NOTES.

177. *Organophosphorus Compounds of Sulphur and Selenium. Part XIV.* The Reaction of Organic Diselenides with Trialkyl Phosphites.*

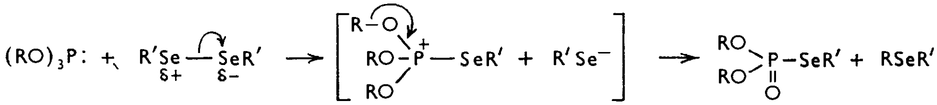
By J. MICHALSKI and J. WIECZORKOWSKI.

IN their reaction with trialkyl phosphites [1] and sodium dialkyl phosphites,[2] various types of organic disulphides have been found by the authors to display cationoid reactivity of the sulphur. Similar observations concerning the reaction of dialkyl disulphides with triethyl phosphite were made by Jacobson *et al.*[3] and by Walling and Rabinowitz.[4] These findings are now extended to diselenides.

Reactions of diphenyl diselenide and bisdiethoxyphosphinyl diselenide with triethyl phosphite in absence of a solvent were as shown in the equations. The diselenides are less active than disulphides and only with bisdiethoxyphosphinyl diselenide was an exothermic effect observed:

$$\mathrm{(EtO)_3P + PhSe{\cdot}SePh \longrightarrow (EtO)_2P(O){\cdot}SePh + EtSePh}$$
$$\mathrm{(EtO)_3P + (EtO)_2P(O){\cdot}Se{\cdot}Se{\cdot}P(O)(OEt)_2 \longrightarrow (EtO)_2P(Se){\cdot}O{\cdot}P(O)(OEt)_2 + (EtO)_2P(O){\cdot}SeEt}$$

We postulate for the above reactions a polar mechanism resembling that accepted for Arbuzov's reaction: [5]



The phosphoroselenolates and the selenide were identified by comparison with known products. Tetraethyl selenopyrophosphate was identical in physical and infrared properties with the condensation product of diethyl phosphorochloridate with sodium *OO*-diethyl phosphoroselenoate [6] for which the selenono-structure seems to be the most likely [7] and is

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* Part XIII, preceding paper.

[1] Michalski and Wieczorkowski, *Bull. Acad. polon. Sci.*, Classe III, 1957, **5**, 917.

[2] Michalski, Wieczorkowski, Wasiak, and Pliszka, *Roczniki Chem.*, 1959, **33**, 247.

[3] Jacobson, Harvey, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 6064.

[4] Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243.

[5] Kukhtin and Pudovik, *Uspekhi Khim.*, 1959, **28**, 96.

[6] Michalski and Wieczorkowski, *Roczniki Chem.*, 1954, **28**, 233.

[7] Coe, Perry, and Brown, *J.*, 1957, 3604.

supported by its nuclear magnetic resonance spectrum.[8] Both compounds exhibit the band 925 cm.$^{-1}$ due to the P·O·P group.[9]

Experimental.—Materials. Bisdiethoxyphosphinyl diselenide was obtained by action of sulphuryl chloride (0·3 mole) on potassium *OO*-diethyl phosphoroselenoate (0·6 mole) in benzene as a red-brown oil, n_D^{20} 1·5260 (yield of undistilled product 74%). Diphenyl diselenide was obtained by oxidation of selenophenol with sulphuryl chloride in benzene or ether.

Reaction of bisdiethoxyphosphinyl diselenide with triethyl phosphite. Triethyl phosphite (24·9 g., 0·15 mole) was added dropwise with stirring to bisdiethoxyphosphinyl diselenide (64·8 g., 0·15 mole). The temperature of the exothermic reaction was kept at 50—55° and decolorisation of the mixture was then observed. The mixture was distilled *in vacuo*, to give (i) *OOSe*-triethyl phosphoroselenolate (33·5 g., 91%), b. p. 39—41°/0·02 mm., 130—131°/24 mm., n_D^{25} 1·4768 (Found: P, 12·8. Calc. for $C_6H_{15}O_3PSe$: P, 12·6%) (lit.,[10] b. p. 134°/18 mm., n_D^{25} 1·4762), and tetraethyl selenopyrophosphate (42·2 g., 80%), b. p. 87—88°/0·01 mm., n_D^{20} 1·4650 (Found: P, 17·6. Calc. for $C_8H_{20}O_6P_2Se$: P, 17·5%) (Michalski and Wieczorkowski[6] reported b. p. 107°/0·05 mm., n_D^{20} 1·4638). The infrared spectrum was identical with that of selenopyrophosphate (b. p. 96—97°/0·1 mm.) prepared by condensation of diethyl phosphorochloridate with sodium *OO*-diethyl phosphoroselenoate. Both compounds exhibit the P·O·P band at 925 cm.$^{-1}$.

Reaction of diphenyl diselenide with triethyl phosphite. Diphenyl diselenide (39 g., 0·125 mole) and triethyl phosphite (30 g., 0·18 mole) were heated with stirring to the b. p. of the phosphite (155°). Then the temperature was increased gradually to 170—180° and was kept at 190—210° for 15 min., until the red-brown colour had disappeared, after which the yellowish mixture was distilled *in vacuo*. After the excess of phosphite had distilled off, two fractions were collected: (i) ethyl phenyl selenide, b. p. 85—86°/9 mm. (22 g.), which was freed from traces of phosphorus ester by 2 hours' boiling with azeotropic hydrochloric acid, extracted with benzene, drying ($MgSO_4$), and redistillation (20 g., 86%); the product had b. p. 97·5°/15 mm., n_D^{25} 1·5845 (Found: C, 52·2; H, 5·5. Calc. for $C_8H_{10}Se$: C, 51·9; H, 5·6%) (lit.,[11] b. p. 102—104°/20 mm., n_D^{25} 1·5825); and (ii) *OO*-diethyl *Se*-phenyl phosphoroselenolate, a yellowish liquid (27·4 g., 75%), b. p. 100°/0·2 mm., n_D^{25} 1·5235 (Found: C, 41·0; H, 5·4; P, 10·5. Calc. for $C_{10}H_{15}O_3PSe$: C, 41·0; H, 5·2; P, 10·6%).

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[8] Jones, Katritzky, and Michalski, *Proc. Chem. Soc.*, 1959, 321.

[9] McIvor, Grant, and Hubley, *Canad. J. Chem.*, 1956, **34**, 1611.

[10] Michalski and Wieczorkowski, *Roczniki Chem.*, 1959, **33**, 105.

[11] Behaghel and Hofmann, *Ber.*, 1939, **72**, 710; Nardelli and Chierici, *Ann. Chim.* (*Italy*), 1952, **42**, 111; *Chem. Abs.*, 1953, **47**, 7454.

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178. *5-Oxo-2-phenyl-1,3-dioxan.*

By A. A. MAREI and R. A. RAPHAEL.

FOR many aspects of carbohydrate synthesis a derivative of 1,3-dihydroxyacetone is needed where the hydroxyl functions are protected by a grouping which is resistant to nucleophilic reagents but subsequently easily removable. The benzylidene derivative, 5-oxo-2-phenyl-1,3-dioxan, fulfils these criteria and a preparative route to this compound has been developed from the readily available tri(hydroxymethyl)nitromethane. Condensation of the latter with benzaldehyde[1] and catalytic reduction of the product furnished 5-amino-5-hydroxymethyl-2-phenyl-1,3-dioxan. Fission of this vicinal amino-alcohol with sodium periodate yielded the stable crystalline hydrate 5,5-dihydroxy-2-phenyl-1,3-

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[1] Scattergood and Maclean, *J. Amer. Chem. Soc.*, 1949, **71**, 4153.

dioxan, which was dehydrated by distillation to give the crystalline 5-oxo-2-phenyl-1,3-dioxan. Alternative routes to this derivative proved unsuccessful; these included oxidation of 1,3-benzylideneglycerol, acidification of the sodium salt [2] of 5-nitro-2-phenyl-1,3-dioxan, and zinc dust reduction of 5-bromo-5-nitro-2-phenyl-1,3-dioxan.[3]

Experimental.—5-*Amino*-5-*hydroxymethyl*-2-*phenyl*-1,3-*dioxan.* A solution of the corresponding nitro-acetal (5 g.) in ethanol (100 ml.) was shaken with a little Raney nickel and the filtrate stirred with fresh Raney nickel (1 g.) under 100 atm. of hydrogen at 80° for 4 hr. Filtration, evaporation, and trituration with light petroleum gave the *amino-acetal* which crystallised in needles, m. p. 117—118°, from ethyl acetate (Found: C, 63·05; H, 6·9; N, 7·2. $C_{11}H_{15}O_3N$ requires C, 63·15; H, 7·2; N, 6·7%).

5-*Oxo*-2-*phenyl*-1,3-*dioxan.* Cold solutions of the amino-acetal (4·2 g. in 75 ml. of water) and sodium metaperiodate (4·4 g. in 75 ml. of water) were mixed at 0° and kept at that temperature for 3 min. After 15 hr. at room temperature the solution was thoroughly extracted with ethyl acetate. Washing with water, drying ($MgSO_4$), and evaporation at 50° under reduced pressure furnished a viscous product which was taken up in dry ether (12 ml.) and filtered. The filtrate was cooled to $-70°$ and light petroleum (b. p. 40—60°) added with thorough scratching of the walls of the container. The resulting *hydrate* (2 g.) crystallised in plates, m. p. 81°, on addition of light petroleum to a cold concentrated ethyl acetate solution; it had $\nu_{\text{max.}}$ (in CCl_4) 3280 cm.$^{-1}$ (strong) but no carbonyl band (Found: C, 61·2; H, 6·3. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%). Cold ethanolic 2,4-dinitrophenylhydrazine sulphate produced the yellow 2,4-*dinitrophenylhydrazone*, m. p. 175° (from dioxan–light petroleum) (Found: C, 53·2; H, 3·35; N, 15·5. $C_{16}H_{14}O_6N_4$ requires C, 53·4; H, 3·9; N, 15·65%). The *semicarbazone*, m. p. 215° (decomp.), crystallised from methanol (Found: C, 56·3; H, 5·3; N, 18·05. $C_{11}H_{13}O_3N_3$ requires C, 56·15; H, 5·55; N, 17·85%). Distillation of the hydrate at 95—99°/0·1 mm. gave a liquid which rapidly solidified. Crystallisation from light petroleum (b. p. 60—80°) gave anhydrous 5-*oxo*-2-*phenyl*-1,3-*dioxan* as needles, m. p. 69—71°, $\nu_{\text{max.}}$ (in CCl_4) 1750 cm.$^{-1}$ (strong) (no hydroxyl band) (Found: C, 67·45; H, 5·8. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·65%). The free ketone slowly liquefies to an oil smelling strongly of benzaldehyde; it is best stored as the much more stable hydrate and regenerated just before use.

5-*Nitro*-2-*phenyl*-1,3-*dioxan.* To a solution of lithamide in liquid ammonia (from 0·15 g. of lithium and 100 ml. of ammonia) was added 5-hydroxymethyl-5-nitro-2-phenyl-1,3-dioxan (3 g.), and the mixture was stirred for 6 hr. Addition of ammonium chloride (1·5 g.), evaporation of the ammonia, addition of water (25 ml.), and filtration gave the *nitro-acetal* (2·1 g.), needles, m. p. 127° (from ethanol or benzene) (Found: C, 57·6; H, 5·05; N, 6·75. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7%). Addition of a sodium hydroxide solution of this product to ice-cold dilute sulphuric acid gave no pure product other than a trace of starting material.

5-*Bromo*-5-*nitro*-2-*phenyl*-1,3-*dioxan.* Water was azeotropically separated from a refluxing mixture of 2-bromo-2-nitropropane-1,3-diol [4] (13 g.), benzaldehyde (7 g.), toluene-*p*-sulphonic acid (0·2 g.), and benzene (200 ml.). The solution was washed with sodium hydrogen carbonate solution and water and dried ($MgSO_4$). Evaporation and addition of light petroleum (b. p. 40—60°) gave the solid *bromonitro-acetal* (16 g.), m. p. 86—87° after crystallisation from ethanol (Found: C, 41·7; H, 3·4; N, 4·8. $C_{10}H_{10}O_4NBr$ requires C, 41·7; H, 3·45; N, 4·85%). Reduction with zinc dust gave a zinc complex, but acid decomposition of this compound gave no useful product.

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[2] Noland, *Chem. Rev.*, 1955, **55**, 137.

[3] Cf. Klager, *J. Org. Chem.*, 1955, **20**, 1348.

[4] Schmidt and Wilkendorf, *Ber.*, 1919, **52**, 389.

179. *Allyl 2,4,6-Triallylphenyl Ether and Derivatives.*

By A. C. DAVIS and R. F. HUNTER.

REACTION of phenol with allyl halide and alkali, known to give the mono- and di-*C*-allyl derivatives, has been found to give allyl 2,4,6-triallylphenyl ether under forcing conditions though the yields are only about 20%. Under the conditions used, *C*-alkylation precedes etherification since allyl phenyl ether is unaffected.

Alkali converts our product into 2,4,6-tripropenylphenol by combined hydrolysis and prototropic rearrangement, as judged by spectral changes and other evidence.

Perbenzoic acid at 0° reacts only with the *C*-allyl groups of allyl 2,4,6-triallylphenyl ether.[1] The tetraepoxide was obtained, though not pure, by oxidation of the glycidyl triallylphenyl ether.

