608. *Unsymmetrical Dialkylphosphinic Acids.*

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Four unsymmetrical dialkylphosphinic acids, $RR'PO_2H$, containing methyl, ethyl, *iso*propyl, and *tert.*-butyl groups have been prepared by reaction of alkylmagnesium chlorides with blocked or sterically hindered alkylphosphonic chlorides.

Derivatives of phosphorus oxychloride, having one of the chlorine atoms replaced by a secondary amino-group, have previously[1] been used for the preparation of symmetrical phosphinic acids (III) by reaction of these phosphoramidic dichlorides (I) with Grignard reagents and hydrolysis of the phosphinamides (II) thus obtained:

$$\mathrm{POCl_3} \longrightarrow \underset{\text{(I)}}{\mathrm{Cl_2PO{\cdot}NR'_2}} \longrightarrow \underset{\text{(II)}}{\mathrm{R_2PO{\cdot}NR'_2}} \longrightarrow \underset{\text{(III)}}{\mathrm{R_2PO{\cdot}OH}}$$

A similar route starting with alkylphosphonic dichlorides (IV; R = Et or Pr^i) and using Grignard reagents containing different alkyl groups has now been used to afford unsymmetrical dialkylphosphinic acids (VII; R = Et, R′ = Me; R = Et, R′ = Pr^i; R = Pr^i, R′ = Me):

(IV) (V) (VI) (VII)

The *NN*-dimethylalkylphosphonamidic chlorides (V; R = Et or Pr^i) were prepared by reaction of the alkylphosphonic dichlorides with two equivalents of dimethylamine in light petroleum. They reacted readily with alkylmagnesium chlorides in ether, to give *NN*-dimethyldialkylphosphinamides (VI; R = Et, R′ = Me; R = Et, R′ = Pr^i; R = Pr^i, R′ = Me). These were not isolated but were hydrolysed by hydrochloric acid to a mixture whence passage through a cation-exchange column and distillation afforded the phosphinic acids (VIII) as colourless liquids; ethylmethylphosphinic acid crystallised at 0°.

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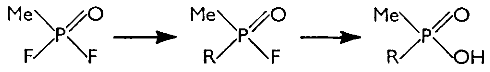
[1] Michaelis and Wegner, *Ber.*, 1915, **48**, 316; Kosolapoff, *J. Amer. Chem. Soc.*, 1949, **71**, 369; 1955, **77**, 6658.

Reaction of alkylphosphonic dichlorides with alkylmagnesium halides would normally be expected to introduce two alkyl groups, forming trialkylphosphine oxides.[2] Monosubstitution has, however, been observed in reactions of this type; *tert.*-butylphosphonic with *tert.*-butylmagnesium chloride gave di-*tert.*-butylphosphinic acid,[3] a result which was ascribed to steric hindrance. It has now been found that *iso*propylmagnesium chloride reacts similarly, giving *tert.*-butyl*iso*propylphosphinic acid.

Relatively few unsymmetrical dialkylphosphinic acids have previously been described. Plets[4] reported the preparation of ethylmethylphosphinic acid (XI) by a route which involved thermal decomposition of diethylmethylphosphine dichloride (VIII) to ethylmethylphosphinous chloride (IX), and oxidation of this to ethylmethylphosphinic chloride (X), which was hydrolysed to the acid. The melting point (7—8°) of our ethylmethylphosphinic acid is however quite different from that (45—48°) of Plets's product.

$$\underset{\text{(VIII)}}{Et_2MePCl_2} \longrightarrow \underset{\text{(IX)}}{EtMePCl} \longrightarrow \underset{\text{(X)}}{EtMePO{\cdot}Cl} \longrightarrow \underset{\text{(XI)}}{EtMePO_2H}$$

Dawson and Kennard[5] recently described the preparation of three alkylmethylphosphinic acids (XIV; R = Bu^i, *n*-pentyl, *cyclo*hexyl) by reaction of alkylmagnesium halides with methylphosphonic difluoride (XII) and hydrolysis of the alkylmethylphosphinic fluorides (XIII) thus obtained. The monosubstitution in this case is a consequence of the low reactivity of the P–F bond.



(XII) (XIII) (XIV)

EXPERIMENTAL

Alkylphosphonic Dichlorides.—Ethylphosphonic dichloride was prepared in 71% overall yield from triethyl phosphite (100 g.) which was isomerised, by heating it with sodium iodide (1·0 g.),[6] to diethyl ethylphosphonate. After distillation, this ester was hydrolysed by refluxing hydrochloric acid. The crude ethylphosphonic acid was heated under reflux for 3 hr. with thionyl chloride, giving ethylphosphonic dichloride which was distilled.

*iso*Propyl- and *tert.*-butyl-phosphonic dichloride were prepared by hydrolysis of the complexes formed by reaction of *iso*propyl and *tert.*-butyl chloride with aluminium chloride and phosphorus trichloride.[7, 3]

NN-*Dimethylethylphosphonamidic Chloride* (V; R = Et).—A solution (90 ml.) of dimethylamine (0·2 mole) in light petroleum (b. p. 30—40°) was added with stirring during 20 min. to ethylphosphonic dichloride (14·7 g.) in light petroleum (200 ml.; b. p. 30—40°). The precipitated dimethylamine hydrochloride was filtered off, and the filtrate distilled, giving NN-*dimethylethylphosphonamidic chloride* (10·5 g., 67%), b. p. 102°/10 mm. (Found: Cl, 22·1. $C_4H_{11}ONClP$ requires Cl, 22·8%).

