

The Preparation of Phosphinic Chlorides from Phosphinic Amides

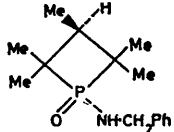
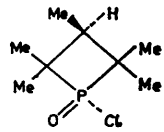
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Phosphinic and phosphinothioic amides react with hydrogen chloride in a suitable inert solvent at room temperature to give high yields of the corresponding phosphinic or phosphinothioic chlorides.

THE preparation of chlorophosphines by the action of hydrogen chloride on phosphinous amides in an aprotic solvent,¹ usually light petroleum, is now well established. However in the P^V field the reaction has been applied only to phosphoramidates.² We now report that phosphinic and phosphinothioic amides give high yields of the corresponding chlorides when treated at room temperature with hydrogen chloride in an inert solvent in which the resulting amine hydrochloride is insoluble (see Table). As expected,³ the phosphetan (1) gave the chloride (2) with retention of configuration at the phosphorus atom, but only racemic methylphenylphosphinothioic chloride was obtained from the di-

astereoisomeric amides (3), presumably because of racemisation of the product by excess of hydrogen

Reaction of P^V amides with hydrogen chloride at room temperature

Amide	Solvent	Time (h)	Chloride
MePhP(:O)NH·CH ₂ Ph Me ₂ P(:S)NH·CH ₂ Ph	Benzene Benzene	4 4	MePhP(:O)Cl Me ₂ P(:S)Cl
	Benzene	12	
MePhP(:S)·NH·CHMePh (3)	Cyclohexane	12	MePhP(:S)Cl
EtP(:S)(OEt)·NH·CHMePh (4)	Cyclohexane	24	EtP(:S)(OEt)Cl (5)

¹ 'Methoden der Organischen Chemie' (Houben-Weyl), Vierte Auflage, Thieme Verlag, Stuttgart, 1963, 12/1, p. 200.

² Z. Skrowaczewska and P. Mastalerz, *Roczniki Chem.*, 1955, 29, 415.

³ J. R. Corfield, N. J. De'ath, and S. Trippett, *Chem. Comm.*, 1970, 1502.

chloride or by amine hydrochloride. The diastereoisomers (3) were obtained from the reaction of methylphenylphosphinous chloride with (–)-1-phenylethylamine followed by the addition of sulphur, or from this amine and the phosphinothioic chloride, and were separated by column chromatography.

The conversion of P^V amides into the corresponding chlorides can be extended to other types of phosphorus amides. Thus, the phosphonamidothioate (4) gave the phosphonochloridothionate (5) on treatment with hydrogen chloride in cyclohexane.

EXPERIMENTAL

Reaction of r-1-Benzylamino-2,2,t-3,4,4-pentamethylphosphetan 1-Oxide with Hydrogen Chloride.—A suspension of the amide (4.1 g) in dry benzene (50 ml) was saturated with hydrogen chloride and set aside at room temperature overnight. Filtration and evaporation of the filtrate gave *r*-1-chloro-2,2,t-3,4,4-pentamethylphosphetan 1-oxide (3.1 g), m.p. 70–72° (from light petroleum); n.m.r. spectrum identical with that of an authentic sample.

All reactions of phosphinic and phosphinothioic amides with hydrogen chloride were carried out in a similar way. Amine hydrochloride was removed by filtration leaving in solution a quantitative yield of phosphinic or phosphinothioic chloride.

