1,3,2-Thiazaphospholidin-2-ones Derived From Ephedrine. Preparation and Stereochemistry of Ring-opening Reactions

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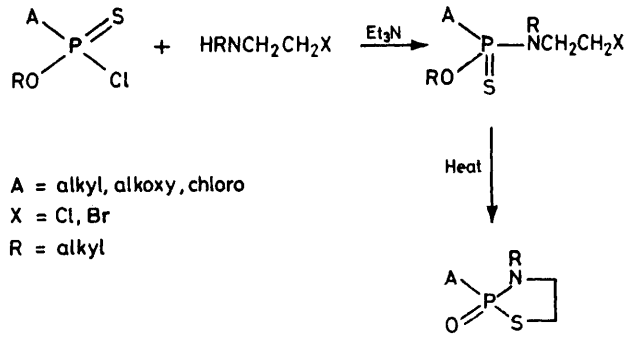
1,3,2-Thiazaphospholidin-2-ones are prepared by rearrangement of the corresponding 1,3,2-oxazaphospholidine-2-thiones. In both the phosphono- and phosphoro-series treatment with alkoxide results in P–N bond cleavage with inversion of configuration, while treatment with Grignard reagents results in P–S bond cleavage with retention of configuration. The products are consistent with a mechanism which involves initial nucleophilic attack opposite endocyclic nitrogen.

THE direction and stereochemical course of bond cleavage on nucleophilic substitution at phosphorus in 1,3,2-oxazaphospholidine-2-thiones varies considerably from similar processes in acyclic analogues.[1,2] To extend such comparisons chiral 1,3,2-thiazaphospholidin-2-ones have been prepared for the first time [3] and the stereochemical course of their reactions which involve endocyclic bond cleavage has been studied.

RESULTS

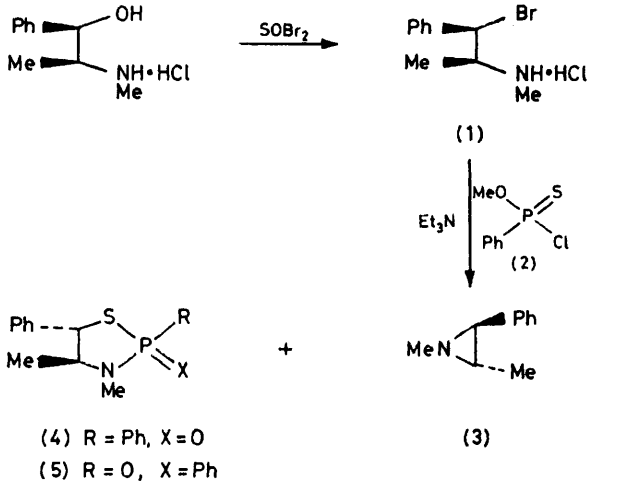
Synthesis.—1,3,2-Thiazaphospholidines have generally received little attention,[4–6] primarily because of the difficulty of synthesis and their ready hydrolysis.[5,6] The most general preparative route is outlined in Scheme 1.[6] It involves condensation of a β-halogenoamine with a phosphorus chloridate followed by a thermally catalysed internal Pishchimuka-type reaction. The sequence is, however, not



SCHEME 1

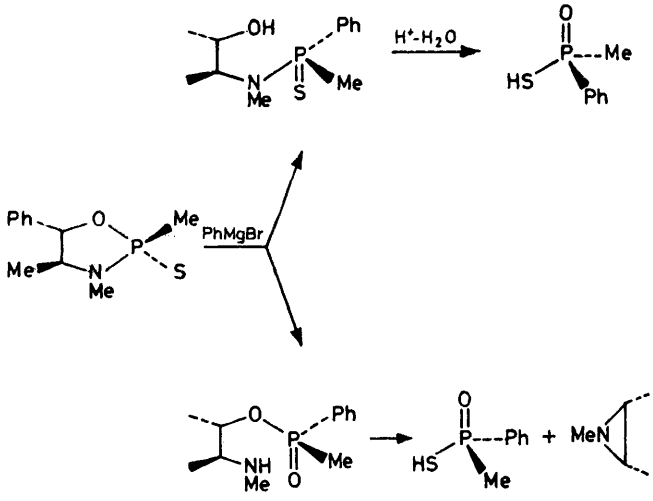
an effective one using β-halogenoamines derived from ephedrine, because of the ease with which such β-halogenoamines cyclise to form aziridines. For example (Scheme 2), treatment of a solution of (1) and (2) with triethylamine resulted only in the *trans*-aziridine (3). In the absence of solvent the reaction was highly exothermic and yields (≤17%) of the two thiazaphospholidin-2-one isomers (4) and (5) could be isolated.

