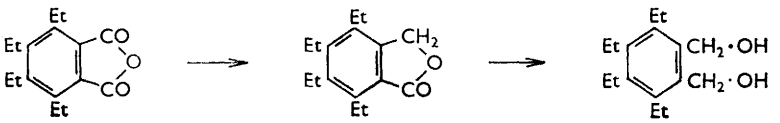
640. *Autoxidation of Hexaethylbenzene.*

By E. G. E. Hawkins and W. F. Maddams.

The autoxidation of hexaethylbenzene, either neat (at 140—170°) or in a solvent, proceeded in a fashion similar to that of tetraisopropylbenzene:[1] the reaction mixture became progressively darker during the oxidation (possibly owing to the formation of phenolic compounds) which ceased after *ca.* 30% conversion of the hydrocarbon.

The product consisted of unchanged hexaethylbenzene (70%), a crystalline compound (2—3%), yellow liquid products (<7·5%), volatile substances (*ca.* 7%), and involatile residue (13%). The crystalline product, which had infrared absorption bands at 910, 1775, 1807, and 1840 cm.$^{-1}$, was shown to be tetraethylphthalic anhydride by (i) analyses of its derivatives with ammonia and with 2,4-dinitrophenylhydrazine, and (ii) its stepwise reduction by lithium aluminium hydride to a phthalide and then a glycol.



The yellow liquid products varied in amount from one oxidation to another, and occasionally only very small quantities were produced. These products, although not satisfactorily separated by use of distillation and chromatography, evidently consisted of a complex mixture of oxidation intermediates. One constituent, boiling lower than hexaethylbenzene, was shown to be an unsaturated, cyclic, aliphatic anhydride by the following evidence: (i) bands at 912, 1778, and 1845 cm.$^{-1}$ (separation of the last two by 67 cm.$^{-1}$) show it to be an anhydride;[2] (ii) the 1778 cm.$^{-1}$ band is much stronger than that at 1845 cm.$^{-1}$, hence the compound must be a cyclic anhydride;[3] (iii) the spectrum has no bands characteristic of an aromatic ring; (iv) the frequencies of the two C=O stretching bands at 1778 and 1845 cm.$^{-1}$ are some 20 cm.$^{-1}$ lower than the average values for saturated cyclic anhydrides, and unsaturation is indicated;[2] failure to add bromine is in line with the behaviour of diethylmaleic anhydride[4] and dimethylmaleic anhydride;[5] (v) the bands of synthetic diethylmaleic anhydride[4] occur at similar frequencies; (vi) it is regenerated on treatment with alkali followed by acid, characteristic of αα′-disubstituted maleic anhydrides;[4,6,7] and (vii) on treatment with lithium aluminium hydride it gave a product with an infrared spectrum similar to that of a phthalide. Although its b. p. was close to that reported for diethylmaleic anhydride, its 2,4-dinitrophenylhydrazine derivative was not identical with that obtained from the latter compound synthesised by Fittig's method.[4] The other liquid products consisted of mixtures of carbonyl compounds: the infrared spectra (ν 1628 cm.$^{-1}$) indicated the presence of 2-hydroxyacetophenones. Unfortunately, no carbonyl derivatives could be obtained owing to steric hindrance (cf. 1,4-diacetyldurene which gives no 2,4-dinitrophenylhydrazone). However, a trace of a yellow solid was isolated from chromatography, and its ultraviolet spectrum and elementary analysis were in agreement with its being tetraethyl-*p*-benzoquinone: a band at 3410 Å ($E^{1\%}_{1\,cm.}$ 10·8) and inflexion at *ca.* 4450 Å ($E^{1\%}_{1\,cm.}$ ~1·17) are characteristic of

[1] Hawkins and Maddams, preceding paper.
[2] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, pp. 127—129.
[3] Bellamy, Connelly, Philpotts, and Williams, *Z. Elektrochem.*, 1960, **64**, 563.
[4] Fittig, *Annalen*, 1877, **188**, 42.
[5] Tarbell and Bartlett, *J. Amer. Chem. Soc.*, 1937, **59**, 407.
[6] Küster, *Annalen*, 1906, **346**, 16.
[7] Couper, Kibler, and Lutz, *J. Amer. Chem. Soc.*, 1941, **63**, 2.

a *p*-benzoquinone, whereas an *o*-benzoquinone has a stronger band between 3800 and 4400 Å ($E^{1\%}_{1cm.}$ ~50). This quinone is presumably derived from a phenolic precursor, *e.g.*, pentaethylphenol, in the same way as 2,6-di-t-butylbenzoquinone is produced from the autoxidation of both 4-methyl-2,6-di-t-butylphenol [8] and 2,4,6-tri-t-butylphenol.[9]

The volatile products consisted of water, formaldehyde, acetaldehyde, acetic acid, propionic acid, methanol, ethanol, esters, and probably hexane-3,4-dione. Some of these products (propionic acid and the hexanedione) indicated considerable oxidative attack on the ring, and others (formaldehyde, acetaldehyde, and acetic acid) could have arisen by scission of the side-chain. Andrews and Keefer [10] noted that the oxidation of hexamethylbenzene with peroxybenzoic acid yielded biacetyl and a compound they thought to be 3,4-dimethylhex-3-ene-2,5-dione, by scission of the benzene ring. The possible sources of related products of low molecular weight from the autoxidation of tetraisopropylbenzene have already been discussed.[1]

Experimental.—Oxidation of hexaethylbenzene. Hydrocarbon (400 g.), containing cobalt and maganese naphthenates (*ca.* 0·5 g. of each) was oxidised at *ca.* 170° (bath) for 55 hr.; the apparent oxygen uptake was 36·8 l. The cold-trap liquid (11·0 g.) was shown by gas chromatography to contain acetaldehyde, acetic acid, methanol, ethanol, propionic acid, ethyl propionate, and some unidentified constituents. It yielded the 2,4-dinitrophenylhydrazones of acetaldehyde (m. p. and mixed m. p. 156—157°) and of hexan-3,4-dione, m. p. 295° (decomp.) (from nitrobenzene) (lit.,[11] 292°) (Found: C, 46·3, 44·75, 44·6; H, 4·05, 3·9, 3·6; N, 22·35, 23·6. Calc. for $C_{18}H_{18}N_8O_8$: C, 45·6; H, 3·8; N, 23·6%). The condenser-trap liquid (15·7 g.) contained formic acid in addition to similar compounds to those in the cold-trap. Distillation of this material gave fractions from which were prepared: (i) the 2,4-dinitrophenylhydrazones of acetaldehyde, formaldehyde, and hexane-3,4-dione; (ii) the phenylurethane of ethanol; and (iii) the *p*-bromophenacyl esters of acetic and propionic acid. The identities of these derivatives (except that of hexane-3,4-dione) were confirmed by mixed m. p.s with authentic samples.

The main reaction product on distillation gave: (1) (306 g.) b. p. 158—180°/13 mm.; (2) (12 g.), b. p. 180—220°/13 mm.; and a black, hard residue (52·5 g.). Fraction 1 consisted largely of hexaethylbenzene and recrystallisation from ethanol–benzene yielded 287 g. of this. Fraction 2, on crystallisation from ethanol, provided *tetraethylphthalic anhydride*, m. p. 142—145° (Found: C, 73·4, 73·7; H, 7·5, 7·7. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%). It had strong absorption bands at 910, 1775, 1807, and 1840 cm.$^{-1}$. It dissolved in sodium hydroxide solution and was re-formed on acidification of the alkaline solution. When heated for several hours on the water-bath with acidified, alcoholic 2,4-dinitrophenylhydrazine it yielded a straw-coloured *derivative*, m. p. 204—206° (Found: C, 59·3, 59·5; H, 5·5, 5·5; N, 12·8, 12·4. $C_{22}H_{24}N_4O_6$ requires C, 60·0; H, 5·45; N, 12·7%). The anhydride was boiled on the bath with concentrated, aqueous ammonia and gave an *imide*, m. p. 195—196·5° (Found: C, 74·6; H, 8·2; N, 5·3. $C_{16}H_{21}NO_2$ requires C, 74·1; H, 8·1; N, 5·4%). Heating with *N*-methylaniline under reflux, followed by cooling, dilution with ether, and washing with hydrochloric acid provided a *derivative*, m. p. 104—106° (Found: C, 78·5, 78·4; H, 7·5, 7·6; N, 3·95, 4·0. $C_{23}H_{27}NO_2$ requires C, 79·1; H, 7·7; N, 4·0%). Reduction of the anhydride was carried out in two stages: (i) the anhydride (2·8 g.) was extracted from a Soxhlet thimble into a stirred suspension of lithium aluminium hydride (1 g.) in refluxing diethyl ether (150 c.c.); when the anhydride had all dissolved the solution was cooled, treated with water and dilute sulphuric acid, and worked up normally. The residue (2·8 g.), on recrystallisation from light petroleum, gave 4,5,6,7-*tetraethylphthalide* (2·3 g.), m. p. 60—61·5° (Found: C, 77·9; H, 9·1. $C_{16}H_{22}O_2$ requires C, 78·05; H, 8·95%), $\nu_{max.}$ 1769 cm.$^{-1}$ (γ-lactone). (ii) The phthalide (0·9 g.) in dry dibutyl ether was heated under reflux for 4 hr. with an excess of lithium aluminium hydride in the same solvent, and finally gave an almost quantitative yield of 3,4,5,6-*tetraethyl*-1,2-*di*(*hydroxymethyl*)*benzene*, m. p. 84—86° (from aqueous ethanol) (Found: C, 76·75; H, 10·4. $C_{16}H_{26}O_2$ requires C, 76·8; H, 10·4%) [*bisphenylurethane*, m. p. 203—204° (from benzene) (Found: C, 73·5; H, 7·5; N, 5·75. $C_{30}H_{36}N_2O_4$ requires C, 73·8; H, 7·4; N, 5·75%)].

[8] Metro, *J. Amer. Chem. Soc.*, 1955, **77**, 2901.
[9] Bickel and Kooyman, *J.*, 1953, 3211.
[10] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 2545.
[11] Freeman and Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 1712.

After the bulk of the crystalline material had been removed from fractions 1 and 2 the mother-liquors were combined, evaporated, and distilled at 12 mm. to give: (i) (2·0 g.), b. p. 103—120°; (ii) (1·4 g.), b. p. 120—130°; (iii) (1·6 g.), b. p. 130—136°; (iv) (2·2 g.), b. p. 136—160°; (v) (13·6 g.), b. p. 160—165°; (vi) (3·6 g.), b. p. 165—177°; (vii) (1·8 g.), b. p. 177—195°; (viii) (4·6 g.), b. p. 195—200°; and residue (2·3 g.). Fraction (i) was separated into acid and neutral parts; the neutral portion probably contained an aromatic ketone ($\nu_{max.}$ 1699 cm.$^{-1}$), whilst the acid portion (0·9 g.) b.p. 205—235°) consisted mainly of an unsaturated, cyclic, aliphatic anhydride ($\nu_{max.}$ 910, 1772, 1842 cm.$^{-1}$) [2,3] and yielded a derivative with 2,4-dinitrophenylhydrazine, m. p. 144—146° (Found: C, 49·8; H, 4·4; N, 16·5. Calc. for $C_{14}H_{14}N_4O_6$: C, 50·3; H, 4·2; N, 16·8%). Fraction (ii) contained the anhydride and a compound having $\nu_{max.}$ 1646 cm.$^{-1}$ (possibly a chelated carbonyl group). Fraction (iii) had *ca.* 70% of this carbonyl compound. Fraction (iv) also contained this compound together with hexaethylbenzene. Fraction (v) also had these two constituents, and from it were obtained crystalline hexaethylbenzene and, on treatment with phenyl isocyanate, a *phenylurethane*, m. p. 190—192° (Found: C, 78·3; H, 8·7; N, 4·25. $C_{23}H_{31}NO_2$ requires C, 78·2; H, 8·8; N, 4·0%). Fraction (vi) had a spectrum with $\nu_{max.}$ 1628 cm.$^{-1}$, probably indicative of a substituted *o*-acetylphenol. Fraction (vii) contained this compound and tetraethylphthalic anhydride which was the major constituent of fraction (viii).

