo*hexanol, two forms (*hydrobromide*, m.p. 160—161°, hydrochloride, m.p. 160°, and *Bz* derivative, m.p. 159—161°, of the α-form; *hydrochloride*, m.p. 144°, and *Bz* derivative, m.p. 148°, of the β-form). (II) is converted by successive treatments with KCNO and 10% HCl into 2-*keto*-3-*benzyloctahydroquinazoline*, m.p. 191°, disproportionated by boiling 20% HCl into the corresponding H_{10}-, m.p. 175°, and H_6-compound, m.p. 153° (decomp.) [*hydrochloride*, m.p. 212° (decomp.)]. If in the above reaction the proportion of CH_2O is doubled, the main product is the *tert.* base (III) (R = CH_2Ph), m.p. 102° (hydrobromide, m.p. 186°; hydrochloride, m.p. 176°; *oxime*, m.p. 186°), reduced (Na–Hg in dil. AcOH) to the $(OH)_2$-base, m.p. 162° (*diacetate*, m.p. 154°). (II), paraformaldehyde, and $COMe_2$ give 10-*hydroxy*-4-*acetyl*-2-*benzyldecahydroisoquinoline* (IV), m.p. 96° (hydrochloride, m.p. 195°; *oxime*, m.p. 131°), reduced (H_2, PtO_2, EtOH) to 10-*hydroxy*-2-*benzyl*-4-*hydroxyethyldecahydroisoquinoline*, m.p. 115—117° (*hydrobromide*, m.p. 240—241°). Conc. H_2SO_4 and (IV) give 4-acetyl-2-benzyloctahydro*iso*quinoline, base *A* (*perchlorate*, m.p. 146°), and non-cryst. base *B* (*perchlorate*, m.p. 201°). *A* or *B* is rapidly hydrogenated to 4-acetyl-2-benzyldecahydro*iso*quinoline (*H oxalate*, m.p. 156°). (II), COPhMe, and CH_2O in boiling dioxan afford 10-*hydroxy*-4-*benzoyl*-2-*benzyldecahydroisoquinoline*, m.p. 164°, the hydrochloride, m.p. 214°, of which is also obtained from (I) and $COPh{\cdot}[CH_2]_2{\cdot}Cl$ in boiling EtOH and is converted by conc. H_2SO_4 into 4-*benzoyl*-2-*benzyloctahydroisoquinoline*, m.p. 97°. $CH_2Ph{\cdot}NH_2,HCl$, paraformaldehyde, and $COMe_2$ yield α-benzylaminobutan-γ-one, b.p. 155°/6 mm. [*hydrochloride* (V), m.p. 162°; hydrobromide, m.p. 124—126°; *oxime hydrochloride*, m.p. 151°]. (V) and KCNO afford α-*benzyl*-α-γ-*ketobutylcarbamide*, m.p. 120—121°. (V) is reduced by Na–Hg in dil. HCl to α-benzylaminobutan-γ-ol (VI), b.p. 122—123°/2 mm. (*hydrobromide*, m.p. 57°; N-p-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}$ derivative, m.p. 236°, and p-*nitrobenzoate hydrochloride*, m.p. 191°). 60% HBr at 160° converts (VI) into γ-bromo-α-benzylaminobutane (*hydrobromide*, m.p. 212°), transformed by $CHNa(CO_2Et)_2$ into α-benzylamino-Δ^β^-butene, b.p. 95°/12 mm. (*hydrochloride*, m.p. 134—135°), hydrogenated to $NHBu^{\alpha}{\cdot}CH_2Ph$. (V) and paraformaldehyde in boiling $COMe_2$ slowly give two diastereoisomeric forms of 4-hydroxy-5-acetyl-1-benzyl-4-methylpiperidine, which could not be obtained pure or converted into cryst. derivatives but are reduced to a mixture of the corresponding 5-OH·$[CH_2]_2$ bases from which a homogeneous *perchlorate*, m.p. 201°, is isolated in 20% yield; this gives a base, b.p. 223°/12 mm. (*hydrobromide*, m.p. 175°; *diacetate*, m.p. 129—131°). $CH_2Ph{\cdot}NH_2,HCl$, 40% CH_2O, and $CHPh{:}CH{\cdot}COMe$ at 100° give a mixture of the very unstable α-benzylamino-δ-benzylidenebutan-γ-one, m.p. 50—51° [*hydrochloride*, m.p. 182—184° (slight decomp.)], reduced to α-*benzylamine*-ε-*phenylpentan*-γ-*ol*, m.p. 87—89° (hydrochloride, m.p. 99—100°), and 4-*hydroxy*-5-*cinnamoyl*-1-*benzyl*-4-*styrylpiperidine*, m.p. 148°. 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene, $NH_2Ph{\cdot}NH_2,HCl$, and 40% CH_2O at 100° afford 1-*keto*-2-*benzylaminomethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. ~160°, converted by KCNO into the *pyrimidine* derivative, $C_{19}H_{18}ON_2$, m.p. 208°, and by $NaNO_2$ into the *NO*-compound, m.p. 94°, which is reduced by Sn and boiling conc. HCl to 2-*benzyltetrahydrobenzindazole hydrochloride*, m.p. 173°. $CH_2Ph{\cdot}NH_2,HCl$, COPhMe, and CH_2O give a mixture of benzylaminopropiophenone (*hydrochloride*, m.p. 163°, converted by KCNO into α-*benzyl*-α-*benzoylethylcarbamide*, m.p. 131°) and 4-*hydroxy*-5-*benzoyl*-4-*phenyl*-1-*benzylpiperidine*, m.p. 116°. 2-*Benzylaminomethyl*cyclo*pentanone hydrochloride*, m.p. 157° (slight decomp.) (whence α-*benzyl*-α-2-*keto*-cyclo*pentylmethylcarbamide*, m.p. 126—127°), is derived from $CH_2Ph{\cdot}NH_2,HCl$, *cyclo*pentanone, and CH_2O. $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}NH_2$, HCl, 40% CH_2O, and *cyclo*hexanone give 2-keto*cyclo*hexylmethyl-3 : 4-methylenedioxybenzylamine [*hydrobromide* (VII), m.p. 155—156°, converted by KCNO into 2-*keto*-3-3′ : 4′-*methylenedioxybenzyloctahydroquinazoline*, m.p. 168°), N-*Bz* compound, m.p. 118°], and the tert. *base* [(cf. (III), R = $CH_2O_2{:}C_6H_3{\cdot}CH_2$], m.p. 167° (hydrobromide, m.p. 250°). 10-*Hydroxy*-4-*acetyl*-2-3′ : 4′-*methylenedioxybenzyldecahydroisoquinoline*, m.p. 127°, is derived from (VII), paraformaldehyde, and $COMe_2$. Methods similar to those described above lead to the following: α-3 : 4-*methylenedioxybenzylaminobutan*-γ-*one hydrochloride*, m.p. 176°, 1-*keto*-2-3′ : 4′-*methylenedioxybenzylaminomethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 186°, and 2-*keto*-3-3′ : 4′-*methylenedioxybenzylhexahydronaphthapyrimidine*, m.p. 228°; ω-3 : 4-*methylenedioxybenzylaminopropiophenone hydrochloride*, m.p. 187°, and the corresponding *carbamide*, m.p. 144°; α-3 : 4-*methylenedioxybenzylamino*-δ-*benzylidenebutan*-γ-*one hydrochloride*, m.p. ~186° (slight decomp.), hydrogenated to α-3 : 4-methylenedioxybenzylamino-ε-phenylpentan-γ-one (*hydrochloride*, m.p. 205°); 2-3′ : 4′-*methylenedioxybenzylaminomethyl*-cyclo*pentanone hydrochloride*, m.p. 161—162° (slight decomp.), and the corresponding *carbamide*, m.p. 160°; α-*benzylamino*-α-2-*keto*-cyclo*hexyl*-β-*phenylethane hydrochloride*, m.p. 154°. H. W.



