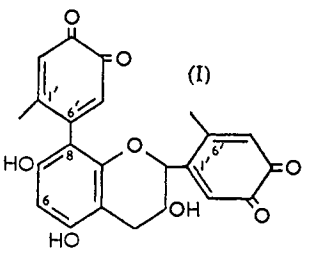
91. *Autoxidation of Polyphenols. Part IV.* Oxidative Degradation of the Catechin-autoxidation Polymer.*

By D. E. Hathway.

It has now been found that permanganate oxidation of the methylated hydrogenation product of catechin-autoxidation polymer (Part III) gives *m*-hemipinic, veratric, and oxalic acid, whereas similar oxidation of the methylation product of the polymer produced by acid catalysis [1] yields veratric and oxalic acid. The difficulty involved in the oxidative degradation of aromatic polymers is shown by the low yield (9%) of veratric acid from the acid-catalysis polymer which is a dimer or trimer.[1] Secondary oxidation which occurs during the preparation of the autoxidation polymer (Part III) is paralleled by a 70% uptake of hydrogen during hydrogenation of the polymer. Its behaviour on dialysis through cellophane indicates that this polymer is a higher polymer than that given by acids, and the more difficult degradation led to a smaller proportion of aromatic acids. *m*-Hemipinic acid (2%) is accompanied by 0·5% of veratric acid, the latter arising presumably from end-groups. These experiments suggest that autoxidation of catechin leads to some polymerisation by type (I) linkages, whereas acids lead to some union of the Freudenberg type.



Catechin-autoxidation polymer is important on account of its close structural similarity to phlobatannins, which have recently been isolated in high yield from the extractives of harvested *Uncaria gambir* leaves and *Acacia catechu* heartwood.[2]

Experimental.—M. p.s were determined on a Kofler block. Paper chromatography was carried out in all-glass apparatus in a constant-temperature enclosure at 25°. Chromatograms were dried in a current of warm air at 60°. Tubes (1·8 cm. in diameter) fitted with a tap of 4 mm. bore and a sintered-glass disc were packed with "chromatographic" silica gel (20 g.) (from Messrs. L. Light & Co.), which had been mixed with 0·5N-sulphuric acid (10 ml.) and made into a slurry with chloroform (60—70 ml.), by Bulen, Varner, and Burrell's method.[3] Eluants were prepared by the equilibration of appropriate volumes of butan-1-ol and chloroform with a little water, and retention of the lower phase.

m-Hemipinic acid (m. p. 179—182°) was prepared from *m*-meconine [4] (Found: C, 53·5; H, 4·8%; equiv., 115. Calc. for $C_{10}H_{10}O_6$: C, 53·1; H, 4·5%; equiv., 113).

Chromatographic separation of veratric and m-*hemipinic acid.* Marker spots (5 μl.) of 0·5% w/v chloroform solutions of the acids were applied to start-lines, 4 cm. from the lower edge of Whatman filter paper No. 1, of length 57 cm. Single-way ascending chromatography was effected with the systems: (1) benzyl alcohol–*tert.*-butyl alcohol–*iso*propyl alcohol–water (3 : 1 : 1 : 1, by vol.) containing 1·8% w/v of formic acid; [5] (2) propanol–35% aqueous ammonia–water (6 : 3 : 1, by vol.).[6] Papers were irrigated for 20 hr. When the chromatograms were developed with solvent system (1), the acids were exposed as yellow spots against a green background by means of a solution of bromocresol-green at pH 5·5; [7] when they were developed with system (2), the acids were revealed by Universal indicator (British Drug Houses Ltd.), adjusted to pH 9—10,[8] as red spots which faded fairly rapidly. *m*-Hemipinic acid had R_F 0·78 (1), 0·53 (2), and veratric acid had R_F 0·95 (1), 0·76 (2).

* Part III, *J.*, 1957, 1562.

[1] Freudenberg and Maitland, *Annalen*, 1934, **510**, 193; *Collegium*, 1934, **776**, 656; Freudenberg, Stocker, and Porter, *Chem. Ber.*, 1957, **90**, 957.
[2] Hathway and Seakins, *Biochem. J.*, 1957, **65**, 32P; **67**, 239.
[3] Bulen, Varner, and Burrell, *Analyt. Chem.*, 1952, **23**, 187.
[4] Edwards, Perkin, and Stoyle, *J.*, 1925, **127**, 195.
[5] Stark, Goodban, and Owens, *Analyt. Chem.*, 1952, **23**, 413.
[6] Hanes and Isherwood, *Nature*, 1949, **164**, 1107.
[7] Lugg and Overell, *ibid.*, 1947, **160**, 87.
[8] Long, Quayle, and Stedman, *J.*, 1951, 2197.

A solution of veratric (50 mg.) and *m*-hemipinic (50 mg.) acid in methanol–chloroform (1 : 1 by vol.; 1 ml.) was added to the top of the column and allowed to drain into the column. The column was eluted successively with chloroform (50 ml.) and 1 : 40 v/v butan-1-ol–chloroform (100 ml.) at a flow-rate of 2 ml./min., solvent being added in 50 ml. volumes before the last 10 ml. of the preceding volume had drained into the column. The effluent was collected in 10 ml. fractions, in which the acid was estimated after the addition of water by titration with 0·01N-sodium hydroxide. Separation was very efficient.

Permanganate oxidation of the methylated hydrogenation product of catechin-autoxidation polymer. A methanolic solution (130 ml.) of catechin-autoxidation polymer (700 mg.) (Part III) was hydrogenated at 1 atm., in the presence of Adams catalyst, and then treated with diazomethane. The product (700 mg.) in dioxan (25 ml.) and saturated aqueous sodium carbonate (2·5 ml.) at 100° was gradually treated with N-potassium permanganate (70 ml.). After the reduction, the filtrate was concentrated to 25 ml., and acidified with 12N-hydrochloric acid. The resinous precipitate (360 mg.) was removed, and the filtrate neutralised to Congo-red with sodium acetate and treated with excess of 0·5M-calcium chloride. The supernatant liquid was centrifuged off, and the calcium oxalate (280 mg.) washed and dried at 100°. Ether-extraction of the combined supernatant liquid and washings, after saturation with sodium chloride and acidification with 12N-hydrochloric acid, afforded a partly crystalline ochreous residue (120 mg.) which on partition chromatography on silica gel gave a sharp fraction (10 mg.) which was recovered by chloroform extraction of the re-acidified fractions. Crystallisation from xylene–light petroleum (b. p. 100—120°) gave *m*-hemipinic acid (9 mg.), m. p. and mixed m. p. 179—182° (anhydride sublimed at 175°). A second fraction (10 mg.), crystallised from xylene–light petroleum, gave veratric acid, m. p. and mixed m. p. 179—180°.

Permanganate oxidation of the methylation product of acid-catalysis polymer. A solution of the methylated polymer [1] (3 g.) in dioxan (100 ml.) and saturated aqueous sodium carbonate (10 ml.) at 100° was similarly treated with aqueous N-potassium permanganate (350 ml.). The filtrate was concentrated to 100 ml. and acidified with 12N-hydrochloric acid, and the precipitate (1·5 g.) obtained was extracted with boiling water (500 ml.) (charcoal). Evaporation of the filtrate to 20 ml. gave a precipitate (200 mg.), m. p. 165—180°, which was removed in the centrifuge, and dried (KOH) at 20°/0·05 mm. When a 30 mg. portion was submitted to partition chromatography on silica gel, a sharp fraction (26 mg.) was eluted which, crystallised from xylene–light petroleum (b. p. 100—120°), gave needles of veratric acid, m. p. and mixed m. p. 179—180°. Absence of *m*-hemipinic acid was shown by paper chromatography.

Calcium oxalate (950 mg.) was separated from the initial filtrate.

The author thanks the Director and the Council of the British Leather Manufacturers' Research Association for their permission to publish this paper. The method of degrading these polymers arose out of a conversation with Professor R. D. Haworth, F.R.S., to whom the author expresses his gratitude.

BRITISH LEATHER MANUFACTURERS' RESEARCH ASSOCIATION,
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92. *Compounds of Silicon. Part III.* Competitive Reactions of Chloro-, Bromo-, and Iodo-triethylsilanes with Phenol.*

By R. A. SHAW.

RECENT work by Wilkins and his co-workers [1,2,3] prompts publication of some results obtained by us several years ago. A theory of the relative ease of displacement of the halogen in trialkylhalogenosilanes has been proposed for reactions proceeding by a simple bimolecular mechanism,[2] $Y^- + R_3SiX \longrightarrow R_3SiY + X^-$. It was suggested that, providing steric effects are here not significant, the relative ease of displacement of the group X

* Part II, *J.*, 1957, 2831.

[1] Wilkins, Brown, and Stevens, *J.*, 1950, 163.
[2] Vaughan and Wilkins, *Nature*, 1951, **167**, 525.
[3] Reid and Wilkins, *J.*, 1955, 4029.

in a competitive reaction, where the same reagent Y^- competes for different halogenosilanes R_3SiX and R_3SiX', depends on the respective values of the electron affinities of the halogen atoms E_X less the bond energies of the silicon–halogen bonds B_{Si-X}, *i.e.* $E_X - B_{Si-X}$, which represents the " ionic bond energy " [4] less a constant (the ionisation potential of silicon). The " ionic bond energies " of the silicon–halogen bonds, which have been discussed,[4,5] and recently revised [5] in the light of the more accurate data now available, are Si–I 167·4, Si–Br 179·0, Si–Cl 190·3, and Si–F 237·4 (kcals. mole^{-1}).