Reduction of these fractions with lithium aluminium hydride in boiling dibutyl ether gave little further information, although the products contained increased amounts of hydroxyl groups (by infrared spectroscopy).

Chromatography on alumina of the non-crystalline products failed to lead to solid materials except for hexaethylbenzene, the anhydride, and a small quantity of a yellow solid, probably *tetraethyl*-p-*benzoquinone*, m. p. 59—61° (Found: C, 76·0; H, 9·7. $C_{14}H_{20}O_2$ requires C, 76·35; H, 9·1%), having an ultraviolet spectrum similar to that reported for tetramethyl-*p*-benzoquinone: [12] a band at 3410 Å ($E^{1\%}_{1\,cm.}$ 10·8) was accompanied by an inflexion at *ca.* 4450 Å ($E^{1\%}_{1\,cm.}$ ~1·7).

The still residue from the distillation of the oxidation products was a black, crisp solid (Found: C, 72·75; H, 6·7; residue 5·0%) having carbonyl groups ($\nu_{max.}$ 1713 and 1775 cm.$^{-1}$: possibly anhydrides) and some hydroxyl content. Attempts to break down suspected anhydride systems by alkali failed to alter appreciably the polymeric nature.

Similar results were obtained on using other catalysts (lead resinate, cobalt, and manganese bromide): oxidation also proceeded in acetic anhydride, propionic acid, and t-butylbenzene but failed in pyridine and acetic acid, possibly owing to the limited temperatures attainable therein.

Diethylmaleic anhydride (*hex*-3-*ene*-3,4-*dicarboxylic anhydride*). This was prepared from citraconic anhydride by the method of Fittig [4] and Küster.[6] It had b. p. 234—238°, n_D^{20} 1·4734 (Found: C, 62·8; H, 6·5. Calc. for $C_8H_{10}O_3$: C, 62·3; H, 6·5%), and gave a 2,4-*dinitrophenylhydrazine derivative*, m. p. 173—174° (Found: C, 50·1; H, 4·1; N, 16·3. $C_{14}H_{14}N_4O_6$ requires C, 50·3; H, 4·2; N, 16·8%).

The authors thank Mr. K. Denbigh for help with experimental work and Mr. D. White for elementary analysis.

THE DISTILLERS COMPANY LIMITED, DEVELOPMENT DIVISION, RESEARCH DEPARTMENT,
GREAT BURGH, EPSOM, SURREY, [*Received, September 28th*, 1962.]

[12] Braude, *J.*, 1945, 490.

641. *The Crystal Structure of Thallium Dibromide.*

By A. C. Hazell.

It has long been recognised [1] that the dihalides of thallium should be formulated as the thallous tetrahalogenothallates(III) $Tl^+[TlX_4]^-$. The structure of thallium dibromide has been studied to determine whether the $[TlBr_4]^-$ ion is tetrahedral as in the analogous Ga_2Cl_4[2] or square-planar as in $CsTlBr_4$.[3]

Experimental.—$TlBr_2$, $M = 364{\cdot}2$, orthorhombic, $a = 8{\cdot}02$, $b = 10{\cdot}35$, $c = 10{\cdot}45$ Å, $U = 867$ Å^3, $Z = 8$, F(000) = 1208. Space-group *Pnna* (D_{2h}^6, No. 52), Cu-K_α radiation, single-crystal oscillation and Weissenberg photographs; absorption coefficient $\mu = 950$ cm.$^{-1}$. The crystals are needle-shaped, elongated in the [100] direction.

0kl and *h0l* Intensity data were obtained from Weissenberg photographs by the multiple-film technique. The cross-sections of the crystals used were $0{\cdot}06 \times 0{\cdot}06$ mm. for the *0kl* zone and $0{\cdot}59 \times 0{\cdot}29$ mm. for the *h0l* zone; absorption corrections were made, treating the crystals as elliptical cylinders, for *0kl* $\mu r_{min.} = \mu r_{max.} = 2{\cdot}8$, for *h0l* $\mu r_{min.} = 14$, $\mu r_{max.} = 28$.

Least-squares refinement of atomic co-ordinates and isotropic thermal parameters reduced the discrepancy factor to $R = 0{\cdot}125$ for the *0kl* zone, and to $R = 0{\cdot}173$ for the less accurate *h0l* zone. The atomic scattering factors used were those of Thomas and Umeda,[4] the thallium values being corrected for the real part of the anomalous scattering ($\Delta f = -4{\cdot}9$ [5]). This showed thallium dibromide to be iso-structural with Ga_2Cl_4. The final fractional co-ordinates and isotropic thermal parameters are given in the Table.

Fractional atomic co-ordinates and thermal parameters (in Å^2).

	x/a	*y/b*	*z/c*	$\bar{u}^2$
Tl(I)	0·676	0·250	0·250	0·068
Tl(III)	0·250	0·000	0·181	0·052
Br 1	0·354	0·187	0·045	0·089
Br 2	0·008	0·050	0·320	0·072

Discussion.—The structure is composed of $[TlBr_4]^-$ tetrahedra and Tl^+ ions; the mean Tl–Br distance in the tetrahedron is 2·51 Å (with standard deviation 0·03 Å), which compares with 2·59 Å in $[Co(NH_3)_6][TlBr_6]$,[6] 2·66 Å in $CsTlBr_4$,[3,6] 2·76 Å in $KTlBr_4,2H_2O$,[3,6] and 2·71 Å in $Rb_3TlBr_6,8/7H_2O$.[7] The Tl^+ ion is surrounded by eight bromine atoms from six different tetrahedra; the mean Tl–Br distance in this irregular dodecahedron is 3·46 Å (cf. the sum of the ionic radii 3·39 Å).[8]

The calculations were carried out on the Durham University Pegasus Computer with a programme devised by Professor D. W. J. Cruickshank and Miss D. E. Pilling. The work was done during the tenure of a British Titan Products Research Fellowship.

Chemistry Department, King's College,
Newcastle upon Tyne, 1.

[*Received, September 24th*, 1962.]

[1] Werner, "Neuere Anschauungen auf dem Gebiet der anorganischen Chemie," Vieweg, Braunschweig, 4th edn., 1920.
[2] Garton and Powell, *J. Inorg. Nuclear Chem.*, 1957, **4**, 84.
[3] Wananabe, Saito, Shiono, and Atoji, Abs. First Congress Internat. Union Crystallography, 1948, p. 30.
[4] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.
[5] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.
[6] Watanabe, Atoji, and Okazaki, *Acta Cryst.*, 1950, **3**, 436.
[7] Hoard and Goldstein, *J. Chem. Phys.*, 1935, **3**, 645.
[8] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York, 3rd edn., pp. 514, 518.

642. *The Absence of the Parent Molecular-ion Peak in the Mass Spectrum of Neopentane.*

By D. S. URCH.

THE purpose of this Note is to demonstrate the instability of the ion CMe_4^+ and thus explain the absence of the parent peak (mass 72) in the mass-spectrum of neopentane.[1]

Carbon–carbon bonds are weaker than carbon–hydrogen bonds, so it is reasonable to suppose that the ejected electron would come from bonds of the former type. The symmetry of the four carbon atoms surrounding the central carbon atom is that of a regular tetrahedron, T_d. x-, y-, and z-Axes pass through the mid-points of the edges of this figure. The four localised carbon–carbon bonds may be transformed into four equivalent molecular orbitals which will belong to classes t_2 and a_1.[2] Molecules containing half-filled orbitals (such as the molecule-ion of neopentane) are described better by the use of molecular orbitals than of localised bonds.[3] The triply degenerate set of orbitals, t_2, will resemble three orthogonal p atomic orbitals and the a_1 orbital will be similar in character to an s orbital. Electrons in t_2 orbitals will be less tightly bound than in the a_1 orbital so that ionisation, $CMe_4 + e \longrightarrow CMe_4^+ + 2e$, probably proceeds by the removal of an electron from one of the t_2 orbitals. A degenerate state of the ion is thus produced and the Jahn–Teller effect [4] will now cause a distortion of the ion.

Suppose that the electron were ejected from the t_2 orbital that resembled a p_z orbital. This would allow the four carbon atoms attached to the central carbon atom to move away from the z-axis, *i.e.*, the ion would become flattened towards the xy-plane. Such a model for CMe_4^+ has symmetry D_{2d} (hydrogen being ignored). The orbitals that correspond to t_2 are b_2 (z) (singly occupied) and e (x and y) (four electrons). The carbon–carbon bond lengths will, of course, remain the same.

The ionisation of neopentane may thus cause a crowding of the four methyl groups. Steric hindrance could result, making the positive ion unstable. The strain may be removed by the elimination of a methyl group, $CMe_4^+ \longrightarrow CMe_3^+ + Me^\bullet$. If this decomposition follows the ionisation immediately, it would provide an explanation of why no peak of mass 72 corresponding to CMe_4^+ is observed in the mass spectrum of neopentane.

QUEEN MARY COLLEGE, MILE END ROAD, LONDON, E.1. [*Received, January 12th,* 1963.]

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[2] Pople, *Quart. Rev.*, 1957, **11**, 273.
[3] Leonnard-Jones and Pople, *Discuss. Faraday Soc.*, 1951, **10**, 9.
[4] Jahn and Teller, *Proc. Roy. Soc.*, 1937, *A*, **161**, 220.

643. *The Reaction of Nitric Oxide with Iron Acetylacetonates.*

By David A. Buckingham, (Miss) J. L. E. Cheong, J. E. Fergusson, and C. J. Wilkins.

It has been suggested that when nitric oxide reacts with iron(II) acetylacetonate [1] there is formed an iron–nitrosyl adduct comparable with the aqueous iron(II) nitrosyl complex, but no products were identified. The reaction (carried out in toluene) may well be initiated by co-ordination of nitric oxide but is found to involve a rapid oxidation. The apparent uptake of gas to almost the 1 : 1 molar ratio is fortuitous. The chief product is iron(III) acetylacetonate; acetate, carbon dioxide, and water are also formed. The nitric oxide is largely reduced to nitrogen, but small amounts of at least two involatile nitrogen-containing products are also formed. The acetate appears in a basic precipitate which separates after the rapid uptake of gas. The iron(III) acetylacetonate formed during the initial reaction is itself oxidised by further nitric oxide but this reaction is much slower and is distinguished by the formation of biacetyl.[2]

There is an increase in the uptake of nitric oxide with decreasing temperature, partly owing to some reversibility of the reaction with iron(III) acetylacetonate at low temperature. For the same reason the uptake of gas becomes pressure-dependent at low temperature (see Table).

That the minor, nitrogenous products are not iron nitrosyl complexes is shown by their failure to yield nitric oxide (or its reduction products) upon treatment with acid and by a high ratio N : Fe(II) ($<2{\cdot}5$).

Effect of temperature and pressure on uptake of nitric oxide by iron (II) acetylacetonate in toluene.

Temp.	20·75°	−35°	−78°	−35°	−35°	−35°	+35°	+35°
Pressure (mm.)	736·5	769·5	773·0	631·6	449·2	231·0	760	260
Moles gas : Fe ...	0·942	1·400	1·515	1·382	1·363	1·268	0·824	0·815

Experimental.—Iron(II) *acetylacetonate.* To a solution of ferrous sulphate (12·9 g.) under carbon dioxide were added piperidine (30 ml.) and acetylacetone (26·6 ml.) in water. The precipitate was filtered off and washed successively with water, alcohol, and ether, all under carbon dioxide. It was dehydrated in a high vacuum, first at room temperature and then at 80° to constant weight (14 hr.) (Found: C, 47·4; H, 5·8; Fe, 21·9. Calc. for $C_{10}H_{14}O_4Fe$: C, 47·2; H, 5·5; Fe, 22·0%). The orange-brown compound [3] was sealed in ampoules. Its solubility (w/v) in methylene chloride at 16° is 4·4%, in benzene at 20° 1·6%, and in toluene at 20° 1·9%. The magnetic susceptibility, measured by the Gouy method, gave a moment of 5·4 B.M.; the compound is thus a high-spin complex.

