CCLXXXVII.—*Tertiary Phosphines containing the Higher Alkyl Radicals.*

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PHOSPHINES containing alkyl groups ranging from methyl to octyl have now been prepared (J., 1929, 33, 1262; 1930, 2298; this vol., pp. 575, 1207), and examination of gradation of properties in the series is therefore possible.

These compounds are liquids at the ordinary temperature, the only exceptions being *tri*-n-*hexyl*-, *-heptyl*-, and *-octyl-phosphines*, which are low-melting solids. Odour in the lower members is unpleasantly phosphinic, but in the higher members it becomes more closely allied to that of the organic radical. In the several instances where the molecular weight of a phosphine has been determined in solution, it has been found to be normal. The tertiary phosphines are difficultly soluble in water, but readily miscible with ether, with benzene, and, usually also, with alcohol. Limited miscibility with absolute ethyl alcohol at 15° is encountered in the cases of tri-*n*-hexyl-, phenyldi-*n*-amyl-, and *p*-tolyldi-*n*-amyl-phosphines and their respective higher homologues. Gradation in this respect is exhibited, the *p*-tolylphosphine being less miscible with alcohol than the corresponding phenylphosphine, which, in turn, is less miscible than the corresponding trialkylphosphine.

Regular changes with increase of molecular weight and with substitution of a phenyl group for an alkyl are illustrated in the following table.

The average increment in molecular volume, V, from one member to its next homologue is 16·5 c.c. per CH_2 group at 25°.

The b. p.'s (Hofmann and Cahours, *Phil. Trans.*, 1857, **147**, 576; Michaelis, *loc. cit.*; Czimatis, *Ber.*, 1882, **15**, 2014; Davies, Pearse, and Jones, J., 1929, 33, 1262) have been reduced, where necessary, to 50 mm. by means of the relation of Ramsay and Young (*Phil.*

Densities, Molecular Volumes, and Boiling Points of Tertiary Phosphines.

	$d_{4^\circ}^{25^\circ}$.		V at 25°.		B. p. /50 mm.	
	Tri-alkyl.	Phenyl-dialkyl.	Tri-alkyl.	Phenyl-dialkyl.	Tri-alkyl.	Phenyl-dialkyl.
Methyl	—	0·977 *	—	—	− 16°	107°
Ethyl	0·800 †	0·957 ‡	—	—	54	132
n-Propyl ...	0·807	0·925	198·5	209·8	103·5	159
n-Butyl	0·812	0·912	249·0	243·6	149·5	185
n-Amyl	0·820	0·902	297·9	277·4	185·5	210
n-Hexyl	—	0·899	—	309·5	227	236
n-Heptyl ...	0·833	0·893	394·1	343·0	260	260
n-Octyl	—	0·888	—	376·5	291	277

† $d_{4^\circ}^{18 \cdot 6^\circ}$ (Zecchini, *Gazzetta*, 1893, **23**, 100).
* $d_{11^\circ}^{11^\circ}$; ‡ [illegible] (Michaelis, *Annalen*, 1876, **181**, 265).

Mag., 1885, **20**, 530) and corrected for thermometric errors. On comparing the members of a given series, it will be found that the difference between the b. p.'s of succeeding homologues falls as the series is ascended, and, on comparing phenyldialkyl with aliphatic phosphines, that up to the heptyl members the b. p.'s converge, but then diverge.

It is noteworthy that equations of the type $T = aM^b$, proposed by Walker (J., 1894, **65**, 193) for the variation of absolute boiling point, T, under a given pressure with molecular weight, M, in an homologous series, hold with fair accuracy for the phosphines given in the table. Thus the equations

$$t = 32{\cdot}014M^{0{\cdot}48587} - 273 \text{ (for tri-}n\text{-alkylphosphines)}$$

and $$t = 41{\cdot}583M^{0{\cdot}44512} - 273 \text{ (for phenyldi-}n\text{-alkylphosphines)}$$

give the b. p. at 50 mm. with an average error of 2°.

Thermally, the phosphines are remarkably stable, tri-*n*-octyl- and phenyldi-*n*-octyl-phosphine being quite unaffected when heated for an hour at 250°. In presence of air, however, the trialkylphosphines readily oxidise even at the ordinary temperature. The affinity of trialkylphosphines for methyl iodide rapidly falls off with increased molecular weight; in the present work no methiodides of the hexyl, heptyl, or octyl compounds could be obtained. The same also applies to affinity for mercuric chloride and for carbon disulphide.

EXPERIMENTAL.

Tri-n-*hexylphosphine* was prepared in an atmosphere of hydrogen by the slow addition of 8·5 c.c. of phosphorus trichloride in 50 c.c. of ether to a cooled solution made from 75 c.c. of *n*-hexyl bromide, 12·1 g. of magnesium, and 300 c.c. of ether. The resulting mixture was decomposed by ammonium chloride solution, the ethereal layer dried over anhydrous sodium sulphate, the ether expelled in a stream of carbon dioxide, the residual oil fractionally distilled, and the phosphinic fraction redistilled under 50 mm. All thermometer readings given have been corrected. Yield of purified phosphine, 3·5 g.; b. p. 227°/50 mm.; m. p. *ca.* 20° (Found: P, 10·5. $C_{18}H_{39}P$ requires P, 10·8%). The determination of phosphorus was made by the method of Davies and Davies (this vol., p. 1207). This compound possesses a mixed phosphinic-hexylic odour, and at the ordinary temperature is only partially miscible with ethyl alcohol.