Competitive reactions of chloro-, bromo-, and iodo-triethylsilanes with phenol in carbon tetrachloride solution confirm this order qualitatively. The reactivity ratio for this reaction of Si–I/Si–Br was found to be 15—20 : 1, and that of Si–Br/Si–Cl 3—4 : 1. From this one would expect a value of 45—80 : 1 for the Si–I/Si–Cl ratio, and the experimental values lay in the region of 45—70 : 1. As neither of the silanes was present in large excess, the concentration of the more reactive halides decreased rapidly in the course of the reaction, and the above ratios are lower limiting values of the true ones. A further effect which also tended to diminish the reactivity ratios was the reversibility of the reaction $Et_3SiX + PhOH \rightleftharpoons Et_3Si{\cdot}OPh + HX$, which was at least partially overcome by aspirating a stream of dry nitrogen through the mixture.

Experimental.—Preparation of reagents. Chloro-,[6] b. p. 145—146°, bromo-,[6] b. p. 162—163°, and iodo-triethylsilane,[7] b. p. 188—188·5°, were prepared by Eaborn's methods.[8,7] Carbon tetrachloride was dried (P_2O_5) and distilled. All these reagents were fractionally distilled in a column of approximately ten theoretical plates. " AnalaR " phenol was distilled and the centre cut collected.

Competitive reactions of halogenosilanes with phenol. Accurately weighed amounts of the two halogenosilanes and phenol (slightly less than the quantity corresponding to the smaller of the two silane concentrations) were dissolved in carbon tetrachloride (10 ml.) and a fast stream of dry nitrogen passed through the solution. The iodine : bromine and the iodine : chlorine ratios were determined at room temperature, the bromine : chlorine ratio at the b. p. of the solvent. The hydrogen halides evolved were absorbed in sodium hydroxide solution; a control flask containing aqueous silver nitrate showed that all of the hydrogen halide was absorbed.

Estimation of the mixed halide ions. The mixed halide ions were determined by potentiometric titration, a quinhydrone electrode, a salt bridge, and a silver electrode being used. Known volumes of the absorbing alkaline solutions were withdrawn from time to time and made up to known volumes, aliquot parts of which were titrated with 0·1N-silver nitrate after acidification with dilute nitric acid. The titrations were followed by means of a Mullard " magic eye " indicator. The accuracy of the method was checked by using standard solutions of mixed halide ions. The reactivity ratios are the results of several runs and of different stages of completion of the reaction. A typical runs was as follows: Bromotriethylsilane (2·804 g., 0·01435 mole), iodotriethylsilane (1·220 g., 0·00505 mole), and phenol (0·440 g., 0·00468 mole) were used in carbon tetrachloride (10 ml.). After ½ hr. (50% reaction) the mean of three titres gave the reactivity ratio (corrected for the different concentrations of the halogenosilanes) as 20 : 1; after 1½ hr. (83% reaction) 15·5 : 1. If the stream of nitrogen was fast enough, the ratio reached a limiting value; slower rates of gas passage decreased this value, owing to the reversible reaction discussed above.

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BIRKBECK COLLEGE, MALET STREET, LONDON, W.C.1. [*Received, June 19th,* 1957.]

[4] Eaborn, *J.*, 1950, 3077.
[5] Shaw, *J.*, 1957, 2831.
[6] Eaborn, *J.*, 1953, 494.
[7] *Idem*, *J.*, 1949, 2755.

93. *Direct 5-Hydroxylation of 3β-Acetoxyandrostane-11 : 17-dione.*

By M. Martin-Smith.

During the work directed towards a partial synthesis of aldosterone,[1] a secondary product was always obtained in small yield in the preparation of 3β-acetoxyandrostane-11 : 17-dione from 3β-acetoxy-17α-hydroxy*allo*pregnane-11 : 20-dione by the action of chromic oxide in aqueous aceti cacid. This compound has now been characterized as 3β-acetoxy-5α-hydroxyandrostane-11 : 17-dione and its direct formation from 3β-acetoxyandrostane-11 : 17-dione demonstrated. Its constitution, which was conclusively shown by its conversion in several steps into adrenosterone, was made apparent from its infrared spectrum, from molecular-rotational considerations,[2] and by analogy with the earlier direct 5-hydroxylation of steroids reported by St. André *et al.*[3]

Extensive investigation of reaction conditions failed to raise the yield of 3β-acetoxy-5α-hydroxyandrostane-11 : 17-dione from 3β-acetoxyandrostane-11 : 17-dione above 14%. It therefore appears not to be feasible to use direct 5-hydroxylation by this method as a means of obtaining 3β : 5α-dihydroxy-steroids for conversion into the 3-keto-Δ^4-compounds which constitute many biologically important steroids (cf. Bladon *et al.*[4]).

In accordance with expectations 3β-acetoxy-5α-hydroxyandrostane-11 : 17-dione was readily dehydrated to 3β-acetoxyandrost-5-ene-11 : 17-dione. Also boiling methanolic sodium hydroxide solution deacetylated 3β-acetoxy-5α-hydroxyandrostane-11 : 17-dione to the corresponding dihydroxy-dione. Oxidation of this compound by chromic oxide in pyridine yielded 5α-hydroxyandrostane-3 : 11 : 17-trione which thionyl chloride in ice-cold pyridine dehydrated smoothly to androst-4-ene-3 : 11 : 17-trione (adrenosterone).

Experimental.—$[\alpha]_D$ are in $CHCl_3$; ultraviolet absorption spectra refer to EtOH solutions; infrared spectra were taken in Nujol suspension. M. p.s were taken on a Kofler block.

3β-Acetoxy-5α-hydroxyandrostane-11 : 17-dione. Maximum yields were to be obtained by the following procedure. A solution of chromic oxide (4·0 g.) in water (3 ml.) was diluted to 100 ml. by glacial acetic acid. 3β-Acetoxyandrostane-11 : 17-dione (500 mg.) was treated with this solution (10 ml.), and the mixture kept at room temperature for 26 hr. Methanol in excess was added and after 3 hr. at room temperature the solution was taken to dryness under reduced pressure. The residue was treated with dilute hydrochloric acid and extracted with chloroform (5 × 20 ml.). The chloroform extracts were washed with sodium hydrogen carbonate solution and water, and taken to dryness under reduced pressure, yielding a colourless oil. This was chromatographed in benzene over alumina (Brockmann grade V). Benzene eluted unchanged starting material. Benzene–chloroform (4 : 1) eluted deacetylated starting material. Chloroform eluted the 5α-hydroxy-compound. Reacetylation of the deacetylated starting material (identical with 3β-hydroxyandrostane-11 : 17-dione [5]) by overnight treatment with acetic anhydride in pyridine afforded a total recovery of 3β-acetoxyandrostane-11 : 17-dione of 60%.

Crystallisation from methanol gave the *3β-acetoxy-5α-hydroxyandrostane-11 : 17-dione* as blunt prisms (70 mg., 14%), showing change of crystal form *ca.* 190° and melting at 244·5—246·5°, $[\alpha]_D$ +86° (*c* 2·08) (Found: C, 69·9; H, 8·7. $C_{21}H_{30}O_5$ requires C, 69·6; H, 8·4%). Longer reaction times did not increase the yield of the 5α-hydroxy-compound, but led to lower recoveries of starting material.

3β-Acetoxy-5α-hydroxyandrostane-11 : 17-dione is soluble in benzene, chloroform, methanol, and ethanol, sparingly soluble in ether, and insoluble in water. The ultraviolet spectrum showed a plateau at *ca.* 290 mμ, ε ~100 (isolated keto-groups) but no other absorption. The infrared spectrum showed a peak at 3480 (OH), a broad peak at 1728—1720 (acetate and 5-membered cyclic ketone), and peaks at 1700 (6-membered cyclic ketone) and 1244 cm.$^{-1}$ (acetate).

[1] Barton, Campos-Neves, and Scott, *J.*, 1957, 2698.
[2] Barton and Klyne, *Chem. and Ind.*, 1948, 755; Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, 3rd edn., 1949, pp. 204—219.
[3] St. André, MacPhillamy, Nelson, Shabica, and Scholz, *J. Amer. Chem. Soc.*, 1952, **74**, 5506.
[4] Bladon, Henbest, Jones, Lovell, and Woods, *J.*, 1954, 125.
[5] Klyne and Ridley, *J.*, 1956, 4825; Steiger and Reichstein, *Helv. Chim. Acta*, 1937, **20**, 817.

3β-*Acetoxyandrost*-5-*ene*-11 : 17-*dione*. 3β-Acetoxy-5α-hydroxyandrostane-11 : 17-dione (140 mg.) in ice-cold pyridine (5 ml.) was treated with ice-cold thionyl chloride (0·2 ml.) and kept at 0° for 10 min. The mixture was then poured into water (50 ml.): the crystalline unsaturated *dione* was deposited. It was collected, dried at the pump, and extracted with warm methanol (20 ml.). Concentration of the solution afforded plates, m. p. 166—167°. Further crystallization from ethyl acetate–light petroleum (b. p. 40—60°) yielded plates, m. p. 170—171·5° (70 mg.) (Found: C, 72·9; H, 8·2. $C_{21}H_{28}O_4$ requires C, 73·2; H, 8·2%). The ultraviolet spectrum showed end-absorption and a weak maximum near 290 mμ, $[\alpha]_D$ +38° (*c* 2·11). The infrared spectrum showed a broad peak at 1740—1727 (acetate and 5-membered cyclic ketone) and peaks at 1707 (6-membered cyclic ketone), 1663 (isolated double bond), 1248 (acetate), and 812 cm.$^{-1}$ (trisubstituted double bond). Hydrogenation in acetic acid solution in the presence of Adams catalyst afforded 3β-acetoxyandrostane-11 : 17-dione (identity proved by infrared spectrum in KCl disc).