For measurement of the uptake of nitric oxide,[4] the solvent (20 ml.) was outgassed in the absorption vessel by repeated freezing in a vacuum. With magnetic stirring, absorption was complete in 30 min.

Reaction with nitric oxide. When nitric oxide was bubbled slowly for 8 hr. through the acetylacetonate solution (1·0 g. in 50 ml.), which was then filtered under carbon dioxide in an apparatus described elsewhere,[5] a precipitate (0·25—0·3 g.) was obtained. This was washed with toluene (2 ml.) and light petroleum (b. p. 40—60°) (2 ml.) and dried in a current of nitric oxide or carbon dioxide. On treatment with cold dilute sulphuric acid this gave acetic acid, acetylacetone, and ferrous ion.

The fraction soluble in toluene yielded iron(III) acetylacetonate, m. p. 183° (Found: C, 50·5; H, 6·1. Calc. for $C_{15}H_{21}O_6Fe$: C, 51·1; H, 6·0%).

[1] Emmert and Gsottschneider, *Ber.*, 1933, **66**, 1871.
[2] Cf. Mendelsohn, Arnett, and Freiser, *J. Phys. Chem.*, 1960, **64**, 660.
[3] Emmert and Jarczynski, *Ber.*, 1931, **64**, 1072.
[4] Buckingham, Thesis, University of Canterbury, N.Z., 1959.
[5] Cheong, Thesis, University of Canterbury, N.Z., 1962.

From the reaction of nitric oxide with iron(III) acetylacetonate (0·5 g), 9·07 of precipitate was obtained after 64 hr. Biacetyl (0·015 g.) was the only volatile product in the solution, as shown by gas chromatography.

Gas analysis. Chemical analysis showed carbon dioxide (3·5 ml. in a 7·9 ml. sample) and a ratio $N_2O : N_2 > 0·06$. Mass-spectrometry analysis showed the presence of water vapour in addition to carbon dioxide, nitrogen, and nitric oxide.

The authors thank Messrs. L. K. Creamer and G. J. Wright for gas-chromatographic analyses, and Miss C. Bishop, University of Auckland, for mass-spectrometric analysis. One of the authors (J. L. E. C.) participated in the work during the tenure of an award under the Colombo Plan.

UNIVERSITY OF CANTERBURY, CHRISTCHURCH, NEW ZEALAND. [*Received, October 2nd,* 1962.]

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644. *Organic Fluorine Compounds. Part XXVII.* Fluorinated α-Aminoisobutyric Acids.*

By ERNST D. BERGMANN and ARNON SHANI.

α-AMINOISOBUTYRIC ACID is of some biological interest because it reduces the clotting time of blood, similarly to histidine.[1] It seemed worthwhile to synthesize and study fluoro-analogues of this acid, and the preparation of fluorinated isobutyronitriles was first investigated. 1-Fluoro- and 1,3-difluoro-propan-2-ol gave easily the corresponding methanesulphonates, but these as well as other sulphonates of the two alcohols were refractory towards sodium cyanide.

Whilst fluoroacetone treated with sodium cyanide in the presence of sulphuric acid gives the cyanohydrin,[2] the reaction carried out in the presence of ammonium chloride as catalyst yielded quite unexpectedly a mixture of β-fluoro-α-hydroxy- and α-amino-β-fluoro-isobutyronitrile. Hydrolysis led to β-fluoro-α-hydroxy- and α-amino-β-fluoro-isobutyric acid, respectively, in the ratio 15 : 85. When 1,3-difluoroacetone was treated analogously, only ββ-difluoro-α-hydroxyisobutyronitrile was formed; its hydrolysis gave the corresponding hydroxy-acid. It was necessary to treat the nitrile with gaseous ammonia to convert it into the amino-nitrile which could be hydrolysed to α-amino-ββ-difluoroisobutyric acid.

When 1,3-difluoro-2-propyl methanesulphonate was treated with potassiophthalimide,[3] preferably in dimethylformamide [4] as solvent, *N*-(1,3-difluoro-2-propyl)phthalimide was obtained and could be converted into the hydrochloride of the free amine.

Experimental.—*1-Fluoro-2-propyl methanesulphonate.* When pyridine (61 g.) was added, dropwise and with stirring, to a mixture of 1-fluoropropan-2-ol (58 g.),[5] methanesulphonyl chloride (80 g.), and benzene (200 ml.), an exothermic reaction took place. The mixture was refluxed for 2 hr., cooled, and diluted with water (400 ml.). The *product* (81 g., 70%) was extracted with benzene; it had b. p. 76—77°/0·1 mm., n_D^{24} 1·4158 (Found: C, 30·6; H, 5·8; F, 11·8. $C_4H_9FO_3S$ requires C, 30·8; H, 5·8; F, 12·1%).

1,3-Difluoro-2-propyl methanesulphonate. Analogously from 1,3-difluoropropan-2-ol (169

* Part XXVI, *J.*, 1961, 4669.

[1] Kohl, *Med. Klin.*, 1947, **42**, 535 (*Chem. Abs.*, 1948, **42**, 8912).
[2] Yakubovich, Bogoslovskii, Pravova, and Rozenshtein, *Zhur. obshchei Khim.*, 1958, **28**, 2288; Voong and Chiang, Hua Hsiieh Hsiieh Pao, 1958, **24**, 155; Cherbuliez, Picciott, and Rabinowitz, *Helv. Chim. Acta*, 1960, **43**, 1143.
[3] Cf. Sakellarios, *Helv. Chim. Acta*, 1946, **29**, 1675.
[4] Sheehan and Bolhofer, *J. Amer. Chem. Soc.*, 1950, **72**, 2786.
[5] Bergmann and Cohen, *J.*, 1958, 2259.

g.), methanesulphonyl chloride (210 g.), benzene (300 ml.), and pyridine (145 g.), the *ester* (207 g., 68%) was obtained, b. p. 76—78°/0·1 mm., n_D^{24} 1·4170 (Found: C, 27·2; H, 4·7. $C_4H_8F_2O_3S$ requires C, 27·6; H, 4·6%).

1,3-*Difluoro*-2-*propyl benzenesulphonate*. At a temperature of −5°, 1,3-difluoropropan-2-ol (48 g.) was added during 30 min. to a suspension of sodium hydride (12 g.) in anhydrous tetrahydrofuran (200 ml.). When the evolution of hydrogen had ceased, benzenesulphonyl chloride (88 g.) was added during 1 hr., at the same temperature, and the mixture gradually permitted to reach room temperature. Addition of water (5 ml.) caused the coagulation of the sodium chloride formed; after filtration the solvent was removed and the *product* (91 g., 78%) distilled, b. p. 115°/0·2 mm. $n_D^{18·5}$ 1·4960 (Found: C, 45·8; H, 4·6; F, 15·6. $C_9H_{10}F_2O_3S$ requires C, 45·8; H, 4·2; F, 16·1%). No reaction took place between sodium cyanide and the above sulphonates in boiling acetonitrile or dimethylformamide.

N-(1,3-*Difluoro*-2-*propyl*)*phthalimide*. When 1,3-difluoro-2-propyl methanesulphonate (47·5 g.), potassiophthalimide (37 g.), and dimethylformamide (150 ml.) were refluxed for 3 hr., white crystals precipitated. After dilution with water, the product was extracted with ether and the extract washed with water, dried, and concentrated. The *product* (22 g., 50%), recrystallized repeatedly from methanol, had m. p. 72—74° (Found: C, 58·8; H, 4·2; F, 16·6; N, 6·1. $C_{11}H_9F_2NO_2$ requires C, 58·7; H, 4·0; F, 16·9; N, 6·2%).

1,3-*Difluoro*-2-*propylamine hydrochloride*. The substituted phthalimide (11·5 g.) was refluxed for 8 hr., with stirring, with concentrated hydrochloric acid (55 ml.) and water (20 ml.), and the phthalic acid (7·5 g.) which precipitated upon cooling, filtered off; it melted at 209—210°. The aqueous filtrate was evaporated to dryness and the residue recrystallized from alcohol. The hygroscopic *product*, m. p. 123—125°, gave a red-violet ninhydrin reaction (Found: C, 27·4; H, 6·2; Cl, 26·8. $C_3H_8ClF_2N$ requires C, 27·5; H, 6·1; Cl, 26·7%).

β-*Fluoro*-α-*hydroxy- and* α-*amino*-β-*fluoro-isobutyric acid*. Into a three-necked flask, cooled at 10°, were introduced successively and with stirring, ammonium chloride (32 g.) in water (90 ml.), fluoroacetone [6] (36 g.) in ether (100 ml.), and sodium cyanide (26 g.) in water (60 ml.). The mixture was stirred for 1 hr. and kept overnight, the ethereal solution was separated, and the aqueous phase extracted with ether. Distillation gave a colourless oil (25 g., 50%), b. p. 45—49°/0·5 mm., n_D^{17} 1·4159, which was refluxed for 3 hr. with concentrated hydrochloric acid (60 ml.). The solution, from which a colourless precipitate had separated, was brought to dryness (without removing the precipitate) and the residue treated with ether. The ether solution, when evaporated, left β-fluoro-α-hydroxy-isobutyric acid (2·7 g., 8%), m. p. 99—100° (lit.,[4] 94·5—95·5°, 101·5—102°) (Found: C, 39·3; H, 6·0. Calc. for $C_4H_7FO_3$: C, 39·3; H, 5·7%).

The ether-insoluble product was dissolved in hot ethanol (which left ammonium chloride undissolved); evaporation of the solvent gave α-amino-β-fluoroisobutyric acid hydrochloride, m. p. 219—220°. When its methanolic solution was brought to pH 5—6 by addition of pyridine, α-*amino*-β-*hydroxyisobutyric acid* (11 g., 50%) crystallized, m. p. 225—226°. It gave a violet ninhydrin reaction (Found: C, 39·8; H, 6·9; F, 15·5; N, 11·5. $C_4H_8FNO_2$ requires C, 39·7; H, 6·6; F, 15·7; N, 11·6%).

ββ-*Difluoro*-α-*hydroxyisobutyric acid*. In the manner described above, 1,3-difluoroacetone (47 g.) in ether (100 ml.) was treated with sodium cyanide (26 g.) in water (60 ml.) and ammonium chloride (38 g.) in water (90 ml.). A product (25 g., 42%) was obtained, b. p. 59—60°/1 mm., n_D^{19} 1·4076 (Found: C, 39·9; H, 4·5; F, 31·6. $C_4H_5F_2NO$ requires C, 39·7; H, 4·1; F, 31·4%). It proved to be ββ-*difluoro*-α-*hydroxyisobutyronitrile*, as hydrolysis with concentrated hydrochloric acid (3 hr.) gave the *acid* (55%), m. p. 87—88° (Found: C, 34·3; H, 4·4. $C_4H_6F_2O_3$ requires C, 34·3; H, 4·3%).

α-*Amino*-ββ-*difluoroisobutyric acid*. Through a solution of the cyanohydrin described in the previous paragraph (13 g.), in methanol (50 ml.), a current of ammonia was passed at 0°. The excess of ammonia was removed by a stream of air and the solvent evaporated *in vacuo*. The residue was refluxed for 3 hr. with concentrated hydrochloric acid (60 ml.) and worked up as described for the monofluoro-analogue. The free *amino-acid* (3 g., 16%) melted at 182—183° (decomp.) and gave a violet ninhydrin reaction (Found: C, 34·5; H, 5·2; N, 10·4. $C_4H_7F_2NO_2$ requires C, 34·5; H, 5·0; N, 10·1%).

ISRAEL INSTITUTE FOR BIOLOGICAL RESEARCH,
NESS-ZIONA, ISRAEL.

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645. *Esters Containing Phosphorus. Part XIX.* The Action of Grignard Reagents on Phosphorofluoridates.*

By B. C. Saunders and P. Simpson.

Dialkyl phosphorochloridates, on treatment with an excess of phenylmagnesium bromide, yield triphenylphosphine oxide,[1] both the ester groups and the chlorine atom being replaced by phenyl groups. Using a reverse-addition technique, first described in connection with phosphorus compounds by Kosolapoff,[2] Burger and Dawson [3] used this reaction to prepare diethyl arylphosphonates from diethyl phosphorochloridate and the appropriate arylmagnesium bromide. The resulting diethyl arylphosphonates were hydrolysed by acid to yield the free arylphosphonic acids. Yields were not high, however, presumably because of the tendency of the reaction to go further, with the replacement of ester groups by aryl groups.

