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REACTION OF OXOPHOSPHORANESULPHENYL CHLORIDES WITH PHOSPHORUS TRICHLORIDE
A NEW SYNTHESIS OF DIALKYL PHOSPHOROCHLORIDOTHIONATES AND THEIR OPTICALLY ACTIVE ANALOGUES

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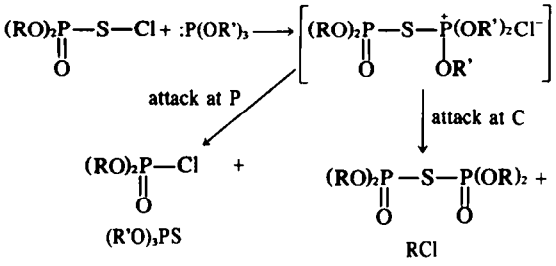
Abstract—The reaction of acyclic oxophosphoranesulphenyl chlorides, >P(O)SCl, with phosphorus trichloride has been found to give thiophosphoryl chlorides, >P(S)Cl, and phosphoryl oxychloride—the products of the exclusive deoxygenation of sulphenyl chloride. Optically active phosphonochloridothionates and phosphorochloridothionates in a high state of optical purity have been obtained with inversion of configuration from optically active sulphenyl chlorides and phosphorus trichloride. It has been shown, however, that cyclic oxophosphoranesulphenyl chlorides undergo simultaneous desulphurisation and deoxygenation when treated with phosphorus trichloride. Using *cis*- and *trans*-isomers of 2-chlorothio-4-methyl-1,3,2-dioxaphosphorinan-2-one it has been demonstrated that deoxygenation is accompanied by inversion, whereas desulphurisation occurs with retention at phosphorus. The mechanism of the title reaction is discussed.

Oxophosphoranesulphenyl chlorides (1) are widely used in phosphoroorganic synthesis and in stereochemical studies mainly as thiophosphorylating agents.[1]

Oxophosphoranesulphenyl chlorides (1) have found a particularly interesting application in the synthesis of monothiopyrophosphate systems which are formed in the reaction with trivalent phosphorus acid esters.[2]

The mechanism of this reaction is shown below:



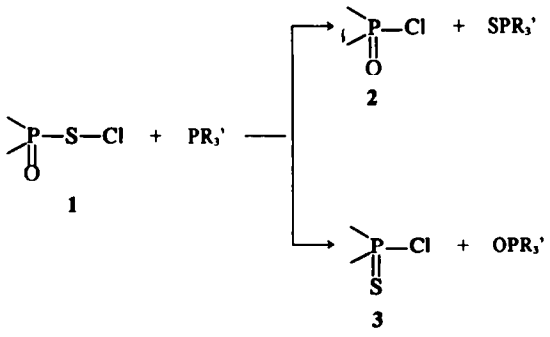
Scheme 1.

Attack at the P atom results in desulphurization of the sulphenyl chloride.

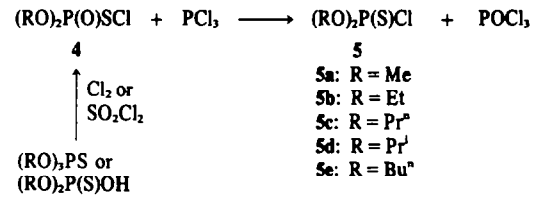
Recently we have found[3] that the reaction of sulphenyl chlorides (1) with trivalent phosphorus compounds such as PPh_3, PBu_3, $P(OPh)_3$ and $P(NMe_2)_3$ is less complex and affords a mixture of products of simultaneous desulphurisation and deoxygenation of sulphenyl chlorides (1).

The ratio of the desulphurisation products to deoxygenation products has been found to be dependent on the kind of P^{III}-compound and on the nature of substituents at the P atom in the starting chloride (1). Our preliminary stereochemical studies, in which we were using optically active (1), showed that chlorides (2 and 3) are formed with inversion of configuration at the P atom.

In our search for other reagents having selective desulphurisating or deoxygenating properties we have investigated the behaviour of phosphorus trichloride



which is a readily accessible trivalent P compound. We have found that its reaction with sulphenyl chlorides (1) leads exclusively to thiophosphoryl chlorides (3) and phosphorus oxychloride, i.e. to deoxygenation products. Dialkoxyoxophosphoranesulphenyl chlorides (4) and PCl_3 gave very good yields of the corresponding dialkyl phosphorochloridothionates (5) which are important starting materials in syntheses of many phosphoroorganic insecticides.