3β : 5α-*Dihydroxyandrostane*-11 : 17-*dione*. 3β-Acetoxy-5α-hydroxyandrostane-11 : 17-dione (100 mg.) was refluxed for 1 hr. with sodium hydroxide (500 mg.) in methanol (10 ml.). The mixture, on being poured into water (75 ml.), deposited a colourless solid (65 mg.). A further 20 mg. of material was obtained by chloroform-extraction of the aqueous solution. Crystallized from methanol, the product formed stout rods which changed to needles at 250° and melted at 273—274° (Found: C, 71·1; H, 8·4. $C_{19}H_{28}O_4$ requires C, 71·2; H, 8·8%). This *dione* is sparingly soluble in ether and only moderately soluble in chloroform and dioxan. $[\alpha]_D$ was therefore taken in pyridine [+137° (*c* 1·96)]. The infrared spectrum showed peaks at 3430, 3350 (OH), 1727 (5-membered cyclic ketone), and 1700 cm.$^{-1}$ (6-membered cyclic ketone).

5α-*Hydroxyandrostane*-3 : 11 : 17-*trione*. Pyridine–chromic oxide complex was prepared by adding finely ground chromic oxide (100 mg.) in small portions to pyridine (1 ml.) with cooling. To the resulting slurry was added 3β : 5α-dihydroxyandrostane-11 : 17-dione (80 mg.), dissolved in pyridine (2 ml.). The mixture, which became homogeneous, was kept overnight at room temperature, then diluted to 100 ml. with water and acidified with dilute hydrochloric acid. Extraction with chloroform (3 × 25 ml.) gave a dark red extract which, on being extracted with dilute aqueous sodium hydroxide solution followed by water, lost nearly all its colour. The chloroform solution was taken to dryness under reduced pressure and the resulting brown amorphous residue exhaustively extracted with ether. The ethereal extracts yielded a white solid which on crystallization from ethanol formed prisms, m. p. 241—243° (Found: C, 71·8; H, 7·9. $C_{19}H_{26}O_4$ requires C, 71·7; H, 8·2%), of the *trione*. Crystallization of this from methanol–ether gives a cubic form, m. p. 252—254°. Slow heating of the prisms of m. p. 241—243° also converts them into the higher-melting form, $[\alpha]_D$ +145° (*c* 1·50). The infrared spectrum showed peaks at 3490 and 3440 (OH), 1730 (5-membered cyclic ketone), and 1705 and 1690 cm.$^{-1}$ (6-membered cyclic ketone).

Adrenosterone. 5α-Hydroxy-3 : 11 : 17-trione (60 mg.), dissolved in pyridine (2 ml.), was cooled to 0°. Then chilled thionyl chloride (0·1 ml.) was added and the mixture set aside at 0° for 10 min. It was then diluted to 100 ml. with water, acidified with hydrochloric acid, and extracted with ether (3 × 100 ml.). The ethereal extracts were washed with water and taken to dryness under reduced pressure, yielding a colourless solid (40 mg.). Crystallization from ether gave cubes, m. p. 218—220°, $[\alpha]_D$ +286° (*c* 0·95), $\lambda_{max.}$ 238 mμ (ε 1·53 × 10^4) [reported for adrenosterone: m. p. 218—220°,[6] 221—225°,[7] 222—224°,[8] $[\alpha]_D$ +284°,[7] $\lambda_{max.}$ 239 mμ (ε 1·38 × 10^4) [8]].

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THE UNIVERSITY, GLASGOW, W.2. [*Received, August 7th*, 1957.]

[6] Mason and Sprague, *J. Biol. Chem.*, 1948, **175**, 451.
[7] Fried, Thoma, Gerke, Herz, Dorin, and Perlman, *J. Amer. Chem. Soc.*, 1952, **74**, 3962.
[8] Sarett, *J. Biol. Chem.*, 1946, **162**, 601.

94. *Sulphide Ratio in the Decomposition of Ethyldimethylsulphonium Bromide.*

By Y. Pocker.

Decompositions of trimethylsulphonium hydroxide and phenoxide in ethanol were found by Gleave, Hughes, and Ingold [1] to give second-order kinetics and were interpreted as bimolecular nucleophilic substitutions. Decomposition of the corresponding carbonate, iodide, bromide, and chloride followed first-order kinetics and had the same rate-constant, being interpreted as unimolecular nucleophilic substitutions.

Streitwieser [2] criticised the unimolecular interpretation, arguing that a bimolecular displacement by solvent ethanol would be equally consistent with the results. This is an unacceptable criticism. Gleave, Hughes, and Ingold gave an independent way of arriving at an answer. The decomposition of the trimethylsulphonium bromide and chloride was measured, by following the disappearance of halide ions. Since ethyl methyl ether is relatively stable under the experimental conditions the primary substitution products must be the corresponding methyl halides. On the other hand, each bimolecular act of substitution by ethanol must yield ethyl methyl ether, dimethyl sulphide, and hydrogen *halide*, leading to $d(Halide^-)/dt = 0$, contrary to observations. Since the various methyl halides are formed at the same rate from the corresponding trimethylsulphonium salts, the decomposition must be a predominantly unimolecular process.

The decomposition of ethyldimethylsulphonium bromide provides an additional test. It is well established that the ease of ionisation is Et > Me, while in a bimolecular nucleophilic displacement the order is reversed. Ethyldimethylsulphonium bromide was decomposed at 100° in water and 4 : 1 water–dioxan. The mixture of sulphides obtained was analysed by gas chromatography. The $[Me_2S] : [EtSMe]$ ratio was determined by gas chromatography.

In water and in 4 : 1 water–dioxan the relative amount of dimethyl sulphide produced was 40 moles %, while that of ethyl methyl sulphide was 60 moles %. The concentration of methyl groups being double that of ethyl in this sulphonium salt, the ratio $\frac{1}{2}[EtSMe] : [Me_2S]$ can, to a first approximation,* be identified with the rate of substitution at a methyl group relative to that at an ethyl group, k_{Me}/k_{Et}. In the Table these rates are summarised, together with those obtained by Dostrovsky, Hughes, and Ingold [3] for alkyl bromides under predominantly unimolecular conditions.

Table

Solvent and temp.	Compound	k_{Me}/k_{Et}
H_2O–$H{\cdot}CO_2H$, 95°	RBr	0·64
Ag^+, 30% H_2O–70% EtOH, 64°	RBr	0·81
H_2O, 100°	$Et\overset{+}{S}Me_2\bar{B}r$	~0·75
80% H_2O–20% Dioxan, 100°	$Et\overset{+}{S}Me_2\bar{B}r$	~0·75

Under predominantly bimolecular conditions, *i.e.*, when ethyldimethylsulphonium bromide was decomposed in 4 : 1 water–dioxan at 100° in the presence of an equivalent amount of triethylamine, 11 moles % of dimethyl sulphide and 88 moles % of ethyl methyl sulphide were produced, leading to $\frac{1}{2}[EtSMe] : [Me_2S] = 4{\cdot}0$.

This result agrees with the expected relation for bimolecular nucleophilic substitutions, namely, $k_{Me} > k_{Et}$. The numerical value, however, provides only a lower minimum for the ratio (k_{Me}/k_{Et}) (S_N2) since under the experimental conditions some of the dimethyl sulphide is produced by a bimolecular elimination process $(E2)$.

* This approximation neglects any possible small difference in the stability of EtSMe and SMe_2.

[1] Gleave, Hughes, and Ingold, *J.*, 1935, 236.
[2] Streitwieser, *Chem. Rev.*, 1956, **56**, 571.
[3] Dostrovsky, Hughes, and Ingold, *J.*, 1946, 190.

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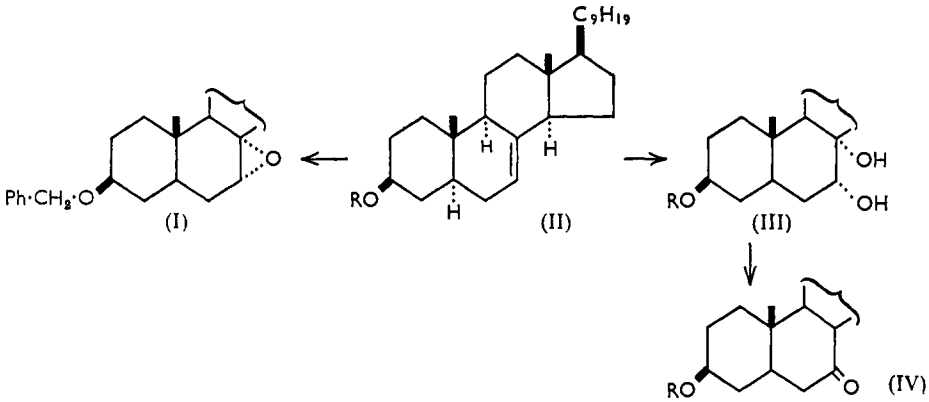
95. *Preparation of 3β-Hydroxyergostan-7-one.*

By G. D. MEAKINS and J. S. STEPHENSON.

IN work concerned with the properties of 9α-methyl-steroids [1] a method was required for converting Δ^7-stenols into the corresponding 7-ketones. This Note describes related experiments with ergost-7-enol.