We now report that the ester groups of dialkyl and diaryl phosphorofluoridates are stable to attack by Grignard reagents, only the fluorine atom being replaced: $FPO(OR)_2 + MgPhBr \longrightarrow Ph{\cdot}PO(OR)_2$. Even after a dialkyl or diphenyl phosphorofluoridate had been heated with a three-fold excess of phenylmagnesium bromide in ether for 20 minutes, the ester groups were still intact. Only insignificant traces of triphenylphosphine oxide were formed, as revealed by a very weak infrared absorption at 724 $cm.^{-1}$ (an intense, characteristic peak in the spectrum of triphenylphosphine oxide).

The importance of Burger and Dawson's method [3] for the preparation of arylphosphonic acids lies in the fact that if the aryl group has other substituents in addition to the phosphonic acid group, then the position in the ring of the latter, newly introduced group is in no doubt. When a phosphorofluoridate is used in place of a phosphorochloridate, the stability of the ester groups of phosphorofluoridates obviates the necessity for reverse addition, whereby the convenience and efficiency of the method are improved. Yields of phenylphosphonic acid (after recrystallisation from ethyl acetate) of 59%, 50%, and 61% were obtained from the diethyl, di-isopropyl and dicyclohexyl phosphorofluoridate, respectively. The yield of crude material (before recrystallisation) obtained by Burger and Dawson [3] was 40·5%.

We have employed this method for the preparation of dialkyl ethynylphosphonates [4] from dialkyl phosphorofluoridates and ethynylmagnesium bromide, omitting the ester-hydrolysis step.

It is interesting that the fluorine atom in dialkyl phosphorofluoridates is, in general, not readily hydrolysed by water, and that these compounds are toxic in virtue of their anticholinesterase activity. On the other hand, the phosphorochloridates are not toxic and the chlorine atom is very readily hydrolysed by water. Further, the parent phosphorofluoridic acid is non-toxic. It is therefore worth while, in toxicological studies, to draw attention to the relation of strength of the P–F link and resistance to dealkylation in the phosphorofluoridates and to the lability of the chlorine atom in the non-toxic phosphorochloridates and ease of dealkylation. In other words, toxic action of these P–F compounds may depend upon the stability of the ester groups.[5]

Experimental.—Action of phenylmagnesium bromide on di-isopropyl phosphorofluoridate. Phenylmagnesium bromide was prepared from bromobenzene (40·2 g.) and magnesium (6·3 g.)

* Part XVIII, this Journal, p. 3351.

[1] Dawson and Burger, *J. Org. Chem.*, 1953, **18**, 207.
[2] Kosolapoff, *J. Amer. Chem. Soc.*, 1942, **64**, 2982.
[3] Burger and Dawson, *J. Org. Chem.*, 1951, **16**, 1250.
[4] Saunders and Simpson, preceding paper.
[5] Cf. Saunders, "Phosphorus and Fluorine. The Chemistry and Toxic Action of their Organic Compounds," Cambridge Univ. Press, 1957, p. 188.

in dry ether (120 ml.). To the cooled stirred solution, di-isopropyl phosphorofluoridate (15·7 g., 0·33 mol.) in ether (50 ml.) was added during 20 min. The reaction was slightly exothermic. The mixture was heated under reflux for 20 min., then cooled to 0°, and dilute hydrochloric acid (120 ml.) was added slowly with stirring. Water (120 ml.) was next added, the ether removed, and the aqueous phase extracted with ether (80 ml.). The last ethereal extracts were dried ($MgSO_4$) and evaporated, leaving a yellow oil (22·4 g.) consisting of di-isopropyl phenylphosphonate and biphenyl. The oil was heated under reflux with concentrated hydrochloric acid (140 ml.) for 6 hr., then steam-distilled to remove biphenyl. After removal of water and hydrochloric acid on the water-bath, a solid (15·12 g.) remained which on recrystallisation from ethyl acetate gave phenylphosphonic acid, m. p. 162·5—164° (6·58 g., 50%) (Burger and Dawson [3] give m. p. 161—163°) (Found: C, 45·9; H, 4·9. Calc. for $C_6H_7O_3P$: C, 45·6; H, 4·4%).

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 27th*, 1962.]

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646. *Replacement of the Diazo-group in a Diazo-oxide by the Cyano-group.*

By EDMOND N. GABALI and ELHOSSEINY M. ABDALLAH.

REPLACEMENT of the diazo-group in diazo-oxides has been reported so far only in respect of replacement by hydrogen.[1] The Sandmeyer reaction for the formation of nitriles from dinitro- and phenolic amines occurs only in limited conditions because of the tendency of the intermediate diazonium compounds to couple with resultant formation of tar.[2] When 4-nitronaphthalene-1-diazo-2-oxide is treated with cuprous cyanide in water, alcohol, aqueous alcohol, benzene, or toluene (which are normally used in the Sandmeyer reaction) only tars result. However, reaction in pyridine is smooth and fast, giving up to 65% of 2-hydroxy-4-nitro-1-naphthonitrile. The nitrile was hydrolysed with sulphuric acid to 2-hydroxy-4-nitro-1-naphthoamide.

Experimental.—4-Nitronaphthalene-1-diazo-2-oxide was prepared from 2,4-dinitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine by hydrolysis with sulphuric acid and treatment with sodium nitrite (cf. Morgan *et al.*[3]). It crystallised from light petroleum (b. p. 60—80°) as yellow needles, m. p. 134° (decomp.) (lit., m. p. 130—134°).

2-*Hydroxy*-4-*nitro*-1-*naphthonitrile*. The above diazo-oxide (10 g.) in redistilled pyridine (100 c.c.) was added slowly with stirring to a freshly prepared solution of cuprous cyanide (12 g.) in water (80 c.c.) containing sodium cyanide (16 g.) at 0° during 30 min. The mixture was kept stirred at 0—5° till a drop of it gave no blue colour with alkaline resorcinol (2 hr.). The mixture was then kept at room temperature for 1 hr. and at 50—60° for 2 hr. It was then cooled and added to dilute hydrochloric acid (200 c.c.). A yellow precipitate was extracted with ether and the extract treated with an excess of 5% sodium hydroxide solution. The aqueous extracts were poured into an excess of 1 : 1 hydrochloric acid; the yellow precipitate (6·1 g.) crystallised from boiling water as yellow needles, m. p. 212—213° (decomp.) (Lindemann *et al.*[4] give m. p. 213—214° for 2-hydroxy-*x*-nitronaphthonitrile) (Found: C, 61·7; H, 2·9; N, 12·4. Calc. for $C_{11}H_6N_2O_3$: C, 61·7; H, 2·8; N, 13·1%).

The nitrile (4 g.) was added to a cooled mixture of sulphuric acid (56 c.c.) and water (12 c.c.),

[1] Hodgson and Birtwell, *J.*, 1943, 468; " Organic Reactions," ed. R. Adams, Wiley, New York, 1944, Vol. II, p. 270 and references therein.
[2] Storrie, *J.*, 1937, 1746; Clark, Heller, and Roth, *J. Amer. Pharmaceut. Assoc.* (*Sci. Edn.*), 1955, **44**, 328.
[3] Morgan and Evens, *J.*, 1919, **115**, 1126.
[4] Lindemann, Konitzer, and Romanoff, *Annalen*, 1927, **456**, 296.

heated at 105—110° for 4 hr. with stirring, cooled, and poured into water (500 c.c.). The mixture was extracted with ether (5 × 100 c.c.). After removal of the ether, the residual *acid amide* (1·9 g.) crystallised from water as rectangular crystals, m. p. 208° (Found: C, 57·4; H, 3·7; N, 12·1. $C_{11}H_8N_2O_4$ requires C, 56·9; H, 3·45; N, 12·1%).

We thank Professor Y. M. Abouzeid of this Faculty for facilities and his interest in the work.

ORGANIC CHEMISTRY DEPARTMENT, FACULTY OF PHARMACY,
CAIRO UNIVERSITY, EGYPT. [*Received, December 19th,* 1962.]

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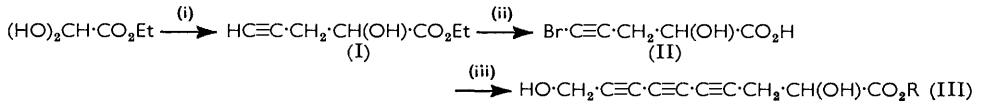
647. *Chemistry of the Higher Fungi. Part XV.*[1] *The Synthesis of two α-Hydroxy-acids from* Poria sinuosa *Fr.*

By R. C. CAMBIE, E. R. H. JONES, and G. LOWE.

IN Part XIV [1] the isolation and structure determination of seven new polyacetylenes from the fungus *Poria sinuosa* was described. These included the two optically active α-hydroxy-acids, 2,10-dihydroxydeca-4,6,8-triynoic acid (III; R = H) and *trans*-2,10-dihydroxydec-4-ene-6,8-diynoic acid (VI; R = H), which were isolated as their methyl esters. The syntheses of their racemic forms are now reported.

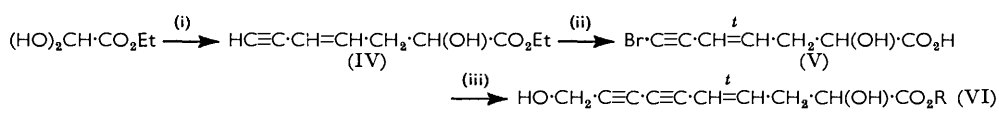
The dihydroxy-acid (III; R = H) and its methyl ester were prepared by the route illustrated. The hydrate of ethyl glyoxylate, prepared by lead tetra-acetate oxidation of



Reagents: (i) $HC{\equiv}C{\cdot}CH_2Br/Zn$. (ii) NaOBr. (iii) $HO{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}C{\equiv}CH/Cu^+/Et{\cdot}NH_2$.

diethyl tartrate,[2] was coupled with propargyl bromide in a Reformatsky reaction [3,4] to give the α-hydroxy-ester (I). Treatment of the ester with sodium hypobromite solution resulted in bromination of the ethynyl group and hydrolysis of the ester to yield 5-bromo-2-hydroxypent-4-ynoic acid (II). Chodkiewicz coupling [5] of the latter compound with penta-2,4-diyn-1-ol [6] gave the racemic dihydroxy-acid (III; R = H); the infrared and ultraviolet absorption spectra of its methyl ester were identical with those of the natural product from *Poria sinuosa*.[1]

The dihydroxy-acid (VI; R = H) was prepared by a similar method, as formulated. Reformatsky coupling of *trans*-1-bromopent-2-en-4-yne [4] with the hydrate of ethyl



Reagents: (i) $HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2Br/Zn$. (ii) NaOBr. (iii) $HO{\cdot}CH_2{\cdot}C{\equiv}CH/Cu^+/Et{\cdot}NH_2$.

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[1] Part XIV, Cambie, Gardner, Jones, Lowe, and Read, *J.*, 1963, 2056.
[2] Weygand, " Organic Preparations," Interscience Publishers Inc., New York, 1947, p. 455.
[3] Henbest, Jones, and Walls, *J.*, 1949, 2696.
[4] Henbest, Jones, and Walls, *J.*, 1950, 3646.
[5] Chodkiewicz, *Ann. Chim.* (*France*), 1957, **2**, 819; Cadiot and Chodkiewicz, *Compt. rend.*, 1957, **245**, 1634.
[6] Armitage, Jones, and Whiting, *J.*, 1952, 1993.

glyoxylate gave ethyl *trans*-2-hydroxyhept-4-en-6-ynoate (IV). Chodkiewicz coupling of propargyl alcohol with the crude bromo-acid (V), formed from (IV) by treatment with sodium hypobromite, gave the racemic dihydroxy-acid (VI; R = H). The methyl ester (VI; R = Me) gave infrared and ultraviolet absorption spectra identical with those of the natural compound.[1]

Experimental.—Ultraviolet absorption spectra were measured for EtOH solutions on a Cary double-beam recording spectrophotometer and infrared spectra, unless otherwise stated, as Nujol mulls on a Perkin-Elmer 21 instrument.