It has been reported [7] that treatment of the various isomers of 2-methyl-1,3,2-oxazaphospholidine-2-thione with phenylmagnesium bromide results in competitive P–N and P–O bond cleavage. P–N Cleavage occurs with inversion, and P–O cleavage with retention of configuration at phosphorus. Thus both enantiomers of methylphenylphosphinothioic acid can be prepared from a single precursor (Scheme 3). Attempts to extend the procedure to prepare benzylphenyl- or t-butylphenyl-phosphinothioic acid by reaction of the 2-phenyl-1,3,2-oxazaphospholidine-2-thione (6) with the appropriate alkylmagnesium halide were unsuccessful. Instead (see *e.g.* Scheme 4) heating (6) and t-butylmagnesium bromide in boiling benzene for several hours resulted in the 1,3,2-thiazaphospholidin-2-one (4) (85%).[3]



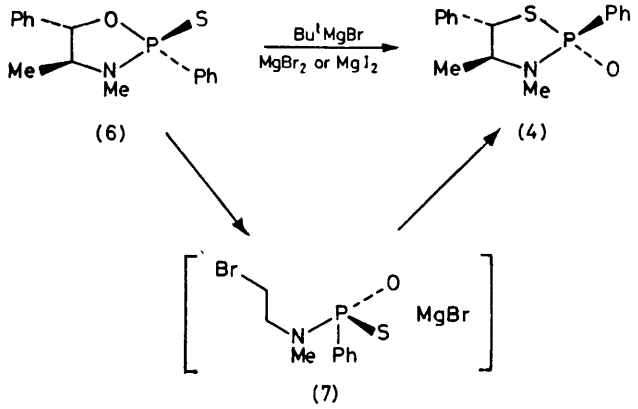
SCHEME 2

The most likely course of the rearrangement is initial



SCHEME 3

C–O bond cleavage by attack of bromide at the benzylic carbon, followed by recyclisation of the intermediate (7) by selective alkylation of sulphur (Scheme 4). This proposal is supported by the fact that the same rearrangement can be catalysed by magnesium bromide or magnesium iodide



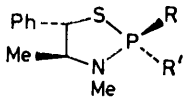
SCHEME 4

etherates. Magnesium iodide is the reagent of choice for preparative procedures.

The rearrangement is a general one (Tables 1 and 2);

TABLE 1

N.m.r. parameters for the (4*S*,5*S*)-1,3,2-thiazaphospholidin-2-ones



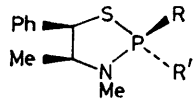
	R	R′	δ_H CMe	δ_H H-4	δ_H H-5 (J_{PH}, J_{HH}/Hz)	δ_P[a]
(4)	Ph	=O	1.20	3.81	4.43 (<1, 9.6)	51.2
(5)	=O	Ph	1.21	3.64	4.64 (1, 9.6)	46.3
(14)	Me	=O	1.09	3.57	4.26 (2, 8.8)	60.5
(15)	=O	Me	1.19	3.37	4.46 (1.5, 8.5)	58.2
(16)	EtO	=O	1.07	3.40	4.27 (0, 10.0)	
(17)	=O	EtO	1.16	3.45	4.46 (3, 8.5)	45.7
(18)	NH_2	=O	1.09	3.49	4.27 (1.6, 9.2)	
(19)[b]	=O	NH_2	1.17		4.37 (3.5, 8.0)	41.7

[a] Downfield from external phosphoric acid. [b] Data obtained from a mixture with (24).

however, only when the precursor is derived from (+)-pseudoephedrine [*e.g.* (6), (8), (9), or (10)] does it yield a single product [*i.e.* (4), (15), (16), or (18), respectively]. For oxazaphospholidines derived from (−)-ephedrine some inversion of configuration at the benzylic carbon occurs.

