NOTES.

352. *The Adsorption of Uranyl Sulphate from 20% Methanol by an Anion-exchange Resin.*

By D. E. B. MORGANS and C. B. MONK.

SEVERAL attempts have been made[1,2] to establish the formulæ of the uranyl sulphate complexes which are adsorbed from solution by anion-exchange resins. Among the suggestions arising from these are[2] (*a*) the complex on the resin is $UO_2(SO_4)_n^{(2-2n)}$ where $n \geqslant 2$, (*b*) $n = 3$ or alternatively an equal mixture of $n = 2$ and sulphate ions. However, there is little evidence from other sources to suggest that $UO_2(SO_4)_3^{4-}$ can be formed. Ahrland[3] roughly estimated the complexity constant of this species in aqueous solution but could not substantiate it by spectrophotometric measurements. This is in accord with similar work[4] and with conclusions derived from solvent extractions.[5] For the present work, 20% methanol has been used, since this is somewhat better than water for promoting complex formation.

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[1] Lower, U.S. Atomic Energy Comm., AECD-4113. O'Connor, *ibid.*, ACCO 61, 1954.
[2] Arden and Wood, *J.*, 1956, 1596; Arden and Rowley, *ibid.*, 1957, 1709.
[3] Ahrland, *Acta Chem. Scand.*, 1951, **11**, 1151.
[4] Davies and Monk, *Trans. Faraday Soc.*, 1957, **53**, 442.
[5] McDowell and Baes, *J. Phys. Chem.*, 1958, **62**, 77; Allen, *J. Amer. Chem. Soc.*, 1958, **80**, 4133.

Experimental.—Deacidite FF was equilibrated with sodium chloride solution, washed, and semi-dried on a Buchner funnel. Before use, the resin was dried (P_2O_5) for 48 hr. at room temperature (40 hr. was a safe minimum); this is superior to drying at 110° since Lower[1] found that heating converts part of a sulphated resin into a non-convertible form, and furthermore, Deacidite becomes brittle above 50°. About 0·5 g. samples were weighed into centrifuge tubes fitted with high-porosity bases.[3] To determine the resin capacity, 0·5N-potassium nitrate was passed through; it was 3·86 ± 0·005 mequiv. of Cl^-/g. of dry resin.

For the exchange work, 0·00569M-uranyl sulphate containing sulphuric acid was dripped through till spectrophotometric estimates of the uranyl concentration (at 300 mμ) were constant. This took 150—200 ml. and 40 hr. The resin in its tube was centrifuged for 1 hr. at[6] 2500 rev./min., then eluted with 0·5M-sodium chloride at 5 drops/min.; this took 150 ml. (ferrocyanide test). Uranium in the eluate was estimated by weighing the oxinate, and sulphate was weighed as barium salt.

The pH of the influent was found by Thymol Blue, the colour being matched against 20% methanol solutions of perchloric acid by spectrophotometer at 540 mμ. The HSO_4^- content of the eluate was found likewise with Methyl Orange and standard sulphuric acid at 540 mμ, the elution process being assumed to be $RHSO_4 + Cl^- \rightleftharpoons RCl + HSO_4^-$. Although the eluate contained uranium, this should not influence the HSO_4^- estimate since it was present mainly as UO_2SO_4.

Adsorption of uranyl, sulphate, and bisulphate ions by Deacidite FF (mmoles/g. of resin).

$-\log [H^+]$, influent	1·90	1·66	1·53	1·42	1·30	1·16	1·13	1·05	0·95	0·85	0·75	0·66	0·51
Total $SO_4^{2-} = b$	3·20	3·39	3·36	3·31	3·31	3·36	3·45	3·39	3·56	3·57	3·69	3·75	3·88
$HSO_4^- = d$	0·18	0·22	0·33	0·39	0·35	0·56	0·63	0·71	0·89	1·10	1·35	1·69	2·10
Total $UO_2^{2+} = x$	1·27	1·35	1·24	1·22	1·20	1·08	1·06	1·03	0·95	0·88	0·81	0·69	0·53
Free SO_4^{2-} ($n = 2$)	0·48	0·47	0·55	0·48	0·56	0·64	0·70	0·62	0·77	0·71	0·72	0·68	0·72
Capacity (calc., a)	3·68	3·86	3·91	3·79	3·87	4·00	4·15	4·01	4·33	4·28	4·41	4·43	4·60
HSO_4^- (calc.)	0·25	0·09	0·31	0·35	0·39	0·63	0·67	0·73	0·89	1·03	1·17	1·41	1·73
Capacity (calc., b)	3·75	3·73	3·89	3·75	3·91	4·07	4·19	4·03	4·33	4·21	4·23	4·15	4·23

Results and Discussion.—The analytical results and relevant calculations are shown in the Table. With x, b, and d as defined in the Table, then nx = complexed sulphate, $b - nx - d$ = free sulphate. Thus the negative charge on the resin = $(2n - 2)x + d + 2(b - nx - d) = 2b - d - 2x$, so than n cannot be deduced from the analysis. A further feature is that, from the Cl^- capacity, $2b - d - 2x$ should be 3·86 mequiv./g., and as the sixth row shows, there is satisfactory accord above pH = 1, but below this the capacity apparently increases. A possible explanation is that the SO_4^{2-} and HSO_4^- determinations include entrapped or permeated free acid, and there is evidence to support this view for, except for the three most acidic solutions, the sum $2x + d$(exptl.) = 2·79 ± 0·05. This produces the HSO_4^- (calc.) values of the seventh row and the last row of capacity values. The latter are still a little high at low pH's but they have not been corrected for the SO_4^{2-} of the free acid (the Kraus and Moore correction[7] proved negligible).