The first approach involved conversion of ergost-7-enol (II; R = H) into the benzyl ether (II; R = CH_2Ph) which, with perbenzoic acid in benzene, gave the 7 : 8-epoxide (I) in excellent yield. Attempts to open the oxide ring by lithium aluminium hydride had no effect, even after prolonged refluxing in tetrahydrofuran.



Oxidation of the ether and ergost-7-enyl acetate (II; R = Ac) with osmium tetroxide yielded the 7α : 8α-diol (III; R = CH_2Ph) and the 3β : 7α : 8α-triol (III; R = H) respectively. [α-Configurations for the epoxide ring in (I) and the new hydroxyl groups in (III) are assumed on the general tendency for rear approach of peracids and osmium tetroxide to the steroid molecule; a close analogy is found in the oxidation of cholest-7-enyl acetate to cholestane-3β : 7α : 8α-triol.[2]] On treatment with methanolic sulphuric acid, the triol (III; R = H) was converted quantitatively into 3β-hydroxyergostan-7-one [3] (IV; R = H), further identified as the acetate [4] (IV; R = Ac). The reaction presumably proceeds by *trans*-elimination of the tertiary 8α-hydroxyl group and subsequent ketonisation. This route to 7-ketones is superior to the alternative (pyrolytic) method from 7 : 8-diols,[5] and to that involving isomerisation of 7 : 8-epoxides.[4]

Experimental.—General features were the same as those described elsewhere.[1]

3β-Benzyloxyergost-7-ene. A solution of ergost-7-en-3β-ol (400 mg.) and benzyl chloride (2 c.c.) in dioxan (10 c.c.) was heated at 100° with powdered potassium hydroxide (4 g.) for 1 hr. The residue obtained on filtration and evaporation *in vacuo* was extracted with light petroleum. The solution so obtained was washed with water and filtered through anhydrous sodium sulphate on to alumina (50 g.; Grade O). Elution with light petroleum–benzene (4 : 1; 150 c.c.) afforded the *benzyl ether* (400 mg.), m. p. 107—108·5° after crystallisation from methanol, $[\alpha]_D$ −1° (*c* 1·6) (Found: C, 85·9; H, 10·8. $C_{35}H_{54}O$ requires C, 85·65; H, 11·1%).

3β-Benzyloxy-7α : 8α-epoxyergostane. 3α-Benzyloxyergost-7-ene (2 g.) in benzene was

[1] Jones, Meakins, and Stephenson, unpublished work.
[2] Fieser and Ourisson, *J. Amer. Chem. Soc.*, 1953, **75**, 4404.
[3] Stavely and Bollenback, *ibid.*, 1943, **65**, 1290.
[4] Alt and Barton, *J.*, 1954, 1356.
[5] Pearlman and Wintersteiner, *J. Biol. Chem.*, 1939, **130**, 35.

treated with an excess of perbenzoic acid in benzene solution at −15° for 15 hr., and the mixture was then poured into dilute aqueous sodium hydrogen carbonate. Isolation with ether afforded the *oxide* (1·8 g.), m. p. 130—135°, which crystallised from ethyl acetate–ethanol to give the pure product, m. p. 136—138°, $[\alpha]_D$ −1° (*c* 1·05) (Found: C, 83·2; H, 10·8. $C_{35}H_{54}O_2$ requires C, 82·95; H, 10·7%). This compound was recovered unchanged after 6 hours' refluxing with lithium aluminium hydride in ether or tetrahydrofuran.

3β-*Benzyloxyergostane*-7α : 8α-*diol.* Osmium tetroxide (275 mg.) in ether (5·5 c.c.) was added to 3β-benzyloxyergost-7-ene (230 mg.) in a mixture of ether (2 c.c.) and pyridine (1 c.c.). The mixture was refluxed for 1 hr., then evaporated under reduced pressure. The residue was refluxed in tetrahydrofuran with an excess of lithium aluminium hydride for 30 min. After addition of ethyl acetate the mixture was stirred for 30 min. with water and extracted with ether. Standard manipulation gave the *diol* (150 mg.), m. p. 153—154·5° (from methanol). Recrystallisation afforded material with m. p. 155—157°, $[\alpha]_D$ −24° (*c* 1·0) (Found: C, 79·8; H, 10·5. $C_{35}H_{54}O_2$ requires C, 80·1; H, 10·8%).

Ergostane-3β : 7α : 8α-*triol.* (*a*) A mixture of osmium tetroxide (2 g.) in ether (25 c.c.) and 3β-acetoxyergost-7-ene (1·7 g.) in ether (25 c.c.)–pyridine (6 c.c.) was refluxed for 1 hr. After subsequent treatment with lithium aluminium hydride as in the preceding experiment, the mixture of products was adsorbed from benzene (20 c.c.) on deactivated alumina (140 g.). Benzene–ether (4 : 1; 250 c.c.) eluted ergost-7-en-3β-ol (400 mg.). A second fraction (1·15 g.), eluted with ether–methanol (50 : 1, 750 c.c.), crystallised from methanol to give the *triol*, m. p. 215—217° (dependent on rate of heating), $[\alpha]_D$ −16° (*c* 0·6) (Found: C, 77·4; H, 11·6. $C_{28}H_{50}O_3$ requires C, 77·4; H, 11·6%).

(*b*) 3β-Acetoxyergost-7-ene (0·8 g.) was converted into the osmic ester as described above. This ester was dissolved in a mixture of tetrahydrofuran (20 c.c.), dioxan (20 c.c.), and an aqueous solution (50 c.c.) containing potassium hydroxide (7·5 g.) and mannitol (7·5 g.). After 30 min. at 20° the mixture was diluted with water and extracted with ether. The material obtained by evaporation of the ether solution was treated with 10% ethanolic potassium hydroxide for 12 hr. at 20° to ensure complete hydrolysis of the 3-acetoxyl group. Dilution of the ethanolic solution with water and isolation with ether afforded the triol (0·6 g.), m. p. 216—218°, $[\alpha]_D$ −15° (*c* 1·0).

3β-*Hydroxyergostan*-7-*one.* A solution of the triol (400 mg.) in methanol (35 c.c.) was warmed with 10% methanolic sulphuric acid (35 c.c.) to 50°, then kept at 20° for 1·5 hr. Water was added and the product isolated by filtration. Crystallisation from methanol gave the *hydroxy-ketone* (342 mg.), m. p. 155—157° raised by recrystallisation to 156·5—157·5°, $[\alpha]_D$ −35° (*c* 1·15) (Found: C, 80·5; H, 11·6. $C_{28}H_{48}O_2$ requires C, 80·7; H, 11·6%), $\nu_{max.}$ 3606, 1709, and 1026 cm.$^{-1}$ (Stavely and Bollenback [3] report m. p. 154° but do not give analytical data).

Recovery of the compound unchanged after 2 hours' boiling with 10% ethanolic potassium hydroxide confirms its possession of the more stable (β)-configuration at position 8. Acetylation with acetic anhydride–pyridine at 20° gave 3β-acetoxyergostan-7-one, m. p. 188—190°, $[\alpha]_D$ −42° (cf. the values, m. p. 183—184°, $[\alpha]_D$ −42°,[3] and m. p. 178—180°, $[\alpha]_D$ −46° [4]). The 2 : 4-*dinitrophenylhydrazone*, crystallised from ethanol, had m. p. 257—258° (Found: C, 68·1; H, 8·6. $C_{34}H_{52}O_5N_4$ requires C, 68·4; H, 8·8%), $\lambda_{max.}$ 365 mμ (ε 23,000).

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96. *Substitution Compounds of Tristrifluoromethylphosphine with Nickel Carbonyl.*

By H. J. EMELÉUS and J. D. SMITH.

THE feeble donor properties of tristrifluoromethylphosphine have been noted [1] but little work has been done on the co-ordination of this compound to atoms which can donate electrons to the empty *d* orbitals of the phosphorus atom. The work of Reppe,[2] Wilkinson,[3]

[1] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.
[2] Reppe and Schweckendiek, *Annalen*, 1948, **560**, 104.
[3] Irvine and Wilkinson, *Science*, 1951, **113**, 742; Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5501.

and Malatesta [4] showed that the carbonyl group in nickel carbonyl can be replaced by certain compounds of tervalent phosphorus, and suggested that tristrifluoromethylphosphine could form similar substitution compounds. Such compounds have now been prepared.

Nickel carbonyl and excess of tristrifluoromethylphosphine react in a sealed tube [5] or, better, in a system from which the carbon monoxide can escape, to form a mixture of $(CF_3)_3P{\cdot}Ni(CO)_3$ and $[(CF_3)_3P]_2Ni(CO)_2$. The reaction takes place at room temperature, but a higher temperature favours the formation of the disubstituted compound. This higher temperature must not be maintained for more than half an hour, as the products decompose slowly. Above 70° decomposition is rapid. The *products* can be separated by trap-to-trap distillation in the vacuum system, but completely pure materials have not been obtained. Hydrolysis at 100° by excess of sodium hydroxide solution yielded fluoroform, which was weighed in the vacuum system; nickel and phosphorus were estimated in the residual solution {Found: CF_3, 56·7; Ni, 14·3; P, 8·2%; *M*, 378; m. p. −71·5 to −70·5°. $(CF_3)_3P{\cdot}Ni(CO)_3$ requires CF_3, 54·4; Ni, 15·4; P, 8·1%; *M*, 381. Found: CF_3, 68·7; Ni, 9·5; m. p. −31·5 to −30°. $[(CF_3)_3P]_2Ni(CO)_2$ requires CF_3, 70·0; Ni, 9·9%}. The vapour pressure of $(CF_3)_3P{\cdot}Ni(CO)_3$ was measured by means of a mercury isoteniscope in the range 0—50° and obeyed the equation

$$\log p(\text{mm.}) = 7{\cdot}161 - 1629/T$$

Slight decomposition occurred. The extrapolated b. p. is 107·5° ± 1°, the latent heat 7450 cal./mole, and Trouton's constant, 19·6. The vapour pressure of $[(CF_3)_3P]_2Ni(CO)_2$ is less than 1 mm. at 20° and a vapour-pressure curve could not be obtained because of the thermal instability of the compound. The substitution compounds are colourless liquids, which remain quite clear when stored in sealed glass ampoules in the dark. They also seem stable to mercury. Exposure to bright sunlight causes them to turn red: the colour may be due to colloidal nickel. The compounds are spontaneously inflammable in air.