It should be mentioned that sulphenyl chlorides (4) are readily accessible from trialkyl phosphorothionates[4] or phosphorus monothioacides.[5] Both reactions, i.e. the synthesis of sulphenyl chlorides (4) and their deoxygenation, can be carried out in two stages in one reaction vessel without the isolation of 4. The physical properties and the yields of dialkyl phosphorochloridothionates (5) prepared by this method are shown in Table 1. The purity

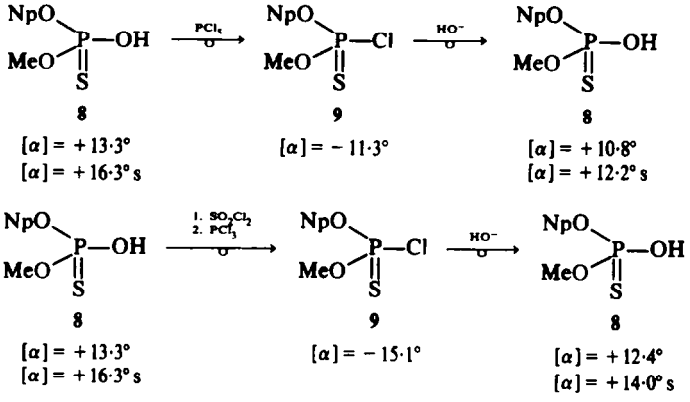
Table 1. Preparation of diakyl phosphorochloridothionates, $(RO)_2P(S)Cl$, (5), from trialkyl phosphorothionates via dialkoxyoxophosphoranesulphenyl chlorides (4)

Product	Yield(%)	B.p.	n_D^{20}	δ_{31_P}, ppm(H_3PO_4)	Literature data[a,b,c]: b.p.	n_D^{20}	δ_{31_P}
5a, R=Me	85	68°/12mm	1.4776	-71.7	70-2°/20mm	1.4795	-72.9
5b, R=Et	71	65-7°/12mm	1.4690	-67.5	90-1°/12-14mm	1.4693	-67.7,-68.1,-68.4
5c, R=Pr^n	83	68-9°/1.5mm	1.4661	-68.2	70-5°/1mm	1.4672	
5d, R=Pr^i	57	53-5°/1mm	1.4588	-65.0	56-9°/1mm	1.4601	-65.1
5e, R=Bu^n	76	88°/1mm	1.4662	-68.2	95°/0.7mm		

[a] K.Sasse "Methoden der Organischen Chemie", E.Miller, Georg Thieme Verlag, Stuttgart, 1964; Vol 12, Part 2, p. 607.

[b] J.H.Flechter et al., J.Amer.Chem.Soc., 72, 2461 (1950).

[c] "Topics in Phosphorus Chemistry", Ed.Grayson and E.J.Griffith, Interscience Publishers, New York, London, Sydney, 1967, Vol 5, p. 364.



Np = 1-naphthyl
s = dicyclohexylammonium salt

Scheme 2.

of the products was determined by ^1H- and ^{31}P-NMR spectra and by gas chromatography.

The new synthesis of 5 from sulphenyl chlorides (4) combined with the preparation of the latter is a very convenient and effective method of the conversion of trialkyl phosphorothionates into phosphorochloridothionates (5). It is undoubtedly superior to the direct chlorination of trialkyl phosphorothionates with phosphorus pentachloride described in the patent literature,[6] since this method gives low yields of the desired products.

Since optically active phosphorus monothioacids are readily available and can be used for the preparation of optically active oxophosphoranesulphenyl chlorides,[7] we have utilised the investigated reaction for the preparation of optically active phosphonochloridothionates. They were obtained in one step by the action of sulphuryl chloride and then phosphorus trichloride on optically active O-alkyl alkylphosphonothioic acids (6). The experiments performed are summarized below.

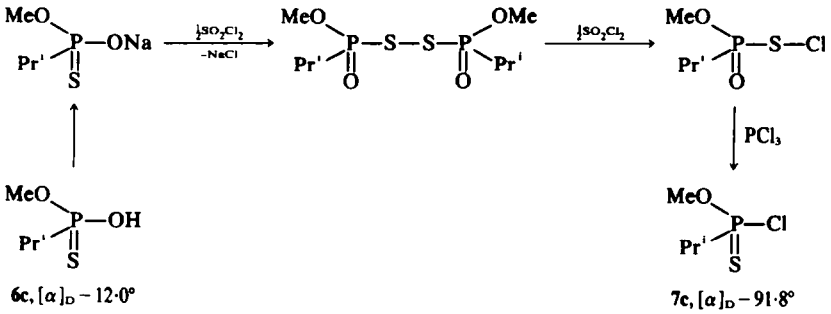
The optical purity of the prepared phosphonochloridothionates (7) was over 85% and their relative configuration was opposite to that of the starting thioacids (6).[8]