Experimental.—*Allyl*-2,4,6-*triallylphenyl ether.* Allyl bromide (121 g.) was gradually added to phenol (23 g., 0·25 mole), toluene (75 c.c.), and sodium hydroxide (48 g.) in water (50 c.c.) which were stirred and boiled under reflux with a water-separating still-head. When separation of water from the condensate became very slow, further allyl bromide (121 g., 1 mole) was added during 3 hr., and the mixture was boiled under reflux for a further 2½ hr. with separation of water. After addition of water and ether, the organic layer was separated, washed with 5% aqueous sodium hydroxide, then with water until neutral, and evaporated. Distillation gave lower allyl ethers (18·1 g.), b. p. 32—98°/0·7 mm., a fraction, b. p. 98—110°, and a small residue. The last two were refractionated, to give *allyl* 2,4,6-*triallylphenyl ether* (13·1 g., 20·6%), b. p. 102—116°/0·8 mm., n_D^{21} 1·5262 (Found: C, 84·7; H, 8·4; OH, 0. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%), which over palladium–charcoal absorbed 369 c.c. of hydrogen per g., though other samples absorbed 344—353 c.c./g. ($4H_2$ = 351 c.c./g.).

Use of xylene as solvent gave 22·3% of the tetra-allyl compound. Heating the low-boiling fraction (95 g.) in xylene at 200° for 8 hr. gave liquid allylphenols (OH content, 9·2%) which with allyl bromide (145 g.) and sodium hydroxide (48 g.) in xylene (275 c.c.) gave a further quantity (44·2 g.) of the allyl triallylphenyl ether, b. p. 101—114°/0·8 mm., n_D^{22} 1·5261. A typical sample was shown to contain less then 2% of the tripropenyl isomer by infrared spectroscopy.

Phenol (70·5 g.), allyl chloride (230 g.), sodium hydroxide (126 g.), and sodium iodide (1 g.) in toluene (225 c.c.) in an autoclave for 5 hr. at 170° gave mixed allyl ethers (129 g.) which contained some phenolic material (Found: OH, 1%). Re-etherification afforded allyl triallylphenyl ether (42·9 g., 22·5%), b. p. 99—115°/0·5 mm., n_D^{19} 1·5282. The higher refractive index probably indicates a trace of triallylphenol.

Other solvents gave similar results but often lower yields.

Rearrangement. The ether was recovered unchanged after treatment with soda-lime in paraffin at 170°.

The ether (5 g.) was distilled with saturated methanolic potassium hydroxide (30 c.c.) until the temperature of the liquid rose to 150° and the mixture was kept thereat for 6 hr., small quantities of solvent being added to maintain the temperature. Working up with ether and water gave crude 2,4,6-tripropenylphenol (1·5 g.), b. p. 130—140°/10^{-5} mm., n_D^{21} 1·5817 [Found: C, 84·05; H, 9·3%; H_2 absorbed (Pd), 295 c.c./g. Calc. for $C_{15}H_{18}O$: C, 84·1; H, 8·5%; $3H_2$, 314 c.c./g.].

After a similar experiment (ether, 5·7 g., KOH solution, 60 c.c.; 2½ hr.), allyl bromide (2·5 g.) and benzene (40 c.c.) were added and the mixture was boiled under reflux for 4 hr. Working up as usual, followed by two distillations, gave allyl 2,4,6-tripropenylphenyl ether (2·0 g.), n_D^{20} 1·5727 (Found: C, 83·5; H, 9·0%; H_2 absorbed, 338 c.c./g. Calc. for $C_{18}H_{22}O$: C, 85·0; H, 8·7%; $4H_2$, 351 c.c./g.).

2,4,6-Triallylphenol, prepared by Claisen rearrangement of allyl 2,6-diallylphenyl ether, had b. p. 101—103°/0·7 mm., n_D^{12} 1·5440 (lit., 159°/14 mm., $n_D^{12\cdot8}$ 1·5445), and gave a phenylurethane, m. p. 92—93°.

Spectra. As liquid capillary films, triallylphenol, had strong infrared bands at 3115 (sharp), 995, and 913 (C–H stretching; bending of $CH{\vdots}CH_2$), 3559 (hindered phenol), and 1639 and 864 $cm.^{-1}$ ($C{\vdots}C$ and 1,2,4,6-tetrasubstitution)[2]

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[1] Cf. Hopff and Jaeger, *Helv. Chim. Acta*, 1957, **40**, 274.

[2] Grisenthwaite and Hunter, *J. Appl. Chem.*, 1956, **6**, 324.

Tripropenylphenol had no band at 3115 cm.$^{-1}$ and only very weak absorption at 995 and 915 cm.$^{-1}$ (little triallylphenol), a very strong band at 965 cm.$^{-1}$ (*trans*-CH:CH), and a doublet 3559 (free OH) and 3333 cm.$^{-1}$ (hydrogen-bonded OH). Conjugation of the double bonds with the aromatic ring [2] led to a shift of the C:C band to 1661 cm.$^{-1}$, and of the 1,2,4,6-tetrasubstitution band to 884 cm.$^{-1}$. Also a band due to conjugation of C:C to the aromatic ring was observed at 1595 cm.$^{-1}$.

In the ultraviolet region (methanol solutions; Unicam spectrometer), triallylphenol showed a strong band at 280 mμ (ε 4000) due to the phenolic chromophore.[3] Tripropenylphenol showed bands at 389, 262, and 245 mμ (ε 2500, 18,350, and 24,700 respectively), the first of which confirms the presence of double bonds conjugated to the aromatic ring.

Allyl 2,4,6-*tri*-(2,3-*epoxypropyl*)*phenyl ether.* Allyl 2,4,6-tripropenylphenyl ether (39·8 g.) was gradually added to perbenzoic acid (4 mols.) in chloroform (810 c.c.) in an ice-bath. An exothermic reaction maintained the temperature at 5° for about an hour, after which the mixture was kept in ice for 43 hr. Titration then showed that about 5% more than the theoretical quantity of the peracid had been consumed. The acid was extracted by aqueous sodium carbonate and sodium hydroxide, and the solution was washed to neutrality and concentrated under reduced pressure, and finally to a constant weight at 70°/0·4 mm. The product (49 g.) was a golden-yellow oil, n_D^{20} 1·5402 (Found: epoxide equiv., 109. Theor., 101).

Glycidyl 2,4,6-*triallylphenyl ether.* 2,4,6-Triallylphenol (15·5 g.) and epichlorohydrin (19·1 g.) in ethanol (5·3 g.) were stirred at 60° whilst sodium hydroxide (3·1 g.) in water (3·5 c.c.) was added during 4 hr. After a further ½ hr., the solvent was removed under reduced pressure, the residue dissolved in water and toluene, and the organic layer was washed with water until neutral, dried (K_2CO_3), and concentrated under reduced pressure; the product, a reddish-brown liquid (18·6 g., 95%), n_D^{20} 1·5333, was distilled, giving the *glycidyl triallylphenyl ether*, n_D^{21} 1·5315 (Found: C, 79·4; H, 8·6%; epoxide equiv., 285. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%; epoxide equiv., 270).

This ether (8·0 g.) reacted with perbenzoic acid (3·5 mol.) in chloroform (125 c.c.) at 0° for 3 days, 0·083 mol. of the peracid disappearing. The acids were removed as before. Concentration gave a tetraepoxide (8·7 g., 92%) (Found: epoxide equiv., 93. Calc. for tetraepoxide $C_{18}H_{22}O_5$: epoxide equiv., 79·5), which appeared to contain 3·5 epoxide groups.

Attempted polymerisation. A solution of benzoyl peroxide (0·022 g.) in the allyl triallylphenyl ether (1·023 g.) was heated at 60° for 18 hr. There was no sign of reaction except a slight rise in refractive index to n_D^{18} 1·5297. Further treatment at 100° for 24 hr. resulted only in the development of a faint yellow colour and an increase in refractive index to n_D^{17} 1·5364.

The infrared spectroscopical data were obtained by Mr. R. J. Grisenthwaite using a Grubb-Parsons S3A Spectrometer.

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[*Received, June* 30*th*, 1959.]

[3] Hunter, Morton, and Carpenter, *J.*, 1950, 441.

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180. *Structure and Reactivity of the Oxy-anions of Transition Metals. Part IX.* Electronic Structure.*

By A. CARRINGTON and M. C. R. SYMONS.

OUR initial structural studies,[1,2] in which we used results obtained by spectrophotometry and electron-spin resonance, were interpreted in terms of an L.C.A.O. molecular-orbital treatment of permanganate and chromate given by Wolfsberg and Helmholz.[3] This level scheme, which accounted qualitatively for the main features of the electronic spectra

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* Part VIII, *J.*, 1960, 290.

[1] Carrington, Ingram, Schonland, and Symons, *J.*, 1956, 4710.

[2] Carrington, Schonland, and Symons, *J.*, 1957, 659.

[3] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

of these ions,[4] was used to interpret the spectra of related ions such as manganate, hypomanganate, and ferrate which have one or two electrons outside the " closed-shell " structure considered by Wolfsberg and Helmholz.

In this orbital scheme the highest filled orbital is a non-bonding orbital (t_1) compounded of oxygen $2p$ atomic orbitals, and the lowest unfilled level is triply degenerate having T_2 symmetry.

This scheme does not fit the detailed results obtained from electron-spin resonance studies of single crystals of potassium chromate containing small amounts of manganate or ferrate, and of sodium vanadate containing hypomanganate.[5] However, an alternative scheme, in which the first unfilled level for closed-shell ions is doubly degenerate (symmetry E) has been suggested by Ballhausen and Liehr [6] and used by them to compute values for the oscillator strengths of the first two electronic transitions of permanganate and chromate.

If the " outer " electrons of manganate, hypomanganate, and ferrate are fed into the e level, which uses $d_{x^2-y^2}$ and d_{z^2} orbitals of the metal atom with π-type overlap with oxygen $2p$ orbitals, the detailed electron-resonance results are explained satisfactorily.[5,7] In particular, the relative insensitivity of the hypomanganate and ferrate spectra to changes in temperature, and the isotropic hyperfine structure from manganese in hypomanganate, can only be understood if the orbital is doubly degenerate.

Schonland [7] has analysed the electron-resonance spectrum obtained from manganate and has found that a good fit of the anisotropic hyperfine splitting and g-values can be obtained if the unpaired electron is in a doubly degenerate orbital, and that the first excited state for this electron is triply degenerate of symmetry T_2. Schonland also concludes that this t_2 orbital is spread over the molecule, whereas the e level is largely localised on the manganese atom. The calculations predict a value for the isotropic hyperfine splitting for hypomanganate which is very close to the experimental value, and they also lead to a value for the quadrupole moment of manganese which is in good agreement with other values quoted in the literature.

The transitions suggested in Part IV [2] to explain the electronic absorption spectra of manganate and related ions are therefore incorrect, and a new assignment has been made, and checked by calculations of intensities [8] similar to those made by Ballhausen and Liehr. Despite certain differences in the detailed calculations, agreement with experiment for " closed-shell " ions, including vanadate, is satisfactory and is also good for ions with " outer " electrons. In this scheme only those orbital levels used in the calculations for the first two transitions of " closed-shell " ions are used. These transitions are represented as $e \longleftarrow t_1$ and $t_2 \longleftarrow t_1$, both for " closed-shell " ions and ions having " outer " electrons. In addition, a transition of an outer electron to the t_2 level is possible,

Interpretation of visible and ultraviolet absorption spectra.

The ground state of the ion is indicated in the first row and the excited state to which the transition is occurring is shown in parentheses with the experimental frequency (in cm.$^{-1}$).

	$(t_1)^6 : {}^1A_1$			$(t_1)^6e : {}^2E$	$(t_1)^6e^2 : {}^3A_2$	
Transition	MnO_4^-	CrO_4^{2-}	VO_4^{3-}	MnO_4^{2-}	MnO_4^{3-}	FeO_4^{2-}
$e \longleftarrow t_1$	18,320($^1T_2$)	26,810	36,900	16,530($^2T_1$) 22,940($^2T_2$)	14,810($^3T_1$)	12,720($^3T_1$)
$t_2 \longleftarrow t_1$	32,210($^1T_2$)	36,630	—	28,490($^2T_1$) 33,440($^2T_2$)	30,800($^3T_1$) —	19,600($^3T_1$) —
$t_2 \longleftarrow e$	—	—	—	12,000($^2T_2$)	—	—

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[4] Teltow, *Z. phys. Chem.*, 1938, *B*, **40**, 397; 1939, *B*, **43**, 198.

[5] Carrington, Ingram, Lott, Schonland, and Symons, *Proc. Roy. Soc.*, in the press.

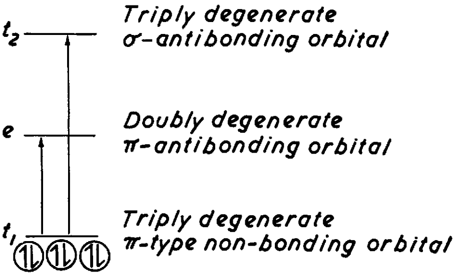
[6] Ballhausen and Liehr, *J. Mol. Spectroscopy*, 1958, **2**, 342.

[7] Schonland, *Proc. Roy. Soc.*, in the press.