Tristrifluoromethylphosphine does not react with tetrakistrichlorophosphinenickel in a sealed tube at temperatures up to 60°, though at 80° complete decomposition of the mixture to nickel, tristrifluoromethylphosphine, and phosphorus trichloride occurs. It does not therefore seem possible to prepare tetrakistristrifluoromethylphosphinenickel $[(CF_3)_3P]_4Ni$ by methods analogous to those used by Wilkinson for the preparation of tetrakistrifluorophosphinenickel and tetrakistribromophosphinenickel. Tristrifluoromethylarsine and -stibine failed to yield substitution compounds.

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[4] Malatesta and Sacco, *Ann. Chim.* (*Italy*), 1954, **44**, 134.
[5] Preliminary experiments were made by Dr. Ram Chand Paul here.

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97. *Studies on Phosphorylation. Part XVI.* Iodides as Debenzylating and Dealkylating Agents.*

By R. J. W. CREMLYN, G. W. KENNER, J. MATHER, and SIR ALEXANDER TODD.

ANIONIC debenzylation of phosphates, pyrophosphates, and phosphites is a conveniently selective technique of general application which has proved important in nucleotide synthesis. When it was first introduced, lithium chloride was the reagent used; [1] later, thiocyanates were found to react under milder conditions [2] but unfortunately they cannot be used if anionic debenzylation is to be followed directly by hydrogenation since the

* Part XV, *J.*, 1957, 1497.

[1] Clark and Todd, *J.*, 1950, 2030.
[2] Morrison and Atherton, B.P. 675,779.

product is usually contaminated by traces of thiocyanate. We have examined other reagents partly to overcome this difficulty and partly to make available a range of techniques needed for nucleotide synthesis. We considered primarily anions with high "nucleophilic constants."[3] Apart from those anions containing sulphur, iodide (5·04) and cyanide[4] (5·1) both stand above thiocyanate (4·77). Iodides proved very effective although, unfortunately, like the thiocyanates they could not be used as a preliminary to hydrogenolysis since iodide ion completely poisoned the usual palladised charcoal catalysts and largely inactivated Raney nickel. The practical value of iodides as reagents for both debenzylation and dealkylation makes it desirable to record our experiments. Since they were completed, experiments with sodium iodide and barium iodide have been described by Zervas and Dilaris;[5] with the exception of tribenzyl phosphate the esters studied by them were different so that the two investigations are complementary and cover most of the field.

Experiments with benzyl diphenyl phosphate showed that iodides react faster than thiocyanates and that the reaction is favoured by lowering the dielectric constant of the medium, as expected for a reaction of the S_N2 type.[6] Tribenzyl phosphate is much less reactive, as it is towards phenolic debenzylation.[7] Two preparations of practical value are those of monobenzyl phosphite and tribenzyl pyrophosphate through their sodium salts. They are slightly superior to the earlier methods, using ammonium thiocyanate[8] and 4-methylmorpholine[9] respectively.

Dealkylation, as well as debenzylation, can be accomplished with lithium chloride;[10] it is relatively rapid with calcium iodide, which usually gives nicely crystalline calcium salts. Variation of the alkyl group affects the velocity in the way typical of an S_N2 reaction, and naturally debenzylation is faster than dealkylations other than demethylation. Reactions between calcium iodide and benzyl dimethyl phosphate or dibenzyl methyl phosphate give mixtures of the debenzylated and demethylated phosphates.

A very convenient feature of all these preparations is the way in which the debenzylated or dealkylated salt separates, usually almost pure, from the reaction medium.

Experimental.—Debenzylation of benzyl diphenyl phosphate. A solution of benzyl diphenyl phosphate[7] (0·205 g.) and *cyclo*hexylammonium iodide, m. p. 197—199° (0·133 g., 1 mol.), in ethyl methyl ketone (5 c.c.) was boiled under reflux during 10 min. The precipitate of *cyclo*hexylammonium diphenyl phosphate,[10] m. p. 199—200° (0·182 g., 86%), was filtered off, washed, and dried. A parallel experiment with *cyclo*hexylammonium thiocyanate, m. p. 99—100°, gave 68% of the salt, while 98% was obtained with either reagent after 1 hour's boiling.

Heating at 51° during 20 min. gave the following yields of salts of diphenyl hydrogen phosphate from the various reagents: *cyclo*hexylammonium iodide, 44%; lithium iodide, 78%; sodium iodide, 62%; sodium thiocyanate, 10%. Runs with sodium iodide in methyl cyanide and 7 : 3 v/v ethyl methyl ketone–dioxan gave 32% and 65% respectively.

Reaction between sodium iodide and tribenzyl phosphate. Experiments like the preceding ones were made with both ethyl methyl ketone and methyl cyanide at 51°. There was no sign of sodium dibenzyl phosphate after 20 min. in either instance. With ethyl methyl ketone the yield was 25% after 1 hr., and with methyl cyanide 20% after 3 hr.

Debenzylation of dibenzyl phosphite. A solution of dibenzyl phosphite (5 g.) and sodium iodide (3·5 g., 1·2 mol.) in ethyl methyl ketone (40 c.c.) was boiled under reflux during 30 min. The precipitated *sodium benzyl phosphite* was recrystallised from aqueous acetone (3·2 g., 87%) (Found: C, 43·0; H, 3·9. $C_7H_8O_3PNa$ requires C, 43·3; H, 4·2%). A similar experiment with ammonium iodide, which dissolved gradually during 1 hr., gave 74% of ammonium benzyl phosphite.[8]

[3] Swain and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141.
[4] Hawthorne, Hammond, and Graybill, *ibid.*, 1955, **77**, 486.
[5] Zervas and Dilaris, *ibid.*, 1955, **77**, 5354.
[6] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, p. 347.
[7] Kenner and Mather, *J.*, 1956, 3524.
[8] Christie, Elmore, Kenner, Todd, and Weymouth, *J.*, 1953, 2947.
[9] Baddiley, Clark, Michalski, and Todd, *J.*, 1949, 815.
[10] Lecocq and Todd, *J.*, 1954, 2381.

Debenzylation of tetrabenzyl pyrophosphate. (*a*) Removal of two benzyl groups. A solution of tetrabenzyl pyrophosphate (0·199 g.) and sodium iodide (0·110 g., 2 mol.) in ethyl methyl ketone (3 c.c.) was boiled under reflux during 40 min. There was very rapid deposition of *disodium* P^1P^2*-dibenzyl pyrophosphate* (0·125 g., 84%), which was recrystallised from aqueous acetone (Found: C, 41·7; H, 3·8. $C_{14}H_{14}O_7P_2Na_2$ requires C, 41·8; H, 3·5%). The same yield was obtained when the solution was boiled during 10 min. Paper chromatography [7] showed that no more than two benzyl groups can be removed in this way.

(*b*) Removal of one benzyl group. A solution of tetrabenzyl pyrophosphate (0·300 g.) and sodium iodide (0·083 g., 1 mol.) in methyl cyanide (15 c.c.) was kept at 51° for either 15 min., 30 min., or 1 hr. and then at 0° for 2 hr. The *sodium tribenzyl pyrophosphate* (53%, 58%, and 61%) was collected and recrystallised from aqueous ethyl methyl ketone (Found: C, 53·0; H, 4·7. $C_{21}H_{21}O_7P_2Na$ requires C, 53·2; H, 4·7%). A similar experiment with *cyclo*hexylammonium iodide (1 mol.) at four-fold concentration gave after 1 hr. at 51° and 15 hr. at 0° 65% of product, m. p. 115—118°. Recrystallisation from ethyl methyl ketone afforded cyclo*hexylammonium tribenzyl pyrophosphate*, m. p. 118—119° (Found: C, 59·3; H, 6·7. $C_{27}H_{35}O_7NP_2$ requires C, 59·2; H, 6·4%).

Dealkylation and debenzylation with calcium iodide. Commercial calcium iodide was dissolved in acetone, which was then diluted with chloroform and evaporated. After two repetitions of this drying process, the calcium iodide was recrystallised from acetone–ether and stored over phosphoric oxide as a colourless, very hygroscopic powder.

The necessary methyl esters were obtained from the corresponding acids and ethereal diazomethane in the usual way. *Methyl diphenyl phosphate* had n_D^{21} 1·5320 (Found: C, 58·9; H, 5·2. $C_{13}H_{13}O_4P$ requires C, 59·1; H, 4·9%). The other esters were made from dibenzyl or diphenyl phosphorochloridate by the procedure of Lecocq and Todd.[10]

A solution of the ester and calcium iodide (0·5 mol.) in ethyl methyl ketone was boiled under reflux during 3 hr. The precipitated calcium salt was washed thoroughly with acetone–ether, examined by ascending paper chromatography in butan-1-ol–water (86 : 14) on Whatman No. 1 paper, and recrystallised from aqueous ethanol or methanol–acetone.