The conclusions that can be drawn are that the resin species are $R_2UO_2(SO_4)_n^{(2n-n)}$ (n = 1 and/or 2), R_2SO_4, and $RHSO_4$. If n = 1 only, the amounts of R_2SO_4 are greater than those shown in the fourth row by x. Since the quantity of adsorbed uranium falls off at lower pH's, where the solution contains higher concentrations of free UO_2^{2+} (there is less SO_4^{2-} to associate with it and HSO_4^- does not appear to do so), n = 1 only seems unlikely. There is the possibility that the resin species is a mixture with n = 1 and 2 and there is no R_2SO_4, but this takes no account of the equilibrium $R_2UO_2(SO_4)_2 \rightleftharpoons R_2SO_4 + UO_2SO_4$ (soln.).

One of us (D. E. B. M.) is indebted to the University College of Wales for the award of a Sir Garrod Thomas fellowship.

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[*Received, August* 31*st*, 1960.]

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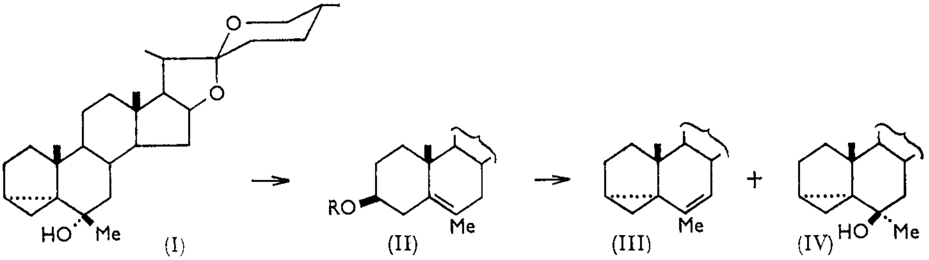
[6] Arden, private communication.

[7] Kraus and Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 1457.

353 *3α,5-Cyclo-6β-methyl-25D-spirostan-6α-ol and 3α,5-Cyclo-6α-methyl-25D-spirostan-6β-ol.*

By G. H. R. SUMMERS.

RECENTLY it has been shown[1] that reaction of methylmagnesium iodide with 3α,5-cyclo-6-oxo-steroids yields the 6α-tertiary alcohols. Thus the compound, m. p. 183—185°, $[\alpha]_D$ —52°, prepared from 3α,5-cyclo-25D-spirostan-6-one by Burn *et al.*[2] is therefore 3α,5-cyclo-6β-methyl-25D-spirostan-6α-ol (I). These workers also isolated in small quantity a second substance, m. p. 175°, $[\alpha]_D$ —130°, believed to be the epimeric tertiary alcohol. Although its analysis and chromatographic properties agree with this formulation, its high negative rotation points to a structure other than that of a cyclosteroid. We now describe the synthesis of authentic 3α,5-cyclo-α-methyl-25D-spirostan-6β-ol.



The alcohol (I) prepared by the method of Burn *et al.*[2] rearranged in presence of toluene-*p*-sulphonic acid in dioxan to 6-methyl-25D-spirost-5-en-3β-ol (II; R = H) the toluene-*p*-sulphonate of which was converted by potassium acetate in boiling aqueous acetone into 3α,5-cyclo-6-methyl-25D-spirost-6-ene (III) and 3α,5-cyclo-6α-methyl-25D-spirostan-6β-ol (IV), m. p. 173°, $[\alpha]_D$ —39°. Both these compounds were rearranged to 6-methyl-25D-spirost-5-en-3β-yl acetate (II; R = Ac) by sulphuric acid in acetic acid. The product of Burn *et al.*[2] is probably 6-methyl-25D-spirost-5-en-3β-ol (II; R = H), formed by rearrangement during the isolation of the alcohol (I). Alcohol (II; R = H) was prepared and had m. p. and $[\alpha]_D$ close to those of the product of Burn *et al.*[2]

Experimental.—$[\alpha]_D$ were measured for $CHCl_3$ solutions.

*6-Methyl-25D-spirost-5-en-3β-yl toluene-*p*-sulphonate.* 6-Methyl-25D-spirost-5-en-3β-ol (5·7 g.) in pyridine (40 ml.) was left at room temperature overnight with toluene-*p*-sulphonyl chloride (6 g.), ice-cold dilute sulphuric acid was added, the product was extracted with chloroform, and the extract washed successively with water, sodium hydrogen carbonate solution, and water. Evaporation of the dried extract gave *6-methyl-25D-spirost-5-en-3β-yl toluene-*p*-sulphonate*, m. p. 165—166° (decomp.) (from ethyl acetate), $[\alpha]_D$ −100° (*c* 1·1) (Found: C, 72·1; H, 8·5. $C_{35}H_{50}O_5S$ requires C, 72·1; H, 8·65%). Unlike the ester of 6-methylcholesterol[1] this did not decompose on storage.