[8] Carrington and Schonland, unpublished work.

and can be represented as $t_2 \longleftarrow e$. The presence of " outer " electrons in the e level can split the former transitions because of Coulomb effects (*e.g.*, manganate spectrum, see Table). Calculations show that the $t_2 \longleftarrow e$ transition should be weak and comparable with the familiar $d \longleftarrow d$ transitions of transition metal ions, whilst the $e \longleftarrow t_1$ and $t_2 \longleftarrow t_1$ transitions should still be fairly intense. The assignments made for permanganate, manganate, hypomanganate, and ferrate are given in the Table, and the orbital level scheme is shown in the Figure.

Highest filled and lowest unfilled levels for ions isoelectronic with MnO_4^-, *showing the first two electronic transitions referred to in the text.*



The main conclusions are the following: (i) There is strong σ-bonding through the a_1 and t_2 levels. In the language of directed valency, the σ-bonds can be pictured as being built up from d^3s hybridised orbitals of the metal atom, overlapping with appropriate oxygen $2p$ orbitals. (ii) The " outer " electrons in manganate, etc., are concentrated mainly on the metal atom in a doubly degenerate orbital and, hence, the electrons in the bonding e level are concentrated mainly on the oxygen atoms. Wolfsberg and Helmholz's calculations appear to have over-estimated the importance of π-bonding. (iii) The intense bands in the visible and near-ultraviolet region, characteristic of transition-metal oxyanions, are due to charge-transfer transitions from oxygen to the metal atom, and $d \longleftarrow d$ type transitions, although fully allowed, still give rise to weak absorptions.

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THE UNIVERSITY, SOUTHAMPTON. [*Received, July 6th,* 1959.]

181. *Inhibition of Proton Transfer to Conjugated Polyenes by Terminal Phenyl Groups.*

By ALBERT WASSERMANN.

AN attempt has been made to transfer a proton from trichloroacetic acid to three αω'-diphenylpolyenes, Ph·[CH=CH]$_n$·Ph, where $n = 4$, 5, and 6, under conditions which were conducive to the protonation of 13 polyenes with 2—15 conjugated double bonds[1,2] but without the phenyl group at both ends. In the systems previously investigated[1,2,3] the time of half protonation was less than two minutes, and the formation of the protonated polyene could easily be detected by marked alteration of the electronic spectra and electrical conductance.[1,2,3] The electronic spectra of the three diphenylpolyenes[4] are, however, not altered when their benzene solutions are made 1M with respect to trichloroacetic acid, the result of a typical experiment being shown in the Figure; and the small

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[1] Wassermann, *J.*, 1954, 4329; 1958, 1014, 3228; *Trans. Faraday Soc.*, 1957, **53**, 1030.

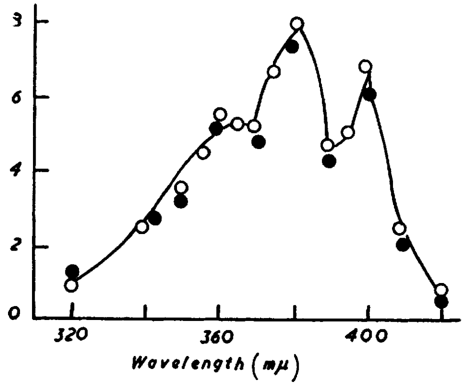
[2] Wassermann, *J.*, 1959, 979, 983 986; *Mol. Phys.*, 1959, **2**, 226.

[3] Wassermann, *J.*, 1955, 581.

[4] The spectra, without acid, were measured by Hausser, Kuhn, and Smakula, *Z. phys. chem.*, 1935, *B*, **29**, 384.

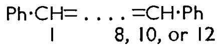
electrical conductance of M-trichloroacetic acid in benzene, at 25°, is not detectably increased by addition of the diphenylpolyenes, the molarities of these polyenes being varied between $1{\cdot}80 \times 10^{-5}$ and $2{\cdot}6 \times 10^{-2}$. Thus, the three αω-diphenylpolyenes are not protonated.

The protonation of conjugated open-chain polyenes involves the withdrawal of two π-electrons and the formation of a methylene group at a position providing for the maximum number of conjugated double bonds and thus for maximum resonance stabilisation of the resulting mesomeric carbonium ion.[2] If this mode of proton transfer is formally applied to the three polyenes, one would expect that the methylene group would be produced in position 1, 8, 10 or 12, adjacent to the phenyl groups, rather than in the phenyl groups or in position 2—7, 2—9, or 2—11. The conclusion is consistent with the mode of proton transfer to vitamin-A acetate, there being no evidence for initiation of reaction at the carbon atoms situated in the middle of the system of conjugated double bonds.[2] It is suggested that the αω-diphenylpolyenes remain unprotonated partly because the addition of a proton to a terminal carbon atom would block the conjugation between one of the phenyl groups and the rest of the cation and partly because the inductive effect of the phenyl groups[5] decreases the basicity of the carbon atoms nos. 1, 8, 10, and 12. These considerations relate to the equilibria between the proton donor and the polyenes. If rate effects played a rôle one would have to take into account that the donor is a bulky hydrogen-bonded dimer and that the specified terminal carbon atoms of the polyene are shielded, to a certain extent, by the bulky phenyl groups. This steric hindrance could not operate if the proton were attached somewhere in the middle part of the system of conjugated double bonds.



Electronic spectrum of 1,8-diphenyloctatetraene (m. p. 232°, recrystallised from acetic anhydride) in benzene at ~20°.

○ . . . . *No acid (cf., ref. 4).* ● . . . . 1·00M *with respect to trichloroacetic acid. Polyene concentration* $6{\cdot}47 \times 10^{-6}$ *to* $1{\cdot}43 \times 10^{-6}$M *in both sets of tests. The symbols* ○ *and* ● *are used to distinguish the tests without and with acid; their number does not indicate the number of optical-density measurements.*



$$\underset{1}{\mathrm{Ph{\cdot}CH}}{=}\ldots\ldots{=}\underset{8,\,10,\,\text{or }12}{\mathrm{CH{\cdot}Ph}}$$

Discussions with Dr. C. A. Bunton, Dr. P. B. D. de la Mare, and Professor Sir Christopher Ingold, F.R.S., are gratefully acknowledged.

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University College, Gower St., London, W.C.1.

[*Received, December* 23*rd*, 1958;
revised, May 3*rd*, 1959.]

[5] Ingold, " Structure and Mechanism in Organic Chemistry," 1953, Cornell Univ. Press, New York, p. 70.

182. *Triterpenoids from Lignite.*

By Raphael Ikan and John McLean.

Previously [1] we described the isolation from a "young" peat of epifriedelanol and an inseparable mixture of β-sitosterol and β-sitostanol. Continuing these studies in an attempt to relate chemical changes with the degree of humification of peat we have examined an "old" peat kindly supplied by the Department of Agriculture for Scotland from the Peat Experimental Station at Gardrum Moss. This peat possessed a high degreee of humification (Von Post Scale value approximately H10); examination of the non-saponifiable portion of a petrol extract revealed the presence of friedelin in addition to epifriedelanol and the mixture of sterols found in the "young" peat. Friedelin and epifriedelanol have been isolated from the bark of *Ceratopetalum apetalum* (coachwood) [2] and from a brown coal,[3] and epifriedelanol from a lichen.[4] Our findings suggest that humification is accompanied by the oxidation of epifriedelanol to friedelin, but such a generalisation is misleading as these peats came from different sources.

Lignite is generally regarded as an intermediate stage in the transformation of peat to coal, and is believed to be the precursor of cannel coal, bituminous coal, and finally anthracite. We have examined lignite and cannel coal to find if the triterpenoids present in peat persist in these more compact fuels, and while a benzene extract of cannel coal did not yield triterpenoid materials, a similar extract of lignite which had been saponified, yielded the following members of the lupeol series: betulin, allobetulin, oxyallobetulin, allobetulone, and oxyallobetulone, along with the aliphatic alcohol tetracosanol.

We did not find any members of the friedelane series present in lignite, although we had previously found those in peat [1] and their presence in Bohemian brown coal has also been established. Šorm [3] has also found allobetulin, oxyallobetulin, and oxyallobetulone in brown coal, but the presence of betulin and allobetulone in brown coal or lignite does not appear to have been shown previously. The presence of oxyallobetul-2-ene in a high-boiling American petroleum fraction has been described by Barton.[5]

Experimental.—Rotations were measured in chloroform unless stated otherwise. Light petroleum refers to the fraction, b. p. 60—80°.

Powdered lignite (38 lb.) was extracted continuously for 30 hr. with hot benzene (15 l.). Removal of benzene *in vacuo* gave semi-solid material (530 g.) which was extracted with boiling isopropyl alcohol (3 l.) for 4 hr. The extract was decanted from insoluble tars (60 g.) and set aside overnight at room temperature. The waxy material (150 g.) which separated was then filtered off. Evaporation of the filtrate *in vacuo* gave a brown solid (310 g.) which was dissolved in benzene (250 ml.) and adsorbed on a column of alumina (4 kg.). Elution with light petroleum (3 l.) gave waxy material.

Allobetulone. The combined benzene–light petroleum (1 : 1) eluates (1·5 l.) were taken to dryness, triturated with light petroleum (40 ml.), and left overnight; allobetulone separated and was recrystallised from chloroform–methanol, forming needles (0·25 g.), m. p. and mixed m. p. 235—236°, $[\alpha]_D$ +84·9° (*c*, 0·9). The infrared spectrum was identical with that of an authentic specimen.

Oxyallobetulone. Elution with benzene (1·5 l.) gave nonterpenoid material (0·770 g.), m. p. 250—251°, which was not identified; continued elution with benzene–ether (1 : 1; 1 l.) and ether (2 l.), after trituration of the solid extracts with light petroleum (40 ml.), gave oxyallobetulone, needles (1·1 g.) (from chloroform–methanol), m. p. and mixed m. p. 331—332°, $[\alpha]_D$ +84·4° (*c* 0·76). The infrared spectrum was identical with that of a specimen prepared from allobetulin.

Allobetulin. After removal of oxyallobetulone from the column, elution was continued with ether–chloroform (9 : 1; 1 l.) and ether–chloroform (1 : 1; 1 l.). Working up as before

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[1] McLean, Rettie, and Spring, *Chem. and Ind.*, 1958, 1515.

[2] Jefferies, *J.*, 1954, 473.

[3] Javolim, Streibl, Hovák, and Šorm, *Chem. and Ind.*, 1958, 1142.

[4] Bruun, *Acta Chem. Scand.*, 1954, **8**, 71; Bruun and Jefferies, *ibid.*, p. 1948.

[5] Barton, Carruthers, and Overton, *J.*, 1956, 788.

gave allobetulin (1·3 g.), which when recrystallised from chloroform–methanol formed plates, m. p. and mixed m. p. 265—266°, $[\alpha]_D$ +51·7° (*c* 0·76). Identity with an authentic specimen was established by infrared spectroscopy.

Betulin. Elution was continued with chloroform alone (7 l.). Early fractions contained betulin (0·8 g.), m. p. and mixed m. p. 255—256° (from ethanol), $[\alpha]_D$ +20·5° (pyridine, *c* 0·83). Infrared identity with an authentic specimen was established.

Oxyallobetulin. The later fractions from elution with chloroform yielded oxyallobetulin, needles (0·35 g.), m. p. 345—346° (from chloroform–methanol), $[\alpha]_D$ +46·6° (*c* 0·76). Identity with an authentic specimen was established as above.

Tetracosanol. Stripping of the column with chloroform–ethanol (1 : 1) gave tetracosanol, needles, m. p. 81—83°, from light petroleum–ethyl acetate (Found: C, 81·8; H, 13·8. Calc. for $C_{24}H_{50}O$: C, 81·4; H, 14·1%); $\nu_{max.}$ 3330 cm.$^{-1}$ (OH group).

We thank Messrs. Watts, Blake, Bearne, and Co. Ltd. for supplying lignite which occurs in association with china clay at Newton Abbot and which belongs to the oligocene period (30—50 million years ago). We also thank the Hebrew University, Jerusalem, for a grant (to R. I.).

THE ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY, GLASGOW. [*Received, June 22nd,* 1959.]

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183. *The Reaction between 2,4-Dinitrotoluene and Phthalic Anhydride in Dimethylaniline.*

By K. J. CLARK and G. I. FRAY.

AN attempt to prepare 3-(2,4-dinitrobenzylidene)phthalide, m. p. 252°, by the reaction of 2,4-dinitrotoluene with phthalic anhydride in dimethylaniline, as described by Porai-Koshits and Chizhevskaya[1] who report a 72% yield, led in our hands instead to two isomers, $C_{15}H_{10}O_4N_2$, m. p. 222° and 234°, which were identified as known phthalimide derivatives by mixed melting point determinations with authentic specimens.

Experimental.—A mixture of 2,4-dinitrotoluene (9·1 g.), phthalic anhydride (7·4 g.), and dimethylaniline (50 c.c.) was refluxed for 2 hr., cooled, and poured into dilute hydrochloric acid. Crystallisation of the tarry product from acetone gave a yellowish solid (3·5 g.), m. p. 190—200°, which on fractional crystallisation from the same solvent finally afforded *N*-(4-methyl-3-nitrophenyl)phthalimide as white needles, m. p. and mixed m. p. 222° (Found: C, 64·1; H, 3·9; N, 9·5. Calc. for $C_{15}H_{10}O_4N_2$: C, 63·8; H, 3·6; N, 9·9%), and *N*-(2-methyl-5-nitrophenyl)-phthalimide as yellow plates, m. p. and mixed m. p. 234° (Found: C, 63·8; H, 3·9; N, 9·7%). Authentic specimens were prepared[2] from phthalic anhydride and the appropriate nitrotoluidines.