The yields of calcium diphenyl phosphate from various alkyl diphenyl phosphates were 98% from methyl, 93% from *n*-propyl, 62% from *iso*propyl, 70% from *n*-butyl. Dimethyl phenyl phosphate furnished 87% of *calcium methyl phenyl phosphate*, m. p. above 300° (Found: C, 39·8; H, 3·9; P, 14·7. $C_{14}H_{16}O_8P_2Ca$ requires C, 40·4; H, 3·9; P, 14·9%).

One benzyl group was removed from the alkyl dibenzyl phosphates, giving the following products: *calcium benzyl ethyl phosphate*, m. p. 267—271°, R_F 0·52 (75%) (Found: C, 45·3; H, 5·2. $C_{18}H_{24}O_8P_2Ca$ requires C, 45·9; H, 5·1%); *calcium benzyl* n*-propyl phosphate*, m. p. 293—297°, R_F 0·58 (50%) (Found: C, 48·1; H, 5·4; P, 12·7. $C_{20}H_{28}O_8P_2Ca$ requires C, 48·2; H, 5·6; P, 12·5%); *calcium benzyl* iso*propyl phosphate*, m. p. 268—272°, R_F 0·58 (63%) (Found: C, 47·8; H, 5·9; P, 11·9%); *calcium benzyl* n*-butyl phosphate*, m. p. above 300°, R_F 0·68 (78%) (Found: C, 50·2; H, 6·0; P, 11·8. $C_{22}H_{32}O_8P_2Ca$ requires C, 50·2; H, 6·1; P, 11·8%); *calcium dibenzyl phosphate*, m. p. 261—263°, R_F 0·80 (87%) (Found: C, 55·9; H, 4·6; P, 9·9. $C_{28}H_{28}O_8P_2Ca$ requires C, 56·5; H, 4·7; P, 10·4%).

Subsequent experiments showed that the yield of precipitated calcium salt was generally between 60 and 70% after only 5 or 10 min. Experiments with boiling acetone solutions gave only 35—40% after 20 min., but the same yields as recorded above after 3 hr.

Dibenzyl methyl phosphate gave a calcium salt (Found: C, 48·9; H, 5·1; P, 11·7%) which appeared to be a mixture of calcium benzyl methyl phosphate, R_F 0·41, and calcium dibenzyl phosphate, R_F 0·80. Similarly benzyl dimethyl phosphate gave a calcium salt (Found: C, 31·1; H, 4·4; P, 16·2%) which was apparently a mixture of calcium benzyl methyl phosphate, R_F 0·40, and calcium dimethyl phosphate, R_F 0·56. In each case the yield of mixed calcium salts was about 75%.

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98. *The Oxidation of Some Naphthalene Derivatives with Peracetic Acid.*

By D. F. Downing and D. Woodcock.

Work on the metabolism of 2-methoxynaphthalene by *Aspergillus niger* van Tiegh required certain substituted 2-carboxycinnamic acids. Oxidation of naphthalene,[1] 1-naphthol,[2] and 2-naphthol [2,3,4] by peracetic acid has been previously used for the preparation of this acid, and this method using the appropriate substituted 2-naphthol was found to be the most convenient for the preparation of 2-carboxy-5-hydroxy-, -5-nitro-, and -3-nitro-cinnamic acid. The acids were easily isolated but yields were low (10—20%). 2-Carboxy-5-methoxycinnamic acid can also be prepared by this method but is obtained in better yield by methylation of the corresponding hydroxy-acid.

Experimental.—*2-Carboxy-5-hydroxycinnamic acid.* 2 : 6-Dihydroxynaphthalene [5] (1 g.) in acetic acid (5 ml.) was treated with 6—9% peracetic acid [6] (25 ml.) dropwise, during 0·5 hr., with stirring and kept at room temperature overnight. After removal of the solvent under reduced pressure, the residual brown solid was crystallised from water (charcoal), to give *2-carboxy-5-hydroxycinnamic acid* as colourless prisms (0·15 g.), m. p. 250—252° (decomp.) (after shrinkage) (Found: C, 57·8; H, 3·6. $C_{10}H_8O_5$ requires C, 57·7; H, 3·8%). In ethanol the acid gave a red-brown colour with a dilute solution of ferric chloride.

2-Carboxy-5-methoxycinnamic acid. (*a*) Methylation of the above acid (0·1 g.) with dimethyl sulphate in sodium hydroxide solution gave the *methoxy-acid* (0·09 g.) as prisms (from water), m. p. 186—187° (Found: C, 59·5; H, 4·5. $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%). (*b*) 6-Methoxy-2-naphthol (see below) (0·3 g.) was oxidised with peracetic acid as described for 2 : 6-dihydroxynaphthalene (above). The acidic product (0·04 g.; m. p. 182—184°) gave no colour with dilute ferric chloride solution and did not depress the m. p. of the product from (*a*) above.

6-Methoxy-2 naphthol. 2 : 6-Dihydroxynaphthalene (3·2 g.) in methanol (20 ml.) was treated with dimethyl sulphate (2·5 ml.) and the mixture stirred at 30—40° during dropwise addition of sodium hydroxide (0·8 g.) in water (3 ml.). After a further 0·5 hour's stirring at the same temperature, water (20 ml.) was added and the solution extracted with ether. The naphtholic material isolated by extraction of the ethereal solution with 10% sodium hydroxide solution was a mixture of mono- and di-methyl ethers which were separated by fractional crystallisation from water, the latter ether being much less soluble. The *monomethyl ether*, recrystallised from water, formed colourless plates, m. p. 149—150° (Found: C, 75·7; H, 5·9. $C_{11}H_{10}O_2$ requires C, 75·9; H, 5·7%). Fischer and Hammerschmidt [7] and Windaus [8] give m. p. 136—137°.

2-Carboxy-5-nitrocinnamic acid. 6-Nitro-2-naphthol [9] (1 g.) in acetic acid (5 ml.) was treated as above with peracetic acid (16 g.). The solution remained at room temperature for two days, during which crystals were deposited. These were filtered off, washed with a little cold water, and recrystallised from 50% ethanol, to give pale yellow needles of *2-carboxy-5-nitrocinnamic acid*, m. p. 195—196° (Found: C, 50·7; H, 3·2; N, 6·1. $C_{10}H_7O_6N$ requires C, 50·6; H, 3·0; N, 5·9%).

2-Carboxy-3-nitrocinnamic acid. 8-Nitro-2-naphthol [10] (2·5 g.) was oxidised as described for 6-nitro-2-naphthol (above). Recrystallisation of the product gave pale yellow plates (from water), m. p. 188—189° (Found: C, 50·9; H, 2·7; N, 6·2%).

Department of Agriculture and Horticulture, University of Bristol, Research Station, Long Ashton, Bristol. [*Received, August 26th*, 1957.]

[1] Böeseken and Sloff, *Rec. Trav. chim.*, 1930, **49**, 100.
[2] Böeseken and von Konigsfeldt, *ibid.*, 1935, **54**, 313.
[3] Bigiavi and Cerchiai, *Atti R. Accad. Lincei*, 1922, **31**, II, 27.
[4] Greenspan, *Ind. Eng. Chem.*, 1947, **39**, 847.
[5] Willstätter and Parnas, *Ber.*, 1907, **40**, 1410.
[6] Swern, *Org. Reactions*, Vol. VII, p. 395.
[7] Fischer and Hammerschmidt, *J. prakt. Chem.*, 1916, **94**, 24.
[8] Windaus, *Ber.*, 1924, **57**, 1731.
[9] Hudson and Ward, *J.*, 1947, 327.
[10] Friedländer and Szymanski, *Ber.*, 1892, **25**, 2076.

99. *The Reaction of Chlorosulphonic Acid with Aminophenols.*

By E. Boyland and D. Manson.

Wiley [1] prepared 2-amino-1-naphthyl hydrogen sulphate, which is a metabolite of 2-naphthylamine, by reaction of 2-amino-1-naphthol hydrochloride with chlorosulphonic (chlorosulphuric) acid in dimethylaniline and carbon disulphide. Boyland, Manson, and Sims [2] found that *o*-aminophenol and chlorosulphonic acid in pyridine yielded *o*-hydroxyphenylsulphamic acid. The formation of 7-hydroxy-2-naphthylsulphamic acid by reaction of chlorosulphonic acid with 2-amino-7-naphthol in quinoline has also been described.[3] These facts suggested that sulphuric esters or sulphamic acid derivatives of aminophenols might be obtained by varying the reaction medium. *o*-, *m*-, and *p*-Aminophenol and 2-amino-6-naphthol have been found to react with one equivalent of chlorosulphonic acid in pyridine and, in one case, in dimethylaniline, also, to give the sulphamic acid derivatives. In dimethylaniline and carbon disulphide the sulphuric esters were formed. In each case only a trace or none of the isomer was detected. Members of each pair of isomers were distinguished from each other by their R_F values and colour reactions. The sulphamic acid derivatives condensed only slowly with *p*-dimethylaminobenzaldehyde whereas the aminophenyl sulphuric esters reacted immediately. Both, however, diazotised immediately and coupled with hexylresorcinol. 2-Amino-6-naphthol hydrochloride gave both a sulphamic acid derivative and a sulphuric ester, but only the sulphuric acid ester was obtained from 2-amino-1-naphthol hydrochloride. Prolonging the reaction time of 2-amino-1-naphthol hydrochloride with chlorosulphonic acid diminished the yield of ester. Boyland, Manson, and Orr [4] found that the free base gave only the sulphuric ester of 1-hydroxy-2-naphthylsulphamic acid. *o*-Aminophenol gives both *o*-hydroxyphenylsulphamic acid and *o*-aminophenyl hydrogen sulphate, which is of interest in view of the existence of only *N*-acyl derivatives.