Ethyl glyoxylate hydrate. This compound was prepared by Weygand's method [2] from diethyl tartrate but without the addition of ethanol. The product had b. p. 66—69°/20 mm., $\nu_{max.}$ (liquid) 3509 (broad, OH), 1754 (ester C=O), 1279, and 1096 cm.$^{-1}$ (C–OH). Attempts to dehydrate the compound by Traube's method [7] were unsuccessful.

Ethyl 2-hydroxypent-4-ynoate (I). The *ester*, prepared in 35% yield from ethyl glyoxylate hydrate and propargyl bromide [8] and distilled in nitrogen, had b. p. 78—80°/1 mm., n_D^{21} 1·4478 (lit.,[8] b. p. 66—68°/0·1 mm.) (Found: C, 59·5; H, 7·1. $C_7H_{10}O_3$ requires C, 59·1; H, 7·1%), $\nu_{max.}$ (liquid) 3436 (OH), 3268 (HC≡C), 2119 (C≡C), 1739 (ester C=O), and 1099 cm.$^{-1}$ (C–OH).

5-Bromo-2-hydroxypent-4-ynoic acid (II). The above compound (5·0 g.) was treated at 0° with sodium hypobromite solution [25 c.c. of a mixture of ice (50 g.), 10N-sodium hydroxide (50 c.c.), bromine (11·0 c.c.), and water (5 c.c.)] in portions with stirring during 15 min. The mixture was then kept at 0° for 15 min., and at 20° for 30 min. before being acidified and extracted with ether. *5-Bromo-2-hydroxypent-4-ynoic acid*, isolated by extraction with saturated aqueous sodium hydrogen carbonate and ether, formed plates (3·8 g.), m. p. 103°, from ether–hexane (Found: C, 31·0; H, 2·7. $C_5H_5BrO_3$ requires C, 31·1; H, 2·6%) and had $\nu_{max.}$ 3279 (OH), 2604 (OH of CO_2H), 2208 (C≡C), 1698 (CO_2H), 1339 and 1094 cm.$^{-1}$ (C–OH).

(±)-*2,10-Dihydroxydeca-4,6,8-triynoic Acid* (III; R = H). Penta-2,4-diyn-1-ol [6] (480 mg.) in methanol (3 c.c.) was added to a stirred solution of cuprous chloride (20 mg.) in 30% aqueous ethylamine (10 c.c.). To the mixture under nitrogen at 20° was added 5-bromo-2-hydroxypent-4-yn-1-oic acid (1·22 g.) in methanol (5 c.c.) during 10 min. Crystals of hydroxylamine hydrochloride were added as required to reduce cupric ion formed. The mixture was stirred for a further 20 min., cooled, acidified, and extracted with ether. (±)-*2,10-Dihydroxydeca-4,6,8-triynoic* acid, isolated by means of extraction with saturated aqueous sodium hydrogen carbonate and ether, formed needles (860 mg., 70%), m. p. 152—153° (decomp.), from ether (Found: C, 62·5; H, 4·2. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%) and had $\lambda_{max.}$ 2830 (ε 120), 2670 (ε 135), 2530 (ε 145), and 2100 Å (ε 178,500), $\nu_{max.}$ 3378 (OH), 3236 (OH), 2700—2550 (OH of CO_2H), 2208 (C≡C), 1712 (CO_2H), 1272, 1110, and 1070 cm.$^{-1}$ (C–OH). The acid slowly became purple on exposure to light at 20°.

(±)-*Methyl 2,10-dihydroxydeca-4,6,8-triynoate* (III; R = Me). The triynoic acid (250 mg.) was esterified with 5% sulphuric acid in methanol at 20° for 3 days. The neutral fraction was recrystallised from dichloromethane–hexane, to yield (±)-*methyl 2,10-dihydroxydeca-4,6,8-triynoate* (230 mg.) as needles, m. p. 108—109° (decomp.) [cf. (+)-enantiomer, m. p. 102—103° (decomp.)] (Found: C, 64·1; H, 5·05. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%). The infrared and ultraviolet spectra were identical with the respective spectra of the dextrorotatory form obtained from *Poria sinuosa*.[1]

Ethyl trans-*2-hydroxyhept-4-en-6-ynoate* (IV). Activated zinc wool (8 g.) was stirred with *trans*-1-bromopent-2-en-4-yne [4] (1 g.) and a crystal of iodine in dry tetrahydrofuran (30 c.c.). A solution of *trans*-1-bromopent-2-en-4-yne (9 g.) and the hydrate of ethyl glyoxylate (10 g.) in dry ether was added dropwise in 1 hr. so that the mixture remained boiling. The mixture was then heated under reflux for 3 hr., kept at 20° for 12 hr., and treated with 20% aqueous acetic acid (100 c.c.), and the product was isolated by extraction with dichloromethane (3 × 100 c.c.). Fractional distillation gave *ethyl* trans-*2-hydroxyhept-4-en-6-ynoate* (3·6 g., 31%), b. p. 132°/1 mm., n_D^{25} 1·4557 (Found: C, 64·1; H, 7·45. $C_9H_{12}O_3$ requires C, 64·3; H, 7·2%), $\nu_{max.}$ (liquid) 3425 (OH), 3257 (HC≡C), 2114 (C≡C), 1736 (ester C=O), 1642 (CH=CH), 1094 (C–OH), and 932 cm.$^{-1}$ (*trans* CH=CH).

[7] Traube, *Ber.*, 1907, **40**, 4942.
[8] Bohlmann, Herbst, and Gleinig, *Chem. Ber.*, 1961, **94**, 948.

trans-7-*Bromo*-2-*hydroxyhept*-4-*en*-6-*ynoic acid* (V). Ethyl 2-hydroxyhept-4-en-6-ynoate (2·5 g.) was treated at 0° with a solution of sodium hypobromite (25 c.c.) as for the preparation of (II). The product, isolated in the usual manner, was obtained as an unstable viscous oil (400 mg.), $\nu_{max.}$ (in CS_2) 3546 (OH), 2653 and 2551 (OH of CO_2H), 1718 (CO_2H), 1274, 1106, and 1020 (C–OH) and 926 cm.$^{-1}$ (*trans* CH=CH).

(±)-trans-2,10-*Dihydroxydec*-4-*ene*-6,8-*diynoic acid* (VI; R = H). Propargyl alcohol (100 mg.) in methanol (2 c.c.) was added to a stirred solution of cuprous chloride (10 mg.) in 30% aqueous ethylamine (10 c.c.), the blue colour of which had been destroyed by the addition of hydroxylamine hydrochloride. To the mixture under nitrogen was added 7-bromo-2-hydroxyhept-4-en-6-ynoic acid (220 mg.) in 5 min. at 20°. Stirring was continued for a further 20 min., the mixture was acidified, and the product isolated with ether. Repeated fractional crystallisation from ether–hexane gave (±)-trans-2,10-*dihydroxydec*-4-*ene*-6,8-*diynoic acid* (52 mg., 27%) as needles, m. p. 163—166° (decomp.) (Found: C, 61·7; H, 5·3. $C_{10}H_{10}O_4$ requires C, 61·85; H, 5·2%), $\lambda_{max.}$ 2820 (ε 21,000), 2660 (ε 26,400), 2520 (ε 17,600), 2390 (ε 8400), 2270 (ε 6500), and 2120 Å (ε 68,200), $\nu_{max.}$ 3344 (OH), 3236 (OH), 2577 (OH of CO_2H), 2088 C≡C), 1712 (CO_2H), 1360, 1099, and 1020 (C–OH), and 957 cm.$^{-1}$ (*trans*-CH=CH). The compound rapidly became pink and then purple on exposure to light at 20°.

(±)-*Methyl* trans-2,10-*dihydroxydec*-4-*ene*-6,8-*diynoate* (VI; R = Me). The above acid (45 mg.) was esterified with 5% sulphuric acid in methanol for 3 days at 20°. Isolation of the product by means of ether, chromatography on deactivated alumina from benzene, and crystallisation from ether–hexane gave (±)-*methyl* trans-2,10-*dihydroxydec*-4-*ene*-6,8-*diynoate* (22 mg.) as unstable needles, m. p. 85—87° (decomp.) (Found: C, 63·3; H, 5·75. $C_{11}H_{12}O_4$ requires C, 63·45; H, 5·8%), $\lambda_{max.}$ 2825 (ε 20,800), 2660 (ε 27,000), 2520 (ε 18,200), 2390 (ε 9600), 2275 (ε 4550), and 2120 Å (ε 49,800), $\nu_{max.}$ 3401 (OH), 2222 and 2128 (C≡C), 1748 (ester C=O), 1096 and 1022 (C–OH), and 954 cm.$^{-1}$ (*trans*-CH=CH). The infrared spectrum was identical with that of the natural product from *P. sinuosa*.[1]

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THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, January 25th*, 1963.]

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648. *Transition-metal Fluorocarbon Complexes. Part IV.*[1] *Hexafluorobut-2-yne Complexes of Manganese and Platinum.*

By J. L. BOSTON, S. O. GRIM, and G. WILKINSON.

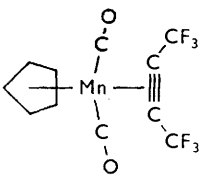
SEVERAL transition-metal complexes have been obtained by interaction of hexafluorobut-2-yne with carbonyl and π-cyclopentadienyl compounds of iron, cobalt, and nickel.[1] The fluoroacetylene was incorporated into complexes in ways similar to those of acetylenic hydrocarbons, *e.g.*, by bridging between two metal atoms, or by dimerisation with incorporation of carbon monoxide to give co-ordinated tetrakistrifluoromethylcyclopentadienone. Two additional types of compound with hexafluorobut-2-yne have now been prepared.

Tricarbonyl-π-cyclopentadienylmanganese(I) and diphenylacetylene interact under the influence of ultraviolet irradiation to give a compound in which one carbon monoxide molecule has been replaced by the acetylene.[2] We find that hexafluorobut-2-yne behaves similarly under irradiation, but not thermally, to give the stable compound π-$C_5H_5Mn(CO)_2C_4F_6$.

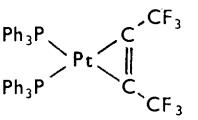
This complex is best formulated as (I), in which the acetylene is merely acting as a donor

[1] Part III, Boston, Sharp, and Wilkinson, *J.*, 1962, 3488.
[2] (*a*) Strohmeier and von Hobe, *Z. Naturforsch.*, 1961, **16***b*, 402. (*b*) Strohmeier, Laporte, and von Hobe, *Chem. Ber.*, 1962, **95**, 455.

in the same way as in the well-known olefin– and other acetylene–metal complexes. Thus the infrared spectrum has very strong absorptions at 2033 and 1969 cm.$^{-1}$ which can be assigned to the two expected C–O stretching frequencies, and a strong band at 1919 cm.$^{-1}$. The latter lies in the region 150—300 cm.$^{-1}$ below the C–C stretching region for disubstituted alkynes, as has been found in other co-ordinated alkyne complexes of various transition metals.[3] Only a slight distortion of symmetry is required for the C–C stretching frequency of the alkyne to become active and the trifluoromethyl groups are probably only slightly bent away from the C–C axis. This is in contrast with the bonding of the acetylene–platinum complexes discussed below where substantial rehybridisation towards sp^2 must occur. That the latter type of bonding is not present in the manganese compound is clear from the fact that there is no infrared absorption in the lower regions where C–C double bond frequencies are to be expected as in the present platinum and other metal complexes;[1,3] it would also lead to an oxidation state of +3 for manganese which is quite unknown in this type of complex.