RESEARCH LABORATORY, SHELL CHEMICAL CO. LTD.,
EGHAM, SURREY.
[*Received, July 23rd,* 1959.]

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[1] Porai-Koshits and Chizhevskaya, *Zhur. obshchei Khim.*, 1956, **26**, 842; *Chem. Abs.*, 1956, **50**, 14,720.

[2] Wanag and Veinbergs, *Ber.*, 1942, **75**, 1558.

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184. *The Replacement of the Diazonium by the Nitro-group. Part VI.*[1] *Further Simplifications in Technique, and the Improved Preparation of* o- *and* p-*Dinitrobenzenes.*

By E. R. WARD, C. D. JOHNSON, and J. G. HAWKINS.

HODGSON, WARD, and their co-workers[1-3] showed that replacement of the diazonium by the nitro-group occurs only in neutral or alkaline medium. Earlier methods largely relied on the neutralisation of the excess of acid used for diazotisation by excess of sodium

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[1] Part V, Hodgson and Heyworth, *J.*, 1949, 1624.

[2] Hodgson and Marsden, *J.*, 1944, 22; Hodgson and Ward, *J.*, 1947, 127; Hodgson, Mahadevan, and Ward, *J.*, 1947, 1392; Hodgson and Ward, *J.*, 1948, 556.

[3] Hodgson, Heyworth, and Ward *J.*, 1948, 1512.

nitrite employed in the subsequent decomposition. Hodgson, Heyworth, and Ward[3] achieved this by neutralisation of the diazonium solution with calcium carbonate before diazo-replacement. We now find that, in certain cases, the diazonium solution can be satisfactorily decomposed by *direct* addition to the decomposition medium containing excess of sodium hydrogen carbonate. Another variation in which a decomposition medium of aqueous sodium nitrite containing cupric carbonate (for neutralisation and catalytic purposes) and cuprous oxide was employed was not successful for the preparation of 2-nitronaphthalene from 2-naphthylamine or of 2,5-dinitrotoluene from 5-nitro-*o*-toluidine. The new techniques provide an extremely simple and rapid method for preparing *o*- and *p*-dinitrobenzenes in almost quantitative yield, the only side products being traces of azo-compound. These preparations are much superior to any alternative procedure in terms of simplicity and rapidity of operation.

The new method has also been applied to the preparation of extremely pure 1,4-dinitronaphthalene, required for kinetic studies,[4] and to the synthesis of 5,6,7-trinitrotetralin from 6-amino-5,7-dinitrotetralin.

5,6,8-Trinitrotetralin was originally prepared by Dean[5] by nitration of 5,6-dinitrotetralin; we have confirmed Dean's work and also synthesised this compound by diazo-decomposition of diazotised 5-amino-6,8-dinitrotetralin.

Attempts to convert these trinitrotetralins, by dehydrogenation, into 1,2,3- and 1,2,4-trinitronaphthalene failed. Nor could the latter be prepared by decomposition of diazotised 1,4-dinitro-2-naphthylamine, the only product being a diazo-nitro-naphthol.[6] Despite the claims that have been made, we believe that these two trinitronaphthalenes (both of which on further nitration could yield the first pentanitronaphthalene) have yet to be prepared. In particular we could not repeat Contardi and Mor's work[7] in which they claimed to have made 1,2,4-trinitronaphthalene from 2,4-dinitro-1-naphthylamine. Their diazotisation procedure is satisfactory but, as one would expect, addition of the diazo-solution to aqueous sodium nitrite containing copper sulphate gives a quantitative yield of 1-diazo-4-nitro-2-naphthol. Further decompositions, involving more efficient catalysts, all gave quantitative yields of diazo-oxide. In any case further doubt is cast on this work by the very high m. p. claimed for the product.

Experimental.—o- *and* p-*Dinitrobenzenes.* *o*-Nitroaniline (10 g.) was dissolved in a warm mixture of sulphuric acid (*d* 1·84; 12 c.c.) and water (30 c.c.). This solution was added with vigorous stirring to ice-cold water (50 c.c.). Crushed ice (20 g.) was added and then, *very* rapidly with vigorous stirring, a solution of sodium nitrite (8 g.) in water (13 c.c.). After 5 minutes' stirring this diazonium solution was added, portionwise, through a *wide*-bore glass tube (projecting well below the level of the decomposition mixture) to a vigorously stirred solution of sodium nitrite (100 g.) and sodium hydrogen carbonate (45 g.) in water (1 l.) at 60° containing a small quantity of silicone " Anti-foam." The diazo-solution was added as rapidly as possible and 5 min. after addition the solids were collected at the pump, and washed with hydrochloric acid (2N) and then much water. The yield of almost pure *o*-dinitrobenzene (m. p. 116—118°) was 11·8 g. (97%). Chromatography of this in benzene on alumina gave very pure material, m. p. 118°, in *ca.* 90% overall yield.

Similar yields were obtained of almost pure and pure *p*-dinitrobenzene from *p*-nitroaniline but in this case the amounts of sulphuric acid and sodium hydrogen carbonate employed were half of those given above.

1,4-*Dinitronaphthalene.* (With A. W. Bamford.) 4-Nitro-1-naphthylamine (10 g.) was made into a paste with water (25 c.c.), and to this was added, with stirring, a mixture of sulphuric acid (*d* 1·84; 11 c.c.) and water (35 c.c.), and then crushed ice (*ca.* 40 g.). This mixture was then treated quickly with sodium nitrite (5 g.) dissolved in water (7 c.c.) and after 5 minutes' stirring was added portionwise, to a solution of sodium nitrite (200 g.) in water (500 c.c.) containing hydrated copper sulphate (40 g.), cuprous oxide (15 g.), and sodium

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[4] Bamford and Broadbank, *Tetrahedron*, 1958, **3**, 321.

[5] Dean, Thesis, London, 1949.

[6] Hardy and Ward, unpublished work.

[7] Contardi and Mor, *Rend. Ist. Lombardi*, 1924, **57**, 645.

hydrogen carbonate (50 g.). Stirring was continued for 1 hr., and next day the solid was washed with water and dried at 40°. Almost pure 1,4-dinitronaphthalene, m. p. 125—130° (yield 50%), was obtained by extracting it with boiling ethanol (3 × 50 c.c.; charcoal) and allowing the filtered extract to crystallise. The material was further purified by chromatography in benzene on alumina (recovery 92—96%), followed by crystallisation from 5 : 1 v/v light petroleum (b. p. 80—100°)–benzene, yielding yellow feathery needles, m. p. 133°.

5,6,8-*Trinitrotetralin.* 5-Amino-6,8-dinitrotetralin (10 g.) was dissolved in a solution of sodium nitrite (3·5 g.) in sulphuric acid (*d* 1·84; 25 c.c.) and this was added portionwise to acetic acid (35 c.c.) below 30°. The mixture was kept for 1 hr. at 0°. Ice-cold anhydrous ether (200 c.c.) was stirred in, and after 30 min. a white solid was collected, washed with dry ether, dried in a current of air, and dissolved in ice-cold water (100 c.c.). This solution was added, portionwise, to a mixture of copper sulphate (65 g.) in water (500 c.c.) and sodium sulphite (65 g.) in water (250 c.c.), which had been treated, *just before use*, with a solution of sodium nitrite (130 g.) in water (500 c.c.). Stirring was continued for 3 hr.; next day the solid was washed with much water, dried, and extracted with boiling ethanol (3 × 50 c.c.; charcoal). On cooling, the filtered extract deposited pure 5,6,8-trinitrotetralin, m. p. 94° (4·4 g., 40% yield) (Dean [9] gives m. p. 94°).

This was also obtained by suspending 5,6-dinitrotetralin (5·0 g.) in oleum (*d* 1·92; 10 c.c.), adding a mixture of nitric acid (*d* 1·5; 15 c.c.) and oleum (*d* 1·92; 10 c.c.) at 20°, and raising the temperature to 95° for 1 hr. After cooling, the mixture was poured on ice, and next day the solid was washed with much water, dried, and extracted by boiling ethanol (3 × 50 c.c.; charcoal). The filtered extract on cooling deposited the pure trinitro-compound (3·2 g., 55%).

5,6,7-*Trinitrotetralin.* 6-Amino-5,7-dinitrotetralin was diazotised as above but addition of ether to the diazonium solution brought about decomposition. Hence the diazonium solution was added directly to the decomposition mixture, containing more than sufficient sodium hydrogen carbonate to neutralise the acid in the diazo-solution. 5,6,7-*Trinitrotetralin* was isolated as above; it had m. p. 132° (from ethanol) (yield 30%) (Found: C, 45·0; H, 3·3. $C_{10}H_9O_6N_3$ requires C, 44·9; H, 3·4%).

The authors thank Genatosan Ltd. for a grant (to J. G. H.).

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185. *The Action of the Methyl Grignard Reagent on 3-Hydroxymethylenecamphor.*

By A. W. BURGSTAHLER and MAX STRUBLE.

IN their study of the reaction of methylmagnesium iodide with 3-hydroxymethylene-(+)-camphor (I; R = OH), Forster and Judd [1] obtained a difficultly purified liquid, giving approximately correct analyses for $C_{12}H_{18}O$, to which they assigned the curious, still quoted,[2] oxeten structure (II; R = Me). The material readily formed a crystalline dibromide, $C_{12}H_{18}OBr_2$, from which it could be regenerated by the action of zinc dust in alcohol. Upon oxidation with potassium permanganate it yielded (+)-camphoric acid. Although the 3-ethylidenecamphor structure (I; R = Me) would appear to be a more likely formula for the Grignard product (arising from conjugate addition and then elimination of water during working-up), Forster and Judd discarded this possibility on the basis of the non-agreement of the specific rotation ($[\alpha]_D$ +195°) of their purified material with an earlier [3] recorded value of +113° for 3-ethylidenecamphor now known [4] to be erroneous.

Because of our interest in the chemistry of 3-hydroxymethylenecamphor in connexion with another problem, we were led to examine the above report. As expected, the product

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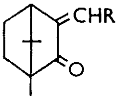
[1] Forster and Judd, *J.*, 1905, 368.

[2] Simonsen and Owen, "The Terpenes," Cambridge Univ. Press, 2nd edn., 1949, Vol. II, p. 461; Elsevier's "Encyclopaedia of Organic Chemistry," Vol. 12A, p. 856.

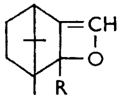
[3] Haller and Minguin, *Compt. rend.*, 1904, **138**, 578.

[4] Rupe and Iselin, *Ber.*, 1916, **49**, 25; Rupe and Burckhardt, *Ber.*, 1916, **49**, 2547.

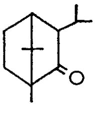
proved to be 3-ethylidenecamphor (I; R = Me), whose identity with an authentic specimen [prepared from 3-chloromethylenecamphor (I; R = Cl) and one equivalent of methylmagnesium iodide by the method of Rupe and Iselin[4] (who apparently were unaware of the work of Forster and Judd)] was confirmed by the exact correspondence of physical and chemical properties, including optical rotation and spectral features, ozonolysis to camphorquinone,[4] and an undepressed mixed m. p. of the dibromide.



(I)



(II)



(III)

In contrast to the behaviour of 3-hydroxymethylenecamphor, both the 3-chloromethylene and the 3-ethylidene derivative reacted with an excess of methylmagnesium iodide to furnish a fragrant, saturated ketonic liquid, $C_{13}H_{22}O$, which is almost certainly 3-isopropylcamphor (III). This substance, presumably because of steric hindrance, gave no carbonyl derivative; however, a strong carbonyl band at 1730 cm.$^{-1}$ (camphor-type carbonyl) was present in its infrared spectrum. An attempt to prepare it by reaction of isopropyl bromide with sodiocamphor was unsuccessful.

Although not examined in the present study, the product from the reaction of ethylmagnesium iodide with 3-hydroxymethylenecamphor, which was formulated by Forster and Judd as (II; R = Et), appears by analogy to have the 3-propylidenecamphor structure (I; R = Et). Recorded[5] physical constants for authentic samples of this substance are in accord with this interpretation.

Experimental.—*3-Ethylidene-(+)-camphor.* The redistilled product obtained by reaction[1] of methylmagnesium iodide with 3-hydroxymethylene-(+)-camphor had b. p. 133—138°/25 mm., n_D^{27} 1·4865, $\nu_{max.}$ (in $CHCl_3$) 1710 and 1655 cm.$^{-1}$, $\lambda_{max.}$ (in EtOH) 238 mμ (ε 14,000), $[\alpha]_D^{28}$ +170° (*c* 2·52) (all rotations in $CHCl_3$). The dibromide, prepared in chloroform, crystallised from benzene–light petroleum (b. p. 30—40°) in elongated, hexagonal prisms, m. p. 154—155°, $[\alpha]_D^{28}$ +157° (*c* 2·62) (Forster and Judd[1] record m. p. 152—153°, $[\alpha]_D$ +157°). Ozonolysis of the Grignard product as described by Rupe and Iselin[4] furnished (−)-camphorquinone, m. p. 198—200°, $[\alpha]_D^{28}$ −104° (*c* 2·04).