TABLE 2

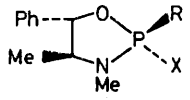
N.m.r. parameters for the (4*S*,5*R*)-1,3,2-thiazaphospholidin-2-ones



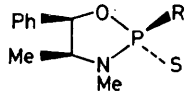
	R	R′	δ_H CMe	δ_H H-4	δ_H H-5 (J_{PH}, J_{HH}/Hz)	δ_P[a]
(20)	Me	=O	0.86	3.75	5.20 (2.5, 5.1)	54.1
(21)[b]	=O	Me	0.98		4.84 (5.1, 5.1)	58.2
(22)	EtO	=O	0.92	3.61	5.13 (4.2, 5.2)	45.9
(23)[c]	=O	EtO	0.93		5.04 (3.3, 5.4)	44.3
(24)[d]	=O	NH_2	0.98		5.05 (2.4, 5.4)	43.7

[a] Downfield from external phosphoric acid. [b] Data obtained from a mixture with (15). [c] Mixture with (17). [d] Mixture with (19).

Thus (11) gives a *ca.* 4 : 1 ratio of (15) and (21); (12) gives a 9 : 1 ratio of (17) and (23); and (13) gives a 1 : 1 ratio of (19) and (24). Halide exchange, with inversion of con-



(8) R = Me, X = S
(9) R = S, X = EtO
(10) R = S, X = NH_2



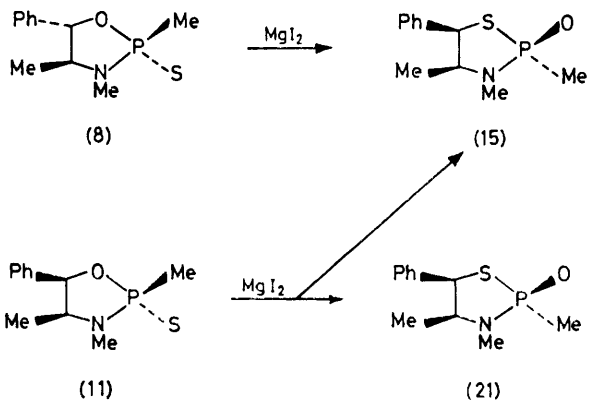
(11) R = Me
(12) R = EtO
(13) R = NH_2

figuration, in an intermediate such as (7), is the most likely explanation for the loss in stereospecificity. That it competes with ring closure only in the (−)-ephedrine-derived case presumably reflects the unfavourable *cis*-relationship of the methyl and phenyl groups generated by ring closure in this series.

The absolute configurations of the 1,3,2-thiazaphospholidin-2-ones have been assigned by comparison of the ^1H n.m.r. spectra of pairs of isomers epimeric at phosphorus (Tables 1 and 2). It was assumed that in such ring systems groups with a *cis*-relationship to the phosphoryl oxygen will be deshielded with respect to those that are *trans*. The assignments are supported by the proposed mechanism of formation from substrates of well established configuration, *e.g.* (11).[8] In the (+)-pseudoephedrine series, where the configurational assignment of the substrate is less solidly based, *e.g.* (8) [7] and (4),[3] the assumption that the rearrangement does not affect the stereochemistry at phosphorus relates the phosphorus configurations of (+)-pseudo- and (−)-ephedrine substrates (Scheme 5). Degradation experiments (*e.g.* Scheme 6, see below) also confirm the above assignments.

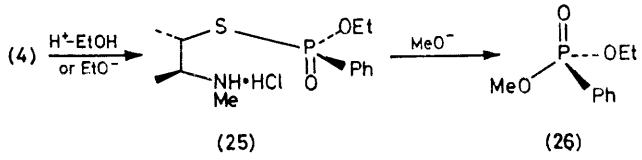
Ring-opening Reactions.—The phosphono-adduct (4) reacts rapidly with a dilute solution of anhydrous hydrogen chloride in ethanol or with sodium ethoxide to give an essentially quantitative yield of the P–N bond cleaved

product (25) (Scheme 6). The reaction is stereospecific and, on the basis of the results of acid-catalysed alcoholyses on similar systems,[9] it can reasonably be assumed to occur with inversion of configuration at phosphorus. Addition of sodium methoxide to a solution of (25) in methanol results



