615. *Organophosphorus Compounds. Part V.* The Preparation of O-Alkyl Hydrogen Methylphosphonothioates.*

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Two new methods for the preparation of *O*-alkyl hydrogen methylphosphonothioates and a convenient synthesis of methylphosphonous dichloride are described.

A CONVENIENT method for the preparation of *O*-alkyl hydrogen methylphosphonothioates (I) was recently described;[1] it was based on the reaction of methylphosphonothioic dichloride (II) with a solution of potassium hydroxide in an aliphatic alcohol. The present paper reports two alternative methods: conversion of methylphosphonous dichloride (III) into the phosphinate (IV) and addition of sulphur;[2] and reaction of methylphosphonic dichloride (V) with an alcohol and sodium hydrogen sulphide.

$Me{\cdot}PO(OR){\cdot}SH$	$Me{\cdot}PSCl_2$	$Me{\cdot}PCl_2$	$Me{\cdot}PHO{\cdot}OR$	$Me{\cdot}POCl_2$
(I)	(II)	(III)	(IV)	(V)

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* Part IV, *J.*, 1962, 3824.

[1] Pelchowicz, Leader, Cohen, and Balderman, *J.*, 1962, 3824.

[2] Cf. Petrov, Bliznyuk, Studnev, and Kolomiets, *Zhur. obshchei Khim.*, 1961, **31**, 179.

Methods for the preparation of methylphosphonous dichloride[3-5] on a laboratory scale include desulphurisation of the chloride (II) by tributylphosphine. Phenylphosphonous dichloride reacts smoothly with the dichloride (II) to give a quantitative yield of the dichloride (III), making this material easily available.

Reaction of the product (III) and an aliphatic alcohol affords an *O*-alkyl methylphosphinate (IV), which can be treated, without isolation, with sulphur in the presence of ammonia to yield ammonium *O*-alkyl methylphosphonothioate. The free acid (I) is obtained by acidification of the salt and distillation.

The yields were satisfactory in all these cases (56—72%) (see Table), except for the *O*-methyl compound (23%). *O*-t-Butyl hydrogen methylphosphonothioate was isolated as the dicyclohexylamine salt as it could not be distilled: heating the crude acid at 150—200° resulted in total decomposition, yielding a very small amount of isobutene (identified as its dibromide), 2-methylpropane-2-thiol as the main distillable product, and a material of m. p. 115—125° whose i.r. spectrum revealed the presence of CH_3–P (1300 cm.$^{-1}$), P=O (1200 cm.$^{-1}$), and P–O–P groups (940, 980 cm.$^{-1}$). Reaction of the last substance with ethanol yielded *O*-ethyl hydrogen methylphosphonate, identified as its dicyclohexylamine salt, and that with water afforded methylphosphonic acid. Reaction of this acid[6] with methylphosphonic dichloride (V) gave a product of very similar properties, as is the case with the pyrolysis of dimethyl phosphite.[7] All these results point to the structure of a metaphosphonate $(Me{\cdot}PO_2)_n$ containing pyrophosphate groups. In keeping with this assumption, thionyl chloride converts the product almost quantitatively into the dichloride (V).

When methylphosphonic dichloride (V) reacts with a solution of 3 mol. of sodium hydrogen sulphide in an alcohol, satisfactory yields (see Table) of sodium *O*-alkyl methylphosphonothioates are obtained:

$$Me{\cdot}POCl_2 + ROH + 3NaHS \longrightarrow Me{\cdot}PO(OR){\cdot}SNa + 2NaCl + 2H_2S$$

The compounds (I) were identified by their physical constants and as their known dicyclohexylamine salts.[8]

EXPERIMENTAL

Methylphosphonous Dichloride (III).—A mixture of methylphosphonothioic dichloride[9] (II) (1 mol.) and phenylphosphonous dichloride[10] (1·1 mol.) was heated in a stream of carbon dioxide in a round-bottomed flask, equipped with mechanical stirrer, gas-inlet, and distillation column. At 150° (bath-temperature) the product (III) began to distil (b. p. 78—90°). Heating was continued, until no more dichloride came over. Redistillation gave >95% of material of b. p. 81—82°.