3α,5-Cyclo-6-methyl-25D-spirost-6-ene and 3α,5-cyclo-6α-methyl-25D-spirostan-6β-ol. The preceding ester (3·5 g.) was refluxed with potassium acetate (3·5 g.) in acetone (150 ml.) and water (45 ml.) for 3 hr. The acetone was removed under reduced pressure and the product extracted with ether, washed with water, dried (Na_2SO_4), and recovered as an oil which was chromatographed on aluminium oxide (90 g.). Elution with pentane–benzene (9 : 1; 6 × 200 ml.) gave an oil (165 mg.) which on crystallisation from acetone gave *3α,5-cyclo-6-methyl-25D-spirost-6-ene* as plates, m. p. 106—110°, $[\alpha]_D$ −144° (*c* 1·1) (Found: C, 81·4; H, 10·3. $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·3%). Elution with benzene (26 × 200 ml.) and benzene–ether (9 : 1; 8 × 200 ml.) gave *3α,5-cyclo-6α-methyl-25D-spirostan-6β-ol* (2·12 g.), m. p. 170—173° (from acetone), $[\alpha]_D$ −39° (*c* 1·2) (Found: C, 78·4; H, 10·4. $C_{28}H_{44}O_3$ requires C, 78·5; H, 10·4%). This compound had m. p. 144—165° on admixture with the isomeric 6α-alcohol.

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[1] Davis, Julia, and Summers, *Bull. Soc. chim. France*, 1960, 742.

[2] Burn, Ellis, Petrow, Stuart-Webb, and Williamson, *J.*, 1957, 4092; see also Grenville, Patel, Petrow, Stuart-Webb, and Williamson, *J.*, 1957, 4105; Ellis, Petrow, and Waterhouse, *J.*, 1960, 2596.

Treatment of the hydrocarbon and the 6β-alcohol in acetic acid with a few drops of concentrated sulphuric acid gave after 1 hr. 6-methyl-25D-spirost-5-en-3β-yl acetate, m. p. 216—218°, $[\alpha]_D$ −130° (*c* 1·0) (plates from chloroform–methanol).

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354. *Preparation and Infrared Spectra of Trimeric Dialkylphosphinoborines and Some B-Halogenated Derivatives.*

By R. H. BIDDULPH, M. P. BROWN, R. C. CASS, R. LONG, and H. B. SILVER.

REPORTED methods of preparation of trimeric dialkylphosphinoborines either have used difficultly accessible materials or have employed high-vacuum techniques.[1-3] We have found that tetra-alkyldiphosphine disulphides, which can be readily prepared from thiophosphoryl chloride and the corresponding Grignard reagent,[4] react with alkali-metal borohydrides to give trimeric dialkylphosphinoborines, with dialkylphosphines as by-products. The use of lithium borohydride gave the highest yields of the desired product (50—60%).

Wagner *et al.*[2] stated, without experimental details, that *B*-halogenated phosphinoborines may be prepared by the action of alkyl halides on trimeric dialkylphosphinoborines in the presence of aluminium halide. Using this general method, we prepared the hexachloro-derivative of trimeric dimethylphosphinoborine and the hexa-chloro-, -bromo-, and -iodo-derivatives of trimeric diethylphosphinoborine. The chloro-derivatives were obtained in good yields by refluxing the phosphinoborine in butyl chloride in the presence of aluminium chloride. Similarly, the hexabromide was obtained from the trimer, propyl bromide, and aluminium bromide. However, the iodo-derivative was prepared by adding iodine to a solution of the trimer in ethyl iodide until the colour was no longer discharged. Chemically, the *B*-halogenated phosphinoborines appeared unreactive. Thus trimeric dimethylphosphinodichloroborine was recovered unchanged after being heated with ammonia at 200° for several days or under reflux with diethylamine. It was also unchanged after refluxing with methylmagnesium iodide in ether.

Infrared Spectra (R.H.B.) (see Fig. and Table).—When the boron atom of a simple molecule BX_3 (where $X =$ halogen) is bonded to a donor atom, the B–X stretching frequencies observed are lower than those found in the simple molecule BX_3; *e.g.*, Bellamy *et al.*[5] quote for the B–Cl stretching frequency a range 850—910 cm.$^{-1}$, whereas we have found a range of 690—770 cm.$^{-1}$ for both the phosphinoborines and the co-ordination compounds R_3NBCl_3 where R_3N is triethylamine or pyridine.[6] This lowering of the asymmetric stretching frequency can be explained in view of the changed electronic environment of the boron atoms owing to the donation of electrons to the bond system by the phosphorus or nitrogen atoms. When X is hydrogen the B–H stretching frequencies which we found occurred at the lower end of the range 2350—2630 cm.$^{-1}$ quoted by Bellamy *et al.*[5] for boron hydrides. The B–H deformation frequencies observed for these phosphinoborines correspond closely to those found previously in the hydrides and are similar to

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[1] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

[2] Wagner, Caserio, Evleth, Freeman, and Stewart, Abs. Papers, 135th Meeting Amer. Chem. Soc., April 1959, p. 49-o.

[3] Burg and Slota, *J. Amer. Chem. Soc.*, 1960, **82**, 2145.

[4] Kabachnik and Schepeleva, *Izvest Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, No. 1, 56; Kosolapoff and Watson, *J. Amer. Chem. Soc.*, 1951, **73**, 5466; Christen, Van Der Linde, and Hooge, *Rec. Trav. chim.*, 1959, **78**, 161; Kuchen and Buckwald, *Angew. Chem.*, 1959, **71**, 162; Issleib and Tzschach, *Chem. Ber.*, 1959, **92**, 704.

[5] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

[6] Katritzky, *J.*, 1959, 2049; Greenwood and Wade, *J.*, 1960, 1130; Waddington and Klanberg, *J.*, 1960, 2339.