SCHEME 5

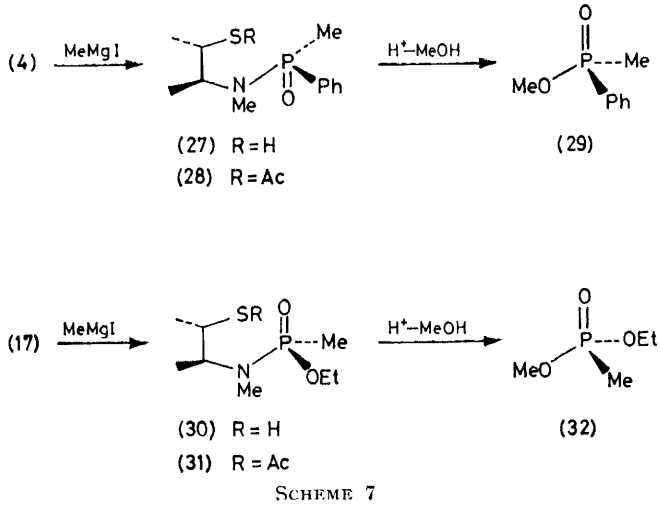
predominantly in enantiomerically pure [10] (+)-(*S*)-ethyl methyl phenylphosphonate (26).[11] Displacement of *S*-alkyl from phosphonothioates by alkoxides occurs with inversion of configuration at phosphorus.[8] This sequence (Scheme 6) therefore either confirms the configuration of (4), or that endocyclic P–N bond cleavage does in fact occur with inversion of configuration. The phosphoro-adduct



SCHEME 6

(17) reacts with both anhydrous hydrogen chloride in methanol and with sodium methoxide to yield the same single product, *i.e.* that resulting from P–N bond cleavage, again presumably occurring with inversion of configuration.

Compound (4) also reacts rapidly and quantitatively with methylmagnesium iodide at room temperature to give the product of P–S bond cleavage (27) (Scheme 7), acetylation



SCHEME 7

of which gives (28). Acid-catalysed (hydrogen chloride or trifluoromethylsulphonic) methanolysis of either (27) or (28) gives enantiomerically pure [8] (+)-(*R*)-methyl methylphenylphosphinate (29).[10,12] Since, under the conditions used, acid-catalysed P–N bond cleavage in phosphinamidates occurs with inversion of configuration at phosphorus,[12] then P–S bond cleavage in (4) must occur with retention of configuration. Similarly, treatment of (17) with methylmagnesium iodide followed by acetylation and acid-catalysed methanolysis yields enantiomerically pure (−)-(*S*)-ethyl methyl methylphosphonate (32) [8] (Scheme 7). Acid-catalysed P–N cleavage can again be assumed to occur with inversion of configuration; therefore endocyclic P–S bond cleavage must occur with retention of configuration.

Direct ^{31}P n.m.r. monitoring of all ring-opening reactions failed to reveal any reaction intermediates.

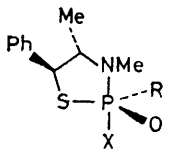
The basic hydrolysis of acyclic *N*-dialkyl phosphoramidothioates results in predominant P–S, with some P–O and C–O, but no P–N, bond cleavage.[13]

DISCUSSION

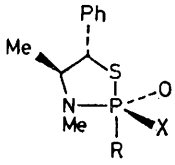
In a review [14] of the recent literature it was concluded that pseudo-rotations, or other ligand reorganisation processes, in trigonal bipyramidal reaction intermediates (TBPs) are limited to the pairwise exchange of apical and equatorial ligands about the P–X as pivot. This means that the stereochemistry of nucleophilic substitution at tetraco-ordinate phosphorus is determined by the direction of initial nucleophilic attack. (Any possible redundant equilibria, such as those between substrate and TBP which result only in regeneration of substrate, are neglected.) Thus if attack occurs opposite the eventual leaving group substitution occurs with inversion of configuration; where this is not the case substitution occurs, after pseudo-rotation, with retention of configuration. When mixed stereochemistry is observed it results from competitive attack opposite more than one substrate ligand. The factors that determine the direction of nucleophilic attack are not yet understood. It is not always correct to assume that attack will occur opposite the most apicophilic group, because apicophilicity is a thermodynamic term that relates the propensity of ligands to occupy apical positions in stable TBPs. The concept of ligand apical potentiality [1,3] is intended to relate the likelihood, during nucleophilic attack at tetraco-ordinate phosphorus, of a ligand being in-line with the nucleophile and therefore of occupying an apical position in the initially formed TBP. The apical potentiality of any ligand will depend on the other ligands attached to phosphorus, the nature of the nucleophile, the solvent, the presence of metal ions, *etc.*, and therefore the term is intended primarily as a descriptive one rather than as a measure of any particular parameter. It should be stressed that the apical potentiality concept does not allow a prediction of which bond to phosphorus will be cleaved, only the stereochemical consequences of cleavage of any bond.