The present synthesis of optically active chlorides (7) is an alternative to the earlier described by us direct chlorination of thioacids (6) with phosphorus pentachloride[9] and in comparison with this method it shows several advantages. In the case of optically active thiophosphoric acids, RO(R'O)P(S)OH, it usually gives the optically active phosphorochloridothionates, RO(R'O)P(S)Cl, having higher optical purity. This is clearly illustrated by the experiments with O-methyl O-1-naphthyl phosphorothioic acid (8) shown in Scheme 2 above.

The optically active O-methyl O-1-naphthyl phosphorochloridothionate (9) obtained from the reaction of thioacid (8) with phosphorus pentachloride had lower optical rotation than that of the same chloride obtained by

the new method via the corresponding sulphenyl chloride. This fact is probably connected with the relatively long time of reaction of thiophosphoric acids with phosphorus pentachloride at room temperature which favours racemization of the resulting phosphorochloridothionates due to the chloride–chloride exchange at the P atom.[10]

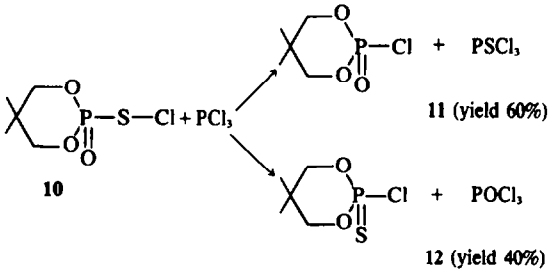
Another advantage of our method consists in the possibility of utilisation of the optically active thioacids salts as the starting materials. It should be pointed out that chlorination of sodium salts of optically active thioacids with phosphorus pentachloride results in the formation of almost completely recemised products. The possibility of using the salts as substrates can be also valuable in the case of unstable free thioacids, since the reaction can be carried out in two stages. Using one half of the molar amount of the chlorinating agent with respect to the thioacid salt it is possible to obtain the corresponding bis-phosphoryl disulphide which can be readily freed from the inorganic salt or isolated. Its further chlorination to sulphenyl chloride and subsequent dexoygenation with phosphorus trichloride lead to the optically active phosphorochloridothionate and phosphorus oxychloride. The preparation of chloride (7c) from thioacid (6c) according to this procedure is shown below.



6c, $[\alpha]_D$ −12·0°

7c, $[\alpha]_D$ −91·8°

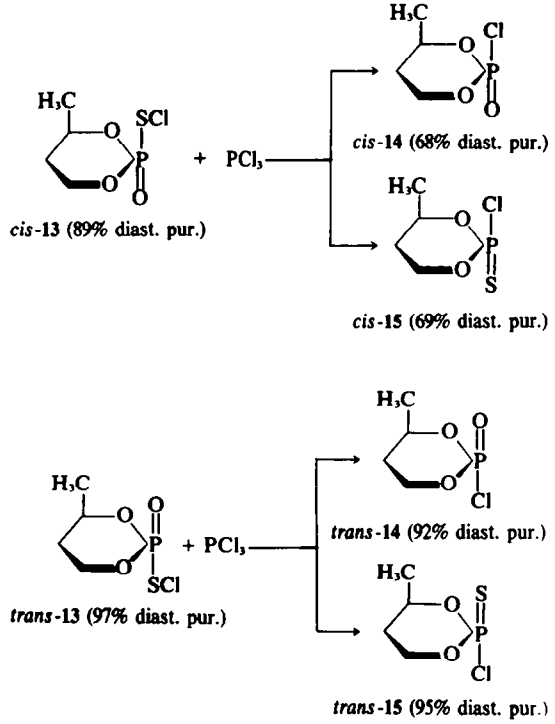
However, in contrast to acyclic oxophosphoranesulphenyl chlorides, phosphorus trichloride has been found to be non-selective with respect to cyclic oxophosphoranesulphenyl chlorides. Thus for example the reaction of phosphorus trichloride with 2-chlorothio-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (10) gave both deoxygenation and desulphurisation products, the latter being predominant.