(III.)

5- and 1-Aminobenzo(*f*)quinoline and derivatives. E. R. Barnum and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1942, **64**, 540—542).—2 : 3-$NH_2{\cdot}C_{10}H_6{\cdot}CO_2R$ (R = H or Me), H_3AsO_4, and glycerol at, successively, 120°, 135°, and 145—150° give 5 : 6-*benzoquinoline*-8-*carboxylic acid* (I) (32%), m.p. 204—205°, the *Me* ester (II), m.p. 86°, of which gives the *amide*, m.p. 205—206°. With hot $SOCl_2$ and then

MeOH, (I) gives the *Me* ester (? 7 : 8-)*dichloride*, m.p. 134—135°, converted by NH_3–MeOH at 40—50° into *Me 7-chloro-5 : 6-benzoquinoline-8-carboxylate*, m.p. 187—189°, and by N_2H_4,H_2O in boiling aq. MeOH into 5 : 6-*benzoquinoline-8-carboxylhydrazide*, m.p. 203—204° [also obtained from (II)], which yields the *azide*, m.p. 65—67°, and thence (Ac_2O–AcOH) 8-*acetamido-*, m.p. 126—127°, and (H_2SO_4 at 0°) 8-*amino-5 : 6-benzoquinoline* (III), m.p. 137—138°. With boiling $Br\cdot[CH_2]_n\cdot NEt_2,HBr$–NaOAc–EtOH ($n$ = 2 or 3) or 2-bromopyridine–NaOAc–BuOH–Cu-bronze (trace), this gives 8-*β-diethylaminoethyl-*, m.p. 85°, 8-*γ*-diethylamino-*n*-propyl-, an oil (hygroscopic *dihydrochloride*, m.p. 235—240°), and 8-2′-*pyridyl-*, m.p. 142—144°, *-amino-5 : 6-benzoquinoline*. 3 : 1-$OH\cdot C_{10}H_6\cdot NH_2,H_2SO_4$ gives, as above, a poor yield of 8-*hydroxy-5 : 6-benzoquinoline*, m.p. 104—106°. 5 : 6-Benzocinchoninic acid gives, as above, the *amide*, m.p. 253—255°, *Me*, 104—105°, and *Et* ester, m.p. 56°, and *hydrazide*, m.p. 224—225°, and thence ($NaNO_2$–dil. AcOH; azide in dioxan at 100°) 4-*amino-5 : 6-benzoquinoline* (IV), m.p. 149—150° (*Ac*, m.p. 192°, and *p-NMe₂·C₆H₄·CH:* derivative, m.p. 136—138°), and N-5 : 6-*benzocinchoninoyl-N′-diethylaminobenzylidenehydrazide*, m.p. 216—218°. (III), but not (IV), can be diazotised and coupled with R-acid or β-$C_{10}H_7\cdot OH$; (IV) resists alkylation. R. S. C.

***N*-Dichlorocarbamates.**—See A., 1942, II, 217.

Benzacridones.—See B., 1942, II, 223.

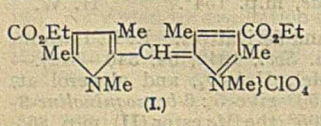
Derivatives of 1′-aza-3 : 4-benzpyrene. M. Weizmann and F. Bograchov (*J.C.S.*, 1942, 377).—3-Aminopyrene and $CH_2Ac\cdot CO_2Et$ in EtOH give *Et β-3-pyrenylaminocrotonate*, m.p. 129°, cyclised in liquid paraffin at 220° to 4′-*hydroxy-2′-methyl-1′-aza-3 : 4-benzpyrene*, m.p. 350°, which with PCl_3 affords the 4′-*Cl*-compound, m.p. 207°. F. R. S.

Synthesis of some four-membered heterocyclic compounds. T. N. Ghosh and D. Das-Gupta (*J. Indian Chem. Soc.*, 1942, **19**, 41—46).—NH_2Ph and dicarbethoxythioacetocarbamic acid in EtOH give N-*phenyl-NN′-dicarbethoxyvinylenecarbamide* (I), m.p. 74—75° (*Br₄*-derivative, m.p. 120—121°), which with N_2H_4 affords N-*phenyl-NN′-(carbethoxycarbohydrazidovinylene)carbamide*, m.p. 171°, remelts 252—253° (decomp.), forming *phenylthiosemicarbazide*, m.p. 188—189° (decomp.), and *CHPh:* derivatives, m.p. 209—210° (decomp.). With NaOEt, (I) is converted into 5-*phenyl-1 : 5-diazo-*(0,2,2)dicyclo-Δ^3-*hexene-2 : 6-dione*, m.p. 245—246°, and when heated at 165—170° is isomerised to N-*phenyl-NN′-dicarbethoxyethenylcarbamide*, m.p. 168—170° (*dianilide*, m.p. 236—238°), which with EtOH–KOH gives the *-carboxy*-derivative, m.p. > 300°. N-p-*Tolyl-NN′-dicarbethoxyvinylenecarbamide*, m.p. 61—62°, is similarly prepared. F. R. S.