The constants for 3-ethylidene-(+)-camphor as obtained from 3-chloromethylene-(+)-camphor by the procedure of Rupe and Iselin[4] were as follows: b. p. 134—138°/25 mm., n_D^{27} 1·4870, $\nu_{max.}$ (in $CHCl_3$) 1710 and 1655 cm.$^{-1}$ (complete infrared spectrum identical with the above), $\lambda_{max.}$ (in EtOH) 238 mμ (ε 14,200), $[\alpha]_D^{28}$ +178° (*c* 2·55). The dibromide had m. p. 154—155°, undepressed on admixture with the above preparation.

3-Isopropyl-(+)-camphor. (*a*) Distillation of the base-equilibrated, neutral product from the reaction of ethereal methylmagnesium iodide (0·2 mole) with 3-chloromethylene-(+)-camphor (14·2 g., 0·071 mole) afforded a fragant liquid *ketone* (7·5 g.), b. p. 132—134°/25 mm., n_D^{27} 1·4690, $\nu_{max.}$ (in $CHCl_3$) 1730 cm.$^{-1}$, $[\alpha]_D^{28}$ +80° (*c* 2·49) (Found: C, 80·6; H, 11·3. $C_{13}H_{22}O$ requires C, 80·4; H, 11·4%).

(*b*) Similarly, reaction of methylmagnesium iodide (0·03 mole) with 3-ethylidene-(+)-camphor (2 g., 0·011 mole) gave a liquid (1·3 g.) whose b. p., refractive index, and infrared spectrum were identical with those of the preceding material; it had $[\alpha]_D^{28}$ +79° (*c* 3·01). Attempted alkylation of (+)-camphor (as the sodio-derivative in benzene and dimethyl sulphoxide at 100°) with isopropyl bromide led only to the recovery of unchanged camphor.

One of us (M. S.) gratefully acknowledges the support of the National Science Foundation for the 1959 Summer High School Teacher Research Program (Grant No. 7537) under which this work was performed.

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[*Received, August 14th,* 1959.]

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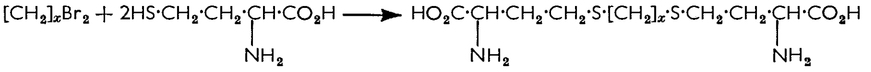
[5] Rupe and Courvoisier, *Helv. Chim. Acta*, 1923, **6**, 1049.

186. *Syntheses of Homologues of Djenkolic Acid.*

By MAX FRANKEL and DAVID GERTNER.

DJENKOLIC ACID, a diamino-dicarboxylic acid containing a methylene group between two cysteine residues, was isolated from plants by Hijman and van Veen.[1] Acids having longer chains between the sulphur atoms of two cysteine residues were isolated [2] from products of hydrolysis of wool samples which had been previously reduced and treated with dihalides in order to give the material better technological properties by cross-linking. Such bis-thioethers of cysteine were also prepared synthetically from cysteine and aliphatic αω-dihalogen compounds.[2,3] In a study of the metabolism of Myleran (1,4-dimethanesulphonyloxybutane), it was found [4] that reaction between cysteine and Myleran in an aqueous medium (*in vitro*) gave, among other products, 3,3′-(tetramethylenedithio)-dialanine.[4]

In the present work, homologues of djenkolic acid derived from homocysteine were synthesised by the action of alkylene dihalides on homocysteine in liquid ammonia or in an aqueous basic medium according to the following scheme:

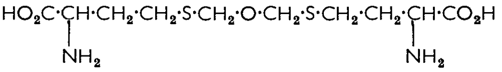


$$[CH_2]_xBr_2 + 2HS{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{NH_2}{CH}{\cdot}CO_2H \longrightarrow HO_2C{\cdot}\underset{NH_2}{CH}{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}[CH_2]_x{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{NH_2}{CH}{\cdot}CO_2H$$

The homocysteine was conveniently prepared by reduction of methionine with sodium in liquid ammonia. In this way homologues of djenkolic acid having up to 5 methylene groups between the sulphur atoms of two homocysteine molecules were prepared.

These substances decompose at ~270°. They are slightly soluble in water and insoluble in ethanol. They can be purified by recrystallisation from a large volume of water or by dissolution in dilute alkali and precipitation with acid. Ascending chromatography, with 1 : 4 aqueous phenol showed that the R_F values increased with the length of the polymethylene chain.

It was interesting to prepare αα′-diamino-dicarboxylic acids having sulphur as well as ether linkages. The acid (I) was prepared by reaction of bischloromethyl ether with homocysteine. Unlike the compounds containing only sulphur linkages, this substance was soluble in water and crystallised from 80% ethanol, and it had a higher R_F value.



$$HO_2C{\cdot}\underset{NH_2}{CH}{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{NH_2}{CH}{\cdot}CO_2H$$

(I)

4,4′-(*Alkylenedithio*)*di*-α-*aminobutyric acids.*

$-[CH_2]_x-$	Yield (%)	R_F	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
$x = 2$	75	0·29	40·3	6·7	9·1	21·4	$C_{10}H_{20}O_4N_2S_2$	40·5	6·7	9·4	21·6
$x = 3$	80	0·34	42·2	7·0	8·8	20·2	$C_{11}H_{22}O_4N_2S_2$	42·5	7·1	9·0	20·6
$x = 4$ [a]	90	0·39	44·2	7·4	8·4	19·4	$C_{12}H_{24}O_4N_2S_2$	44·4	7·4	8·6	19·7
$x = 5$	90	0·49	46·2	7·8	8·0	18·5	$C_{13}H_{26}O_4N_2S_2$	46·1	7·7	8·2	18·9

[a] Prepared by use of tetramethylene chloride.

Experimental.—The ascending method of paper chromatography was used (80% phenol). One synthesis is described. Properties of the other acids are tabulated.

4,4′-(*Methylenedithio*)*di*-α-*aminobutyric acid.* DL-Methionine (3 g., 0·02 mole) was dissolved in liquid ammonia (75 ml.). Sodium was added slowly until the solution became permanently blue. Powdered ammonium chloride was added cautiously until the solution was just decolorised. Methylene dibromide (2·2 g., 0·011 mole) was added dropwise, and the solution shaken and left until most of the ammonia had evaporated (1—2 hr.). The residual ammonia was evaporated at a water-pump and the residue left in a desiccator over sulphuric acid, then

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[1] Hijman and van Veen, *Rec. Trav. chim.*, 1935, **54**, 493.
[2] Shikanova, *J. Appl. Chem. U.S.S.R.*, 1950, **23**, 703.
[3] Zahn and Wollemann, *Makromol. Chem.*, 1953, **10**, 122.
[4] Roberts and Warwick, *Nature*, 1959, **183**, 1509; *Biochem. J.*, 1959, **72**, 3P.

dissolved in water (10 ml.), cooled, and acidified with hydrochloric acid to pH 5—6. The precipitated *acid* was filtered off and washed with water (yield, 2·6 g., 70%). Recrystallised from water, it decomposed at 270° and had R_F 0·18 (Found: C, 38·0; H, 6·4; N, 10·0; S, 22·2. $C_9H_{18}O_4N_2S_2$ requires C, 38·3; H, 6·4; N, 9·9; S, 22·6%).

4,4'-(Oxydimethylenedithio)di-α-aminobutyric acid. DL-Homocysteine, prepared from DL-methionine (3 g., 0·02 mole) was dissolved in 2N-sodium hydrogen carbonate (25 ml.). Bischloromethyl ether (1·1 g., 0·01 mole) in ethanol (20 ml.) was added. The solution was shaken from time to time and left for 8 hr. at room temperature. The solution was acidified with acetic acid and evaporated *in vacuo* until crystals started to form. The whole was cooled and filtered. The *product* (2·5 g., 70%), recrystallised from 80% alcohol, decomposed at 250° and had R_F 0·86 (Found: C, 38·5; H, 6·7; N, 8·7; S, 20·6. $C_{10}H_{20}O_5N_2S_2$ requires C, 38·4; H, 6·4; N, 8·9; S, 20·5.)

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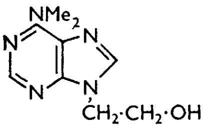
187. *An Anomalous Ring Closure obtained from a Purine Synthesis.*

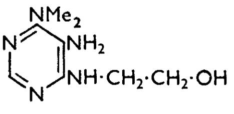
By J. H. LISTER.

IN an attempted preparation [1] of the purine (I) by heating the pyrimidine (II) in formamide with a small amount of hydrochloric acid, a product (" substance X ") was isolated in small yield which gave correct analyses for the purine hydrochloride. However, in 0·1N-hydrochloric acid, this product did not show the single ultraviolet absorption maximum in the 268 mμ region characteristic of 9-substituted 6-dimethylaminopurines, but gave two peaks, at 245 and 278 mμ. Two structures considered were (III) (formed by ring closure on to the 5-amino-group followed by formylation) and (IV; R = CHO) (formed by ring closure on a ring-nitrogen atom and subsequent formylation). The former was ruled out on spectroscopic evidence,[2] and the glyoxalinopyrimidine (IV; R = CHO) was therefore synthesised. This type of compound has been investigated by Ramage and his co-workers [3] who found that a 4-2'-chloroethylaminopyrimidine having either a 5-amino-group or a potentially tautomeric group at position 2 readily cyclises to a glyoxalinopyrimidine.

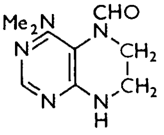
The pyrimidine alcohol (II) was treated with thionyl chloride and the product cyclised by heating it in aqueous ethanol. The resulting hydrochloride was converted into the base (IV; R = H), formylated to give the amide (IV; R = CHO), and converted to its hydrochloride. The spectra of this compound and of " substance X " in hydrochloric acid were similar, but not identical. " Substance X " was then examined chromatographically on paper with 5% aqueous ammonium chloride as solvent. Two spots were obtained (R_F 0·72 and 0·90) which were separately eluted with 0·1N-hydrochloric acid; the faster-moving spot gave a spectrum identical with that of the glyoxalinopyrimidine (IV; R = CHO), whilst the other was spectroscopically identical with the hydroxyethylpurine (I) prepared by another route.[1] The pure hydrochlorides of the purine and the glyoxalinopyrimidine gave the same R_F values as " substance X."



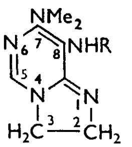
(I)



(II)



(III)



(IV)

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[1] Lister and Timmis, *J.*, 1960, 327.

[2] Lister and Ramage, *J.*, 1954, 4109.

[3] Ramage and Trappe, *J.*, 1952, 4410; Clark and Ramage, *J.*, 1958, 2821.

It thus seems that esterification of the hydroxyethylpyrimidine (II) by the hydrochloric acid present occurred to some degree before formylation and cyclisation. Supporting this, others[4] have shown that constant-boiling hydrobromic acid cyclises hydroxyethylpyrimidines to glyoxalinopyrimidines. In contrast, preparation of the analogous 9-2′-hydroxyethyladenine[1] by the formamide method proceeded smoothly, no indication of isomeric glyoxalinopyrimidine being obtained.

Experimental.—Analyses are by Mr. P. R. W. Baker, Beckenham.

Preparation of "substance X." 5-Amino-6-dimethylamino-4-2′-hydroxyethylaminopyrimidine (5 g.) in formamide (10 ml.) and hydrochloric acid (*d* 1·16; 1 ml.) was heated at 170° for 25 min. After evaporation under reduced pressure the residue was extracted with chloroform, and the extracts were dried (Na_2SO_4) and evaporated. The residue was washed with acetone and recrystallised (charcoal) from propan-1-ol. "Substance X" was obtained as colourless needles (0·5 g.), m. p. 205° (decomp.) (Found: C, 44·3; H, 5·7; N, 29·3; Cl, 14·2. Calc. for $C_9H_{13}ON_5$,HCl: C, 44·3; H, 5·8; N, 28·75; Cl, 14·6%).

8-*Amino*-7-*dimethylamino*-2,3-*dihydroglyoxalino*[1,2-c]*pyrimidine hydrochloride.* 5-Amino-4-dimethylamino-6-2′-hydroxyethylaminopyrimidine (1 g.) was added portionwise to thionyl chloride (10 ml.) and heated gently for 1 hr. After evaporation to dryness and treatment with aqueous sodium carbonate to pH 10, the mixture was extracted with chloroform. The extracts were dried (Na_2SO_4) and evaporated, and the oil remaining was heated under reflux with 1 : 1 aqueous ethanol for 90 min., then evaporated under reduced pressure. The residue crystallised from ethanol, giving the *hydrochloride* (0·15 g.) of base (IV; R = H) as prisms, m. p. 262—264° (Found: N, 32·2; Cl, 16·5. $C_8H_{13}N_5$,HCl requires N, 32·5; Cl, 16·4%). Basification and extraction with chloroform gave the crude base (IV; R = H), hygroscopic prisms (from cyclohexane, m. p. 119—121°, for which a satisfactory analysis could not be obtained owing to decomposition.