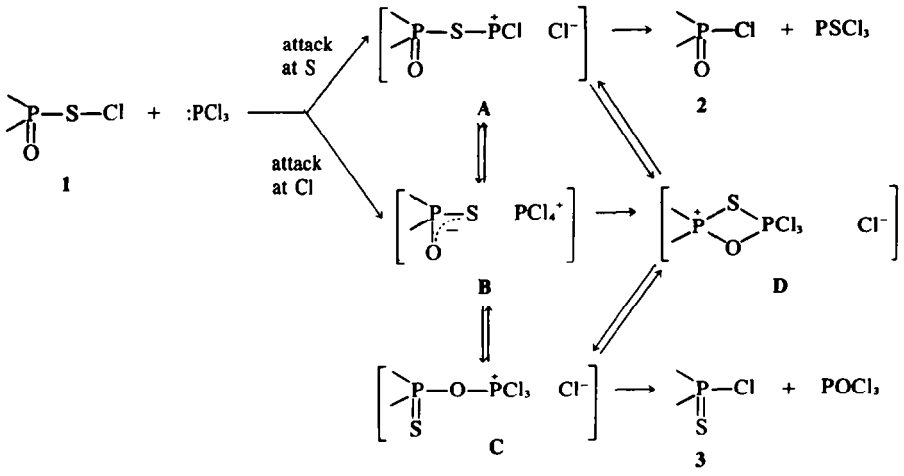
Using diastereomeric *cis*- and *trans*-2-chlorothio-4-methyl-1,3,2-dioxaphosphorinan-2-ones (13)[11] the stereochemical course of the discussed reaction was investigated.

It should be mentioned that the configurational relationship in the diastereomeric chlorides (14 and 15) formed as well as the corresponding values of chemical shifts in the ^{31}P-NMR spectra, used for analytical purposes in the present work, were determined by us earlier.[12] An inspection of the results shown in Scheme 4 reveals a very interesting phenomenon. While the deoxygenation of sulphenyl chloride (13) takes place with the expected inversion of configuration at the P atom, its desulphurisation leads to chloride (14) with retention at phosphorus. This indicates that the steric course of the reaction of cyclic oxophosphoranesulphenyl chlorides with PCl_3 is different from that of the reaction of acyclic oxophosphoranesulphenyl chlorides with PCl_3, since we have found that in the latter case both desulphurisation and deoxygenation are accompanied by inversion of configuration at the P atom.

It is evident that the stereochemistry at phosphorus upon transformation of the sulphenyl chloride into the final reaction products is closely related to the reaction mechanism involved. In accord with our previous suggestions[3] as well as with the facts reported here it seems reasonable to suppose that the intermediate quasiphosphonium complex (A) is first formed as the result of nucleophilic attack by phosphorus trichloride on the S atom of the sulphenyl chloride (1). This complex may break down into phosphorochloridate (2) and thiophosphoryl chloride. Since an exclusive deoxygenation of acyclic sulphenyl chlorides (1) by PCl_3 has been



Scheme 3.



Scheme 4.

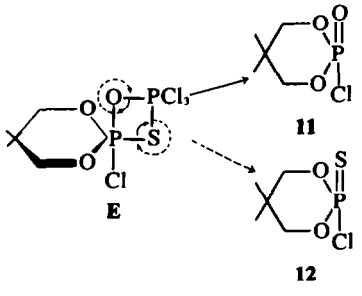
observed it is reasonable to expect that the complex (A) initially formed undergoes transformation into an ion pair (B) which in turn gives the quasiphosphonium complex (C). Decomposition of the latter by nucleophilic attack of chloride ion on thiophosphoryl phosphorus results in the formation of phosphorochloridothionate (3) and phosphorus oxychloride. In the case of the optically active thiophosphoryl centre this process is accompanied by inversion.

It is interesting to point out that an ion pair (B) may also result from the direct attack of phosphorus trichloride on the Cl atom of the sulphenyl chloride (1). However, although an ionic mechanism involving nucleophilic attack of the trivalent P atom on the positive chlorine of the sulphenyl chloride (1) has been suggested for other reactions,[13] our results do not support or eliminate its operation in the reaction under discussion.

Furthermore, the quasiphosphonium complex (A) may undergo conversion into the complex (C) through the transient quasiphosphonium salt (D) and not via an ion pair (B).

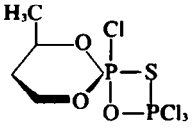
The stereochemical results obtained with the cyclic sulphenyl chloride (13) may be considered to favour this reaction pathway since it allows the reasonable explanation of the different stereochemistry of the deoxygenation and desulphurisation products, i.e. chlorides (14 and 15).