(I)



(II)

Although with diphenylacetylene there is evidence [2b] for replacement of more than one carbon monoxide molecule from tricarbonyl-π-cyclopentadienylmanganese, similar indications have not been observed for the hexafluorobut-2-yne compound. The complex is soluble with decomposition in concentrated sulphuric acid; since tricarbonyl-π-cyclopentadienylmanganese and other hexafluorobut-2-yne derivatives are not so decomposed,[1,4] the rapid attack in this case is presumably due to protonation of the co-ordinated acetylene. The compound does not react with triphenylphosphine in the melt or in refluxing benzene, and neither the fluoroacetylene nor carbon monoxide can be displaced by boiling phenylacetylene. The compound is decomposed with loss of carbon monoxide by pyridine but no replacement complexes could be isolated.

Interaction of hexafluorobut-2-yne with bis(triphenylphosphine)- and bis(triphenylarsine)-phenylacetyleneplatinum(II) leads to displacement of phenylacetylene. The resulting compounds undoubtedly have the structure (II) suggested for the alkyne complexes, with square-planar platinum(II). The infrared spectra of both the phosphine and the arsine complex show a strong band at 1775 cm.$^{-1}$ indicating that the C–C bond has been substantially reduced in order; for other similar complexes [5] the band is in the region 1700 cm.$^{-1}$ and for the phenylacetylene complex we find the band at 1675 cm.$^{-1}$.

The ^{19}F nuclear resonance spectrum of these platinum complexes is of some interest. While the arsine complex shows only the splitting of the fluorine resonance line due to the ^{195}Pt nucleus (80 c./sec.) the triphenylphosphine complex shows additional well-defined splitting due to coupling with the rather remote ^{31}P nuclei, the splittings being 65·1 c./sec. due to ^{195}Pt and 10·3 c./sec. due to ^{31}P, respectively.

Experimental.—Microanalyses and molecular-weight determinations (ebullioscopic in benzene) were made by the Microanalytical Laboratory, Imperial College.

Preparations were carried out in nitrogen atmospheres; the light petroleum used had b. p.

[3] See, *e.g.*, Chatt, Guy, and Duncanson, *J.*, 1961, 827 (cf. *Chem. and Ind.*, 1959, 431); Coates and Parkin, *J. Inorg. Nuclear Chem.*, 1961, **22**, 59; *J.*, 1962, 3220; Chatt and Shaw, *J.*, 1959, 4020; 1960, 1718.

[4] Davison, McFarlane, Pratt, and Wilkinson, *J.*, 1962, 3653.

[5] Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208; cf. Chatt, Rowe, and Williams, *J.*, 1962, 3269.

30—40° Infrared spectra was taken on a Perkin-Elmer model 21 instrument with sodium chloride and calcium fluoride optics where appropriate. Nuclear resonance spectra were taken on a Varian spectrometer V4311 and 4310C at frequencies of 40 and 56·45 Mc./sec.; proton resonances are referred to tetramethylsilane (internal) and are given as τ values, while fluorine resonances are referred to benzotrifluoride (internal) and are all on the low-field side.

Dicarbonylhexafluorobut-2-yne-π-cyclopentadienylmanganese(I). An excess of hexafluorobut-2-yne [1] (5 g.) was condensed on to tricarbonyl-π-cyclopentadienylmanganese (0·5 g.) in light petroleum, in a thick-walled glass tube. After 60 hr. at 110° there was no obvious interaction, so the tube was exposed for 48 hr. to strong ultraviolet radiation. After freezing and opening, the excess of acetylene was collected and the filtered petroleum solution chromatographed on alumina (Brockmann grade III). The eluate was evaporated and the residue crystallised from light petroleum at −10° to give orange-yellow crystals of the *compound*, m. p. 68° [*ca.* 0·4 g., *ca.* 50% based on π-$C_5H_5Mn(CO)_3$] (Found: C, 38·9; H, 2·0; F, 33·6; Mn, 16·3%; *M*, 342. $C_{11}H_5F_6MnO_2$ requires C, 39·1; H, 1·5; F, 33·7; Mn, 16·3%; *M*, 338).

The compound is moderately soluble in light petroleum and very soluble in other common organic solvents such as benzene and chloroform. In solution and also in the solid state the compound slowly decomposes in the presence of air. It sublimes slowly at 55° in a high vacuum to a probe at −78°. It has infrared maxima (CCl_4 solution and Nujol mulls) at: 3115w (C–H str.); 2033vs, 1969vs (C–O str); 1919s (C–C str); 1433m; 1255vs, 1227vs, 1128vs (C–F str); 1011m, 911w, 893s, 868w, 848s, 786w, 706w, 652m, 632w. The nuclear resonance is τ 5·2, ^{19}F 9·3 p.p.m.

Bis(triphenylphosphine)hexafluorobut-2-yneplatinum(II). Hexafluorobut-2-yne (5g.) was condensed on to bis(triphenylphosphine)phenylacetyleneplatinum(II) [5] (1·2g.) in light petroleum (5 ml.) in a thick-walled glass tube. After 24 hr. at 70° the tube was cooled in liquid air, then opened, and the excess of acetylene and solvent were removed under reduced pressure. The residue was extracted with dichloromethane, the extract filtered and concentrated, and the product crystallised by addition of an excess of diethyl ether and cooling to −78°. Recrystallisation from diethyl ether at −78° gave white crystals of the *compound*, m. p. 215—216° (*ca.* 0·3 g., *ca.* 17% based on $C_{18}H_{15}P_2PtC_6H_6$) (Found: C, 54·5; H, 3·5%; *M*, 860. $C_{40}H_{30}F_6P_2Pt$ requires C, 54·5; H, 3·4%; *M*, 882). The compound is stable indefinitely in the solid state. It is readily soluble in common organic solvents, the solution decomposing slowly in air over a period of days. It has infrared maxima (CCl_4 solution, Nujol mulls) at: 3055w, 1775m, 1480w, 1436m, 1376w, 1263s, 1223s, 1180m, 1160m, 1130—1080s, 808m, 748s, 736s, 698s, 685s.

The nuclear resonance is: ^{19}F 9·0 p.p.m. (central position of triplet, each peak of which is a doublet); 8·38, 9·53 p.p.m. (centres of satellite doublets).

Bis(triphenylarsine)hexafluorobut-2-yneplatinum(II). Hexafluorobut-2-yne (3g.), bis(triphenylarsine)phenylacetyleneplatinum(II) (0·5 g.) in light petroleum (5 ml.) in a sealed tube were heated at 80° for 48 hr. After opening and removal of volatile contents, the residue was extracted with ether, and the solution filtered, concentrated, and cooled to −78°. The *product* recrystallised at −78° from ether to give a pale yellow powder (*ca.* 100 mg.) (Found: C, 51·5; H, 3·9%; *M*, 980. $C_{40}H_{30}As_2F_6Pt$ requires C, 49·5; H, 3·1%; *M*, 970). It is oxidised in air slowly in the solid state and quite rapidly in solution so that it must be handled in nitrogen. It had infrared maxima (CCl_4 solution, Nujol mulls) at: 3050w, 1775m, 1484m, 1439m, 1380w, 1325m, 1260s, 1222s, 1180w, 1163w, 1135—1110s, 1078m, 816m, 746s, 737s, 697sh, 691s.

The nuclear resonance is: ^{19}F 9·0 p.p.m. (central peak of triplet).

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Inorganic Chemistry Research Laboratories,
Imperial College of Science and Technology,
London, S.W.7.

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649. *Chemistry of the* Coprosma *Genus. Part XII.*[1] *The Glycoside of Morindone from* Coprosma australis.

By Lindsay H. Briggs and P. W. Le Quesne.

The constitution of morindin, a glycoside of morindone (1,5,6-trihydroxy-2-methylanthraquinone) and originally isolated from *Morinda citrifolia*, is still uncertain as regards the sugars present and their mode of union.[2] This also applies to a "morindin" isolated from *M. umbellata*,[3] which could be identical with morindin. A "morindin," $C_{27}H_{30}O_{14}$, m. p. 264·5°, from *Coprosma australis* was shown [4] to contain a disaccharide moiety consisting of glucose and rhamnose, joined to morindone through the 6-hydroxyl group. From *Morinda persisæfolia*, Paris and Tuoc [5] isolated a "morindin," $C_{26}H_{28}O_{14}$, m. p. 264°, and showed, by analogy with the "morindin" from *Coprosma australis*, that it was a primeveroside of moridone linked in the 6-position. More recently a new morindone glycoside, morindonin, $C_{27}H_{30}O_{15}$, m. p. 256°, has been isolated from *Morinda tinctoria* by Balakrishna, Seshadri, and Venkataramani [6] and shown to be a 6-disaccharide (most probably a gentiobioside) of morindone.

Further investigation of the "morindin" from *Coprosma australis* has shown it to be the 6-rutinoside of morindone. Enzymic hydrolysis afforded rutinose, identified by co-chromatography with that simultaneously liberated by enzymic hydrolysis of rutin isolated from *C. rhamnoides*.[7] Earlier methylation experiments [4] had indicated that the disaccharide was linked to morindone through the 6-position. This is supported by the absence of non-chelated carbonyl absorption in the infrared spectrum, which exhibits only a single carbonyl peak characteristic of a 1,5-dihydroxyanthraquinone.[8]

Experimental.—The analysis is by Dr. A. D. Campbell, University of Otago.

Repeated crystallisation of morindone 6-rutinoside, isolated as previously described,[4] from glacial acetic acid afforded golden-yellow needles which darkened above 150°, coalesced and resolidified at 170—173°, began to sublime at *ca.* 245°, and melted at 264·5° (decomp.); $\lambda_{max.}$ (in EtOH) 230, 261, and 448 mμ (log ε 4·15, 3·93, and 3·57); $\nu_{max.}$ (in KBr) 1626 cm.$^{-1}$ (chelated quinonoid C=O). An *X*-ray powder photograph, taken on a Guinier focusing camera with Cu-*K*α radiation, gave the following *d* values: 5·53m, 4·90m, 4·51s, 4·43s, 3·88w, 3·69w, 3·57vvw, 3·44vw, 2·73vw, and 2·58vw.

Octabenzoylmorindone 6-rutinoside. Benzoylation of morindone 6-rutinoside with benzoyl chloride–pyridine under reflux for 40 min. yielded the *product* as short yellow rods, m. p. 158—161° with softening above 145° (from acetone–ethanol) (Found: C, 70·6; H, 4·4. $C_{83}H_{62}O_{22}$ requires C, 70·6; H, 4·7%).

Acid hydrolysis of moridone 6-rutinoside. A solution of morindone 6-rutinoside (8 mg.) in 2N-hydrochloric acid (0·3 c.c.) and water (0·8 c.c.) was heated under reflux for 5·5 hr. The initial yellow precipitate of "β-morindin" [4] gradually became orange. Water and hydrochloric acid were removed *in vacuo* at room temperature (over sodium hydroxide, sulphuric acid) and the product partitioned between ether and water. Evaporation of the ethereal fraction afforded morindone, orange needles from benzene–n-hexane, m. p. and mixed m. p. 279—280°. Circular

[1] Part XI, Brooker, *J.*, 1959, 470.
[2] Anderson, *Annalen*, 1849, **71**, 216; Stenhouse, *J.*, 1864, **17**, 333; Stein, *J. prakt. Chem.*, 1866, **97**, 234; Thorpe and Greenall, *J.*, 1887, **51**, 52; Thorpe and Smith, *J.*, 1888, **53**, 171; Oesterle and Tisza, *Arch. Pharm.*, 1907, **245**, 534; 1908, **246**, 150; Simonsen, *J.*, 1918, **113**, 766.
[3] Perkin and Hummell, *J.*, 1894, **65**, 851; Perkin, *Proc. Chem. Soc.*, 1908, **24**, 149.
[4] Briggs and Dacre, *J.*, 1948, 564.
[5] Paris and Tuoc, *Ann. pharm. franç.*, 1954, **12**, 794.
[6] Balakrishna, Seshadri, and Venkataramani, *J. Sci. Ind. Res., India*, 1960, **19**, *B*, 433.
[7] Briggs and Taylor, *J.*, 1955, 3298.
[8] Bloom, Briggs, and Cleverley, *J.*, 1959, 178.

paper chromatography of the colourless aqueous fraction against reference sugars in butan-1-ol–pyridine–water (5 : 3 : 2) (solvent A) and butan-1-ol–ethanol–water (5 : 2 : 2) [9] (solvent B) (Whatman No. 1 paper; aniline hydrogen phthalate as indicator) confirmed the presence of glucose and rhamnose only.