Identification of carbonyl compounds by conversion into hydantoins. H. R. Henze and R. J. Speer (*J. Amer. Chem. Soc.*, 1942, **64**, 522—523).—Aldehydes and ketones are identified by conversion into hydantoins by $KCN–(NH_4)_2CO_3$ in 50% EtOH at 58—60°. A few fail to react. The following are described. 4-n-, m.p. 139·5°, and 4-iso-*Butyl-*, m.p. 212·5—216°, 4-n-*amyl-*, m.p. 144·5°, 4-2′-*furyl-*, m.p. 147°, 4-n-*hexyl-*, m.p. 148°, 4-*βζ-dimethyl-*Δ^{ζ}-n-*heptenyl-*, m.p. 172—172·5°, 4-*α-ethyl-*n-*propyl-*, m.p. 175·7—176·1°, 4-p-*tolyl-*, m.p. 182·5°, 4-o-*phenetyl-*, m.p. 185—186°, 4-o-*anisyl-*, m.p. 186—187°, 4-o-*chloro-*, m.p. 176°, 4-3′ : 4′-*dimethoxy-*, m.p. 182·5—183°, 4-3′ : 4′-*methylenedioxy-*, m.p. 207°, 4-m-, m.p. 212°, and 4-p-*hydroxy-*, m.p. 263° (decomp.), 4-p-*dimethylamino-*, m.p. 234—235°, and 4-3′-*methoxy-4′-hydroxy-phenyl-*, m.p. 276° (decomp.), 4-*methyl-*4-n-, m.p. 123—124·5°, and -iso-*propyl-*, m.p. 177°, -n-, m.p. 107·5—108·5°, and -iso-*butyl-*, m.p. 148°, -n-*amyl-*, m.p. 102·5—103·5°, -n-*hexyl-*, m.p. 107·5—108°, *-hydantoin*; 4-p-*tolyl-*, m.p. 203·5°, and 4-p-*anisyl-*, m.p. 210°, -4-*methylhydantoin*; 4-*ethyl-*4-n-*propyl-*, m.p. 144—145°, and -iso*amyl-hydantoin*, m.p. 153°; 4-*methyl-5-β-carboxyethyl-*, m.p. 156·5—157·5°, 4-n-*propyl-*4-n-*butyl-*, m.p. 175°, and 4-*methyl-*4-Δ^{α}-iso*butenyl-hydantoin*, m.p. 194°; 4 : 4-*tetramethylene-*, m.p. 204—205°, -*diisopropyl-*, m.p. 207°, -1′-, m.p. 215·5—216°, -2′-, m.p. 268·5—269°, and -3′-*methylpentamethylene-*, m.p. 279—280°, *-hydantoin*; *hydantoins* from carvone, m.p. 193·5—194°, α-hydrindone, m.p. 240°, thujone, m.p. 254·5—255°, and fluorenone, m.p. 324—325° (decomp.). Many other *hydantoins* are listed in American Documentation Document No. 1603. M.p. are corr. R. S. C.

Barbituric acids.—See B., 1942, III, 172.

Pyrrole series. VI. Steric influences on the aromaticity of dipyrrylmethenes. Synthesis and properties of a di-*N*-methyldipyrrylmethene. K. J. Brunnings and A. H. Corwin (*J. Amer. Chem. Soc.*, 1942, **64**, 593—600; cf. A., 1941, II, 338).—A *NN′*-dimethyldipyrrylmethene is synthesised. It is much less stable than the unmethylated homologue, *e.g.*, to Br; this is ascribed to steric interference of the *N*-Me opposing the planar alignment of rings necessary for resonance. 4 : 4′-Dicarbethoxy-1 : 3 : 5 : 1′ : 3′ : 5′-hexamethyldi-2-pyrrylmethene perchlorate (I), decomp. 160—170° (explosive), is obtained from (*a*) 4 : 4′-dicarbethoxy-1 : 3 : 5 : 1′ : 3′ : 5′-hexamethyldi-2-pyrrylmethane (II) by, best (50% yield), 1 mol. of Br in CCl_4, (*b*) 3-carbethoxy-1 : 2 : 4-trimethylpyrrole (III) (best, 2 mols.; 73% yield), 2-formyl-4-carbethoxy-1 : 3 : 5-trimethylpyrrole (IV), and gaseous HCl in CCl_4, and (*c*) (III) and 98% HCO_2H in conc. aq. HCl–Et_2O, best (54% yield) at 50°. The structure of (I) is proved by hydrogenation (Pd–C) in MeOH to (II) and conversion by 2·5% KOH–MeOH at room temp. into 4 : 4′-*dicarbethoxy-1 : 3 : 5 : 1′ : 3′ : 5′-hexamethyldi-2-pyrrylcarbinyl Me ether*, $CHR_2\cdot OMe$ (R = substituted pyrryl group) (82%), m.p. 113—114°, whence (I) (80—85%) is regenerated by HCl–Et_2O or –hexane and later $HClO_4$. The bromide solution intermediate in method (*a*) above with 2·5% aq. NaOH gives 4 : 4′-*dicarbethoxy-1 : 3 : 5 : 1′ : 3′ : 5′-hexamethyldi-2-pyrrylcarbinol* (V) (42%), m.p. 142—143°. The chloride and bromide corresponding with (I) are red oils, sol. in dil. acid to solutions which gradually decompose. Treatment of the chloride at p_H 1·5—2 with NaOH to give p_H 3·5—4 decolorises the red solution and 88% of (V) is gradually deposited; the same reaction is caused at p_H 1·5 by adding NaF. All these reactions indicate ready transformation of the methene salts into the covalent forms, *e.g.*, CHR_2Br, and show the great effect of the anion on the ease of the change. The absorption spectrum of (I) (max. at 4700 A., log E ~1·1) differs only as expected from that of the 3 : 5 : 3′ : 5′-Me_4 homologue (max. at 5100 A., log E ~1·9; narrower band) (both $1·3 \times 10^{-5}$M. in $CHCl_3$). Use of 2 mols. of Br in method (*a*) above gives only (IV) and 2-*bromo-4-carbethoxy-1 : 3 : 5-trimethylpyrrole* (VI), m.p. 57—58°, which are also obtained from the methene bromide and Br in CCl_4 or H_2O. (IV) is also obtained from the mother-liquor from (I) in method (*a*). This decomp. probably proceeds by cleavage of the bromide to the 5-$CHBr_2$ compound + (III), hydrolysis of the former product, and bromination of the latter (realised in a separate experiment: product, m.p. 54—55°, decomp. 145—150°). R. S. C.



(I.)

Pyrimidines. CLXXVI. Action of keten on 5 : 5-dibromohydroxyhydrouracil. M. Fytelson and T. B. Johnson (*J. Amer. Chem. Soc.*, 1942, **64**, 306—308).—Keten does not react with hydrouracil, uracils, or 5 : 5-dibromo-4-hydroxyhydrouracil (I) at room temp. In boiling $COMe_2$, (I) and keten give 5-bromouracil (II) or alone at 90—95° gives (II) and some ? impure $CH_2Br\cdot CO_2H$. In presence of SiO_2 gel at 90°, (I) and keten give 5-*bromo-3-acetyluracil* (III), m.p. 175·5—177° [in HCl gives (II)], (II), and $COMe\cdot CH_2Br$ [formed by decomp. of (III) to (II) and HOBr, followed by addition of HOBr to diketen]; after partial interaction at 60°, (III), $COMe\cdot CH_2Br$, and $CH_2Br\cdot CO_2H$ are obtained. With Ac_2O at room temp., (I) gives the O-*acetate*, m.p. 146—148°. In presence of SiO_2 gel at 100° or 80°, 5 : 5-dibromo-4-hydroxy-4-methylhydrouracil gives 5-bromo-4-methyluracil, m.p. 226—230° (decomp.). R. S. C.