O-*Alkyl Hydrogen Methylphosphonothioates*.—*Method A*. Freshly distilled methylphosphonous dichloride (0·5 mol.) was added dropwise to the appropriate alcohol (4 mol.) at 0°, with stirring at 30 mm. After 2 hr. solid sodium hydrogen carbonate was added. After the removal of sodium chloride and the excess of the hydrogen carbonate, the remaining alcohol was distilled off *in vacuo*. Sublimed sulphur (16 g.) was added and dry ammonia passed into the mixture with stirring and cooling (if necessary). An exothermic reaction took place, leading to the disappearance of most of the sulphur. Ammonia was passed through the product for another 30 min., the semisolid mass dissolved in water (100 ml.), and the filtered solution acidified with concentrated hydrochloric acid to pH 1. The free acid was extracted with ether (3 × 200 ml.), and the extract dried and concentrated under reduced pressure. The remaining

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[3] Komkov, Karavanov, and Ivin, *J. Gen. Chem.* (*U.S.S.R.*), 1958, **28**, 2963.

[4] Parshall, *J. Inorg. Nuclear Chem.*, 1960, **12**, 372.

[5] Ulmer, Groenweghe, and Maier, *J. Inorg. Nuclear Chem.*, 1961, **20**, 82.

[6] Michaelis, *Annalen*, 1896, **293**, 193; 1901, **315**, 43; Guichard, *Ber.*, 1899, **32**, 1572; Hersmann and Audrieth, *J. Org. Chem.*, 1958, **23**, 1889.

[7] See Bergmann, Pelchowicz, and Brukson, *J.*, 1961, 4348.

[8] Hoffmann, Kagan, and Canfield, *J. Amer. Chem. Soc.*, 1959, **81**, 148.

[9] Kabachnik and Godovikov, *Doklady Akad. Nauk S.S.S.R.*, 1956, **110**, 217.

[10] *Org. Synth.*, 1951, **31**, 88.

acids were distilled at <1 mm.; the yields and physical constants obtained are shown in the Table. The dicyclohexylamine salts were prepared according to directions of Hoffmann *et al.*[8] and recrystallised from ethanol or acetone. Mixed m. p.s with authentic samples were not depressed.

O-Alkyl hydrogen methylphosphonothioates (I).*

	Yield (%)				Dicyclohexylamine salt
R	Method A †	Method B ‡	B. p./mm.	n_D^{25}	m. p.
Me	23	41	77°/0·45 (54—56°/0·2)	1·5015 (1·5005)	180—181° (179·5—181°)
Et	67	55	77—78°/0·35 (63°/0·22)	1·4910 (1·4912)	162—163 (159·5—161)
Pr^n	72	48	80—81°/0·3 (74°/0·35)	1·4825 (1·4820)	146—147 (143·5—144·5)
Pr^i	56	34	75—76°/0·3 (61/0·2)	1·4800 (1·4810)	170—172 (168·5—170)
Bu^n	70	55	90°/0·3 (83—84°/0·1)	1·4820 (1·4829)	160—161 (157·5—159)
Bu^i	70	54	95°/0·5	1·4770	160—162
Bu^s	63·5	28	91°/0·3	1·4790	149—151
Bu^t	52	—	—		175—176

* Values in parentheses are from Hoffmann *et al.*[8] † Calc. on methylphosphonous dichloride. ‡ Calc. on methylphosphonic dichloride.

Method B. A solution of sodium (37 g., 1·6 g.-atoms) in the appropriate alcohol (600 ml.) was saturated with dry hydrogen sulphide at 0—4°. Methylphosphonic dichloride (0·5 mole) was added dropwise and with stirring, which was continued at room temperature for 30 min. The mixture was refluxed until no more hydrogen sulphide was liberated (1 hr.). After cooling, sodium chloride was filtered off and the excess of alcohol removed under reduced pressure. The residue was dissolved in water, acidified with concentrated hydrochloric acid, and extracted with ether (3 × 200 ml.). After drying, the product was distilled; yields are shown in the Table.

O-Isobutyl hydrogen methylphosphonothioate (I; R = Bu^i). This new *acid* was prepared by method A in 70%, by method B in 54% yield. It had b. p. 95°/0·5 mm., n_D^{25} 1·4770 (Found: C, 36·1; H, 7·8; P, 18·7; S, 19·0. $C_5H_{13}O_2PS$ requires C, 35·7; H, 7·7; P, 18·5; S, 19·0%). The *dicyclohexylamine salt* melted at 160—162° (Found: C, 58·5; H, 10·3; P, 9·0; S, 9·0; N, 4·1. $C_{17}H_{36}NO_2PS$ requires C, 58·4; H, 10·3; P, 8·9; S, 9·2; N, 4·0%).