It is now well-accepted that the presence of the cyclic substituents at phosphorus promotes the formation of the penta-coordinated phosphorus intermediate during nucleophilic substitution.[14] Therefore, the quasiphosphonium complex of the type (D) formed from the cyclic sulphenyl chloride (10) may further react to give the final reaction product via the phosphorane intermediate (E) described below:

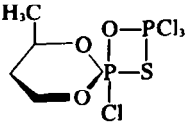


in which the dioxaphosphorinan ring spans basal positions in the trigonal bipyramid and the O and S atoms of the 4-membered ring occupy apical and basal positions, respectively. This situation is most favourable from the point of view of the apicophility order of substituents and ring-strain in pentacovalent phosphorane structure.[15] Decompositions of the complex (E) leads to the cyclic phosphoryl and/or thiophosphoryl chloride.

From the diastereomeric sulphenyl chlorides *cis*-13 and *trans*-13 two intermediates of the type (E) should be formed which have different stereochemistry at phosphorus, i.e. opposite geometrical relationship between the Me group and the 4-membered ring as depicted below.



(from *cis*-13)



(from *trans*-13)

Their decomposition should afford the cyclic diastereomeric chloride (14 and 15) with retention and inversion at phosphorus, respectively. Further studies on the reaction of oxophosphoranesulphenyl chlorides with P^{III}-compounds are continued.

EXPERIMENTAL

Optical activity measurements were made with a Hilger and Watts polarimeter (sensitivity ±0·01°) or with a Perkin–Elmer 141 photopolarimeter (sensitivity ±0·002°). Rotations refer to neat compounds unless otherwise stated. The chemical purity of 0,0-dialkyl phosphorochloridothionates was checked by GLPC (Varian Chromatograph 10) and/or by ^{31}P-NMR spectra (Jeol C-60 H). Racemic thioacid (**6a**) was resolved into optical antipodes via diastereomeric salts with quinine.[16] Thioacids (**6b** and **6c**) were resolved with α-phenyl ethylamine.[17,18] Resolution of **8** was accomplished with (-)ephedrine according to the preliminary description by Donninger and Hudson[19] (full experimental details are given below). Trialkyl phosphorothionates were prepared from thiophosphoryl chloride and the appropriate alkoxides.[20]

Dialkyl phosphorochloridothionates (5) *from trialkyl phosphorothionates*

General procedure. To a soln of trialkyl phosphorothionate in benzene a soln of SO_2Cl_2 (equimolar amount) in benzene was added dropwise at 0–5°. When SO_2Cl_2 was added the mixture was allowed to come to room temp and degassed under vacuum. Then the benzene soln of 4 obtained was treated with PCl_3 (small molar

excess) at −5 to 5° and the mixture was stirred at room temp for 2 hr. Removal of solvent and $POCl_3$ gave the residue which was fractionated in vacuum to afford **5**. In order to remove the small amounts of dialkylphosphorochloridates (0–3%) formed it is advantageously to dissolve the crude product in benzene and wash it with 10% Na_2CO_3 aq and water. After drying and removal of benzene **5** was purified by distillation. Table 1 summarises the results obtained with a five representative dialkyl phosphorothionates.

Dimethyl phosphorochloridothionate (**5a**). SO_2Cl_2 (5·5g, 40·7 mmol) was added dropwise to a soln of trimethyl phosphorothionate (6·3 g, 40·3 mmol) in benzene (20 ml) at 0–5°. The mixture was stirred at room temp for 1 hr and degassed under vacuum. The resulting soln of **4a** was then added to a soln of PCl_3 (7 g, 51 mmol) in benzene (15 ml) at 0–5°. The mixture was left overnight at room temp. After removal of the solvent and $POCl_3$ the residue was fractionated to give **5a**; 5·6 g (85%), b.p. 68°/12 mm, n_D^{20} 1·4776, δ_{31_P} − 71·7 ppm.

(+)-O-*Methyl isopropylphosphonochloridothionate* (**7c**) *from* (+)-O-*methyl isotpopylphosphonothioic acid* (**6c**). To a soln of (+)-**6c**, $[\alpha]_D$ + 13·20° (2·8 g, 18·1 mmol) in benzene (20 ml) a soln of SO_2Cl_2 (2·5 g, 18·5 mmol) in benzene (5 ml) was added at 0–5°. After stirring for 0·5 hr at room temp the mixture was deganesed under vacuum. Then, PCl_3 (2·6 g, 19 mmol) in benzene (5 ml) was slowly added at 5°. The mixture was stirred at room temp for 2 hr and evaporated. The residue was dissolved in ether (30 ml). The ether soln was washed with dil $NaHCO_3$ aq (2 × 15 ml) and then with water (2 × 10 ml). The ether layer was dried over $MgSO_4$. After removal of the solvent the crude product was distilled in vacuum to give (+)-**7c**, $[\alpha]_D$ + 93·90°, 2·2 g (70%), b.p. 72°/5 mm, n_D^{20} 1·4972 (lit. b.p. 72°/4 mm, n_D^{20} 1·4978).