Chemotherapy. IV. Sulphanilamidopyrimidines. R. O. Roblin, jun., P. S. Winnek, and J. P. English (*J. Amer. Chem. Soc.*, 1942, **64**, 567—570; cf. A., 1941, II, 288).—Pharmacological activity (A = active, S = slightly active, I = inactive), solubility in H_2O, and max. blood level are recorded for 2-*sulphanilamido-4-methoxy-* (*A*), m.p. 241—242°, -4-*ethoxy-* (*S*), m.p. 255—256°, and -4 : 6-dimethyl- (I) (*A*), m.p. 198—199° (lit. 178—180°) [Ac derivative, m.p. 249—250° (lit. 246·8—247·4°)], 5-*chloro-2-sulphanilamido-* (*S*), m.p. 246—247°, 4-*sulphanilamido-2-methyl-* (*S*), m.p. 207—208°, 5-*sulphanilamido-* (II) (*A*), m.p. 260—261°, 2-*chloro-5-sulphanilamido-* (*S*), m.p. 206—207°, 2-*amino-5-sulphanilamido-* (*S*), m.p. 293—298°, 5-*sulphanilamido-2-methoxy-* (*A*), m.p. 232—234°, and 2 : 5-*disulphanilamido-* (*I*), m.p. 231—232°, *-pyrimidine* and other derivatives (A., 1940, II, 359). 4-Sulphanilamidopyrimidine, inactive *in vitro*, is active *in vivo*, possibly by hydrolysis, which is facile. Only (I) is as active as sulphadiazine (the 2-$SO_2\cdot NH_2$-derivative). Activity and max. blood level do not always parallel solubility in H_2O. The Na salt, anhyd. and +$2H_2O$ (prep. by NaOH–EtOH on the 5-nitro-2-amino-compound at 70—75°), of 5-nitro-2-hydroxypyrimidine with $POCl_3$, finally at the b.p., gives 2-*chloro-5-nitropyrimidine* (II), m.p. 110—111°. With boiling NaOMe–MeOH, (II) gives 5-nitro- and thence (H_2–Pd; MeOH; 50 lb.) 5-amino-2-methoxypyrimidine. With Fe in 1·5% aq. AcOH, (II) gives 2-*chloro-5-amino-*, m.p. 198—199° (decomp.), reduced by H_2–Pd–$CaCO_3$ and BaO in MeOH at 25°/60 lb. to 5-*amino-pyrimidine* (III), m.p. 170—171°. 4-Chloro-2-amino- with boiling NaOEt–EtOH gives 2-*amino-4-ethoxypyrimidine*, m.p. 154—156°. 5-*Chloro-2-amino-*, m.p. 234—236° (sealed tube), and 5-nitro-2-acetamido-pyridine, m.p. 187—188° (decomp.) (lit. 172°), are also recorded. (II) is not obtained from $NO_2\cdot CH(CHO)_2$ and $NH{:}CH\cdot NH_2$ and is not hydrogenated directly to (III). M.p. are corr. R. S. C.

Dicyclic compounds and their analogy with naphthalene. VI. Indazole series. K. Fries, K. Fabel, and H. Eckhardt (*Annalen*, 1941, **550**, 31—49; cf. A., 1937, II, 124).—The general behaviour of indazole and many of its derivatives shows that it belongs to the naphthoid dicyclic series. The slight divergencies from the substitution regularities characteristic of this series are ascribed to the influence of NH of the hetero-ring. The solid diazonium sulphate from 5-amino-1 : 3-diphenylindazole is converted by warming with a mixture of AcOH and conc. H_2SO_4 into 5-*hydroxy-1 : 3-diphenylindazole*, m.p. 196° (*acetate*, m.p. 82°), converted by Br in AcOH into 4-*bromo-5-hydroxy-1 : 3-diphenylindazole* (I), m.p. 146°; this by further treatment with Br in AcOH gives a keto-bromide, reduced by $SnCl_2$ in AcOH to (I) and hydrolysed by H_2O to 1 : 3-*diphenyl-4 : 5-indazolequinone*, m.p. ~208° after becoming black (*quinoxaline*

derivative, $C_{25}H_{16}N_4$, m.p. 165° and, after re-solidification, m.p. 185°). HNO_3 (*d* 1·52) and conc. H_2SO_4 at 10° convert 6-nitro- into 5 : 6-*dinitro-indazole*, m.p. 224° (after decomp.), reduced by $SnCl_2$ and conc. HCl to 5 : 6-*diaminoindazole* (**II**), m.p. 275° after decomp. at ~265°, which with HNO_2 affords 1 : 2 : 3-*triazoloindazole*, decomp. >300° after blackening at ~280°. (**II**) is converted by 2N-HCl at 170—180° into 5 : 6-*dihydroxyindazole* (**III**), m.p. 235° (*diacetate*, m.p. 143°), transformed by Br in AcOH into 4 : 7-dibromo-5 : 6-dihydroxyindazole (**IV**), m.p. 184° (decomp.) [*hydrobromide*, m.p. ~200° (decomp.); Ac_3 derivative, m.p. 162°]. Attempts to oxidise (**III**) or (**IV**) to an *o*-quinone were unsuccessful. Chlorination of (**II**) or (**III**) in sunlight gives 7 : 7-*dichloro*-4 : 5 : 6-*triketo*-4 : 5 : 6 : 7-*tetrahydroindazole dihydrate*, m.p. 170° (decomp.), also obtained by chlorination of (**III**) and converted by NaOAc followed by acid into 5 : 6-*dihydroxy*-4 : 7-*indazolequinone* (**V**), m.p. 330° to a dark melt after decomp. at 290°, and reduced by $SnCl_2$ and conc. HCl to 4 : 5 : 6 : 7-*tetrahydroxyindazole* (**VI**) [*hydrochloride* (**VII**), m.p. ~225° (decomp.); *tetraacetate*, m.p. 181°]. (**VII**) when dissolved in H_2O passes into (**V**) and is oxidised by HNO_3 (*d* 1·52) in AcOH to 4 : 5 : 6 : 7-tetraketo-4 : 5 : 6 : 7-tetrahydroindazole. Hot, fuming, HNO_3 oxidises (**VI**) to pyrazole-4 : 5-dicarboxylic acid, which could not be converted into an internal anhydride. When heated alone it gives pyrazole-4-carboxylic acid, m.p. 275°, whilst with Ac_2O it affords the N-*Ac* derivative, m.p. 169°, which is transformed ($SOCl_2$) through the dichloride into *pyrazole*-4 : 5-*dicarboxanilide*, m.p. 244°. Indazole is scarcely hydrogenated in presence of Pd–$BaSO_4$ in AcOH or of Ni-Co–Cu in EtOH at 20°/100 atm. or at 130° but in presence of much Pt it gives 4 : 5 : 6 : 7-tetrahydroindazole. 1-Methylindazole is slowly reduced to the non-cryst. tetrahydride (*picrate*, m.p. 148°) but the 2-Me compound is much more rapidly and similarly reduced. The behaviour of an equimol. mixture of C_6H_6 and $C_{10}H_8$ shows that $C_{10}H_8$ is much the more rapidly hydrogenated (Pt–AcOH). 5-Aminoindazole with PhN_2Cl gives 5-*amino*-4-*benzeneazoindazole*, m.p. 164°, reduced by $SnCl_2$ to 4 : 5-*didminoindazole*, m.p. 181°, which affords a *quinoxaline* derivative, $C_{21}H_{14}N_2$, m.p. 257°. 5-*Amino*-4-*benzeneazo*-1-, m.p. 202°, and -2-, a viscous mass [*hydrochloride*, m.p. 237° (decomp.)], -*methylindazole* are obtained similarly whereas the corresponding *diazoamino*-compounds have m.p. 125° and 176° (decomp.), respectively. 6-, m.p. 196°, and 5-, m.p. 155° after sotening at 145°, -*benzylideneaminoindazole* are readily converted into *dihydroacridone* derivatives, $C_{20}H_{15}N_5$, both of m.p. >360°.
H. W.