Dicyclohexylammonium O-t-butyl methylphosphonothiate (as I; R = Bu^t). The crude acid obtained by method A was dissolved in dry ether, and dicyclohexylamine added in excess. The *salt* was filtered off and the ether solution concentrated under reduced pressure, giving a second crop. After recrystallisation from acetone, the product melted at 175—176° [yield 52%, based on (III)] (Found: C, 58·3; H, 10·1; P, 8·9; S, 8·9; N, 4·0. $C_{17}H_{36}NO_2PS$ requires C, 58·4; H, 10·3; P, 8·9; S, 9·2; N, 4·0%).

Pyrolysis of O-t-butyl hydrogen methylphosphonothioate. When the crude acid obtained from methylphosphonous dichloride (0·5 mole) and t-butyl alcohol (method A) was heated at 120°, visible decomposition took place, accompanied by elimination of a low-boiling material (10 g.) which was identified as 2-methylpropane-2-thiol,[11] b. p. 64°, n_D^{25} 1·4230 (Calc. for $C_4H_{10}S$: C, 53·3; H, 11·2; S, 35·5. Found: C, 53·5; H, 10·8; S, 35·4%). The most volatile material formed was passed through a solution of bromine in carbon tetrachloride and proved to be isobutene, identified *via* its dibromide [12] (~300 mg.), n_D^{22} = 1·5060 (Found: C, 22·0; H, 3·3. Calc. for $C_4H_8Br_2$: C, 2·2; 2H, 3·7.%).

The viscous residue (18·0 g.) solidified and had m. p. 115—125°; it did not recrystallise from the usual organic solvents. When it was refluxed with ethyl alcohol and the unchanged alcohol removed, *O*-ethyl hydrogen methylphosphonate was obtained, having b. p. 112—115°/0·1 mm., n_D^{23} 1·4250 (Calc. for $C_3H_9O_3P$: C, 29·0; H, 7·3; P, 25·0. Found: C, 28·6; H, 6·9; P, 25·3%), identified as its *dicyclohexylamine salt*, m. p. 145—146° (from acetone) (Calc. for $C_{15}H_{32}NO_3P$: C, 59·0; H, 10·4; P, 10·2; N, 4·6. Found: C, 59·1; H, 10·5; P, 10·1; N, 4·6%).

Reaction of the viscous residue with boiling water gave methylphosphonic acid, m. p. and mixed m. p. 103—104°.

Other Methods for the Preparation of the Assumed Methyl Metaphosphonate.—(*a*) To a stirred mixture of methylphosphonic acid (0·1 mole) in dry benzene (50 ml.), methylphosphonic

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[11] Dobbin, *J.*, 1890, **57**, 641.

[12] Spiegel and Kaufmann, *Ber.*, 1906, **39**, 2638.

dichloride (V) (0·1 mole) in benzene (100 ml.) was added, and the mixture refluxed for 10 hr. (until the evolution of hydrogen chloride had ceased). The product solidified overnight; it was filtered off and washed several times with acetone, and had m. p. 115—125°.

(*b*) Dimethyl phosphite (220 g., 2 moles) containing boron trifluoride–ether complex (2 ml.) was refluxed. The boiling temperature rose gradually, dimethyl ether (identified as boron trifluoride complex) and phosphines (destroyed by sodium hypochlorite solution) being liberated. At 210—220° (internal temperature), a violent exothermic reaction set in, accompanied by distillation of a large volume of volatile products, identified as dimethyl ether and water. Heating was continued until the internal temperature reached 300° (3—4 hr.). The total loss of weight was 20—22%. Most (90%) of the viscous residue solidified and, after being collected and washed with light petroleum or acetone, had m. p. 115—125°.

The products obtained by the three methods had identical infrared spectra. They also reacted with thionyl chloride in the following manner: Thionyl chloride (2 moles) was added at 30° to the product obtained from 1 mole of dimethyl phosphite. When the clear solution was heated cautiously, sulphur dioxide and hydrogen chloride were evolved. At the end of the reaction the mixture was heated to 130°, to remove the excess of thionyl chloride; finally the methylphosphonic dichloride (nearly quantitative yield) was distilled (b. p. 163°).

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