Enzymic hydrolysis of morindone 6-rutinoside. Suspensions of rhamnodiastase (8 mg. and 9 mg., respectively), in solutions of morindone 6-rutinoside (46 mg.) in water (100 c.c.) and of rutin (50 mg.) in water (100 c.c.), were kept at room temperature for 9 days. The flocculent orange and yellow precipitates, respectively, were dried and extracted with acetone to remove unchanged glycosides. Crystallisation from ether afforded morindone, m. p. and mixed m. p. 282·5—283·5°, and quercetin, m. p. 313—315° (decomp.), respectively. The aqueous filtrates were concentrated and chromatographed against flanking spots of glucose. After development for 18 hr. only one spot appeared in each hydrolysate.

Rhamnomorindin hydrolysate...	R_F 0·24, R_G 0·84 } Solvent A	R_F 0·06, R_G 0·53 } Solvent B
Rutin hydrolysate.....	,, 0·25, ,, 0·85 } Solvent A	,, 0·06, ,, 0·51 } Solvent B

No appreciable difference appeared in the relative R values after development for 50 hr.

We are indebted to Professor R. Paris for a specimen of rhamnodiastase and to Mr. C. E. F. Rickard for the X-ray measurement. Assistance is gratefully acknowledged from the Chemical Society, the Rockefeller Foundation of New York, the Australian and New Zealand Association for the Advancement of Science, and the Research Grants Committee of the University of New Zealand.

UNIVERSITY OF AUCKLAND, AUCKLAND, NEW ZEALAND. [*Received, January 25th,* 1963.]

[9] Avigad, *Biochem. J.*, 1959, **73**, 587.

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650. *Agricultural Fungicides.* p-*Aminoazobenzenes.*

By J. A. SILK and L. A. SUMMERS.

IT has been known for a number of years that certain azo- and hydrazo-compounds [1] protect seeds from attack by pathogenic seed- and soil-borne micro-organisms. In pursuance of our finding [2] that 4-amino-4′-hydroxyazobenzene was highly effective for the control of *Pythium ultimum* on peas, we have made a series of azo-compounds by standard methods of coupling benzenediazonium salts with phenols and anilines. Details of tests with these compounds as seed disinfectants and protectants, and a report on their mammalian toxicity, are given elsewhere.[2]

Experimental.—*4-Amino-4′-hydroxyazobenzenes* (Table 1). (*a*) Compounds 1—23 were prepared essentially as described by Meldola.[3] *p*-Nitroanilines were diazotised and coupled with phenols. The hydroxynitroazobenzenes thus obtained were not purified (those crystallised for analysis are listed in Table 2) but were reduced by boiling (5 hr.) with aqueous sodium sulphide. The aminohydroxyazobenzenes were precipitated (42—68%) on neutralisation of the cold solutions.

(*b*) Compounds 24—35 were prepared by a modification of the method of Hewitt and Thomas.[4] *p*-Acetamidoaniline was diazotised and coupled with phenols. The crude acetamidohydroxyazobenzenes (those which were purified and analysed are in Table 3) were

[1] Bonrath and Urbschat, G.P. 732,816 (1943) (*Chem. Abs.*, 1944, **38**, 830); G.P. 696,766 (1940) (*Chem. Abs.*, 1941, **35**, 6054); Petersen, Gauss, and Urbschat, *Angew. Chem.*, 1955, **67**, 217; Frohberger, *Phytopath. Z.*, 1956, **27**, 427; Urbschat, *Angew. Chem.*, 1960, **72**, 981; Leach, Garber, and Lange, *Plant Dis. Reptr.*, 1959, Suppl. 259, 213.

[2] Fox, Geoghegan, Silk, and Summers, *Ann. Appl. Biol.*, in the press; see also Geoghegan and Silk, B.P. 907,811 (1962); Geoghegan and Summers, B.P. Appl. 36,286 (1959).

[3] Meldola, *J.*, 1885, **47**, 657.

[4] Hewitt and Thomas, *J.*, 1909, **95**, 1292.

TABLE 1.

4-Amino-4′-hydroxyazobenzenes.

No.	Substituents	M. p.	Solvent *	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
1	3-Me	179°	F	$C_{13}H_{13}N_3O$	68·7	6·0	68·7	5·7
2	2-Me	151	D	$C_{13}H_{13}N_3O$	69·3	5·8	68·7	5·7
3	2-MeO	191	C	$C_{13}H_{13}N_3O_2$,0·25MeOH	63·0	5·2	63·3	5·6
4	3-MeO	152	C	$C_{13}H_{13}N_3O_2$	64·0	5·3	64·2	5·3
5	2-Cl	170	C	$C_{12}H_{10}ClN_3O$	57·9	4·1	58·2	4·0
6	2,3′-Me_2	204	C	$C_{14}H_{15}N_3O$	69·1	6·15	69·7	6·2
7	2,2′-Me_2	192	C	$C_{14}H_{15}N_3O$	69·3	6·3	69·7	6·2
8	2-Me,3′-MeO	172	C	$C_{14}H_{15}N_3O_2$	65·0	5·8	65·4	5·8
9	2-Me,2′-MeO	199	C	$C_{14}H_{15}N_3O_2$	65·4	5·8	65·4	5·8
10	3,3′-$(MeO)_2$	154	C	$C_{14}H_{15}N_3O_3$,0·25MeOH	60·6	5·5	60·9	5·7
11	2-Me,3′-EtO	135	C	$C_{15}H_{17}N_3O_2$,0·25MeOH	65·5	6·4	65·6	6·45
12	2-Me,3′-Et	154	E	$C_{15}H_{17}N_3O$	70·3	6·7	70·6	6·7
13	2-Me,2′-OH	196	D	$C_{13}H_{13}N_3O_2$,0·25MeOH	63·1	5·4	63·3	5·6
14	2-Me,3′-Cl	176	D	$C_{13}H_{12}ClN_3O$,0·25MeOH	58·9	4·9	58·4	5·0
15	2-Et, 3′-MeO	155	C	$C_{15}H_{17}N_3O_2$	66·1	6·35	66·4	6·3
16	2-Cl,3′-MeO	165	C	$C_{13}H_{12}ClN_3O_2$	56·5	4·6	56·2	4·3
17	2,3′-Cl_2	135	C	$C_{12}H_9Cl_2N_3O$	51·0	3·2	51·1	3·2
18	2,3′,5′-Me_3	144	C	$C_{15}H_{17}N_3O$,0·25MeOH	69·7	6·6	69·5	6·8
19	3,3′,5′-Me_3	177	C	$C_{15}H_{17}N_3O$	70·6	6·6	70·6	6·7
20	2,5-Me_2,3′-MeO	147	C	$C_{15}H_{17}N_3O_2$	66·0	6·3	66·4	6·3
21	2-Cl,3′,5′-Me_2	160	C	$C_{14}H_{14}ClN_3O$,0·25MeOH	60·0	5·4	60·3	5·3
22	3-MeO,3′,5′-Me_2	187	C	$C_{15}H_{17}N_3O_2$	66·2	6·6	66·4	6·3
23	2,5,3′,5′-Me_4	156	C	$C_{16}H_{19}N_3O$	71·6	6·9	71·4	7·1
24	2′-Me	199	A	$C_{13}H_{13}N_3O$	68·5	5·7	68·7	5·7
25	3′-Me	178	A	$C_{13}H_{13}N_3O$	68·7	5·7	68·7	5·7
26	2′-MeO	163	B	$C_{13}H_{13}N_3O_2$	64·0	5·6	64·2	5·3
27	2′-NH_2	185 †	A	$C_{12}H_{12}N_4O$	63·4	5·5	63·1	5·3
28	2′-OH ‡	195	A	$C_{12}H_{11}N_3O_2$	62·7	4·8	63·0	4·8
29	3′-Pr^i	164	E	$C_{15}H_{17}N_3O$	70·8	6·5	70·6	6·7
30	3′,5′-Me_2	138	D	$C_{14}H_{15}N_3O$	69·9	6·2	69·7	6·2
31	2′-Me,3′-Pr^i	126	B	$C_{16}H_{19}N_3O$	71·1	7·4	71·4	7·1
32	3′,5′-Pr^i_2	140	B	$C_{18}H_{23}N_3O$	72·5	7·6	72·7	7·7
					N		N	
33	3′-MeO	143	A	$C_{13}H_{13}N_3O_2$	17·4		17·3	
34	3′-EtO	120	B	$C_{14}H_{15}N_3O_2$	16·2		16·3	
35	3′,5′-$(MeO)_2$	102	B	$C_{14}H_{15}N_3O_3$	15·4		15·4	

* A, ethanol; B, aqueous ethanol; C, methanol; D, aqueous methanol; E, benzene; F, benzene–methanol. † With decomp. ‡ Hydrolysis under nitrogen. Prepared previously [3, 5] but not characterised.

TABLE 2.

4′-Hydroxy-4-nitroazobenzenes.

Substituents	M. p.	Solvent *	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
3-Me	165°	G	$C_{13}H_{11}N_3O_3$	60·7	4·4	60·6	4·3
3-MeO	198	G	$C_{13}H_{11}N_3O_4$	57·6	4·0	57·1	4·0
2-Cl †	209	E	$C_{12}H_8ClN_3O_3$	52·0	2·8	51·9	2·9
2,3′-Me_2	153	G	$C_{14}H_{13}N_3O_3$	61·7	4·4	62·0	4·8
2,2′-Me_2	183	G	$C_{14}H_{13}N_3O_3$	61·5	4·8	62·0	4·8
2-Me,3′-MeO	151	G	$C_{14}H_{13}N_3O_4$	58·2	4·6	58·5	4·5
2-Me,2′-MeO	188	C	$C_{14}H_{13}N_3O_4$	58·5	4·3	58·5	4·5
3,3′-$(MeO)_2$	159	G	$C_{14}H_{13}N_3O_5$	55·3	4·2	55·4	4·3
2-Me,3′-EtO	124	C	$C_{15}H_{15}N_3O_4$	60·2	4·6	59·8	5·0
2-Me,3′-Et	134	A	$C_{15}H_{15}N_3O_3$	62·6	5·2	63·2	5·3
2-Me,3′-Cl	170	G	$C_{13}H_{10}ClN_3O_3$	53·3	3·6	53·5	3·4
2-Et,3′-MeO	121	C	$C_{15}H_{15}N_3O_4$	59·8	4·9	59·8	5·0
2,3′-Cl_2	192	G	$C_{12}H_7Cl_2N_3O_3$	46·8	2·2	46·2	2·2
2,3′,5′-Me_3	192	E	$C_{15}H_{15}N_3O_3$	62·6	5·3	63·2	5·3
2,5-Me_2,3′-MeO	128	C	$C_{15}H_{15}N_3O_4$	59·9	4·9	59·8	5·0
2-Cl,3′,5′-Me_2	217	E	$C_{14}H_{12}ClN_3O_3$	55·4	4·0	55·0	3·9
3-MeO,3′,5′-Me_2	201	G	$C_{15}H_{15}N_3O_4$	60·0	5·0	59·8	5·0
2,5,3′,5′-Me_4	200	A	$C_{16}H_{17}N_3O_3$	64·3	5·6	64·2	5·7

* As in Table 1; G, acetic acid. † Higashino (*Yakugaku Zasshi*, 1959, **79**, 69; *Chem. Abs.*, 1959, **53**, 10,096) gives m. p. 205°.

[5] Large and Hinshelwood, *J.*, 1956, 620.

TABLE 3.

4-Acetamido-4′-hydroxyazobenzenes.

Substituent	M. p.	Solvent	Formula	Found (%) N	Required (%) N
2′-Me	225°	B	$C_{15}H_{15}N_3O_2$	15·6	15·6
3′-Me	192	B	$C_{15}H_{15}N_3O_2$	15·6	15·6
3′-MeO	209	A	$C_{15}H_{15}N_3O_3$	14·8	14·8

hydrolysed by boiling (5 hr.) with 5N-sodium hydroxide. The aminohydroxyazobenzenes were obtained (50—73%) by neutralisation of the cold solutions. In some cases they tenaciously retained methanol of crystallisation which could not always be removed by heating *in vacuo* at 100° for 2 hr.