Cinnolines. I. New examples. J. C. E. Simpson and O. Stephenson (*J.C.S.*, 1942, 353—358).—*Phenyl-(5-bromo-2-aminophenyl)-methylcarbinol*, m.p. 100° (N-*Ac*, m.p. 181—182°, and N-*Bz* derivatives, m.p. 196°), prepared from $COPh{\cdot}C_6H_3Br{\cdot}NH_2$-5 : 2 and MgMeI, is dehydrated (H_2SO_4) to *α-phenyl-α-(5-bromo-2-benzamidophenyl)ethylene*, m.p. 113·5—114° [*sulphates* (+$2H_2O$), m.p. 107° and 154°], which with HNO_2 affords 6-*bromo*-4-*phenylcinnoline*, m.p. 143·5—144·5°. Reduction (Fe–AcOH) of the anthroxan (**I**) from *o*-$NO_2{\cdot}C_6H_4{\cdot}OH$ and PhOH gives 2 : 5-$NH_2{\cdot}C_6H_3Cl{\cdot}CO{\cdot}C_6H_4{\cdot}OH$-4′ (**II**) ($Bz_2$ derivative, m.p. 143°), deaminated to 3-$C_6H_4Cl{\cdot}CO{\cdot}C_6H_4{\cdot}OH$-4′, m.p. 169·5—171° (lit. m.p. 161°), and converted (HNO_2–CuCl) into 2 : 5-*dichloro*-4′-*hydroxybenzophenone*, m.p. 171—172·5° (under different conditions, a *substance*, m.p. 224—226°, is obtained), which is oxidised ($KMnO_4$) to 2 : 5-$C_6H_3Cl_2{\cdot}CO_2H$ (m-*nitroanilide*, m.p. 151—152°). Na–MeOH and (**I**) give the *chloro-methoxyanthroxan*, m.p. 143—145°, reduced (Fe–AcOH) to 5-*chloro*-2-*amino*-4′-*methoxybenzophenone*, m.p. 100—101°. MgMeI and (**II**) yield, after decomp., *α-(5-chloro-2-aminophenyl)-α-(4′-hydroxyphenyl)ethylene*, m.p. 159° (Bz_2 derivative, m.p. 130·5—132°), which with HCl–$NaNO_2$ gives 6-*chloro*-4-(4′-*hydroxyphenyl*)-*cinnoline*, m.p. 257—259° (decomp.) (*Bz* derivative, m.p. 156°). The anthroxan from *p*-cresol and *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ is reduced to 2 : 5-$NH_2{\cdot}C_6H_3Cl{\cdot}CO{\cdot}C_6H_3Me{\cdot}OH$-5′ : 2′ (**III**) ($Bz_2$ derivative, m.p. 156—157°), which is converted into the 2 : 5-Cl_2-compound, m.p. 149—150°. This anthroxan with Na–MeOH yields the *methoxyanthroxan*, m.p. 96—98°, which is reduced (Fe–AcOH) to 5-*chloro*-2-*amino*-2′-*methoxy*-5′-*methylbenzophenone*, m.p. 100—101° (N-*Ac* derivative, m.p. 136—137°). MgMeI and (**III**) give a resin, converted through the *hydrochloride*, m.p. 222—223° (decomp.), into *α-(5-chloro-2-aminophenyl)-α-(2′-hydroxy-5′-methylphenyl)ethylene*, m.p. 108° [Bz_2 derivative, m.p. 119°; Bz_3 (?) derivative, m.p. 235°], which with HCl–$NaNO_2$ affords 6-*chloro*-4-(2′-*hydroxy*-5′-*methylphenyl*)*cinnoline*, m.p. 260—261° (decomp.) (*Bz* derivative, m.p. 140°).
F. R. S.

Pyridylquinolines.—See B., 1942, II, 255.

Alkaline hydrolysis of fluorenone*spiro*hydantoin. W. H. McCown with H. R. Henze (*J. Amer. Chem. Soc.*, 1942, **64**, 689—690).—Fluorenone*spiro*hydantoin (**I**), m.p. 324—325° (decomp.) (lit. 308—310°), is obtained in 78% yield from fluorenone, KCN, and $(NH_4)_2CO_3$ at 110°. In ~50% aq. $Ba(OH)_2$ at 110—120° it gives 9-*amino*-9-*carbamylfluorene* (**I**) (80%), m.p. 254—256° (decomp.; sealed tube), and some fluorenone. In HCl–EtOH at 120°, (**I**) gives 9-chlorofluorene, m.p. 91—92°, and with boiling NH_2Ph gives NH_3 and 9-*aminofluorene*-9-*carboxylanilide*, m.p. 292—297° (decomp.). 9-Hydroxyfluorene-9-carboxylic acid (prep. from phenanthraquinone by 20% NaOH at 100°; 42% yield), new m.p. 167—168°, with PCl_5 at 0° gives 9-chlorofluorene-9-carboxyl chloride (30%), m.p. 111°, converted by NH_3–Et_2O into the amide, which with $NaNH_2$–NH_3 gives an amorphous product, m.p. 60—70° (decomp.). M.p. are corr.
R. S. C.

Technics in the synthesis of porphyrindin. H. A. Lillevik, R. L. Hossfeld, H. V. Lindstrom, R. T. Arnold, and R. A. Gortner (*J. Org. Chem.*, 1942, **7**, 164—168).—The prep. of porphyrindin from $CMe_2{:}N{\cdot}OH$ (**I**) is described. The yield of $OH{\cdot}NH{\cdot}CMe_2{\cdot}CN$ (**II**) from (**I**) is improved by cold room technique and by extractions with light petroleum instead of crystallisation. The most difficult step [conversion of (**II**) into $OH{\cdot}NH{\cdot}CMe_2{\cdot}C(OEt){:}NH,2HCl$] gives good yields under anhyd. conditions.
H. W.