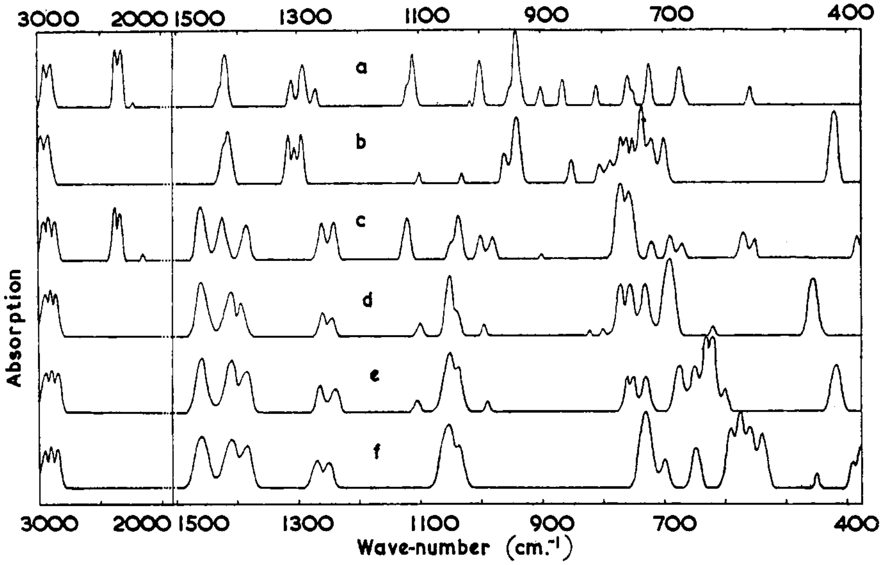
Assignments of bands observed in the spectra of $[R_2P{\cdot}BX_2]_3$.

R	Me	Me	Et	Et	Et	Et	
X	H	Cl	H	Cl	Br	I	Ref.
CH stretch	2910 2965	2918 2979	2870 2922 2955	2859 2911 2940	2852 2905 2940	2855 2910 2950	*a*
BH stretch	2332 2370	—	2345 2380	—	—	—	5
CH_3 deform. as.	1420	1418	1462	1460	1458	1457	*a*
CH_3 deform. s.	1268 1294 1310	1298 1303 1314	1388	1388	1382	1386	*a*
CH_2 scissor	—	—	1422	1412	1410	1410	*a*
CH_2 wag	—	—	1242 1260	1244 1260	1239 1258	1250 1268	*a*
BH_2 scissor	1111	—	1118	—	—	—	5
CH_3 rock	938	940	1043	1050	1050	1054	*a*
BH_2 wag	1000	—	982 1003	—	—	—	5
B Hal_2 stretch as.	—	738	—	691	620 630	576	
BH_2 rock	557	—	570	—	—	—	
B Hal_2 stretch s.	—	420	—	455	415	<375	

a, Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

those for the SiH_2 group as found by Ebsworth, Onyszchuk, and Sheppard.[7] This is to be expected, since the stretching force constants calculated from the observed mean BH and SiH are 2·9 and 2·7 × 10^5 dynes/cm. The bending force constants are probably similar to one another.

Spectra of $(R_2P{\cdot}BX_2)_3$. (*a*) R = Me, X = H; (*b*) R = Me, X = Cl); (*c*) R = Et, X = H; (*d*) R = Et, X = Cl; (*e*) R = Et, X = Br; (*f*) R = Et, X = I.



N.B. The featureless part of the spectra between 1500 and 2000 cm.⁻¹ has been omitted.

Experimental.—Trimeric dimethylphosphinoborine. Tetramethyldiphosphine disulphide (9·3 g.) and lithium borohydride (3·3 g.) were ground together and placed in a flask provided with a 5 ft. air-condenser, to the top of which was connected a U-trap cooled in liquid nitrogen. The apparatus was completely flushed with dry nitrogen. The flask was heated to 250° at atmospheric pressure. After 1 hr. the pressure in the system was reduced to 25 mm. and the heating was continued for a further 3 hr. During the reaction, crystals of the product sublimed into the air-condenser. The volatile material collected in the U-trap was shown to be dimethylphosphine (0·2 g.) (v. p. at 0° = 342·5 mm.; Wagner and Burg [8] give 342 mm.). The contents of the air-condenser and the reaction flask were extracted with light petroleum (b. p. 40—60°), the solution was chromatographed (Woelm alumina, neutral grade), and the solid (3·5 g.) obtained by evaporation of the eluant was crystallised from methanol, giving trimeric dimethylphosphinoborine, m. p. 87—88° (Burg and Wagner [1] give m. p. 85—86°).

Numerous other preparations which were carried out with sodium and potassium borohydride showed that the amount of dimethylphosphine formed tended to increase (10—30%) whilst the yields of trimeric dimethylphosphinoborine were reduced (20—25%) (yields based on the amount of initial tetramethyldiphosphine disulphide). Use of 2,2′-dimethoxydiethyl ether as a reaction medium in the initial stages offered no advantage.

Trimeric diethylphosphinoborine. A mixture of tetraethyldiphosphine disulphide (12·1 g.) and lithium borohydride (6·5 g.) was heated at 280—300° under nitrogen for 7 hr. Volatile material, assumed to be diethylphosphine (0·3 g.), was collected in a trap cooled at $-196°$. The mixture was extracted with light petroleum (b. p. 40—60°), and removal of the solvent left an oil (6·15 g.). The crude oil was distilled, giving trimeric diethylphosphinoborine, b. p. 106—108°/0·1 mm., n^{20} 1·5312 (Found: C, 47·0, 46·7; H, 11·9, 12·2. Calc. for $C_{12}H_{36}B_3P_3$: C, 47·1; H, 11·9%). Burg and Slota [3] give b. p. 133—134°/1·5 mm.