This base (0·35 g.) was heated in 4 : 1 formic acid–acetic anhydride for 1 hr., then evaporated. Trituration of the oily residue with triethylamine gave a solid from which the *formamido-derivative* (IV; R = CHO) (0·17 g.) was obtained as deliquescent cream-coloured prisms, m. p. 168—170°, which decomposed on drying *in vacuo*. Treatment with ethanol saturated with hydrogen chloride gave the *hydrochloride* as prisms (from propan-1-ol), m. p. 275—278° (Found: C, 44·2; H, 5·7; N, 28·5; Cl, 15·1. $C_9H_{13}ON_5$,HCl requires C, 44·3; H, 5·8; N, 28·75; Cl, 14·6%), $\lambda_{max.}$ (in 0·1N-HCl) 245 (ε 18,900) and 285 mμ (ε 9200), $\lambda_{min.}$ 262 mμ (ε 5000).

6-*Dimethylamino*-9-2′-*hydroxyethylpurine hydrochloride.* 6-Dimethylamino-9-2′-hydroxyethylpurine[1] was taken up in ethanol saturated with hydrochloric acid. Removal of the solvent and crystallisation of the residue from methanol gave the *hydrochloride* as needles, m. p. 223—225° (Found: C, 44·5; H, 5·3; N, 28·5; Cl, 14·6. $C_9H_{13}ON_5$,HCl requires C, 44·3; H, 5·8; N, 28·75; Cl, 14·6%), $\lambda_{max.}$ (in 0·1N-HCl) 268 mμ (ε 14,200), $\lambda_{min.}$ 235 mμ (ε 3000).

I am indebted to Miss J. M. Wiseman for the ultraviolet absorption data and to Mr. M. H. Black for technical assistance. The work has been supported by grants to this Institute from the British Empire Cancer Campaign, the Jane Coffin Childs Memorial Fund for Medical Research, the Anna Fuller Fund and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

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[*Received, August* 13*th*, 1959.]

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[4] Martin and Mathieu, *Tetrahedron*, 1957, **1**, 75.

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188. *Absorption Spectra of Oximes from Acetoacetamides.*

By J. S. Dave and A. M. Talati.

Naik, Trivedi, and Mankad[1] reported the ultraviolet absorption spectra of unsubstituted and *N*-aryl-α-chloro- and -α-hydroxyimino-acetoacetamides in aqueous solution. We now report similar data for *N*-aryl-α-hydroxyiminoacetoacetamides and their β-oximes in water and alcohol.

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[1] Naik, Trivedi, and Mankad, *J. Indian Chem. Soc.*, 1943, **20**, 407, 414.

N-Aryl-αβ-bishydroxyiminobutyramides in water have $\lambda_{max.}$ 228—240 mμ (see Table), attributed to the crossed conjugation in ·C(:N·OH)·C(:N·OH)·C(:O)·NHAr. A *para*-substituent (OEt, Cl) increases the polarity and the length of the absorbing system and so causes a shift of the band to red. An *ortho*-substituent (Me, Cl) is, however, in a " side chain " of the absorbing system, so the band is unaffected or moves to shorter wavelength.

These oximes have nearly the same $\lambda_{max.}$ in water as in alcohol, indicating the absence of solvent–solute interaction. It is suggested that hydrogen-bonded chelate rings may be present in the solute molecules.

N-Aryl-α-hydroxyiminoacetoacetamides absorb maximally in the same region in aqueous and alcoholic solution. Replacement of $>C:N\cdot OH$ by $>C:O$ causes a shift of 0—8 mμ. These mono-oximes have a second band, at 264—285 mμ in aqueous, but not in alcoholic solution.

Experimental.—The *N*-aryl-α-hydroxyiminoacetoacetamides (see Table) were prepared by slow addition of a solution of sodium nitrite and the arylamide in sodium hydroxide to an excess of ice-cold sulphuric acid (cf. Knorr [2]). The precipitates were filtered off and recrystallised from aqueous alcohol. These *oximes* were converted into the *dioximes* by Knorr and Reuter's method.[3]

	N (%)			In H_2O		In MeOH	
Aryl	Found	Reqd.	M. p.	$\lambda_{max.}$ (mμ)	*E*	$\lambda_{max.}$ (mμ)	*E*
			N-*Aryl-α-hydroxyiminoacetoacetamides*				
Ph †	—	—	99—100° [1, 2]	237—239	14,570	236—238	18,940
				280—281	9043		
o-C_6H_4Me †	—	—	130 [1]	224—227	14,940	—	—
				264—268 *	3900—4000		
o-C_6H_4Cl †	11·5	11·6	122	231—233	17,800	231—233	17,280
				280—281	9759	264 *	6233 *
o-$MeO\cdot C_6H_4$ †	12·0	11·9	131—132	233—235	23,620	—	—
				282—284	9840		
p-C_6H_4Cl	11·6	11·6	178	—	—	242—246	21,220
p-$EtO\cdot C_6H_4$ †	11·8	11·2	117—118	—	—	241—244	18,310
2,4-$C_6H_3Me_2$ †	12·2	12·0	136	268—276 *	4800—4900	—	—
			N-*Aryl-αβ-bishydroxyiminobutyramides*				
Ph	—	—	192 [3]	233—234	19,820	236—238	25,930
o-C_6H_4Me	17·5	17·9	195	230—231	18,820	—	—
o-C_6H_4Cl	16·9	16·4	144	231—232	18,660	—	—
p-C_6H_4Cl	16·25	16·4	203—204	238—239	18,090	—	—
p-EtO-C_6H_4	16·1	15·8	202—203	234—239	21,330	235—240	12,290
2,4-$C_6H_3Me_2$	17·0	16·9	194—195	228—231	18,630	230—232	20,300
				310—320 *	9454		

* Inflexion. † Yellow (others colourless).

Ultraviolet absorption spectra of aqueous and alcoholic solutions were investigated with a Beckman model DU spectrophotometer.

The authors thank Messrs. National Carbon Ltd. for the gift of chemicals and Professor S. M. Sethna for his interest in the work. One of them (A. M. T.) is indebted to the Dean, Faculty of Technology and Engineering, for facilities.

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[*Received, August* 17*th*, 1959.]

[2] Knorr, *Annalen*, 1887, **236**, 80.
[3] Knorr and Reuter, *Ber.*, 1894, **27**, 1169.

189. *Pyrolytic Formation of* p-*Diacetylbenzene from Vinyl* p-*Acetylbenzoate.*

By P. D. RITCHIE and A. E. WRIGHT.

ALLAN, IENGAR, and RITCHIE[1] found that 2-benzoyloxyethyl terephthalate (I) yielded no detectable amount of *p*-diacetylbenzene (III) on pyrolysis at 400—500°, even though earlier work[2] had indicated the very strong probability that the various competitive thermal breakdown-reactions of ester (I) would include the annexed sequence.

$$\text{(I) } BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OBz \xrightarrow[A^1]{-BzOH} BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH{:}CH_2 \xrightarrow[A^1]{-BzOH}$$

$$CH_2{:}CH{\cdot}O_2C{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH{:}CH_2 \xrightarrow[R/C^1]{-CO} \underset{\text{(II)}}{CH_2{:}CH{\cdot}O_2C{\cdot}C_6H_4{\cdot}COMe} \xrightarrow[R/C^1]{-CO} Me{\cdot}CO{\cdot}C_6H_4{\cdot}COMe\text{-}p \text{ (III)}$$

In explanation, it was suggested[1] that: " Either . . . the diketone is produced in amounts too small to be detected (owing to predominating destruction of its precursor . . .), or the R/C^1 breakdown of one vinyl ester group so modifies the electronic structure of the (unsymmetrical) product, vinyl *p*-acetylbenzoate, that the second vinyl ester group breaks down preferentially by one of the other competitive routes." The former explanation was preferred, and this view is now confirmed. Vinyl *p*-acetylbenzoate (II) has been prepared and characterised; on pyrolysis at *ca.* 500° (vapour phase) it yields a pyrolysate containing *p*-diacetylbenzene as a major component. Other predictable[1,2] products were also observed (carbon monoxide and dioxide, acetylene, *p*-acetylbenzoic acid, acetophenone, and an acid anhydride).

Experimental.—Apparatus and procedure were those described previously.[1,2]

p-Diacetylbenzene, prepared, as a reference standard, as described previously,[1] had b. p. 120°/1 mm., m. p. 114° (lit.,[3] m. p. 114°). It yielded a 2,4-*dinitrophenylhydrazone*, orange needles, m. p. 233—234° (from acetic acid) (Found: C, 56·0; H, 4·4; N, 16·0. $C_{16}H_{14}O_5N_4$ requires C, 56·1; H, 4·1; N, 16·4%).

Preparation of p-*acetylbenzoic acid.* 4-Ethylacetophenone was oxidised to *p*-ethylbenzoic acid by aqueous sodium hypochlorite: the reagent prepared according to Newman and Holmes[4] gave 90—95% yields but that prepared according to Emerson and Deebel[5] only *ca.* 15%. The acid was converted into its methyl ester: this was oxidised to methyl *p*-acetylbenzoate by air in presence of chromium sesquioxide–calcium carbonate.[5] The product was purified by distillation: alkaline hydrolysis yielded *p*-acetylbenzoic acid, m. p. 208° (lit.,[6] m. p. 208°). It yielded a 2,4-dinitrophenylhydrazone as orange needles (from glacial acetic acid), m. p. *ca.* 280° (decomp.) [Allan[7] gives m. p. 280° (decomp.)] (Found: C, 52·7; H, 4·0; N, 16·4. Calc. for $C_{15}H_{12}O_6N_4$: C, 52·3; H, 3·5; N, 16·3%). Various other recorded preparations[8] gave very poor yields of the acid.

Preparation of vinyl p-*acetylbenzoate.* Standard ester-exchange methods[9] were used. *p*-Acetylbenzoic acid (50 g.) and vinyl acetate (172 g.) were shaken for 30 min. with mercuric acetate (1·3 g.): concentrated sulphuric acid (0·13 ml.) was then added dropwise, and the whole was refluxed for 9 hr. and left overnight. The filtered solution was treated with sufficient sodium acetate to neutralise free sulphuric acid; excess of vinyl acetate was removed under reduced pressure (nitrogen atmosphere) and the residue fractionally distilled, yielding fractions (i) b. p. 50—60°/18 mm., (ii) b. p. 128—138°/4 mm., and (iii) b. p. 138—150°/4 mm. Fraction (i) was acetic acid: fractions (ii) and (iii) solidified to crude vinyl *p*-acetylbenzoate, from which 8 g. (14%) of the pure *ester* were obtained as colourless needles (from methanol), m. p. 88°. A second preparation, with a reflux period of 18 hr., gave a yield of 38% [Found: C, 69·5;

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[1] Allan, Iengar, and Ritchie, *J.*, 1957, 2107.
[2] Allan, Forman, and Ritchie, *J.*, 1955, 2717; Allan, Jones, and Ritchie, *J.*, 1957, 524.
[3] Ingle, *Ber.*, 1894, **27**, 2527.
[4] Newman and Holmes, *Org. Synth.*, 1937, **17**, 65.
[5] Emerson and Deebel, *ibid.*, 1952, **32**, 81.
[6] Fichter and Meyer, *Helv. Chim. Acta*, 1925, **8**, 255.
[7] Allan, Ph.D. Thesis, Glasgow University, 1956, p. 102.
[8] Raadsveld, *Rec. Trav. chim.*, 1922, **41**, 657; Ahrens, *Ber.*, 1887, **20**, 2956.
[9] Burnett and Wright, *Trans. Faraday Soc.*, 1953, **49**, 1108.

H, 5·7%; *M* (cryoscopic in benzene), 196. Calc. for $C_{11}H_{10}O_3$: C, 69·5; H, 5·3%; *M*, 190]. The ester decolorises bromine water and aqueous potassium permanganate: it is sparingly soluble in ether, cold methanol, and hot light petroleum (b. p. 60—80°), and very soluble in benzene and hot methanol. It has major infrared absorption bands at *ca.* 1264s, 1195m, 1188m, 1170m, 1107s, 1025m, 956m, 950m, 882m, and 865m cm.$^{-1}$. It yields a 2,4-*dinitrophenylhydrazone* as orange needles, m. p. 221°, from glacial acetic acid (Found: C, 55·0; H, 4·3. $C_{17}H_{14}O_6N_4$ requires C, 55·1; H, 3·8%).

Pyrolysis of vinyl p-*acetylbenzoate.* The general experimental results for two runs are summarised in the Table.

Pyrolysis of vinyl p-*acetylbenzoate at* 500°.

Run no.	1	2	Run no.	1	2
Feed-rate (g./min.)	0·18	0·15	Compn. of pyrolysate (*c*) (%)		
Residence time (sec.)	52	151	CO	79·0	75·7
Wt. pyrolysed (g.)	24·5	41·5	CO_2	5·5	11·7
(*a*) In main receiver	22·5	34·5	Unsatd. hydrocarbons	15·5	13·4 *
(*b*) In cold trap	Nil	Nil			
(*c*) Gaseous pyrolysate (l.)	0·9	2·9			

* Including acetylene, 1·7%.