Chlorophyll. CXI. Purpurins. 10-Hydroxymesophæophorbide *a* and its direct transformation into mesopurpurin 7. M. Strell (*Annalen*, 1941, **550**, 50—66).—Oxidation of mesophæophorbide with $KMnO_4$ in C_5H_5N (cf. Fischer and Kahr, A., 1937, II, 470), removal of the "unstable chlorin," and treatment of the residue with CH_2N_2 leads to 10-*hydroxymethylmesophæophorbide* (**I**), m.p. 255°, $[\alpha]^{20}$ −348° in $COMe_2$, isomerised by HI in AcOH at 100° to 10-hydroxyphæoporphyrin a_5 (**II**), m.p. 270°, identified by spectrum, mixed m.p., and transformation into phæoporphyrin a_7. Oxidation of cryst. phæophorbide (cf. *loc. cit.*) and further treatment of the product described above gives a flocky hydroxyphorbide which softens at 265° but does not melt completely. The mixed m.p. with a material obtained by hydrolysis of 10-acetoxymethylphæophorbide (**III**) shows the same phenomenon. The spectrum is identical with that of (**III**). Addition of $CHN_2{\cdot}CO_2Et$ causes slight displacement towards blue. Isomerisation by HI leads to 10-hydroxyphæoporphyrin a_5. Oxidation of mesomethylphæophorbide by $KMnO_4$ gives (**I**) and "*unstable mesochlorin* 7" *Me*$_2$ *ester*, non-cryst., m.p. 225°. Although fully esterified this substance can be removed from Et_2O by dil. NaOH but not by dil. NH_3, thus giving further evidence of the lactonic nature of the compound. It is esterified by CH_2N_2 quantitatively to mesopurpurin 7. Catalytic hydrogenation of (**I**) in $COMe_2$ gives unchanged material and its leuco-compound whilst the product obtained in AcOH is re-oxidised to (**II**). The tendency towards passage into the porphyrin system exceeds that of reduction of OH. (**I**) is very stable towards protracted boiling in C_5H_5N. Treatment of (**I**) with MeOH–Na_2CO_3 quickly leads through a red-violet to a red solution which ultimately becomes green and then contains almost exclusively mesorhodochlorin, identified spectroscopically and by isomerisation (HI) to rhodoporphyrin. The red stage is due to the presence of *mesopropurpurin* 7 (**IV**). Pptn. of the Et_2O solution with MeOH gives mesopurpurin 7 (**V**), also obtained in poor yield when the Et_2O solution is exposed to air and almost quantitatively by oxidation with $FeCl_3$–MeOH. If methanolysis is effected in presence of O_2, (**IV**) is not formed and (**V**) is obtained directly. (**IV**) is also produced during the catalytic hydrogenation of (**V**) in dioxan. Tentatively (**IV**) is regarded as a γ-glycollic acid. The propurpurin reaction is shown by 10-acetoxy- and 10-hydroxymethyl-phœophorbide but scarcely by methylphæophorbide and appears to be the best criterion of allomerised phæophorbide. Methanolysis by CH_2N_2–MeOH gives similar results. When shaken with 10% KOH–MeOH for 3 hr. (**I**) yields "unstable mesochlorin 7" whereas after very short action with much more dil. alkali the presence of (**IV**) in small amount is established. The *Cu*, m.p. 245°, and *Zn*, m.p. 220°, complex salts of purpurin 7 Me_3 ester are described.
H. W.

Structure of imidoporphyrin in relation to phthalocyanines. F. Endermann (*Z. physikal. Chem.*, 1942, **A**, **190**, 129—173).—The structure of these compounds is discussed and formulæ are proposed.
C. R. H.

***N*-β-Morpholinoethyl furoate and tetrahydrofuroate.**—See B., 1942, II, 261.

Isosteric and structurally similar compounds. XV. Thiazole-5-carboxylamide. H. Erlenmeyer, E. Schmid, and A. Kleiber (*Helv. Chim. Acta*, 1942, **25**, 375—376).—*Thiazole*-5-*carboxylamide*, m.p. 196°, is obtained from conc. NH_3 and the acid chloride or from Et thiazole-5-carboxylate and NH_3–EtOH at room temp. It does not form mixed crystals with nicotinamide.
H. W.

Structural chemical investigations. V. *cyclo*Hexenothiazole. H. Erlenmeyer and M. Simon (*Helv. Chim. Acta*, 1942, **25**, 362—364).—2-Bromo*cyclo*hexanone slowly condenses with $HCS{\cdot}NH_2$ in Et_2O to cyclo*hexenothiazole*, b.p. 126—127°/22 mm. (*picrate*, m.p. 183—184°; hygroscopic hydrochloride and hydrobromide; oxalate, m.p. 112°), which resembles quinoline in its power of forming sparingly sol. metallic complexes. Similarly $MeCS{\cdot}NH_2$ yields 2-*methyl*cyclo*hexenothiazole*, b.p. 146—148°/22 mm. (*picrate*, m.p. 123—124°), which readily forms metallic complexes and condenses with *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ in presence of anhyd. $ZnCl_2$ to 2-p-*dimethylaminostyrylcyclohexenothiazole*, m.p. >190° (decomp.). 2-*Thiol*cyclo*hexenothiazole*, m.p. 176°, gives sparingly sol. Cd^{II}, Cu^{II}, and Ag^{I} salts.
H. W.

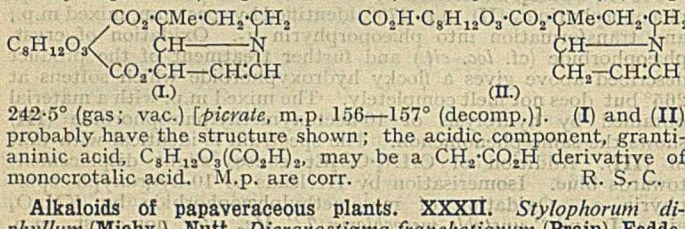
Benzthiazoles.—See B., 1942, II, 223.

Action of chlorine on arylthiocarbimides and reactions of aryl *iso*cyanodichlorides. III. Addition of chlorine to α-naphthylthiocarb-

imide and the structure of the compounds obtained. G. M. Dyson and T. Harrington (*J.C.S.*, 1942, 374—375; cf. A., 1942, II, 169).—α-$C_{10}H_7$·NCS (I) and Cl_2–$CHCl_3$ give an unstable additive compound, converted in air into *bis-(α-naphthylthiocarbimide) oxide*, m.p. 80°. Further addition of Cl_2 produces 2 : 4′-*dichloronaphtha*(1′ : 2′ : 4 : 5)-*thiazole*, m.p. 113°, also obtained by chlorination of 4-*chloro-α-naphthylthiocarbimide*, m.p. 87°. Prolonged chlorination of (I) yields a *compound*, $C_{11}H_2NCl_5S$. A. T. P.