Trimeric dimethylphosphinodichloroborine. Trimeric dimethylphosphinoborine (1·22 g.) was heated in butyl chloride (20 c.c.). Aluminium chloride (0·45 g.) was added, and after 5 min. a very vigorous reaction ensued, the mixture became yellow, and hydrogen chloride was evolved. Heating was continued until evolution of hydrogen chloride ceased (1·5 hr.). The mixture was decomposed with water (50 c.c.) and extracted with chloroform. Removal of the solvents gave a residue (2·26 g.) which crystallised from benzene, giving *trimeric dimethylphosphinodichloroborine,* m. p. 393—394° (Found: C, 17·3, 17·5; H, 4·2, 4·4; Cl, 49·6, 50·1. $C_6H_{18}B_3Cl_6P_3$ requires C, 16·8; H, 4·2; Cl, 49·7%).

Trimeric diethylphosphinodichloroborine. In a similar manner this *compound* was prepared from trimeric diethylphosphinoborine (0·22 g.), aluminium chloride (0·13 g.), and butyl chloride (10 c.c.). The crude product (0·35 g.) crystallised from light petroleum (b. p. 40—60°) as rods, m. p. 181·5° (Found: C, 28·9, 28·95; H, 5·9, 6·0; Cl, 41·2, 41·5. $C_{12}H_{30}B_3Cl_6P_3$ requires C, 28·1; H, 5·9; Cl, 41·5%).

Trimeric diethylphosphinodibromoborine. This *compound* was prepared from trimeric diethylphosphinoborine (0·83 g.), aluminium bromide (0·3 g.), and propyl bromide (10 c.c.). The crude solid (1·93 g.) crystallised from chloroform–light petroleum (b. p. 40—60°) as rods, m. p. 304—305° (Found: C, 18·5, 18·7; H, 4·1, 3·85; Br, 61·0, 61·2. $C_{12}H_{30}B_3Br_6P_3$ requires C, 18·5; H, 3·9; Br, 61·5%).

Trimeric diethylphosphinodi-iodoborine. Iodine was added in small portions to a refluxing solution of trimeric diethylphosphinoborine (0·74 g.) in ethyl iodide (10 c.c.). The crude product (2·18 g.) obtained by evaporation was washed with ether and crystallised from carbon tetrachloride–light petroleum (b. p. 40—60°), giving small rhombic crystals, m. p. 325—330° (decomp.) (Found: C, 14·8, 14·6; H, 2·8, 2·6; I, 71·3, 71·7. $C_{12}H_{30}B_3I_6P_3$ requires C, 13·6; H, 2·85; I, 71·6%).

Infrared spectra. With the exception of trimeric diethylphosphinoborine, which is liquid and was prepared as a thin film between potassium bromide plates, substances were examined in pressed potassium chloride discs. The spectrophotometer was a Unicam S.P. 100 fitted with sodium chloride and potassium bromide prisms. The accuracy was ±5 cm.$^{-1}$ between 375 and 2000 cm.$^{-1}$ and ±10 cm.$^{-1}$ between 2000 and 3500 cm.$^{-1}$.

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COX LANE, CHESSINGTON, SURREY.
[*Received, September 26th,* 1960.]

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[7] Ebsworth, Onyszchuk, and Sheppard, *J.*, 1958, 1453.

[8] Wagner and Burg, *J. Amer. Chem. Soc.*, 1953, **75**, 3869.

355. *The Diazo-exchange Reaction studied with Nitrogen-*15: p-*Nitrophenyldiazonium Chloride Solution.*

By P. F. HOLT and C. J. MCNAE.

A PREVIOUS paper [1] described the application of nitrogen-15 to the study of the diazo-exchange in which a diazonium group appears to change places with an amino-group. Of the two mechanisms which had been suggested one was rejected. This, due to Bamberger,[2] assumed an equilibrium between diazonium salts and nitrous acid and suggested that the acid diazotised free amino-groups. No such equilibrium could be observed; when potassium [^{15}N]nitrite was added to diazonium salts it was not incorporated in the diazonium ion.

In support of Bamberger's theory, Bucherer and Wolff [3] claimed to have demonstrated that nitrous acid was present in a solution of *p*-nitrophenyldiazonium chloride purified by converting it into sodium *p*-nitrophenylisodiazoate and acidifying this. This observation appeared directly contradictory to our results. We therefore repeated the experiments of the previous paper on a solution of *p*-nitrophenyldiazonium chloride.

Experimental.—*p*-Nitroaniline (B.D.H.), recrystallised to m. p. 145·5—146·5° (lit., 146°) (0·340 g.) was dissolved in hydrochloric acid (8 ml.; 2N) and water (17 ml.), and the solution was diazotised with sodium nitrite (0·215 g.). A solution containing potassium [^{15}N]nitrite (0·0589 g.; 35·8 atom % of nitrogen-15) was then added, and the mixture left for 4 days at 0—3°. Free nitrous acid was then removed by addition of urea, and the mixture poured into 2-naphthol (0·410 g.) in aqueous sodium carbonate (1 g. in 100 ml.). The precipitated 1-*p*-nitrophenylazo-2-naphthol was washed with water (150 ml.), recrystallised once from dimethylformamide, and thoroughly dried; it had m. p. 251° (lit.,[4] 251—252°).