Run 1. Product (*a*), a pale yellow pasty solid, which contained an acid anhydride (Davidson–Newman test [10]), was treated with ether. The insoluble residue was *p*-acetylbenzoic acid: the same product was obtained from the ether-soluble portion by extraction with aqueous potassium carbonate (m. p. and mixed m. p. 207—208°: total acid recovered, *ca.* 2 g.). The residue from the ether-soluble fraction, on distillation, yielded (i) 12·5 g., b. p. 106°/1 mm. (solidified), (ii) 1 g., b. p. 106—112°/1 mm. (remained liquid), and (iii) a residue. Fraction (i) was unchanged ester (mixed m. p. 87°). After several days, the liquid fraction deposited 0·1 g. of *p*-diacetylbenzene (mixed m. p. 112—113°).

A small portion of product (*a*) was converted into a mixture of the 2,4-dinitrophenyl hydrazones of all carbonyl compounds present: and this crude mixture was examined by paper chromatography (Burton method [11]). By using reference samples of *p*-acetylbenzoic acid, vinyl *p*-acetylbenzoate, and *p*-diacetylbenzene, all these compounds were identified in the pyrolysate (*a*), the eluant employed being acetone (20%) in light petroleum (b. p. 60—80°) (80%). The spot corresponding to the diketone was not moved by this eluant. There were also two unidentified spots.

Run 2. Product (*a*), worked up as for run 1, again yielded *p*-acetylbenzoic acid; after its removal, distillation of the residue yielded (i) 7·2 g., b. p. 130—135°/4 mm. (solidified), (ii) 0·5 g., b. p. 130—135°/4 mm. (liquid), (iii) 19 g., b. p. 135—140°/4 mm. (solidified), and (iv) a dark brown residual tar. Fraction (i) was unchanged ester, which was also present in fraction (ii) along with acetophenone (infrared spectrum); fraction (iii) was *p*-diacetylbenzene (mixed m. p.).

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[*Received, August* 20*th*, 1959.]

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[10] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.
[11] Burton, *Chem. and Ind.*, 1954, 576.

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190. *Syntheses of Some Benzylcycloalkanes.*

By D. W. Hughes and John C. Roberts.

In connexion with other work, we required some benzyl-cyclopropanes and -cyclobutanes, the aryl group carrying one or more methoxyl substituents. At the time, no compounds of this type appeared to have been made. We now report syntheses for four such compounds by the route:

$$\underset{\text{(I)}}{\text{R·CO·Ar}} \xrightarrow[\text{reduction}]{\text{Modified Wolf–Kishner}} \underset{\text{(II)}}{\text{R·CH}_2\text{Ar}}$$

(a; R = cyclobutyl, Ar = *p*-MeO•C_6H_4)
(b; R = 1-1′-methylcyclopropyl, Ar = *p*-MeO·C_6H_4)
(c; R = cyclobutyl, Ar = 2,4-dimethoxyphenyl)
(d; R = cyclobutyl, Ar = 3,5-dimethoxyphenyl)

The ketones (Ia, c, and d) were synthesized from cyclobutyl cyanide and a Grignard reagent prepared from the appropriate aryl halide. The structures of these ketones and of the final products (IIa, c, and d) are therefore unambiguous.

The ketone (Ib) was conveniently prepared by a Friedel–Crafts reaction between anisole and the acid chloride prepared from 1-methylcyclopropane-1-carboxylic acid. The orientation of this ketone was established by oxidation of its reduction product (IIb) to *p*-anisic acid. The possibility that the cyclopropane ring had opened, during the acid conditions obtaining in this route, and that the ketone and the final product possessed ethylenic structures, was excluded by the following observations: first, the product (IIb) gave no detectable reaction (during 40 min.) with cold, aqueous, alkaline potassium permanganate; secondly, it did not react with monoperphthalic acid (during a time when anethole consumed one equivalent); thirdly, attempted ozonolysis of the substance yielded no volatile carbonyl compounds.

Experimental.—Cyclobutyl cyanide. Cyclobutanecarboxylic acid[1] was converted[2] *via* the acid chloride (prepared by using thionyl chloride) into the amide. Distillation of a mixture of the amide and phosphoric oxide gave[3] cyclobutyl cyanide, b. p. 146—149°, in an overall yield of 40% (based on the acid). An alternative method[4] proved less convenient and gave a lower overall yield.

4-*Methoxybenzylcyclobutane* (IIa). Cyclobutyl cyanide (2·9 g.) in dry ether (20 ml.) was added to a Grignard reagent prepared from *p*-bromoanisole (18 g.) and magnesium (2·7 g.) in dry ether (35 ml.). The mixture was stirred for 2 hr. and left overnight, and the complex was decomposed with ice (80 g.) and concentrated hydrochloric acid (50 ml.) to give an aqueous solution of the imine hydrochloride which was heated under reflux for 1 hr. The ketone (Ia) separated as an oil which was collected in ether and distilled, the fraction boiling at 92—96°/0·1 mm. being collected (5·1 g., 70%). The 2,4-*dinitrophenylhydrazone* crystallised from ethanol in red plates, m. p. 200° (Found: C, 58·0; H, 4·9; N, 15·5. $C_{18}H_{18}O_5N_4$ requires C, 58·4; H, 4·9; N, 15·1%), and the *semicarbazone* from aqueous methanol in needles, m. p. 162° (Found: C, 63·1; H, 6·9; N, 17·1. $C_{13}H_{17}O_2N_3$ requires C, 63·1; H, 6·9; N, 17·0%). The semicarbazone (4·1 g.), potassium hydroxide (3·3 g.), 80% hydrazine hydrate (2·3 ml.), and diethylene glycol (21 ml.) were heated under reflux for 2 hr. Water and some oil were distilled off until the temperature reached 195°. The remaining liquid was heated under reflux for a further 4 hr., cooled, combined with the distillate, and diluted with water, and the product was isolated by extraction with ether. 4-*Methoxybenzylcyclobutane* (IIa) was obtained (2·5 g., 85%), having b. p. 146—147°/25 mm. (Found: C, 82·0; H, 9·3; OMe, 18·0. $C_{11}H_{13}{\cdot}OMe$ requires C, 81·8; H, 9·2; OMe, 17·6%). Heating this compound under reflux with hydriodic acid (*d* 1·7) and glacial acetic acid, gave 4-*hydroxybenzylcyclobutane* which, after two distillations at 100° (bath)/0·1 mm., formed colourless needles, m. p. 35—37° (Found: C, 81·0; H, 8·4. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%). Oxidation of this phenol with cold chromic–sulphuric acid yielded succinic acid.

2,4-*Dimethoxybenzylcyclobutane* (IIc). The ketone (Ic) was prepared, by a method similar to that described above, from cyclobutyl cyanide (3·0 g.) and a Grignard reagent made from 1-iodo-2,4-dimethoxybenzene[5] (28·5 g.) and magnesium (2·62 g.) in dry ether (70 ml.). The crude product was distilled and the fraction of b. p. 138—140°/1·5 mm. was chilled and then crystallised from light petroleum (b. p. 40—60°) to yield the *ketone* (Ic) as prisms (4·1 g., 50%), m. p. 43° [Found: C, 71·3; H, 7·4; OMe, 29·1. $C_{11}H_{10}O(OMe)_2$ requires C, 70·9; H, 7·3; OMe, 28·2%]. The 2,4-*dinitrophenylhydrazone* crystallised from methanol in orange needles, m. p. 106° (Found: C, 57·3; H, 5·0; N, 13·9. $C_{19}H_{20}O_6N_4$ requires C, 57·0; H, 5·0; N, 14·0%). Reduction of the ketone, by the modified Wolff–Kishner method,[6] gave (in 68% yield) the *cyclobutane derivative* (IIc), b. p. 170—172°/22 mm. (Found: C, 75·5; H, 9·1. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

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[1] *Org. Synth.*, Coll. Vol. III, p. 213.
[2] Perkin, *J.*, 1894, **65**, 957.
[3] Freund and Gudeman, *Ber.*, 1888, **21**, 2696.
[4] Carpenter and Perkin, *J.*, 1899, **75**, 932.
[5] Kauffmann and Kieser, *Ber.*, 1912, **45**, 2334.
[6] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

1-*Bromo*-3,5-*dimethoxybenzene*. This was prepared from 3,5-dimethoxybenzamide[7] by successive Hofmann and Sandmeyer reactions.[8]

3,5-*Dimethoxybenzylcyclobutane* (IId). Reaction of cyclobutyl cyanide (0·7 g.) with a Grignard reagent prepared from magnesium (0·24 g.) and 1-bromo-3,5-dimethoxybenzene (2·1 g.) in dry ether (10 ml.) gave (in 30% yield) the *ketone* (Id), b. p. 190° (bath)/20 mm., which crystallised from light petroleum (b. p. 40—60°) in prisms, m. p. 77—78°, raised to 79° after sublimation at 70°/2 mm. [Found: C, 70·8; H, 6·9; OMe, 28·6. $C_{11}H_{10}O(OMe)_2$ requires C, 70·9; H, 7·3; OMe, 28·2%]. Reduction of this ketone gave the *product* (IId) (yield, 55%), b. p. 185° (bath)/24 mm. (Found: C, 75·7; H, 8·8%).

1-*Chlorocarbonyl*-1-*methylcyclopropane*. Methyl 1-methylcyclopropanecarboxylate[9] was hydrolysed[10] to the acid, which was converted, in 55% yield, into the acid chloride, b. p. 132—134°, by means of thionyl chloride.

1-4′-*Methoxybenzyl*-1-*methylcyclopropane* (IIb). The foregoing acid chloride (19 g.) in dry carbon disulphide (15 ml.) was added dropwise, during ¾ hr., to a stirred and ice-cooled mixture of anisole (17·5 g.), aluminium chloride (29 g.), and dry carbon disulphide (47 ml.). After having been stirred for a further 2 hr., the mixture was poured on ice and concentrated hydrochloric acid. The product (impure Ib; 18 g.), isolated in the usual way, was an oil, b. p. 124—129°/0·5 mm. The 2,4-*dinitrophenylhydrazone* crystallised from ethanol or from benzene in red plates, m. p. 236° (Found: C, 58·6; H, 4·9; N, 15·1. $C_{18}H_{18}O_5N_4$ requires C, 58·4; H, 4·9; N, 15·1%). The main portion (17 g.) of the product was converted into the *semicarbazone* which formed, after repeated crystallisation from methanol, colourless needles (5·0 g., 14%), m. p. 174—175° (Found: C, 63·3; H, 7·0; N, 17·0. $C_{13}H_{17}O_2N_3$ requires C, 63·1; H, 6·9; N, 17·0%). This semicarbazone was converted, as described above for the preparation of (IIa), into the *product* (IIb) (yield 45%), b. p. 116—118°/12 mm. (Found: C, 81·5; H, 8·8. $C_{12}H_{16}O$ requires C, 81·8; H, 9·2%). Oxidation of this compound with hot, aqueous, alkaline potassium permanganate solution gave *p*-anisic acid (30%), m. p. and mixed m. p. 182°.

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[7] Suter and Weston, *J. Amer. Chem. Soc.*, 1939, **61**, 232.
[8] Dean and Whalley, *J.*, 1954, 4638.
[9] Siegel and Bergstrom, *J. Amer. Chem. Soc.*, 1950, **72**, 3815.
[10] Kohn and Mendelewitsch, *Monatsh.*, 1921, **42**, 241.

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191. *The Skraup Reaction with 2-Aminobiphenyl.*

By D. H. HEY and C. W. REES.

THERE is wide variation in the reported melting points of 8-phenylquinoline and its picrate. The base has been described as an oil[1,2,3,4] and as a solid with m. p. 48—49°[5,6] and its monopicrate as having m. p. *ca.* 210°,[2] 200°,[3] and 156°.[6] These differences prompted a re-examination of the preparation described by Hey and Walker.[3] An exact repetition of their Skraup reaction with 2-aminobiphenyl gave, on fractionation of the resulting oil, two components. The first was shown to be 8-hydroxyquinoline and the second 8-phenylquinoline, obtained as a solid, m. p. 48°, with a picrate of m. p. 154°. The picrate with m. p. 200° reported[3] for 8-phenylquinoline was actually that of the unexpected 8-hydroxyquinoline (picrate, m. p. 205°), and a second lower-melting picrate obtained in greater yield in the same preparation, and thought to be impure, had m. p. 154°, and was in fact the picrate of 8-phenylquinoline. Hey and Walker's method[3] thus readily gave a 60% yield of crystalline 8-phenylquinoline, m. p. 48° (picrate, m. p. 154°; methiodide, m. p. 174°). The 8-hydroxyquinoline was identified by its reactions (ferric chloride), analysis, mixed melting point determination, and infrared comparison with an authentic sample.

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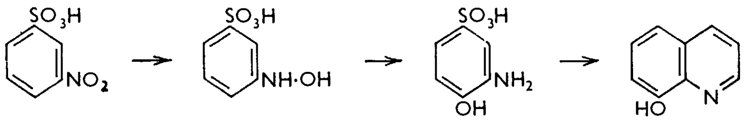
[1] LaCoste and Sorger, *Annalen*, 1885, **230**, 38.
[2] Möhlau and Berger, *Ber.*, 1893, **26**, 2004.
[3] Hey and Walker, *J.*, 1948, 2213.
[4] Kaslor and Hayek, *J. Amer. Chem. Soc.*, 1951, **73**, 4986.
[5] Bergstrom, *J. Org. Chem.* 1939, **3**, 424.
[6] Avramoff and Sprinzak, *J. Org. Chem.*, 1957, **22**, 573.