VII.—ALKALOIDS.

Alkaloid of *Crotolaria Grantiana*. I. Grantianine. R. Adams, M. Carmack, and E. F. Rogers (*J. Amer. Chem. Soc.*, 1942, **64**, 571—573).—The seeds of this plant yield to 95% EtOH at room temp. *grantianine* (I), $C_{18}H_{23}O_7N$, m.p. 204—205° (decomp.), $[\alpha]_D^{27}$ +50·6° in $CHCl_3$ [*methiodide*, m.p. 242—243° (vac.); *picrate*, m.p. 225—228° (decomp. from ~210—215°); hydrochloride, m.p. 221—222° (decomp.; vac.)], hydrolysed by hot KOH–MeOH to retronecine (44%) and hydrogenated (PtO_2–EtOH–AcOH) to a H_4-derivative (II), m.p.

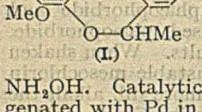


242·5° (gas; vac.) [*picrate*, m.p. 156—157° (decomp.)]. (I) and (II) probably have the structure shown; the acidic component, grantianinic acid, $C_8H_{12}O_3(CO_2H)_2$, may be a CH_2·CO_2H derivative of monocrotalic acid. M.p. are corr. R. S. C.

Alkaloids of papaveraceous plants. XXXII. *Stylophorum diphyllum* (Michx.), Nutt., *Dicranostigma franchetianum* (Prain), Fedde, and *Glaucium serpieri*, Heldr. XXXIII. *Corydalis cheilantheifolia*, Hemsl. R. H. F. Manske (*Canad. J. Res.*, 1942, **20, B**, 53—56, 57—60).—XXXII. *S diphyllum* and *D. franchetianum* contain protopine (I) (~0·03%), chelidonine (0·05, 0·02%, respectively), and *l*- + *dl*-stylopine (II), and their separate generic rank is chemically unjustified. *G. serpieri* contains glaucine, *iso*corydine (0·004%), (I), aurotensine (0·002%), and an amorphous base (? cheilanthifoline or an isomeride) which with CH_2N_2 gives partly racemised sinactine.

XXXIII. *C. cheilantheifolia* contains *l*-canadine, berberine, (II), *l*-corypalmine, *l*-cheilanthifoline (0·0002%), (I) (0·14% from the aerial parts; 0·74% from the roots), *allo*cryptopine (0·06%), and a neutral nitrogenous *compound*, m.p. >360°. The structure of ophiocarpine is confirmed by oxidation by $KMnO_4$ to 1-keto-6 : 7-methylenedioxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. R. S. C.

New degradation product from morphine. L. Small (*J. Org. Chem.*, 1942, **7**, 158—163).—3-*Methoxy-5-methyl-5-phenanthro*[4 : 5-bcd]-*pyran* (I), m.p. 118·5°, $[\alpha]_D^{25}$ ±0·0° in EtOH (*picrate*, m.p. 107—108°), is isolated from the residues from the purification of methylmorphenol prepared by the degradation of morphine according to Mosettig *et al.* (A., 1935, 366).



(I) is not sol. in aq. or alcoholic alkali, gives no colour with $FeCl_3$, and does not react with NH_2OH. Catalytic hydrogenation is negative and it is not dehydrogenated with Pd in boiling $C_{10}H_8$. It is not oxidised by $KMnO_4$ in boiling $COMe_2$ and yields a non-cryst. product with CrO_3. With Br in glacial AcOH (I) gives a Br_1-derivative, m.p. 104—105°. With boiling 48% HBr (I) gives a transient, intense purple colour but appears otherwise unchanged. With boiling Ac_2O–HI (*d* 1·7) (I) gives a *compound*, $C_{16}H_{12}O_3$, m.p. 84—84·5°. Distillation of (I) with Zn dust gives pyrene. In addition to (I) the isolation of a *liquid* (C 80·23, H 10·42%) and a cryst. N-free *solid*, m.p. 270—272° (slight decomp.; becomes yellow at 265°), $[\alpha]_D^{20}$ ±0·0° in dioxan, is described. Thebenol (II) could not be converted into (I) since (II) is unchanged by NH_3–$(NH_4)_2SO_3$ at 140° and converted into a black tar by NaOAc, NH_4Cl, and AcOH at 270°. The pyran ring of (II) could not be opened. Attempts to resolve (II) were unsuccessful. H. W.

Thalictrum foliolosum, **DC. Isolation and characterisation of a new alkaloid thalictrine.** S. K. Vashistha and S. Siddiqui (*J. Indian Chem. Soc.*, 1941, **18**, 641—645).—The rhizome contains berberine and *thalictrine*, $C_{20}H_{27}O_4N$, m.p. 208°, a quaternary hydroxide containing $(OMe)_2$, NMe, phenolic OH, and two double bonds [*chloride*, softens 161°, frothes 163—165°; *chloroplatinate*, darkens 215°, swells 231°, decomp. 233—234°; *iodide*, m.p. 265° (decomp.); *picrate*, m.p. 207—208°; *tetrabromide acetate*, blackens 200°, decomp. 248—250°]. F. R. G.

Argentine plants. IV. Alkaloids from *Erythrina* species. R. A. Gentile and R. Labriola (*J. Org. Chem.*, 1942, **7**, 136—139).—The isolation of hypaphorine (I), erysodine (II), m.p. 204—205°, $[\alpha]_D$ +250° in EtOH, erysopine (III), m.p. 241°, $[\alpha]_D$ +265° in EtOH–glycerol, and erysovine (IV), m.p. 175—176°, from *E. crista galli* is described. *E. falcata* yields (I), (II), (III), erysocine, m.p. 160—161°, $[\alpha]_D$ +236·4° in EtOH, and (IV) whilst (I), (II), (III), and (IV) are obtained from *E. dominguezzii*. H. W.

Koto-tsuzurafuji alkaloids.—See B., 1942, III, 172.

VIII.—ORGANO-METALLIC COMPOUNDS.

Preparation and properties of dimethylphosphine. N. Davidson and H. C. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 718).—Prep. of $PHMe_2$ from PH_4I, ZnO, and MeI at 100° (Hofmann, 1871) is modernised. The v.p. is given by log $p = -1370/T + 7·539$, whence are calc. b.p. 21·1°, ΔH (vapour) 6·27 kg.-cal., and Trouton's const. 21·2. R. S. C.

IX.—PROTEINS.

Recent advances in protein chemistry. S. Moore (*Wallerstein Lab. Comm.*, 1942, **5**, 27—34).—The discussion relates to mol. wt., analysis of hydrolysates (solubility product and isotope dilution methods), and *in vivo* equilibria. I. A. P.