4-p-*Aminophenylazo*-1-*naphthol*, m. p. 160° (from methanol) was prepared as in (*b*) above from 1-naphthol (Found: N, 15·7. Calc. for $C_{16}H_{13}N_3O$: N, 16·0%). It was reported by Meldola [3] but not characterised.

TABLE 4.

4,4′-Diaminoazobenzenes.

No.	Substituents	M. p.	Solvent	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
36	3-Me	148°	B	$C_{13}H_{14}N_4$	69·2	6·6	69·0	6·2
37	2-Me	185	B	$C_{13}H_{14}N_4$	69·4	6·1	69·0	6·2
38	3-MeO	119	B	$C_{13}H_{14}N_4O$	64·1	5·8	64·5	5·8
39	3,5-Me_2	175	B	$C_{14}H_{16}N_4$	70·2	6·8	70·0	6·7
40	2′,3,5-Me_3	171	A	$C_{15}H_{18}N_4$	70·8	7·4	70·9	7·1

4-*Amino*-2′-*hydroxy*-5′-*methylazobenzene*,[6] m. p. 138—140° (from aqueous ethanol) (Found: C, 69·1; H, 5·8. Calc. for $C_{13}H_{13}N_3O$: C, 68·7; H, 5·7%), was likewise prepared from *p*-cresol.

4,4′-*Diaminoazobenzenes* (Table 4) (cf. Saunders [7]). (*a*) To prepare compounds 36—38 the appropriate toluidine or anisidine (0·1 mol.) and sodium formaldehyde bisulphite (0·1 mol.) in water (200 c.c.) were warmed (to 80°) until the solution was clear. Sodium acetate (0·3 mol.) was added and the solution cooled to 5°. Diazotised *p*-acetamidoaniline solution (0·1 mol.) was added. The precipitate of the sodium *N*-methylenesulphonate of the 4′-acetamido-4-aminoazobenzene was hydrolysed by refluxing it for 5 hr. in ethanol (100 c.c.) and water (200 c.c.) containing potassium hydroxide (40 g.) The diaminoazobenzene (60—65%) precipitated on cooling.

(*b*) Compound 39 was prepared by adding diazotised *p*-acetamidoaniline solution to 2,6-dimethylaniline and sodium acetate (3 equiv.) in aqueous methanol. The tar which formed initially solidified to an orange precipitate of 4′-*acetamido*-4-*amino*-3,5-*dimethylazobenzene*, m. p. 184° (from ethanol) (Found: N, 19·8. $C_{16}H_{18}N_4O$ requires N, 19·9%). Without purification it was hydrolysed as in (*a*) above.

(*c*) To obtain compound 40 a diazotised solution of 2-amino-5-nitrotoluene was added to 2,6-dimethylaniline and sodium acetate (3 equiv.) in aqueous methanol. The crude 4-*amino*-4′-*nitro*-2′,3,5-*trimethylazobenzene* (analytical sample, m. p. 117°, from methanol) (Found: C, 63·3; H, 5·6. $C_{15}H_{16}N_4O_2$ requires C, 63·3; H, 5·6%) was reduced with sodium sulphide in aqueous ethanol.

4-(p-*Hydroxybenzylideneamino*)*aniline*, m. p. 194—196° (from ethanol) (Found: N, 13·2. $C_{13}H_{12}N_2O$ requires N, 13·0%), was prepared from *p*-phenylenediamine and *p*-hydroxybenzaldehyde in hot ethanol.

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[6] Sandoz, Ltd., Swiss P. 276,609 (1951) (*Chem. Abs.*, 1952, **46**, 6845); Baker and Imperial Chemical Industries Limited, B.P. 822,948 (1959) (*Chem. Abs.*, 1960, **54**, 8094).

[7] Saunders, "The Aromatic Diazo-compounds and their Technical Applications," 2nd edn., Edward Arnold & Co., London, 1949, p. 202.

651. *Fluoro- and Difluoro-benzodicarboxylic Acids and Their Anhydrides.*

By G. VALKANAS and H. HOPFF.

THE preparation of fluorophthalic acids from the corresponding nitro-acids has already been described but, even in those cases in which one isomeric nitro-acid is formed after nitration, the yields obtained are small, and several steps are involved, as the fluorination is carried out through the amino-esters. 4-Fluorophthalic acid and the anhydride,[1] and 5-fluoroisophthalic acid [2] are prepared in this way. 3-Fluorophthalic acid has been prepared by oxidising 3-fluoro-*o*-xylene with potassium permanganate in pyridine,[3] and then converted by distillation into the anhydride, which could also be isolated by an exchange reaction of 3-chlorophthalic anhydride and potassium fluoride.[4]

Fluorotoluenes and certain nitrofluorotoluenes with a nitric acid solution at elevated temperature and pressure are oxidised to fluorobenzoic [6] and nitrofluorobenzoic acid.[7] When fluoroxylenes are similarly treated, the fluorobenzodicarboxylic acids are obtained in about 80% yield, free of nitrated by-products. In general the reaction is carried out with the stoicheiometric amount of nitric acid, though with fluoro-*m*- or fluoro-*p*-xylenes it is advantageous to use an excess of the acid.

The fluoro-*p*-xylenes are oxidised to water-soluble products and the two isomeric 3-fluoro- and 4-fluoro-phthalic acids are obtained as clear yellow solutions. Fluoroterephthalic and 2-fluoro-, 4-fluoro-, and 5-fluoro-isophthalic are water insoluble. When half the stoicheiometric amount of nitric acid is used fluorotoluic acids are formed in very good yield. When the fluorobenzodicarboxylic acids are dissolved in refluxing thionyl chloride the corresponding acid chlorides are formed. This conversion is slower with fluoroterephthalic acid than with the other acids.

Difluoroxylenes,[8] when oxidised by nitric acid under the conditions described for fluoroxylenes, are readily converted into the difluorobenzodicarboxylic acids with yields up to 80%. The acids so far prepared are 2,5-difluoroterephthalic, 2,5-difluoroisophthalic, and 3,6-difluorophthalic acid, isolated as the anhydride. With the oxidation of 2,5-difluoro-*p*-xylene and 2,5-difluoro-*m*-xylene, water-insoluble crystalline products are obtained. The 3,6-difluorophthalic acid obtained from 3,6-difluoro-*o*-xylene is water soluble, as are the 3-fluoro- and 4-fluoro-phthalic acids described.

As expected, the introduction of fluorine into the dicarboxylic acids increases their acidity. The dissociation constants measured indicate a decrease in pK value for the one fluorine substituted of, *m*-fluorine 0·15, *p*-fluorine 0·19, and *o*-fluorine substitution 0·30 pK units.[2]

Experimental.—Fluoroterephthalic Acid. Fluoro-*p*-xylene (15 g.) and 22% nitric acid solution (150 ml.) were heated in a glass-lined autoclave (½ l. capacity) for 75 min. to 200°. The temperature was maintained for 4 hr., and the final pressure was 52 kg./cm.². The *acid* was washed with cold water, and dried at 100° (yield, 17·6 g., 79%); it had m. p. 330° (subl.) (Found: C, 52·3; H, 2·6; F, 10·7, 11·1. $C_8H_5FO_4$ requires C, 52·2; H, 2·7; F, 10·3%).

2-Fluoroisophthalic acid. By a similar reaction, 2-fluoro-*m*-xylene (15 g.) gave the *acid* (17·2 g., 75%) as fine needles, m. p. 286—287° (Found: F, 10·5. $C_8H_5FO_4$ requires F, 10·3%).

4-Fluoroisophthalic Acid. Similarly, oxidation of 4-fluoro-*m*-xylene (15 g.) gave the

[1] Blick and Smith, *J. Amer. Chem. Soc.*, 1929, **51**, 1865.
[2] Seidel, Dissertation, E.T.H., Zurich, 1960, p. 17.
[3] Newman and Wiseman, *J. Org. Chem.*, 1961, **26**, 3208.
[4] Heller, *J. Org. Chem.*, 1960, **25**, 834.
[5] Korshak, Kolesnikov, and Federova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 353; *Chem. Abstr.*, 1958, **52**, 12,804.
[6] Hopff and Valkanas, *J. Org. Chem.*, 1962, **27**, 2923.
[7] Valkanas and Hopff, *J.*, 1963, 359.
[8] Valkanas, unpublished work.

crystalline acid (17·4 g., 75·5%), m. p. 282—283° (Found: F, 10·55. Calc. for $C_8H_5FO_4$: F, 10·3%).

5-*Fluoroisophthalic acid.* 5-Fluoro-*m*-xylene (15 g.), was treated as described, (*a*) with 22% nitric acid solution (150 ml.; 10% excess), and (*b*) with 20% nitric acid solution (150 ml., no excess). In expt. (*a*) the final pressure at 200° was 63 kg./cm.^{2}, and the yield of 5-fluoroisophthalic acid was 68%. In (*b*) the pressure at 200° was below 52 kg./cm.^{2}, and the yield was increased to 78%. In both cases the acid was obtained crystalline, m. p. 291—292° (Found: F, 10·35. Calc. for $C_8H_5FO_4$: F, 10·3%).

3-*Fluorophthalic acid and anhydride.* 3-Fluoro-*o*-xylene (15 g.) was oxidised with the stoicheiometric amount of nitric acid solution (20%, 150 ml.). The oxidation products were water soluble, and the 3-fluorophthalic acid was extracted three times from the water solution with ether. The *anhydride* was formed at about 200° and distilled at 281—283°/730 mm. (14·2 g., 70%), m. p. 153—155° (lit.,[3,4] 160°) (Found: F, 10·3. Calc. for $C_8H_3FO_3$: F, 10·65%).

If in the oxidations described only half the required quantity of nitric acid is used, then products are obtained which are insoluble in water. These were identified as *fluorotoluic acids* (Found: F, 12·1. $C_8H_7FO_2$ requires F, 12·35%).

4-*Fluorophthalic acid and anhydride.* As in the preceding experiment, 4-fluoro-*o*-xylene (15 g.) gave water-soluble oxidation products from which the 4-fluorophthalic acid was extracted with ether. The acid, recrystallised from acetic acid, had m. p. 152—153° (sealed tubes). The *anhydride* (14·5 g., 73%) was distilled off at 261—262°/730 mm.; it had m. p. 74—75° (lit.,[1] m. p. 76—78°) (Found: F, 10·6. Calc. for $C_8H_3FO_3$: F, 10·65%).

3,6-*Difluorophthalic acid and anhydride.* 3,6-Difluoro-*o*-xylene (11·4 g.) and 15% nitric acid solution (140 ml.; no excess) were heated in a glass-lined autoclave for 3 hr. at 190—200° to give a clear solution, which was extracted three times with ether. The ether extract was dried and the 3,6-*difluorophthalic acid* recovered as a yellowish powder; this was distilled at 730 mm. to give the *anhydride* (9·5 g., 61%), m. p. 206—207° (Found: C, 52·4; H, 1·1; F, 20·3. $C_8H_2F_2O_3$ requires C, 52·2; H, 1·1; F, 20·6%).

2,5-*Difluoroisophthalic acid.* 2,5-Difluoro-*m*-xylene (17·2 g.) was oxidised with 15% nitric acid solution (220 ml.). 2,5-*Difluoroisophthalic acid* was crystallised from the reaction solution and washed with cold water; it had (16·7 g., 75%) m. p. 282—283° (Found: C, 47·5; H, 2·0; F, 18·75. $C_8H_4O_2F_4$ requires C, 47·5; H, 2·0; F, 18·8%).

2,5-*Difluoroterephthalic acid.* By reaction as described above, 2,5-difluoro-*p*-xylene (15·0 g.) gave the acid (16·6 g., 78%), which had m. p. 325—330° (Found: C, 47·6; H, 2·1; F, 18·35%).

LABORATORY OF ORGANIC CHEMICAL TECHNOLOGY,
SWISS FEDERAL INSTITUTE OF TECHNOLOGY,
ZURICH, SWITZERLAND.

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