Tri-n-*hexylphosphine oxide* (Found: C, 70·9; H, 12·5. $C_{18}H_{39}OP$ requires C, 71·5; H, 13·0%) is a white crystalline solid obtained by aerial oxidation.

Phenyldi-n-*hexylphosphine* (yield, 8 g.), obtained by adding 11·5 c.c. of phenyldichlorophosphine in 50 c.c. of ether to magnesium *n*-hexyl bromide (from 47 c.c. of *n*-hexyl bromide, 8 g. of magnesium, and 300 c.c. of ether), has b. p. 236°/50 mm., $d^{20^\circ}_{4^\circ}$ 0·901 (Found: C, 77·6; H, 11·1; P, 10·9. $C_{18}H_{31}P$ requires C, 77·6; H, 11·2; P, 11·2%). The phosphine yields the *oxide* (Found: C, 73·8; H, 10·6. $C_{18}H_{31}OP$ requires C, 73·5; H, 10·6%), a white crystalline solid, and the *mercurichloride* (Found: Cl, 12·9. $C_{18}H_{31}P,HgCl_2$ requires Cl, 12·9%) which, after recrystallisation first from alcohol and then from glacial acetic acid, forms white needles, m. p. 140°. *Phenylmethyldi*-n-*hexylphosphonium iodide* is precipitated when ethereal solutions of its components are mixed. It forms white needles, m. p. 67° (Found: I, 29·8. $C_{19}H_{34}IP$ requires I, 30·2%). The *chloroplatinate* [Found: Pt, 19·6. $(C_{19}H_{34}P)_2PtCl_6$ requires Pt, 19·6%] was prepared from the phosphonium hydroxide. It crystallises from alcohol as clusters of pale orange needles, m. p. 135°.

Tri-n-*heptylphosphine* (Found: P, 9·6. $C_{21}H_{45}P$ requires P, 9·4%) is obtained from 10·7 c.c. of phosphorus trichloride, 79 c.c. of *n*-heptyl bromide, and 12·1 g. of magnesium in ether. Yield, 9 g.; b. p. 260°/50 mm.; m. p. *ca.* 20°; $d^{25^\circ}_{4^\circ}$ 0·833. The *oxide* (Found: C, 72·7; H, 13·0. $C_{21}H_{45}OP$ requires C, 73·2; H, 13·2%) is a crystalline solid. The phosphine gives a dark red coloration with carbon disulphide, but crystals of the addition compound could not be obtained.

The preparation of *phenyldi*-n-*heptylphosphine* is effected by adding 17 c.c. of phenyldichlorophosphine dissolved in 50 c.c. of ether to the Grignard reagent obtained from 79 c.c. of *n*-heptyl bromide, 12·1 g. of magnesium, and 300 c.c. of ether. Yield, 18 g. It has b. p. 260°/50 mm.; $d^{20^\circ}_{4^\circ}$ 0·895 (Found: C, 78·4; H, 11·7; P, 9·9. $C_{20}H_{35}P$ requires C, 78·3; H, 11·5; P, 10·1%). The *mercurichloride* (Found : Cl, 12·7. $C_{20}H_{35}P,HgCl_2$ requires Cl, 12·3%), recrystallised from alcohol, forms white needles, m. p. 102°.

Phenylmethyldi-n-*heptylphosphonium iodide* (Found : I, 28·2. $C_{22}H_{48}IP$ requires I, 28·3%) is obtained as white plates, m. p. 87°. The *chloroplatinate* {Found : Pt, 18·3. $[P(CH_3)(C_6H_5)(C_7H_{15})_2]_2PtCl_6$ requires Pt, 18·6%}, on recrystallisation from alcohol, forms deep orange, flat prisms, m. p. 105°.

Tri-n-*octylphosphine* (Found : C, 77·6; H, 14·0; P, 8·3. $C_{24}H_{51}P$ requires C, 77·8; H, 13·9; P, 8·4%) has m. p. *ca.* 30°, b. p. 291°/50 mm. In its preparation, 13 c.c. of phosphorus trichloride in 100 c.c. of ether are added to magnesium *n*-octyl bromide, made from 107 c.c. of *n*-octyl bromide, 15 g. of magnesium, and 300 c.c. of ether. Yield, 6 g.

Phenyldi-n-*octylphosphine* (Found : C, 78·6; H, 11·8; P, 9·0. $C_{22}H_{39}P$ requires C, 79·0; H, 11·8; P, 9·3%) is obtained by adding a solution of 11·5 c.c. of phenyldichlorophosphine in 50 c.c. of ether to the Grignard reagent prepared from 57 c.c. of *n*-octyl bromide, 8 g. of magnesium, and 240 c.c. of ether. Yield, 8 g.; b. p. 277°/50 mm.; $d_{4°}^{20°}$ 0·890. The *oxide* (Found : C, 74·7; H, 11·3. $C_{22}H_{39}OP$ requires C, 75·4; H, 11·2%) is a white solid. The *methiodide* [Found : I, 26·6. $(CH_3)(C_6H_5)(C_8H_{17})_2PI$ requires I, 26·7%] has m. p. 81°. *Phenylmethyldi*-n-*octylphosphonium chloroplatinate* (Found : Pt, 17·6. $C_{46}H_{84}Cl_6P_2Pt$ requires Pt, 17·6%) forms fine orange needles, m. p. 102°.

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