P-Methyl-P-phenyl-N-(1-phenylethyl)phosphinothioic Amide.—(a) (–)-1-Phenylethylamine (28.6 g) was added to a solution of methylphenylphosphonous chloride (18.7 g) in ether (200 ml) at a rate sufficient to maintain gentle reflux. The mixture was refluxed for a further 24 h and filtered. Sulphur (4 g) and aluminium chloride (0.1 g) were added to the filtrate and the resulting suspension was refluxed for 24 h. The solvent was then evaporated off and the residue chromatographed on basic alumina. Elution with ether–light petroleum (1:1) gave *one isomer* of *P-methyl-P-phenyl-N-(1-phenylethyl)phosphinothioic amide* as a viscous oil, $[\alpha]_D -37.7^\circ$ (MeOH), τ 1.7–2.2 (2H, m), 2.4–2.83 (8H, m), 5.07–5.67 (1H, m), 8.22 (3H, d, *J* 14 Hz), and 8.63 (3H, d, *J* 7 Hz). Continued elution with the same solvent mixture gave the *second isomer*, m.p. 94–95° (from cyclohexane), $[\alpha]_D -58.8^\circ$ (MeOH), τ 1.8–2.3 (2H, m), 2.38–2.7 (3H, m), 2.73 (5H, s), 5.4–5.98 (1H, m), 7.03br (1H, s), 8.08 (3H, d, *J* 14 Hz), and 8.48 (3H, d, *J* 7 Hz), *m/e* 275, 156, 155, 138, 121, 120, and 105

(Found: C, 65.6; H, 8.45; P, 9.8. C₁₅H₁₈NPS requires C, 65.8; H, 8.7; P, 10.0%).

(b) (–)-1-Phenylethylamine (5.2 g) in ether (50 ml) was added slowly to a solution of methylphenylphosphinothioic chloride (4.0 g) in ether (100 ml) at room temperature and the mixture was refluxed for 2 h and filtered. The filtrate was washed with dilute hydrochloric acid and with water and dried. Solvent was removed and the residue chromatographed as in (a).

N-Benzyl-PP-dimethylphosphinothioic Amide.—Benzylamine (3.42 g) in dichloromethane (20 ml) was added slowly to a solution of dimethylphosphinothioic chloride (1.82 g) in dichloromethane (30 ml) at 0°. The mixture was stirred at room temperature for 1 h, washed with dilute hydrochloric acid and water, and dried. Removal of solvent and crystallisation of the residue from light petroleum gave the *amide* (2.64 g), m.p. 91–92°, τ 2.67 (5H, s), 5.87 (2H, d, *J* 11 Hz), and 8.27 (6H, d, *J* 14 Hz), *m/e* 199, 166, 106, 94, and 91 (Found: C, 54.5; H, 7.1; N, 6.9. C₉H₁₄NPS requires C, 54.2; H, 7.1; N, 7.0%).

N-Benzyl-P-methyl-P-phenylphosphinic Amide.—Benzylamine (2.14 g) in dichloromethane (20 ml) was added slowly to a solution of methylphenylphosphinic chloride (1.58 g) in dichloromethane (20 ml) at 0°. The mixture was stirred at room temperature for 2 h, washed with dilute hydrochloric acid and water, and dried. Solvent was removed and the residue chromatographed on basic alumina. Elution with ether–methanol (20:1) gave the *amide*, m.p. 73–74° (from dichloromethane–light petroleum), τ 1.9–2.33 (2H, m), 2.4–2.63 (3H, m), 2.70 (5H, s), 5.77–6.23 (2H, m), 6.67br (1H, s), and 8.33 (3H, d, *J* 14 Hz), *m/e* 245, 139, 125, 106, and 91 (Found: C, 68.3; H, 6.5; N, 5.5. C₁₄H₁₆NOP requires C, 68.6; H, 6.5; N, 5.7%).

O-Ethyl P-Ethyl-N-(1-phenylethyl)phosphonamidothioate.—(–)-1-Phenylethylamine (4.84 g) in tetrahydrofuran (50 ml) was added slowly to a solution of *O*-ethyl ethylphosphonochloridothionate (3.44 g) in tetrahydrofuran (60 ml) and the mixture was stirred and refluxed overnight. Solvent was removed and ether (200 ml) added. The resulting suspension was filtered; the filtrate was washed with dilute hydrochloric acid and water and dried. Removal of solvent and distillation gave the *amide*, b.p. 165–170° (bath temp.) at 2 mmHg, $[\alpha]_D -69.0^\circ$ (MeOH), τ 2.65 (5H, s), 5.27–6.83 (4H, m), 7.63–8.37 (2H, m), and 8.4–9.35 (9H, m), *m/e* 257, 224, 178, 138, 137, 121, 120, 109, 106, and 105. The amide is a mixture of diastereoisomers which could not be separated by chromatography.

[1/2343 Received, 7th December, 1971]