The nitrogen-15 abundance in the nitrogen of the azo-compound was 0·40 atom % (atmospheric abundance, 0·37 atom %). If the equilibrium existed, some nitrogen-15 would have been incorporated into the diazonium ion, resulting in a calculated abundance for the product of 6·93 atom % of nitrogen-15 under the experimental conditions.

This result confirms the view that a mechanism involving an equilibrium between nitrite and diazonium ions is unacceptable and leaves the mechanism suggested by Bayer,[5] involving the formation and decomposition of a triazen, as the only reasonable mechanism suggested so far. It is possible that Bucherer and Wolff failed to free their sodium *p*-nitrophenylisodiazoate from nitrite. Any mechanism involving the nuclear nitro-group has already been eliminated.[1]

We are grateful to Dr. D. H. Tomlin who assayed the nitrogen samples, and to the Department of Scientific and Industrial Research for a grant (to C. J. M.).

THE UNIVERSITY, READING. [*Received, October* 17*th*, 1960.]

[1] Holt, Hopson-Hill, and McNae, *J.*, 1960, 2245.
[2] Bamberger, *Ber.*, 1895, **28**, 827.
[3] Bucherer and Wolff, *Ber.*, 1909, **42**, 881.
[4] Bamberger and Meimberg, *Ber.*, 1895, **28**, 1894.
[5] Bayer, D.R.-P. 1890, 51,576.

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356. *Phosphonitrilic Derivatives. Part VI.*[1] N-*Methyltrichlorophosphinimine Dimer.*

By A. C. CHAPMAN, W. S. HOLMES, N. L. PADDOCK, and H. T. SEARLE.

PRODUCTS of the condensation of phosphorus pentachloride with amides have often been described; a large number of such derivatives, apparently containing the P=N group, have been obtained by Kirsanov and his co-workers.[2] The parent compound, trichlorophosphophinimine NH:PCl$_3$, is believed to be formed in the reaction between phosphorus

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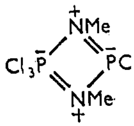
[1] Part V, Chapman, Paine, Searle, Smith, and White, *J.*, 1961, 1768.

[2] Kirsanov, *Khim. i Prim. Fos. Akad. Nauk S.S.S.R. Trudy I-O Konferents*, 1955, 99 (Pub. 1957).

pentachloride and ammonium chloride,[3] subsequently condensing either with itself or with further phosphorus pentachloride to give the linear phosphonitrilic derivatives previously described.[4] Gilpin [5] prepared *N*-phenyltrichlorophosphinimine by reaction of aniline hydrochloride with phosphorus pentachloride; we report here the preparation of dimeric *N*-methyltrichlorophosphinimine, which displays some new structural features.

The compound has the dimeric formula $(CH_3{\cdot}N{:}PCl_3)_2$; it is a non-conductor in nitrobenzene. Its molecular weight is independent of temperature (5—74°) and of the dielectric constant of the solvent (2·3—34·8). The two monomer units are therefore united by primary valencies rather than by dipolar forces. The spectroscopic data agree most nearly with a centrosymmetric structure in which the phosphorus and nitrogen atoms form a 4-membered planar ring. The ring bonds are strong, as Mortimer [6] found a minimum average value for *E*[P–N] of 74·3 kcal. mole^{-1}. The infrared peak at 2812 cm.$^{-1}$ is characteristic of an *N*-methyl group bearing an unshared pair of electrons,[7] but its low intensity compared with that of the C–H stretching band at 2941 cm.$^{-1}$ suggests some delocalisation. The transfer of one electron from each nitrogen atom would allow the formation of polar $d\pi$–$p\pi$ bonds, one of a pair of symmetrically related structures being as shown (inset), the ring bonds now resembling those in the phosphonitrilic chlorides, in which [8] *E*[P–N] = 72·3 kcal. mole^{-1}. This interpretation is consistent with the absence of a peak in the region 1290—1325 cm.$^{-1}$ associated [9] with the $P{\cdot}N{\cdot}CH_3$ group; the strong peak at 847 cm.$^{-1}$ may correspond to a P–N stretching vibration, normally expected [9,10] in the range 680—750 cm.$^{-1}$. If the bonds are of the type proposed, the natural ring angle at the nitrogen atoms would be close to 120°, and at the phosphorus atoms should not be less than 90°. It is remarkable that a dimer is formed, rather than a trimer in which the angular requirements could be easily satisfied by slight puckering of the ring. Related compounds, notably the phosphoric imido-amides RN:P(O)·NHR, are often associated,[11] and Michaelis [12] has postulated 4-membered ring structures for several classes of phosphorus–nitrogen compound on the basis of their molecular weights. The type of structure deduced here for *N*-methyltrichlorophosphinimine may therefore occur frequently.



Experimental.—Methylammonium chloride (74·3 g., 1·1 moles), phosphorus pentachloride (208·5 g., 1 mole), and *sym*-tetrachloroethane (1 l.), all commercial materials, were heated together under reflux for 5 hr.; when reaction had practically ceased, the amount of hydrogen chloride evolved corresponded closely to that required by the reaction $Me{\cdot}NH_3Cl + PCl_5 \longrightarrow MeN{:}PCl_3 + 3HCl$. The excess of salt was filtered off, and the solvent distilled off *in vacuo* (yield 150 g., 90%). The product was recrystallised from carbon tetrachloride and sublimed at 150°/0·5 mm., giving hygroscopic monoclinic needles of dimeric N-*methyltrichlorophosphinimine*, m. p. 160° (decomp.) (Found: C, 7·1; H, 1·8; N, 8·5; Cl, 63·4; P, 18·9. CH_3Cl_3NP requires C, 7·2; H, 1·8; N, 8·4; Cl, 64·0; P, 18·6%). Phosphorus was estimated as magnesium pyrophosphate or as phosphomolybdate after hydrolysis by a solution of silver nitrate in nitric acid.