Denaturation of edestan by acid: T. B. Osborne's edestan. K. Bailey (*Biochem. J.*, 1942, **36**, 140—154).—The kinetics of HCl-denaturation of edestin (I) to edestan (II) are recorded at various p_H. The initial reaction is rapid at p_H below 4, but becomes slower, partly because of a rise in p_H. (II) is a monodispserse fragmentation product of (I). Edestin chloride freshly pptd. from aq. NaCl has the same *X*-ray diffraction pattern as (I), but after removal of NaCl it changes to one typical of denatured proteins. The no. of SH groups ∝ the amount of (II), in which it represents ~¼ of the cystine-S. Total N and tryptophan are lower in (II) than in (I), the fall in total N being mainly due to hydration of the mol. There is a small loss of sol. N as NH_3 and tryptophan. R. L. E.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Resins. VI. Determination of *d*-pimaric acid in mixtures of native resin acids. W. Sandermann (*Ber.*, 1942, **75**, [*B*], 174—178).—The mixture of acids is isomerised by boiling with AcOH for 2 hr., after which only *d*-pimaric (I) and abietic acid (II) are present. The final val. $([\alpha]_D)_e$ of the sp. rotation is determined. % (I) = $\{([\alpha]_D)_e + 8\} \times 100/138$. The method is not valid for colophony. (II) has $[\alpha]_D$ −103·5° in Et_2O, −81·0° in AcOH, −103° in dioxan, −12·5° in C_6H_6, and −70° to −79° in *cyclo*hexane whereas (I) has +70° in Et_2O, +75° in $CHCl_3$, +75° in C_6H_6 and +57° in AcOH. H. W.

Purification of penicillin. E. P. Abraham and E. Chain (*Nature*, 1942, **149**, 328).—Penicillin (I) has been obtained in the form of a highly purified Ba salt by extraction from amyl acetate into H_2O, chromatography (Al_2O_3), treatment of the active fraction with Al-Hg, and finally repeated chromatography. Its activity is 450—500 Oxford (I) units per mg. A. A. E.

Nitrogenous character of penicillin. E. P. Abraham, W. Baker, E. Chain, H. W. Florey, E. R. Holiday, and R. Robinson (*Nature*, 1942, **149**, 356).—Analysis of the Ba salt of penicillin (I) (cf. preceding abstract) corresponds with $C_{24}H_{32}O_{10}N_2Ba$. The salt is lævorotatory (H_2O); the absorption spectrum does not suggest the presence of aromatic rings. A. A. E.

XI.—ANALYSIS.

Rapid chromic-nesslerisation determination of nitrogen in biological materials.—See A., 1942, III, 503.

Micro-analytical determination of sulphur in organic compounds by catalytic hydrogenation. K. Bürger (*Angew. Chem.*, 1941, **54**, 392—394).—A modified method is described. A. T. P.

Determination of glycerol, ethylene glycol, and propylene αβ-glycol in presence of one another. G. Hoepe and W. D. Treadwell (*Helv. Chim. Acta*, 1942, **25**, 353—361).—The mixture, dissolved in H_2O, is oxidised by KIO_4 at room temp. and HCO_2H is determined in one portion of the solution by titration with 0·1N-NaOH using Me-red as indicator [$OH·CH(CH_2·OH)_2$ (I) + $2KIO_4$ = $2CH_2O$ + HCO_2H + $2KIO_3$ + H_2O]. In a second portion the total aldehyde is determined by addition of Na_2SO_3 and titration of NaOH formed by 0·1N-HCl in presence of thymolphthalein [$(CH_2·OH)_2$ (II) + KIO_4 = $2CH_2O$ + KIO_3 + H_2O; $OH·CHMe·CH_2·OH$ (III) + KIO_4 = CH_2O + MeCHO + KIO_3 + H_2O]. CH_2O is determined by successive addition of 0·1N-KCN, HNO_3, and 0·1N-$AgNO_3$ and titration of excess of the latter by NH_4CNS; residual KIO_3 and KIO_4 are determined in a blank experiment. The amount of MeCHO formed is a measure of (III) whilst (II) is determined from CH_2O after deduction of the amounts due to (I) and (III). H. W.

Identification of carbonyl compounds.—See A., 1942, II, 271.

Action of vanadous sulphate on organic compounds.—See A., 1942, I, 279.

Colorimetric determination of cyclic ketones in solvent mixtures. G. Zeidler and H. Kreis (*Angew. Chem.*, 1941, **54**, 360—361).—The Lange colorimeter is used after interaction of the product with *o*-NO_2·C_6H_4·CHO–aq. PhOH. A. T. P.

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AUGUST, 1942.

JUDACTAN

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ACTUAL

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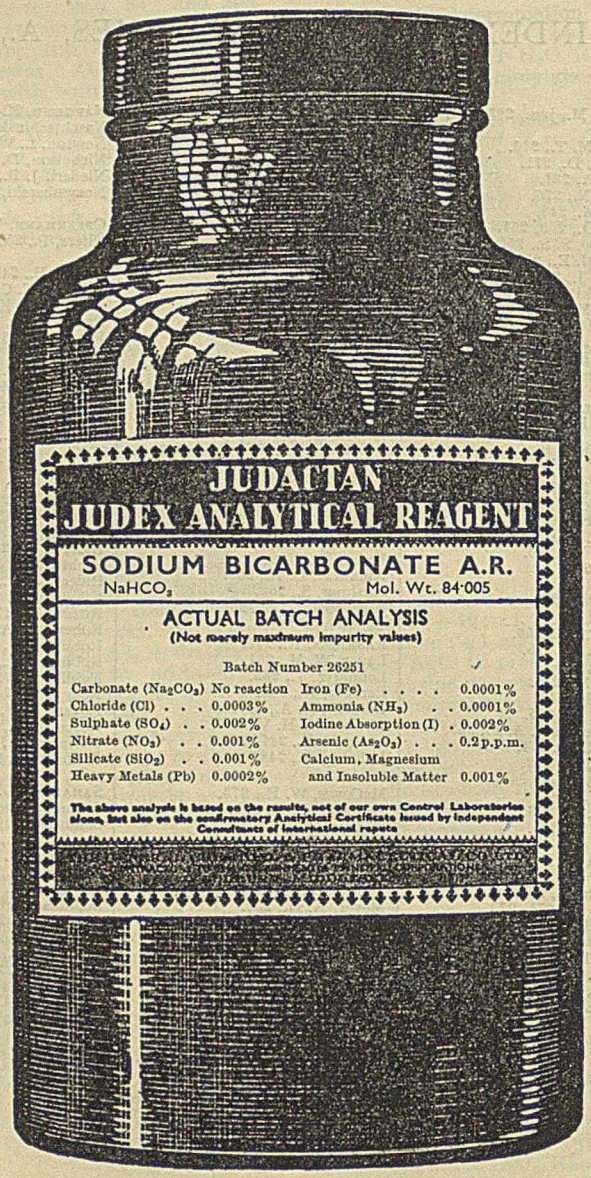
ANALYSIS



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