Experimental.—Paper chromatography was carried out on Whatman No. 1 chromatography paper, ascending development being used with propan-1-ol–butan-1-ol–0·1N-ammonia (1 : 2 : 1 v/v). The compounds were detected on chromatograms by the following reagents: (*a*) Ehrlich's reagent (*p*-dimethylaminobenzaldehyde, 0·5%, in ethanol containing 1 ml. of concentrated hydrochloric acid per 100 ml.); (*b*) N-hydrochloric acid followed by sodium nitrite (0·5%) and hexylresorcinol (0·5% in 2N-sodium hydroxide); (*c*) 10% aqueous sodium carbonate followed by diazotised sulphanilic acid [1·6 ml. sodium nitrite (0·5%) added to 10 ml. of sulphanilic acid (0·2% in N-hydrochloric acid)].

Sulphuric esters. o-Aminophenol (1·1 g.) was added with stirring to chlorosulphonic acid (1·1 g.), dimethylaniline (2 ml.), and carbon disulphide (10 ml.). After 16 hr. at room temperature, the mixture was poured into water containing potassium hydroxide (2 g.). The mixture was extracted several times with ether and then evaporated to dryness. The residue was extracted several times with hot methanol, and the combined extracts were evaporated to small bulk: *o*-aminophenyl potassium sulphate separated on cooling. After recrystallisation from aqueous ethanol 0·5 g. of ester was obtained (Found: S, 14·1. Calc. for $C_6H_6O_4NSK$: S, 14·1%). Under similar conditions *m*-aminophenol (5 g.) gave *m*-aminophenyl potassium sulphate (1·5 g.) (Found: N, 6·0; S, 14·0. Calc. for $C_6H_6O_4NSK$: N, 6·2; S, 14·1%), and similarly *p*-aminophenol (5 g.) gave *p*-aminophenyl potassium sulphate (1·3 g.) (Found: N, 5·9; S, 13·1. Calc. for $C_6H_6O_4NSK,H_2O$: N, 5·7; S, 13·1%). 2-Amino-6-naphthol hydrochloride (1·5 g.) in chlorosulphonic acid (0·9 g.), dimethylaniline (4·5 ml.), and carbon disulphide (27 ml.) gave 2-amino-6-naphthyl potassium sulphate (0·5 g.), needles (Found: N, 4·8; S, 11·6. Calc. for $C_{10}H_8O_4NSK$: N, 5·05; S, 11·55%). All the compounds gave precipitates when heated with 2N-hydrochloric acid and barium chloride. Paper chromatography of the mixtures showed that none or only a trace of the isomeric sulphamate was formed. The properties of

[1] Wiley, *J. Biol. Chem.*, 1938, **124**, 627.
[2] Boyland, Manson, and Sims, *J.*, 1953, 3623.
[3] F.P. 684,356.
[4] Boyland, Manson, and Orr, *Biochem. J.*, 1957, **65**, 417.

the sulphuric esters on paper chromatograms are compared with those of the sulphamates in the Table. All the compounds gave yellow colours with Ehrlich's reagent. The colour reactions and analytical figures of the sulphuric esters agreed with those of the products obtained by the reduction of the corresponding nitro-derivatives.[5]

A: Diazotisation and coupling with hexylresorcinol.
B: Treatment with diazotised sulphanilic acid.

	R_F	A	B	R_F	A	B
	Aminophenyl hydrogen sulphate			Hydroxyphenylsulphamic acid		
o-Isomer	0·35	Orange	No colour	0·3	Mauve	Orange-red
m-Isomer	0·28	Orange-red	,,	0·22	Orange	Yellow
p-Isomer	0·21	Yellow	Yellow	0·2	Mauve	Pink
From	Hydrogen sulphate			Sulphamic acid		
6 : 2-NH_2·$C_{10}H_6$·OH ...	0·47	Orange	Pink	0·33	Red	Mauve
2 : 1-NH_2·$C_{10}H_6$·OH ...	0·58	Mauve	Pink	(0·16	Mauve	No colour) *

* Sulphate ester of sulphamic acid.

Sulphamates. The preparation of potassium *o*-hydroxyphenylsulphamate from chlorosulphonic acid and *o*-aminophenol in pyridine has been described.[2] *o*-Aminophenol (1·1 g.) in dimethylaniline (5 ml.) and chlorosulphonic acid (1·1 g.) also gave this sulphamic acid derivative (0·5 g.). *m*-Aminophenol (5 g.) was added to pyridine (25 ml.) containing chlorosulphonic acid (5·8 g.), and the solution kept at room temperature overnight. The solution was poured into water (100 ml.) containing potassium hydroxide (7·5 g.). The mixture was adjusted to pH 6·0 and extracted several times with ether, after which it was made alkaline and evaporated to dryness under reduced pressure. The residue was extracted with hot methanol, and the combined extracts were evaporated to dryness and crystallised from aqueous ethanol, to yield *potassium* m-*hydroxyphenylsulphamate* (2·5 g.; plates) (Found: N, 5·5; S, 13·0. $C_6H_6O_4NSK,H_2O$ requires N, 5·7; S, 13·1%). *p*-Aminophenol (5 g.) was treated in the same way, but the residue from the methanol extraction was tarry and required treatment on porous tile before crystallisation from aqueous ethanol, to yield *potassium* p-*hydroxyphenylsulphamate* (0·5 g.), needles (Found: N, 5·4; S, 12·2. $C_6H_4O_4NSK,2H_2O$ requires N, 5·3; S, 12·2%). The use of dimethylaniline gave much tar and no sulphamate. 2-Amino-6-naphthol hydrochloride (1 g.), in pyridine (5 ml.) containing chlorosulphonic acid (0·58 g.), was treated in the same way as the aminophenols and gave *potassium* 6-*hydroxy*-2-*naphthylsulphamate* (0·25 g.), plates (Found: N, 4·7; S, 10·8. $C_{10}H_8O_4NSK,H_2O$ requires N, 4·7; S, 10·9%). On evaporation of the ether extracts unchanged 2-amino-6-naphthol was recovered (0·25 g. as the hydrochloride). Potassium 6-hydroxy-2-naphthylsulphamate gave erratic analytical figures if it was dried at 100° and this and the other sulphamates were dried at room temperature. All the compounds gave precipitates with barium chloride in warm 2N-hydrochloric acid.

Reaction of 2-*amino*-1-*naphthol hydrochloride with chlorosulphonic acid.* This hydrochloride (6 g.) was added to dimethylaniline (20 ml.), chlorosulphonic acid (3·5 g.), and carbon disulphide (100 ml.). The mixture was kept for 16 hr. at room temperature and added to water (100 ml.) containing potassium hydroxide (5 g.). The whole was extracted several times with benzene, evaporated to small volume under reduced pressure, and cooled, to yield 2-amino-1-naphthyl potassium sulphate (2·3 g.), plates. The mother-liquors were then evaporated to dryness, the residue dissolved in the minimum amount of a mixture of butan-1-ol, propan-1-ol, and water (2 : 1 : 1 v/v) and sufficient Whatman cellulose powder added to form a paste. A cellulose column (12 × 3 cm.) was prepared with the same solvent mixture, the paste added to the top, and the column developed and eluted with the solvent mixture, collection of fractions being guided by paper chromatography. The fraction containing 2-amino-1-naphthyl sulphuric ester yielded 0·7 g. as the potassium salt. Continued elution of the column gave fractions containing a trace of the sulphuric ester of 1-hydroxy-2-naphthylsulphamic acid.[4] The total yield of 2-amino-1-naphthyl potassium sulphate (Found: N, 5·3%) was 35%, which is more than was obtained when the free acid was isolated.[2] The preparation was repeated, the reaction being allowed to proceed at room temperature for 3 days. The alkaline aqueous solution of the products was evaporated to dryness and the residue chromatographed on a cellulose column as before. Fractions containing 2-amino-1-naphthyl potassium sulphate (300 mg.) and the

[5] Burkhardt and Wood, *J.*, 1929, 141; Bernstein and McGilvery, *J. Biol. Chem.*, 1952, **198**, 195; Booth, Boyland, and Manson, *Biochem. J.*, 1955, **60**, 62.

dipotassium salt of the sulphuric ester of 1-hydroxy-2-naphthylsulphamic acid (60 mg.) (Found: N, 3·3; S, 16·25. Calc. for $C_{10}H_7O_7NS_2K_2$: N, 3·5; S, 16·2%) were obtained. The properties of these compounds were the same as those of previous preparations.[2,4] 1-Hydroxy-2-naphthylsulphamic acid could not be prepared by reaction of the aminonaphthol with chlorosulphonic acid in pyridine or dimethylaniline.

Analyses were carried out by Mr. P. Baker of Wellcome Research Laboratories. 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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100. *Vapour Pressure of* NN'-*Diphenylacetamidine.*

By A. S. DUNN and A. HANRAHAN.

