

LXXVI.—*Tertiary Arylalkyl Phosphines. Part II.*

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IN the present communication, *p*-xylyldialkylphosphines (2 : 5-dimethylphenyldialkylphosphines) and some of their derivatives are described.

The *p*-xylene was prepared from recrystallised *p*-xylydine hydrochloride by the method of Clemo, Haworth, and Walton (J., 1929, 2375), and was subjected to purification by the repeated operation of freezing and drawing off the mother-liquor, whereby crystals, m. p. 13°, were finally obtained.

In the preparation of *p*-xylyldichlorophosphine (compare Weller, *Ber.*, 1887, 20, 1720; 1888, 21, 1494), 150 g. of *p*-xylene, 125 c.c. of phosphorus trichloride, and 30 g. of aluminium trichloride were vigorously refluxed for 36 hours. The product was distilled under 20 mm. pressure until all liquid had passed over, and the distillate was fractionally redistilled, whereby 60 c.c. of the dichlorophosphine, b. p. 129°/12 mm., 140°/23 mm., were obtained.

The phosphines were prepared in the way already described (J., 1930, 2298); the precautions, there referred to, for the exclusion of air were found to be necessary in the present preparations, the methylphosphine in particular being quickly oxidised.

p-Xylyldimethylphosphine (Found: C, 72.0; H, 9.4. $C_8H_9PMe_2$ requires C, 72.2; H, 9.1%) is prepared by introducing a solution of 20 c.c. of *p*-xylyldichlorophosphine in 50 c.c. of ether into a Grignard reagent made from 21 c.c. of methyl iodide, 8 g. of magnesium, and 240 c.c. of ether (yield of purified phosphine, 14 c.c.); b. p. 106°/12 mm., d_4^{25} 0.9541. When the phosphine is boiled in a current of air, *p*-xylyldimethylphosphine oxide (Found: C, 65.1; H, 8.4. $C_8H_9 \cdot PMe_2O$ requires C, 65.9; H, 8.3%) separates as colourless

radiating needles, m. p. 94—95°, which may be distilled without decomposition.

p-Xylyldimethylphosphine combines directly with carbon disulphide to give the *inner anhydride* of *p*-xylyldimethylhydroxyphosphinocarbitronic acid (compare Meyer-Jacobson, "Lehrbuch der organischen Chemie," 1 Aufl., Bd. 1, 263; Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1510; Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 612). This compound, after recrystallisation from alcohol, forms deep red plates, m. p. 76° (Found: C, 54.9; H, 6.5.

$C_8H_9 \cdot \overline{PMe_2} \cdot CS_2$ requires C, 54.5; H, 6.2%). Although colorations were given by carbon disulphide with all the *p*-xylylphosphines, no solid compound could be isolated except in the above case. This is in agreement with the observation of Czimatis (*Ber.*, 1882, **15**, 2014) that arylmethylphosphines combine very easily with carbon disulphide, but arylethylphosphines only with difficulty.

p-Xylyldimethylphosphine mercurichloride (Found: Cl, 16.8. $C_8H_9 \cdot PMe_2 \cdot HgCl_2$ requires Cl, 16.2%) is prepared by mixing alcoholic solutions of its components; the white precipitate is extracted with boiling glacial acetic acid, from which the double compound crystallises as needles, m. p. 225° after recrystallisation from alcohol.

In ethereal solution, methyl iodide combines with the phosphine to give *p*-xylyltrimethylphosphonium iodide (Found: I, 41.1. $C_8H_9 \cdot PMe_3I$ requires I, 41.2%), which crystallises from alcohol as long white prisms, m. p. 204°.

p-Xylyltrimethylphosphonium mercu-tri-iodide (Found: I, 50.3; Hg, 26.1. $C_8H_9 \cdot PMe_3I \cdot HgI_2$ requires I, 49.9; Hg, 26.3%), m. p. 152°, is obtained as prismatic plates when the precipitate resulting from the treatment of excess of the phosphonium iodide with mercuric iodide in alcohol is recrystallised from the same solvent. The *chloroplatinate* (Found: Pt, 25.1. $[(C_8H_9)P(CH_3)_3]_2PtCl_6$ requires Pt, 25.3%), on recrystallisation from alcohol, forms orange needles, m. p. 236°.

Hot alcoholic solutions of iodine and the phosphonium iodide were mixed; on cooling, metallic-lustred, dark red plates of the *tri-iodide*, $C_8H_9 \cdot PMe_3I_3$ (Found: I, 67.9. $C_{11}H_{18}I_3P$ requires I, 67.8%), m. p. 91°, separated, which were recrystallised from alcohol.

p-Xylyldiethylphosphine (Found: C, 74.0; H, 9.9; P, 16.0. $C_8H_9 \cdot PEt_2$ requires C, 74.2; H, 9.9; P, 16.0%) is obtained by adding 10 c.c. of the dichlorophosphine in 50 c.c. of ether to magnesium ethyl bromide prepared from 25 c.c. of ethyl bromide, 8 g. of magnesium, and 240 c.c. of ether (yield, 9 g.); b. p. 157°/52 mm., d_4^{25} 0.9392. Like all the *p*-xylyldialkylphosphines, this phosphine possesses a

penetrating, persistent, agreeable smell, somewhat reminiscent of hyacinths.