(+)-O-*Ethyl ethylphosphonochloridothionate* (**7a**) *from* (+)-O-*ethyl ethylphosphonothionic acid* (**6a**). According to the procedure described above from (+)-**6a**, $[\alpha]_D$ + 13·56°, (0·8 g, 5·2 mmol), (+)-**7a** was obtained, $[\alpha]_D$ − 71·10°, 0·5 g (63%).

(−)-O-*Isopropyl methylphosphonochloridothionate* (**7b**) *from* (−)-O-*isopropyl methylphosphonothioic acid* (**6a**). According to the procedure as for **7a** yielded from (−)-**6b**, $[\alpha]_D$ − 14·25° (2 g, 13 mmol), (−)-**7b**, $[\alpha]_D$ − 71·50°, 1·2 g (54%).

(−)-O-*Methyl isopropylphosphonochloridothionate* (**7c**) *from* (−)-*sodium* O-*methyl isopropylphosphonothionate*. To the stirred suspension of sodium salt (2·42 g, 13·6 mmol) of (−)-**6c** [prepared from 2·1 g of (−)-**6c**, $[\alpha]_D$ − 12·0°, and the soln of NaOMe (0·74 g Na 13·7 mmol)] in benzene (20 ml) the soln of SO_2Cl_2 (0·92 g, 6·8 mmol) in benzene (5 ml) was added at −5 to 0°. The benzene solution of the resulting disulphide was washed with water (2 × 15 ml) and dried over $MgSO_4$. To the benzene soln hexane (10 ml) was added. Then SO_2Cl_2 (0·92 g, 6·8 mmol) in benzene (5 ml) and PCl_3 (1·92 g, 14 mmol) in benzene (5 ml) were added at 0°. After stirring for 0·5 hr the solvents and the gaseous products were evaporated. The residue was distilled in vacuum to give (−)-**7c**, $[\alpha]_D$ − 91·80°, 1 g (43%), b.p. 72°/5 mm, n_D^{20} 1·4967.

Synthesis and resolution of O-*methyl* O-1-*naphthyl phosphorothioic acid* (**8**)

(a) 0,0-*Dimethyl* O-1-*naphthyl phosphorothionate*. Na (4·1 g; 0·178 mol) was dissolved in MeOH (70 ml). 1-Naphthole (25·6 g, 0·178 mol) was added and MeOH was completely removed. Sodium 1-naphthoxide obtained was dissolved in dimethoxyethane (200 ml) and treated with dimethyl phosphorochloridothionate (30 g, 0·187 mol). The mixture was stirred under reflux for 3 hr and evaporated. To the residue ether (100 ml) was added. The ether soln was washed with water, dried and evaporated to give the crude 0,0-dimethyl-O-1-naphthyl phosphorothionate. After distillation under reduced pressure 35 g (75·4%) of the pure product were obtained, b.p. 120°/0·05 mm, n_D^{23} 1·5948. ^{1}H-NMR (CCl_4): δ 3·75 ppm (d, 6H, $^3J_{P-CH_3}$ 13·3 Hz); 7·10–8·30 ppm (m, 7H).

(b) *Tetramethylammonium* O-*methyl* O-1-*naphthyl phosphorothioate*. To a soln of 0,0-dimethyl O-1-naphthyl phosphorothionate (35 g, 0·132 mol) in benzene (100 ml) a soln of trimethylamine (50 g) in benzene (100 ml) was added and the mixture was allowed to stand for 2 days. The precipitated tetramethylammonium O-methyl O-1-naphthyl phosphorothioate was filtered off; 42 g (98·5%), m.p. 108–110°, ^{31}P-NMR ($CHCl_3$): δ −53 ppm (Found: C, 54·92; H, 6·65; N, 3·89; P, 9·28. Calc. for $C_{15}H_{22}NO_3PS$: C, 55·00; H, 6·74; N, 4·28; P, 9·50%).