With regard to the genesis of 8-hydroxyquinoline from carefully purified 2-aminobiphenyl, sodium *m*-nitrobenzenesulphonate, glycerol, and sulphuric acid, it was found that, when the nitro-compound was replaced by arsenic pentoxide as oxidising agent, no 8-hydroxyquinoline was formed, but when replaced by nitrobenzene 8-hydroxyquinoline was again formed, together with 6-hydroxyquinoline, 8-phenylquinoline, and a small amount of quinoline. Furthermore, 8-phenylquinoline did not yield any hydroxyquinolines when heated with sulphuric acid alone, under the reaction conditions, but if it was treated with sulphuric acid, glycerol, and sodium *m*-nitrobenzenesulphonate some 8-hydroxyquinoline was formed. These facts suggested that the 8-hydroxyquinoline arose from a reaction between the reagents used in the Skraup reaction, not involving the aromatic amine; and indeed, when the sulphonate, glycerol, and sulphuric acid were heated together, 8-hydroxyquinoline was formed, though in smaller yield than in the presence of the amine. No 6-hydroxyquinoline was detected in this case.

The formation of quinolines directly from nitro-compounds in the Skraup reaction has only been observed with certain nitrophenols; *e.g.*, 8-hydroxyquinoline was prepared in small yield by heating *o*-nitrophenol with glycerol and sulphuric acid.[7] The formation of 6- and 8-hydroxyquinoline from aniline, nitrobenzene, glycerol, and sulphuric acid has been reported by Sucharda and Mazonski,[8] who assumed that the nitrobenzene was reduced to phenylhydroxylamine, probably by 1,2-dihydroquinoline formed from the aniline, which then rearranged to *o*- and *p*-aminophenol, which underwent ring-closure to 8- and 6-hydroxyquinoline, respectively. Our isolation of 8-hydroxyquinoline in experiments with no aromatic amine initially present may be explained similarly, but shows that a dihydroquinoline is not essential, the initial reducing agent presumably being acraldehyde. However, this appears to be a less effective reducing agent, since the yields of hydroxyquinolines are much smaller in the absence of added amine. In the formation of 8-hydroxyquinoline from sodium *m*-nitrobenzenesulphonate the necessary desulphonation must have taken place after reduction of the nitro-group and rearrangement of the hydroxylamine, since only 8-hydroxyquinoline was formed, whilst from nitrobenzene both 6- and 8-hydroxyquinoline were formed, the 6-isomer predominating. These facts lead to the overall reaction scheme shown. The formation [9] of 8-hydroxyquinoline by a Skraup reaction on 3-amino-4-hydroxybenzenesulphonic acid supports this, although, in contrast, *m*-hydroxyaminobenzenesulphonic acid is said [10] to rearrange when heated with *dilute* sulphuric acid to 5-amino-2-hydroxybenzenesulphonic acid which could yield 6-hydroxyquinoline and not the 8-isomer.



Experimental.—The light petroleum used had b. p. 40—60°. The 2-aminobiphenyl was recrystallised from light petroleum and melted sharply at 50°. Glycerol was dried by heating at 180°.

Skraup reactions with 2-*aminobiphenyl.* (i) The method of Hey and Walker [3] was repeated on twice the scale described and the resulting oil was fractionated to give fractions, (*a*) b. p. 140—145°/16 mm. (0·5 g.), and (*b*) b. p. 196—200°/16 mm. (4·84 g.). Fraction (*a*) solidified and had m. p. 58—63°, raised to 73° on crystallisation from light petroleum (Found: C, 74·9; H, 4·8; N, 9·6. Calc. for C_9H_7ON: C, 74·5; H, 4·9; N, 9·65%), and gave a picrate, m. p. 205° (Found: C, 48·4; H, 3·2. Calc. for $C_9H_7ON,C_6H_3O_7N_3$: C, 48·1; H, 2·7%). It gave an intense green-black colour with ferric chloride. A mixed m. p. with 8-hydroxyquinoline was undepressed and their infrared spectra were superposable. Fraction (*b*) solidified and had m. p. 42—46°, raised

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[7] Ghosh, Banerjee and Lasker, *J. Indian Chem. Soc.*, 1944, **21**, 354.

[8] Sucharda and Mazonski, *Ber.*, 1936, **69**, 2719.

[9] Claus, *J. prakt. Chem.*, 1890, **41**, 32.

[10] Raschig, "Schwefel und Stickstoffstudien," Leipzig–Berlin, 1924, p. 268; *Chem. Zentr.*, 1924, II, 1082.

to 48° by crystallisation from light petroleum (Found: C, 88·5; H, 5·65. Calc. for $C_{15}H_{11}N$: C, 87·8; H, 5·4%), and gave a picrate, m. p. 154° (Found: C, 58·8; H, 2·9. Calc. for $C_{15}H_{11}N,C_6H_3O_7N_3$: C, 58·1; H, 3·25%), a methiodide, m. p. 174° (Found: C, 55·3; H, 4·45. Calc. for $C_{16}H_{14}NI$: C, 55·3; H, 4·0%), and a dichromate, m. p. 130—131° (decomp.). LaCoste and Sorger [1] reported m. p. 163° for the methiodide and m. p. 125—126° for the dichromate of 8-phenylquinoline.

(ii) 2-Aminobiphenyl (7 g.), anhydrous glycerol (10 ml.), and arsenic pentoxide (7 g.) were intimately mixed and heated to 100° in an oil-bath. Concentrated sulphuric acid (8 ml.) was added in 30 min. and the bath-temperature was then slowly raised to 160° and held there for 7 hr. The mixture was cooled to 100°, poured on ice, and treated as in (i), to yield 8-phenylquinoline (4·7 g., 56%) only. No 8-hydroxyquinoline could be detected with ferric chloride.

(iii) The method of Hey and Walker [3] was followed, but sodium *m*-nitrobenzenesulphonate was replaced by an equivalent amount of purified nitrobenzene. After the reaction mixture had been poured on ice the solution was neutralised and extracted with chloroform. The extracts were dried ($MgSO_4$), and the chloroform was removed. The resulting oil (3·9 g.) was distilled under reduced pressure and fractions were collected at: (*a*) b. p. 110—125°/16 mm. (0·1 g.); (*b*) b. p. 145—155°/16 mm. (0·1 g.); (*c*) b. p. 170—200°/16 mm. (1·65 g.). Fraction (*a*) was quinoline (picrate, m. p. and mixed m. p. 203°), and fraction (*b*) was 8-hydroxyquinoline (picrate, m. p. and mixed m. p. 205°). Fraction (*b*) gave an intense dark green colour with ferric chloride. Fraction (*c*) was a mixture of 8-phenylquinoline (m. p. and mixed m. p. 47°) and 6-hydroxyquinoline, which were separated by extraction of an ethereal solution of the mixture with aqueous sodium hydroxide. The 6-hydroxyquinoline had m. p. 188—192°, raised to 195° by crystallisation from water, gave a picrate of m. p. 235°, and coupled with benzenediazonium chloride to give a red dye.

Action of concentrated sulphuric acid on 8-phenylquinoline. 8-Phenylquinoline (0·5 g.) was heated with concentrated sulphuric acid (3 ml.) at 160° and at intervals portions were removed, diluted with water, neutralised with aqueous sodium hydroxide, and tested with ferric chloride. No 8-hydroxyquinoline was formed in 8 hr.

8-Phenylquinoline subjected to the conditions of the Skraup reaction. The reaction was performed as before,[3] but 2-aminobiphenyl was replaced by 8-phenylquinoline (2 g.). The product, isolated as before, was dissolved in ether and extracted with aqueous sodium hydroxide which, on neutralisation, gave 8-hydroxyquinoline (0·1 g.); this was identified by its m. p. and the m. p. and mixed m. p. of its picrate. 8-Phenylquinoline (1·2 g.) was recovered from the ethereal solution.

Reaction of sodium m-*nitrobenzenesulphonate with glycerol and sulphuric acid.* Sodium *m*-nitrobenzenesulphonate (8 g.), anhydrous glycerol (9 ml.), and concentrated sulphuric acid (7 ml.) were thoroughly mixed and heated very slowly to 130° (bath-temperature), held at this temperature for 2 hr., and then heated for a further 5 hr. at 170°. (More rapid heating causes extensive carbonisation.) The mixture was cooled, diluted with water, neutralised with sodium hydroxide, and extracted with chloroform. The chloroform solution was treated with charcoal, dried ($MgSO_4$), and evaporated. The residue was dissolved in a small volume of 2N-sodium hydroxide, which was filtered and neutralised. The solid which separated was dried and crystallised from light petroleum as white needles of 8-hydroxyquinoline (0·04 g.), m. p. 74°, which gave a picrate of m. p. and mixed m. p. 205°.

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192. *Sodium and Lithium Hexafluororuthenates*(V).

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ALTHOUGH the hexafluororuthenates M(I)Ru(V)F_6 are known [1] for M = K, Cs, Ag, or Tl, previous attempts to prepare the sodium salt have been unsuccessful and it was presumed that $NaRuF_6$ was completely solvolysed in solution in bromine trifluoride; it was considered that an important factor in the solvolysis was the small size of the cation. The method of preparation attempted previously involved treating a 1 : 1 mixture of metallic ruthenium and alkali-metal bromide or chloride with bromine trifluoride. We have found that treatment of a mixture of a slight excess of ruthenium trichloride and sodium or lithium chloride with bromine trifluoride yields the appropriate hexafluororuthenate(v). Hepworth, Peacock, and Robinson [1] record that the reaction between metallic ruthenium and bromine trifluoride is extremely vigorous and it is possible that under the conditions used for their preparation the ruthenium pentafluoride was entirely removed from solution before combination could take place with the base. The procedure used in the rest of the preparation was the same as that in the present work. Ruthenium trichloride reacts with bromine trifluoride quietly and the salts were obtained as cream-coloured, hygroscopic solids on removal of excess of solvent.

The salts are rhombohedral, having the $NaOsF_6$ structure, and it has been found that lithium hexafluoro-osmate(v) and hexafluoroiridate(v) are also isomorphous with sodium hexafluoro-osmate(v). The lattice constants are given in the Table. Infrared spectra confirm the existence of the appropriate $M(v)F_6^-$ ions in these salts. The extra peaks observed in the spectra of some of the lithium and sodium salts may be due to slight distortions of the MF_6^- octahedra by the strongly polarising cations.

Unit cell constants for rhombohedral unit cells.

	RuF_6^-	OsF_6^-	IrF_6^-
Na	a = 5·80 Å [a]	a = 5·80 Å [b]	a = 5·80 Å [b]
	α = 54° 32′	α = 55° 10′	α = 55° 10′
Li	a = 5·39 Å [a]	a = 5·41 Å [a]	a = 5·41 Å [a]
	α = 56° 2′	α = 56° 2′	α = 56° 2′

[a] Present work. [b] Jack, personal communication.

Experimental.—Preparations. Sodium chloride or lithium chloride (from lithium carbonate) mixed with a slight excess of ruthenium trichloride was treated with excess of bromine trifluoride. The excess of solvent was removed and the products were heated to 140° *in vacuo* to remove all traces of bromine trifluoride. There is only slight decomposition at this temperature. Analysis was by decomposition with alkali followed by ignition of the hydrated oxide in hydrogen [Found for *sodium hexafluororuthenate*(v): Ru, 43·1%; equiv. (based on alkali halide), 211. $NaRuF_6$ requires Ru, 42·6%; equiv., 239. Found, for *lithium hexafluororuthenate*(v): Ru, 46·2%; equiv., 244. $LiRuF_6$ requires Ru, 45·7%; equiv., 223].

Hexafluoro-osmates(v) and hexafluoroiridates(v) were prepared as described by Hepworth, Robinson, and Westland [2] [Found for sodium hexafluoro-osmate(v): Os, 57·2. Calc. for $NaOsF_6$: Os, 58·1%. Found for lithium hexafluoro-osmate(v): Os, 60·4. Calc. for $LiOsF_6$: Os, 61·2%. Found for lithium hexafluoroiridate(v): Ir, 61·1. Calc. for $LiIrF_6$: Ir, 61·5%].

X-*Ray powder photography.* Unit-cell dimensions are given in the Table. *X*-Ray powder photographs were taken with Cu-K_α radiation; samples were filled into Lindemann glass capillaries, the " dry-box " technique being used for all specimens, and the capillaries were sealed with warm picein wax.

Infrared absorption spectra. Spectra were measured in suspension in Nujol mulls (prepared and kept in the " dry-box ") on a Perkin–Elmer Model 21 spectrometer with potassium bromide optics. Infrared peaks were recorded as follows:

$NaRuF_6$, 636 and 565 cm.$^{-1}$; $LiRuF_6$, 625 and 552 cm.$^{-1}$; $KRuF_6$,[3] 640 cm.$^{-1}$.
$NaOsF_6$, 630 cm.$^{-1}$; $LiOsF_6$, 626 cm.$^{-1}$; $KOsF_6$,[3] 616 cm.$^{-1}$.
$LiIrF_6$, 668 cm.$^{-1}$. $KIrF_6$,[3] 667 cm.$^{-1}$.

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[1] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.
[2] Hepworth, Robinson, and Westland, *J.*, 1954, 4269.
[3] Peacock and Sharp, *J.*, 1959, 2762.