THE vapour pressure of *NN'*-diphenylacetamidine has been determined by Knudsen's effusion method[1] over the range 70—110°. The rate of effusion of the vapour through an orifice, measured by means of the contraction of a spiral spring, was related to vapour pressure by calibrating the orifice with stable solid benzophenone, whose vapour pressure was accurately determined by Neumann and Völker[2] as $4 + \log p^b(\text{mm}). = 17{\cdot}46 - (4966/T)$ where p^b is the vapour pressure of benzophenone and T the absolute temperature. The vapour pressure p of the substance is calculated from the p^b at the same rate of effusion by means of the relation $p = p^b[(M_b/M)(T/T_b)]^{\frac{1}{2}}$, where M and T are the molecular weight and absolute temperature of the substance and M_b, T_b those of benzophenone.

The vapour pressures of *NN'*-diphenylacetamidine at various temperatures thus measured are as follows:

Orifice diam. (in.)	0·025				0·050				
Temp. (°c)	110·0	105·0	100·0	95·0	90·0	86·6	83·4	80·0	70·0
$10^3 \times$ Pressure (mm. Hg)	26·45	16·31	9·26	5·46	3·45	2·364	1·315	1·102	0·302

The points were fitted by the method of least squares which gave the relation

$$4 + \log p = 19{\cdot}156 \pm 0{\cdot}038 - (6409{\cdot}2 \pm 136{\cdot}8)/T$$

The limits quoted are the standard errors.

The latent heat of sublimation of diphenylacetamidine was derived as $29{\cdot}3 \pm 0{\cdot}9$ kcal./mole.

Experimental.—Majury's apparatus[3] was used. The "Pyrex" glass spring was similar to that used by him but had a sensitivity of 3·39 mg./mm. The orifices were those calibrated by Majury and a check point with benzophenone fell precisely on his calibration. Two orifices, diameters 0·025 and 0·05 in. were used. The points obtained were satisfactorily collinear apart from one with the larger orifice at 100° where the rate of effusion was 0·275 mg./min.; evidently this rate was too great for the required conditions to be satisfied. All other rates of effusion were less than 0·2 mg./min.

NN'-Diphenylacetamidine, received from British Celanese Ltd. and recrystallised from methylated spirit, had m. p. 131° (uncorr.). Before use it was sublimed *in vacuo* at about 96° on a finger cooled by solid carbon dioxide–methanol, with continuous pumping to free it from occluded solvent.

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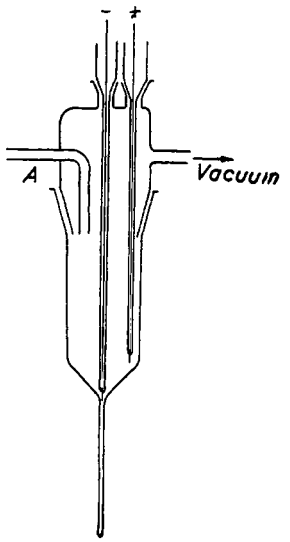
[1] Knudsen, *Ann. Physik*, 1909, **28**, 999.
[2] Neumann and Völker, *Z. phys. Chem.*, 1932, **161**, *A*, 33.
[3] Majury, *J. Soc. Dyers Colourists*, 1956, **72**, 41.

101. *Organomercury Groups. Part II.*[1] *Electron Resonance Measurements.*

By B. G. Gowenlock, P. Pritchard Jones, and D. W. Ovenall.

In a recent investigation and extension [1] of Kraus's work [2] on organomercury groups, it was suggested that they were best described in terms of " organic metals " or the Pauling theory of metals. It was also shown chemically that free-radical behaviour participated to only a very minor extent. To obtain further evidence for the understanding of these novel substances, the methyl-, *iso*propyl-, and *n*-butyl-mercury groups, prepared as cathode deposits on electrolysis of organomercuric chlorides in liquid ammonia, were examined at 90° K in an electron resonance spectrometer. No resonance absorption being detected, we infer that the organomercury groups do not contain free radicals.

Experimental.—A modification of Gowenlock and Trotman's method for the electrolytic production of organomercury groups was employed. Liquid ammonia was saturated with RHgCl (R = Me, Pr^i, Bu^n) and then carefully displaced into the glass reaction vessel shown, at *A*: these operations and the electrolysis were carried out at −78°. The cathode was mounted just above the narrow tube (external diam. 5 mm.) attached to the reaction vessel. In the case of the methyl group gentle tapping of the vessel sufficed to detach the small particles of the solid from the cathode and to send them to the bottom of the tube. For the *iso*propyl and *n*-butyl groups it was necessary to remove the bath of solid carbon dioxide and warm the tube carefully by hand. The subsequent violent agitation of the liquid ammonia removed the group from the cathode and the heavy solid settled when the cooling bath was replaced. A run of about 3 hr. was sufficient to give a layer of 1 in. depth in the narrow tube. Air was then admitted, the vessel and contents were detached, and most of the liquid ammonia was sucked off under vacuum. The vessel then contained the solid group at the base of the narrow tube covered by some six inches of liquid ammonia. The whole was then immersed in liquid oxygen, air admitted, the reaction vessel detached, and the narrow portion of the tube studied at 90° K in the electron resonance spectrometer of Abraham, Ovenall, and Whiffen.[3] It is very unlikely that oxygen from the air can diffuse through the liquid ammonia (15 in. depth) or through the solid ammonia (at least 6 in. depth) and react with the solid at the base of the narrow tube. At 90° K there is no detectable decomposition of the groups and the solid ammonia present has little or no dielectric loss at the microwave frequency. Absorptions were sought at a microwave frequency of approximately 9300 Mc./sec. over the magnetic-field range 1·9—3·5 kilogauss, which corresponds to the range of " *g* " values 4·55 to 1·9, but none was detected.



Discussion.—It is difficult accurately to estimate the detection limit of the spectrometer since this is directly proportional to the line width of the resonance. However, if it is assumed that the microwave cavity contained about 200 mg. of each group and that the resonance expected had a half-height width of 50 gauss, the sensitivity was such that one unpaired electron per 10^4 RHg units would have been detected. A theoretical study of the CH_3Hg radical [4] has shown that the wave function of the unpaired electron is represented predominantly by the term involving a free methyl radical at the van der Waals distance from a mercury atom in the ground state. This implies that the angular

[1] The paper by Gowenlock and Trotman, *J.*, 1957, 2114, is regarded as Part I.
[2] Kraus, *J. Amer. Chem. Soc.*, 1913, **35**, 1732.
[3] Abraham, Ovenall, and Whiffen, to be published.
[4] Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **219**, 270.

momentum of the unpaired electron would be quenched, and that the resonance would occur not far from $g = 2{\cdot}00$. In view of the fact that over a wide range of g values, as well as near $g = 2{\cdot}00$, no resonance was detected, the RHg radical structure can be discounted. This is in accord with the lack of radical reactivity already demonstrated.[1]

From previous evidence it was concluded [1] that the groups were best described in terms of organic metals, and that the plausible assumption of an organomercurous compound was untenable. The data here presented afford no evidence against organomercurous compounds. Rochow, Hurd, and Lewis [5] recently stated that the groups are not mercurous compounds but gave no evidence for this assumption. It may be expected, if the metal theory for the groups be correct, that resonance from conduction electrons would be observed. However such resonance absorption has been detected only when a metal was in the form of particles small compared with the microwave skin depth. Thus Solt and Strandberg's [6] measurements on particles of sodium less than 4μ in diameter gave a g value of $2{\cdot}0014 \pm 0{\cdot}0002$ and a line-width of 10 gauss. Therefore, it seems unlikely because of particle size that conduction electrons would have been detected in the present investigation. Another possible objection to the metal theory of the groups would be that if they behaved as metals the microwave field patterns inside the cavity would be distorted and tuning would be difficult. No such difficulties were experienced, the groups behaving similarly to normal non-metallic samples. With samples of both zinc dust and mercury at 90° K it was impossible to tune and consequently pure metallic behaviour for the groups is difficult to uphold. However it was possible to tune when samples of powdered chalk containing up to 15 molar % of zinc dust were placed in the cavity. It may therefore be concluded that partial metallic behaviour is not disproved by this work, but that the groups cannot be regarded as radicals or pure metals.

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Department of Chemistry,
The University, Birmingham, 15. [*Received, September 30th*, 1957.]

[5] Rochow, Hurd, and Lewis, " The Chemistry of Organometallic Compounds," Wiley, New York, 1957, p. 121.
[6] Solt and Strandberg, *Phys. Rev.*, 1954, **95**, 607.

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102. *The Dipole Moment of* 5 : 5′-spiro*Bis*-1 : 3-*dioxan: A Correction.*

By I. T. Millar, C. T. Mortimer, and H. D. Springall.

Professor R. J. W. Le Fèvre has kindly drawn our attention to the marked difference between the value for the dipole moment of 5 : 5′-*spiro*bis-1 : 3-dioxan recorded in his recent paper [1] ($\mu = 2{\cdot}69$ D in carbon tetrachloride) and that recorded recently by us [2] ($\mu = 0$ D in benzene). We have recalculated the moment from our experimental data by the established expressions for ${}_{T}P_2$ and ${}_{E}P_2$ and have found an arithmetical error in the earlier record.

Our experimental data, in fact, yield for this compound values of ${}_{T}P_2$, ${}_{E}P_2$, and μ of 179·3 c.c., 34·3 c.c., and 2·66 D, respectively, in close agreement with the corresponding values found by Professor Le Fèvre and his collaborators.

This error invalidates the final piece of supporting evidence we adduced [2] but does not affect the general argument as to the freedom of rotation about the CH_2–O bonds in pentaerythritol and its derivatives.

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Keele, Staffordshire. [*Received, November 14th*, 1957.]

[1] Le Fèvre, Le Fèvre, and Smith, *J.*, 1958, 16.
[2] Millar, Mortimer, and Springall, *J.*, 1957, 3456.