(c) *Resolution of* (+)-O-*methyl* O-1-*naphthyl phosphorothioic acid* (**8**) *with* (−)-*ephedrine*. Tetramethylammonium O-methyl O-1-naphthyl phosphorothioate (18·1 g) and (−)-ephedrine hydrochloride (11·1 g) when mixed as hot aqueous solns (2 × 320 ml) gave 14·8 g (64%) of crystalline, insoluble in water (−)-ephedrinium O-methyl O-1-naphthyl phosphorothioate, $[\alpha]_D$ + 11·0° (*c*, 2·44; $CHCl_3$). Two recrystallizations from aqueous EtOH afforded a pure sample of (−)-ephedrinium (+)-O-methyl O-1-naphthyl phosphorothioate; 9·5 g (82%), $[\alpha]_D$ + 32·2° (*c*, 2·82; $CHCl_3$).

In order to obtain the free (+) thioacid (**8**), an excess of hydrochloric acid was added to a suspension of (−)-ephedrinium (+)-O-methyl O-1-naphthyl phosphorothioate (9·5 g) in water and the mixture was shaken with ether. The etheral soln was dried and evaporated to give 5·39 (93·5%) (+)-(**8**) as a stable, slightly yellow oil; $[\alpha]_D$ + 13·3° (*c*, 1·94; $CHCl_3$); ^{1}H-NMR (CCl_4): δ 3·67 ppm (d, 3H, $^3J_{P-CH_3}$ 13·3 Hz), 6·75–8·06 ppm (m, 7H_{arom} + $^1H_{acidic}$).

Since the acid contained small amounts of ether difficult to remove under vacuum it was characterised as a dicyclohexylammonium salt, m.p. 150–152° (cryst. from aqueous EtOH), $[\alpha]_D$ + 16·3° (*c*, 2·14; $CHCl_3$), ^{31}P-NMR ($CHCl_3$): δ −55 ppm (H_3PO_4) (Found: C, 63·05; H, 8·01; N, 3·48; P, 7·12; Calc. for $C_{23}H_{34}NO_3PS$: C, 63·45; H, 7·82; N, 3·22; P, 7·13%). (−)-**8** was obtained from the filtrate after separating (+) isomer by treatment with HCl and extraction with ether. The ether layer was dried and evaporated to give 4·8 g of (−)-O-methyl O-1-naphthyl phosphorothioic acid, $[\alpha]_D$ − 13·2° (*c*, 1·99; $CHCl_3$); dicyclohexylammonium salt: $[\alpha]_D$ − 14·7° (*c*, 2·17; $CHCl_3$), m.p. 132–137°.

(−)- *and* (+)-O-*Methyl* O-1-*naphthyl phosphorochloridothionate* (**9**) *from* (+)-*and* (−)-O-*naphthyl phosphorothioic acid* (**8**) *and phosphorus pentachloride*. To a suspension of PCl_5 (0·82 g, 3·93 mmol) in CCl_4 (15 ml) a soln of (+)-thioacid (**8**), $[\alpha]_D$ + 13·3° (1 g, 3·93 mmol) was added at 10°. The mixture was stirred at room temp until PCl_5 disappeared (*ca.* 2 hr). After removal of the solvent and $POCl_3$ the residue was dissolved in benzene (10 ml) and washed with aq $NaHCO_3$ aq and water. The benzene soln was dried and evaporated to give (−)-**9** as a slightly yellow oil; 0·84 g (78·5%), $[\alpha]_D$ − 11·3° (*c*, 1·9; $CHCl_3$); ^{1}H-NMR (CCl_4): δ 3·92 ppm (d, 3H, $^3J_{P-CH}$, 16 Hz), 7·00–8·20 ppm (m, 7H).

Starting from (−)-thioacid (**8**), $[\alpha]_D$ − 13·3°, (1 g, 3·93 mmol) (+)-**9** was obtained; 0·89 g (83·1%), $[\alpha]_D$ + 10·2° (*c*, 3·34; $CHCl_3$).

(−)- *and* (+)-O-*Methyl* O-1-*naphthyl phosphorochloridothionate* (**9**) *from* (+)- *and* (−)-O-*methyl* O-1-*naphthyl phosphorothioic acid* (**8**) *and sulphuryl chloride and phosphorus trichloride*. (+)-Thioacid **8** (1 g, 3·93 mmol), $[\alpha]_D$ + 13·3°, was dissolved in benzene (10 ml) and hexane (15 ml) and SO_2Cl_2 (0·53 g, 3·93 mmol) in benzene (5 ml) was added dropwise at −10°. The mixture was stirred at this temp for 0·5 hr and then the gaseous products were removed under vacuum below 10°. To the soln of O-methyl-O-1-naphthyloxophosphoranesulphenyl chloride PCl_5 (0·57 g, 4·15 mmol) was dropped at 0° and the mixture was stirred for an additional 3 hr. The organic soln was washed with $NaHCO_3$ aq, then with water, dried and evaporated to afford (−)-**9**, $[\alpha]_D$ − 15·1° (*c*, 3·57; $CHCl_3$), 0·7 g (65·5%).