Molecular weights were determined in carbon tetrachloride with a special Menzies–Wright ebulliometer, in which the solvent was dried *in situ* by circulation through activated alumina before the sample was added to it by breakage of a phial within the apparatus. They were also determined cryoscopically in benzene and in nitrobenzene; the values obtained by the three methods (315, 348, 330) are close to that (333) for the dimer. The molar conductance

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[3] Proctor, Thesis, London, 1958.

[4] Lund, Paddock, Proctor, and Searle, *J.*, 1960, 2542; Becke-Goehring and Koch, *Chem. Ber.*, 1959, **92**, 1188.

[5] Gilpin, *Amer. Chem. J.*, 1897, **19**, 352.

[6] Mortimer, *Chem. and Ind.*, 1960, 444.

[7] Braunholtz, Ebsworth, Mann, and Sheppard, *J.*, 1958, 2780.

[8] Hartley, Paddock, and Searle, *J.*, 1961, 430.

[9] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 2nd edn., p. 323.

[10] Holmstedt and Larsson, *Acta Chem. Scand.*, 1951, **5**, 1179.

[11] Kosolapoff, " Organo-Phosphorus Compounds," Wiley, New York, 1950, p. 295.

[12] Michaelis, *Annalen*, 1903, **326**, 129.

of the compound in nitrobenzene at 25° was near 1·7 ohm^{-1} mole^{-1} cm.^{2} over the range (0·5—2·0) × 10^3 l. mole^{-1}. Since values near 30 ohm^{-1} mole^{-1} cm.^{2} are obtained [13] for 1 : 1 electrolytes in nitrobenzene, the small conductance observed is attributed to ionic impurities (principally water or hydrogen chloride), and *N*-methyltrichlorophosphinimine itself is taken to be a non-electrolyte.

Infrared spectra, for CS_2 or CCl_4 solutions, were obtained with a Perkin–Elmer model 21 spectrometer, calibrated with polystyrene. Raman spectra, for CS_2 or benzene solutions, were obtained with a Hilger direct-recording Raman spectrograph. Depolarisation factors were determined approximately by Edsall and Wilson's method.[14] Solutions were prepared and cells were filled inside a dry-box. The following fundamental frequencies were observed, relative intensities and state of polarisation, where appropriate, being also given.

Raman lines (cm.$^{-1}$): 204ms,dp, 268s,dp, 352vs,p, 412w,dp, 458m,dp, 544s,dp, 2946m, 2999vw.

Infrared bands (cm.$^{-1}$): 434m, 575s, 658s, 700m, 747vw, 847vs, 1162s, 1184s, 1210s, 1429m, 1461m, 2812w, 2941m, 2996m.

Since the two methyl groups in a dimeric molecule will be very weakly coupled, the Raman active–infrared active methyl vibrations are likely to be unresolved, leading to apparent Raman–infrared coincidences for methyl group vibrations irrespective of molecular symmetry. All the bands above 1150 cm.$^{-1}$ are tentatively assigned to methyl group vibrations, and the two remaining series of bands are mutually exclusive, leading to the conclusion that the molecule is centrosymmetrical, the phosphorus and nitrogen atoms alternating in a 4-membered ring. These remaining bands are fewer than predicted on the basis of the proposed symmetry [15 Raman lines, either all polarised (C_i) or 10 polarised (C_{2h}), and 15 infrared bands], but this is not unexpected, because many of the predicted infrared bands are probably of too low a frequency to be observed, while some of the weaker Raman lines may have escaped observation.

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[13] Kraus and Witschonke, *J. Amer. Chem. Soc.*, 1947, **69**, 2472.
[14] Edsall and Wilson, *J. Chem. Phys.*, 1938, **6**, 124.

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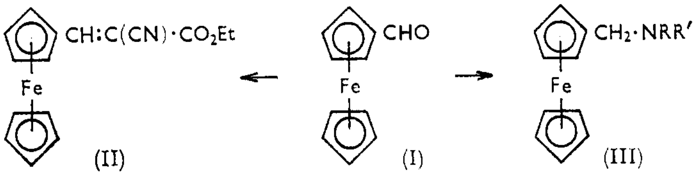
357. *Some Substituted Ferrocenes.*

By I. K. Barben.