The following derivatives were obtained by the methods described in the case of the methyl compounds.

p-Xylyldiethylphosphine mercurichloride (Found: Cl, 15.7. $C_8H_9 \cdot PEt_2 \cdot HgCl_2$ requires Cl, 15.2%), white needles, m. p. 184°; *p*-xylylmethyl-diethylphosphonium iodide (Found: I, 37.4.



requires I, 37.8%), colourless rhombic prisms, m. p. 137°; the chloroplatinate (Found: Pt, 23.3. $[(C_8H_9)P(C_2H_5)_2(CH_3)]_2PtCl_6$ requires Pt, 23.6%), orange needles, m. p. 217°; the phosphonium mercuri-iodide (Found: Hg, 25.4; I, 48.4. $C_8H_9 \cdot PMeEt_2 I \cdot HgI_2$ requires Hg, 25.4; I, 48.2%), long, pale yellow needles, m. p. 105°; the tri-iodide (Found: I, 64.3. $C_8H_9 \cdot PMeEt_2 I_3$ requires I, 64.6%), glistening, chocolate-coloured needles, m. p. 85°.

p-Xylyldi-*n*-propylphosphine (Found: C, 75.8; H, 9.9; P, 13.7. $C_8H_9 \cdot PPr_2$ requires C, 75.6; H, 10.4; P, 13.9%) has b. p. 161°/2.5 mm. and d_4^{25} 0.9281. It is prepared (9 g.) by the addition of 10 c.c. of *p*-xylyldichlorophosphine to the Grignard reagent obtained by using 30 c.c. of *n*-propyl bromide and 8 g. of magnesium.

p-Xylyldi-*n*-propylphosphine mercurichloride (Found: Cl, 14.2. $C_8H_9 \cdot PPr_2 \cdot HgCl_2$ requires Cl, 14.4%), needles, m. p. 188°; *p*-xylylmethyl-di-*n*-propylphosphonium iodide (Found: I, 34.6. $C_8H_9 \cdot PMePr_2 I$ requires I, 34.8%), needles, m. p. 105°; the chloroplatinate (Found: Pt, 21.6. $[(C_8H_9)P(C_3H_7)_2(CH_3)]_2PtCl_6$ requires Pt, 22.1%), orange needles, m. p. 141°; the phosphonium mercuri-iodide (Found: I, 46.8; Hg, 24.1. $C_8H_9 \cdot PMePr_2 I \cdot HgI_2$ requires I, 46.5; Hg, 24.5%), flaky yellow needles, m. p. 90°; the tri-iodide (Found: I, 61.8. $C_8H_9 \cdot PMePr_2 I_3$ requires I, 61.6%), needles, m. p. 76°.

The preparation of *p*-xylyldi-*n*-butylphosphine [Found: C, 76.8; H, 11.1; P, 12.3. $C_8H_9 \cdot P(C_4H_9)_2$ requires C, 76.7; H, 10.9; P, 12.4%] is effected by adding 10 c.c. of *p*-xylyldichlorophosphine in 50 c.c. of ether to the Grignard solution obtained from 36 c.c. of *n*-butyl bromide, 8 g. of magnesium, and 240 c.c. of ether (yield, 10 g.); b. p. 171°/16 mm., d_4^{25} 0.9124. *p*-Xylyldi-*n*-butylphosphine mercurichloride [Found: Cl, 13.9. $C_8H_9 \cdot P(C_4H_9)_2 \cdot HgCl_2$ requires Cl, 13.6%], needles, m. p. 179°; *p*-xylylmethyl-di-*n*-butylphosphonium iodide [Found: I, 32.1. $C_8H_9 \cdot PMe(C_4H_9)_2 I$ requires I, 32.3%], recrystallised from water, forms needles, m. p. 93°; the chloroplatinate (Found: Pt, 20.4. $[C_8H_9 \cdot PMe(C_4H_9)_2]_2PtCl_6$ requires Pt, 20.8%), orange needles, m. p. 215°; the tri-iodide [Found: I, 59.0. $C_8H_9 \cdot PMe(C_4H_9)_2 I_3$ requires I, 59.0%], m. p. 70°. All the phosphonium tri-iodides herein described decompose at their melting points, liberating iodine.

p-Xylyldiisobutylphosphine (Found: C, 75.9; H, 10.2; P, 12.0%) was obtained by the action of 10 c.c. of the dichlorophosphine in 50 c.c. of ether on magnesium isobutyl bromide prepared from 36 c.c. of freshly distilled isobutyl bromide and 8 g. of magnesium in 240 c.c. of ether. B. p. 184°/20 mm. The mercurichloride (Found: Cl, 13.7%), after recrystallisation, first from glacial acetic acid, and then from alcohol, was obtained as fern-like aggregated crystals, m. p. 227°. The methiodide (Found: I, 31.2%), m. p. 120°, was recrystallised from alcohol.

The preparation of *p*-xylyldi-*n*-amylphosphine [Found: C, 76.8; H, 11.4; P, 10.7. $C_8H_9 \cdot P(C_5H_{11})_2$ requires C, 77.6; H, 11.2; P, 11.1%] is effected by adding 10 c.c. of the dichlorophosphine in ether to a Grignard reagent made from 40 c.c. of *n*-amyl bromide and 8 g. of magnesium. It has b. p. 214°/23 mm. Its mercurichloride [Found: Cl, 13.4. $C_8H_9 \cdot P(C_5H_{11})_2 \cdot HgCl_2$ requires Cl, 12.9%] forms minute cubes, m. p. 117°. *p*-Xylylmethyl-di-*n*-amylphosphonium chloroplatinate (Found: Pt, 19.5.

$[C_8H_9 \cdot PMe(C_5H_{11})_2]_2PtCl_6$
requires Pt, 19.6%) forms orange crystals, m. p. 151°.

The authors are indebted to the Chemical Society for a grant which has partly defrayed the expenses of this work.

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[Received, February 2nd, 1931.]