According to this procedure in other run optically active (+)-chloride **9**, $[\alpha]_D$ + 12·0° (*c*, 2·54; $CHCl_3$), 0·7 g (71%), was obtained from (−)-thioacid (**8**), $[\alpha]_D$ − 13·3°.

Hydrolysis of optically active O-*methyl* O-1-*naphthyl phosphorochloridothionate* (**9**). A soln of (−)-chloride **9**, $[\alpha]_D$ − 11·3°, (0·84 g, 3·08 mmol), in dioxane (10 ml) was added to a soln of KOH (0·3 g) in water (10 ml). The mixture was stirred at room temp for a few hr and left overnight. After addition of water (15 ml) the soln was extracted with ether. The aqueous soln was the acidified with conc HCl and extracted with ether. The organic soln was dried and evaporated to give (+)-O-**8**, $[\alpha]_D$ + 10·8° (*c*, 2·18; $CHCl_3$), 0·5 g (64·1%); dicyclohexylammonium salt, $[\alpha]_D$ + 12·2° (*c*, 2·07; $CHCl_3$).

Starting from (+)-chloride **9**, $[\alpha]_D$ + 10·2° (0·89 g, 3·26 mmol) (−)-thioacid **8** was obtained, $[\alpha]_D$ − 8·7° (*c*, 1·72; $CHCl_3$), 0·6 g (76·9%); dicyclohexylammonium salt $[\alpha]_D$ − 11·6° (*c*, 1·51; $CHCl_3$).

Hydrolysis of (−)-chloride (**9**), $[\alpha]_D$ − 15·1° (0·7 g, 2·57 mmol) gave (+)-thioacid **8**, $[\alpha]_D$ + 12·4° (*c*, 1·83; $CHCl_3$), 0·5 g (80·5%);

dicyclohexylammonium salt $[\alpha]_D$ +14·0° (*c*, 2·25; $CHCl_3$).

Under similar reaction conditions from (+)-chloride **9**, $[\alpha]_D$ +12·0°, (0·76 g, 2·78 mmol) (−)-thioacid **8** was obtained, $[\alpha]_D$ −9·6° (*c*, 1·35; $CHCl_3$), 0·52 g (77%), dicyclohexylammonium salt $[\alpha]_D$ −13·1° (*c*, 1·03; $CHCl_3$).

Reaction of 2-chlorothio-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (**10**) *with phosphorus trichloride.* To a soln of 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione (3·92 g, 0·02 mol) in CH_2Cl_2 (10 ml) SO_2Cl_2 (2·7 g, 0·02 mol) in CH_2Cl_2 (10 mol) was added dropwise with stirring at −15°. Stirring was continued for 20 min and PCl_3 (2·75 g, 0·02 mol) in CH_2Cl_2 (10 ml) was added at −20°. Evaporation of solvent under reduced pressure afforded a mixture containing 60% of **11**, δ_{31_P} +2·5 ppm (neat, H_3PO_4) and 40% of **12**, δ_{31_P} −58 ppm (neat, H_3PO_4).

Reaction of cis- *and* trans-*2-chlorothio-4-methyl-1,3,2-dioxaphosphorinan-2-one* (**13**) *with phosphorus trichloride.* According to the procedure described above from **13**[11] (89% *cis* and 11% *trans*) and PCl_3 a mixture of **14** (32% *trans*, δ_{31_P} +3·5 ppm, and 68% *cis*, δ_{31_P} +5·8 ppm) and **15** (29% *trans*, δ_{31_P} −59 ppm, 69% *cis*, δ_{31_P} −58 ppm) was obtained.

Compound **13**[11] (97% *trans* and 3% *cis*) when treated with PCl_3 it gave a mixture consisted of **14** (91% *trans*, δ_{31_P} +3·5 ppm, and 9% *cis*, δ_{31_P} +5·8 ppm) and **15** (85% *trans*, δ_{31_P} −59 ppm, and 15% *cis*, δ_{31_P} −58 ppm).

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