Formylferrocene [1] (I) condensed with ethyl cyanoacetate at room temperature, in ethanol containing a trace of piperidine, to give ethyl α-cyano-β-ferrocenylacrylate (II). Condensation also took place in boiling benzene containing a little piperidine and acetic acid.[2] No addition of phenylmagnesium bromide to this acrylate occurred even in the presence of cuprous chloride.[3] 2-Dimethylaminoethylamine reacted with the ferrocene aldehyde (I) and the product was reduced by sodium borohydride to (2-dimethylaminoethylaminomethyl)ferrocene (III; R = $CH_2·CH_2·NMe_2$, R' = H) which was isolated as a



[1] Graham, Lindsey, Parshall, Peterson, and Whitman, *J. Amer. Chem. Soc.*, 1957, **79**, 3416.
[2] Cope, Hofmann, Wyckoff, and Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.
[3] Brandström and Forsblad, *Arkiv Kemi*, 1954, **6**, 561.

dihydrochloride. This same aldehyde and aniline in boiling toluene containing a trace of phosphoryl chloride[4] gave anilinomethylferrocene (III; R = Ph, R' = H) after reduction with sodium borohydride. Similarly, 2-pyridylaminomethylferrocene (III; R = 2-C_5H_4N, R' = H) was obtained, but in better yield when the reactants condensed at 100°. An attempted alkylation of the anilino-derivative (III; R = Ph, R' = H) with 2-dimethylaminoethyl chloride in boiling xylene in the presence of sodamide failed but chloroacetyl chloride in the presence of triethylamine[5] in ether gave the amide (III; R' = Ph, R = $CO{\cdot}CH_2Cl$) whence the piperidinoacetyl compound (III; R = $C_5H_{10}N{\cdot}CH_2{\cdot}CO$, R' = Ph) was obtained.

Experimental.—*Ethyl α-cyano-β-ferrocenylacrylate.* (*a*) A solution of formylferrocene[1] (1·07 g.) and ethyl cyanoacetate (0·57 g.) in ethanol (10 c.c.) containing a few drops of piperidine deposited red cubes (0·9 g., 58%) of *ethyl α-cyano-β-ferrocenylacrylate*, m. p. 88—90° [from light petroleum (b. p. 60—80°) or ethanol] (Found: C, 62·4; H, 5·1; N, 4·55. $C_{16}H_{15}FeNO_2$ requires C, 62·2; H, 4·9; N, 4·5%).

(*b*) The aldehyde (1·07 g.) and ethyl cyanoacetate (0·57 g.) in benzene (50 c.c.) containing a few drops of piperidine and acetic acid (0·6 g.) were heated under reflux in a Dean and Stark apparatus. When the theoretical amount of water had been collected the benzene solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent left the acrylate ester (1·3 g., 84%).

(*2-Dimethylaminoethylaminomethyl*)*ferrocene.* A mixture of formylferrocene (2·14 g.) and 2-dimethylaminoethylamine (0·88 g.) was set aside for several days. The resulting red oil was dissolved in methanol (20 c.c.), and sodium borohydride (0·38 g.) was added, with stirring, during 15 min. After being boiled for a further 15 min. the solution was poured into water and extracted with ether. The dried ($MgSO_4$) solution, on saturation with hydrogen chloride, deposited (*2-dimethylaminoethylaminomethyl*)*ferrocene dihydrochloride* (1·7 g., 54%), yellow needles (from 1 : 1 ethanol–ether), m. p. 203—205° (decomp.) (Found: C, 50·0; H, 6·4; Fe, 15·3; N, 7·7. $C_{15}H_{22}N_2Fe,2HCl$ requires C, 50·2; H, 6·7; Fe, 15·5; N, 7·8%).

Anilinomethylferrocene. Aniline (1·12 g.) and formylferrocene (2·14 g.) in toluene (50 c.c.) containing phosphoryl chloride (0·1 c.c.) were refluxed in a Dean and Stark apparatus until the theoretical amount of water had been collected. The filtered solution was washed with water and dried ($MgSO_4$). The red oil obtained on evaporation of the solvent was reduced with sodium borohydride as described above. *Anilinomethylferrocene* (2·6 g., 90%), m. p. 85—86°, crystallised as yellow plates from aqueous ethanol (Found: C, 70·1; H, 5·9; N, 5·0. $C_{17}H_{17}FeN$ requires C, 70·1; H, 5·9; N, 4·8%).

2-Pyridylaminomethylferrocene. Similar conditions afforded *2-pyridylaminomethylferrocene* (35%), m. p. 138—140°, as red needles [from light petroleum (b. p. 60—80°)] (Found: C, 66·3; H, 5·4; N, 9·25. $C_{16}H_{16}FeN_2$ requires C, 65·8; H, 5·5; N, 9·6%). When equimolar quantities of the amine and the aldehyde were heated on a steam-bath for 9 hr. and then reduced with sodium borohydride a 62% yield was obtained.

N-*Chloroacetylanilinomethylferrocene.* Addition of chloroacetyl chloride (0·57 g.) to a stirred ethereal solution of anilinomethylferrocene (1·46 g.) and triethylamine (0·51 g.) gave the *chloroacetyl derivative* (1·49 g., 81%) on removal of the solvent. Recrystallisation from benzene–light petroleum (b. p. 60—80°) afforded yellow needles, m. p. 140—141° (Found: C, 61·6; H, 5·0; Cl, 9·2; Fe, 14·9; N, 3·8. $C_{19}H_{18}ClFeNO$ requires C, 62·1; H, 4·9; Cl, 9·6; Fe, 15·2; N, 3·8%). The chloroacetyl compound (6·7 g.) and piperidine (3·05 g.) were heated under reflux in dry benzene for 10 hr. The filtered benzene solution was extracted with 2N-hydrochloric acid (3 × 20 c.c.). The acid extract was basified and the product isolated with ether as an oil (6 g., 79%) which slowly solidified. Recrystallisation from light petroleum (b. p. 38—42°) gave yellow rods of N-(*piperidinoacetyl*)*anilinomethylferrocene*, m. p. 71—73° (Found: C, 69·7; H, 7·25; N, 6·75. $C_{24}H_{28}FeN_2O$ requires C, 69·2; H, 6·8; N, 6·7%).

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