Ethylmethylphosphinic Acid (VII; R = Et, R′ = Me).—*NN*-Dimethylethylphosphonamidic chloride (24·2 g.) in dry ether (100 ml.) was added with stirring during 2 hr. to methylmagnesium chloride (from 4·8 g. of magnesium) in dry ether (70 ml.). The mixture was heated under reflux for 4 hr. and kept overnight. Hydrochloric acid (100 ml.) and water (100 ml.) were added and the ether was distilled off. The aqueous solution remaining was evaporated, and the residue heated in hydrochloric acid (100 ml.) under reflux overnight, then evaporated, and this residue, after being kept *in vacuo* over potassium hydroxide pellets overnight was dissolved in water. The solution was passed through a cation-exchange column (Zeo-Karb 225, H form)

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[2] Kosolapoff, "Organophosphorus Compounds," John Wiley & Co., New York, 1950, pp. 132—133.

[3] Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3379.

[4] Plets, Diss., Kazan, 1938, cited in ref. 3.

[5] Dawson and Kennard, *J. Org. Chem.*, 1957, **22**, 1671.

[6] Coates and Crofts, B.P. 713,669/1954.

[7] Clay, *J. Org. Chem.*, 1951, **16**, 892; Kinnear and Perren, *J.*, 1952, 3437.

and the effluent was concentrated *in vacuo*. The yellow oil which remained was distilled, giving *ethylmethylphosphinic acid* (14·6 g., 88%). This was purified by five fractional distillations, fractions of similar refractive index being combined, and finally yielded acid (2·5 g., 15%) of b. p. 170—172°/11 mm., m. p. 7—8°, n_D^{20} 1·4514 (Found: C, 33·8; H, 7·8%; equiv., 108·9. $C_3H_9O_2P$ requires C, 33·3; H, 8·3%; equiv., 108·1).

*Ethyl*iso*propylphosphinic Acid* (VII; R = Et, R′ = Pr^i).—*NN*-Dimethylethylphosphonamidic chloride (21·8 g.) in dry ether (100 ml.) was added with stirring during 30 min. to a solution of *iso*propylmagnesium chloride prepared from *iso*propyl chloride (12·8 g.) and magnesium (3·8 g.) in dry ether (140 ml.). The mixture was worked up as in the preceding experiment. The brown liquid obtained by evaporation of the effluent from the ion-exchange column was distilled three times, to give *ethyl*iso*propylphosphinic acid* (6·0 g., 31%), b. p. 89·5°/0·017 mm., n_D^{20} 1·4567 (Found: C, 44·2; H, 9·9%; equiv., 136·7. $C_5H_{13}O_2P$ requires C, 44·1; H, 9·6%; equiv., 136·1).

NN-*Dimethyl*iso*propylphosphonamidic Chloride* (V; R = Pr^i).—Dimethylamine (0·20 mole) and *iso*propylphosphonic dichloride (16·0 g.) in light petroleum gave, as above, NN-*dimethyl*iso-*propylphosphonamidic chloride* (13·2 g., 78%), b. p. 104°/12 mm., n_D^{25} 1·4628 (Found: Cl, 21·2. $C_5H_{13}ONClP$ requires Cl, 21·0%).

*Methyl*iso*propylphosphinic Acid* (VII; R = Pr^i, R′ = Me).—*NN*-Dimethyl*iso*propylphosphonamidic chloride (17·0 g.) in dry ether (90 ml.) was added with stirring during 20 min. to methylmagnesium chloride (from 2·4 g. of magnesium) in ether (200 ml.). The mixture was heated for 2 hr. and worked up as in the preparation of ethylmethylphosphinic acid. Distillation of the residue left after evaporation of the effluent from the ion-exchange column gave *methyl*iso*propylphosphinic acid* (7·0 g., 58%), b. p. 96—98°/0·05 mm., n_D^{24} 1·4502 (Found: C, 39·5; H, 9·2. $C_4H_{11}O_2P$ requires C, 39·3; H, 9·0%).

tert.-*Butyl*iso*propylphosphinic Acid*.—*tert*.-Butylphosphonic dichloride (17·0 g.) in dry ether (100 ml.) was added with stirring during 30 min. to *iso*propylmagnesium chloride [from *iso*propyl chloride (10·0 g.) and magnesium (2·4 g.)] in ether (150 ml.). There was a vigorous reaction and a large amount of pale grey solid was precipitated. After being kept overnight the mixture was poured on ice (100 g.) and hydrochloric acid (2 ml.), and the ethereal layer was separated and evaporated. The resulting yellow oil was heated in ethanol (60 ml.) and hydrochloric acid (50 ml.) for 10 hr., then evaporated, leaving an oil which was dissolved in water. Charcoal and Celite were added to the solution which was then boiled, allowed to cool, filtered, and evaporated to *ca*. 40 ml. The *phosphinic acid* separated as an oil from the hot solution and crystallised on cooling. It was filtered off (0·8 g.; m. p. 73—78°). Continued evaporation of the solution gave a further 1·9 g. of the acid. The two crops were combined and recrystallised five times from light petroleum (b. p. 40—60°), to give 0·8 g. (5%) of colourless crystals, m. p. 82—84° (Found: C, 51·5; H, 10·4; P, 18·5. $C_7H_{17}O_2P$ requires C, 51·2; H, 10·4; P, 18·8%).

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