The difference in the stereochemical course of nucleophilic substitution between 1,3,2-oxazaphospholidine-2-

thiones and their acyclic analogues may be rationalised if in the cyclic case nitrogen has a higher apical potentiality than oxygen, but that in the acyclic case the reverse is true.[1] The stereochemical results of ring cleavage of 1,3,2-thiazaphospholidin-2-ones reported here are consistent with nitrogen having a higher apical potentiality than sulphur in this system. Thus the mechanism of ring opening can be envisaged as involving attack of the nucleophile (X) opposite endocyclic nitrogen to form a TBP intermediate such as (33). When the nucleophile is alkoxide, apical P–N cleavage occurs, resulting in a product formed with inversion of configuration. When the nucleophile is alkyl, pseudo-rotation of (33) to the new TBP (34) is presumably fast compared with the rate of



(33)



(34)

P–N bond cleavage. P–S Bond cleavage in (34) results in a product formed with retention of configuration.

If it is assumed that the TBP (33), once formed, has a sufficiently long lifetime to enable it to adopt (by pseudo-rotation if necessary) the lowest energy form (as determined by a comparison of the relative apicophilicities of all the groups at phosphorus; RS > RO > R_2N > Me > Ph [15]) before bond cleavage occurs, then it can be argued that the observed reaction products are those that would be predicted except for the case where X = OMe and R = OEt, where P–S cleavage with retention of configuration might be expected. It is, however, likely that the rate of P–N bond cleavage in the relatively proton-rich MeONa–MeOH is fast (compared with pseudo-rotation) but in the non-protic MeMgI–Et_2O it is slow. Thus only in the latter does reaction occur, through the thermodynamically most stable TBP.

As was argued for nitrogen and oxygen in the 1,3,2-oxazaphospholidine case,[1] endocyclic nitrogen in 1,3,2-thiazaphospholidines may have a greater apical potentiality than endocyclic sulphur, either because of the stereoelectronic effects [1,14,16] of the fixed lone pairs on sulphur, or because nucleophilic attack opposite sulphur is sterically hindered by the alkyl substituent on nitrogen. In either case the results reported here constitute a further example [1,14,17] of how the confining of ligands within a five-membered ring can alter the stereochemistry and course of nucleophilic substitution reactions compared with the acyclic analogues.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded at 100 MHz in deuteriochloroform as solvent and with tetramethylsilane as internal standard, and optical rotations were measured in chloroform (path length 1 dm) unless otherwise stated. ^{31}P N.m.r. shifts are quoted in δ downfield from external phosphoric acid. Column chromatography was performed over Merk Kieselgel 60, particle size 0.040—0.063 mm, under a slight positive pressure. All organic solutions of reaction products were dried over magnesium sulphate. Light petroleum refers to the fraction of b.p. 60—80 °C.

1,3,2-*Thiazaphospholidin-2-ones. General Procedure.*—A solution of the 1,3,2-oxazaphospholidine-2-thione [3,7-9] substrate and an excess of t-butylmagnesium bromide, magnesium bromide, or magnesium iodide in benzene or ether was refluxed until t.l.c. indicated that reaction was complete (1—30 h). The mixture was then cooled, poured into ammonium chloride solution or water, and extracted with benzene. The combined extracts were concentrated and the residue purified by crystallisation or by rapid column chromatography,[18] eluting with benzene–acetone or benzene–acetone–methanol. Isolated yields were in the range 20—90%. ^{1}H N.m.r. spectra of the crude reaction products demonstrated that where isolated yields were low this was primarily because of loss during the purification procedure (chromatography). The following were obtained: (2*S*,4*S*,5*S*)-2,3,4-trimethyl-5-phenyl-1,3,2-thiazaphospholidin-2-one (14), m.p. 111—113 °C (from di-isopropyl ether), $[\alpha]_D$ +74° (*c* 1.1); (2*R*,4*S*,5*S*)-2,3,4-trimethyl-5-phenyl-1,3,2-thiazaphospholidin-2-one (15), m.p. 93—95 °C (from di-isopropyl ether), $[\alpha]_D$ −75° (*c* 0.9); (2*S*,4*S*,5*R*)-2,3,4-trimethyl-5-phenyl-1,3,2-thiazaphospholidin-2-one (20), m.p. 125 °C (from di-isopropyl ether), $[\alpha]_D$ −1.5° (*c* 1.2); (2*S*,4*S*,5*S*)-2-ethoxy-3,4-dimethyl-5-phenyl-1,3,2-thiazaphospholidin-2-one (16), m.p. 55 °C (from light petroleum), $[\alpha]_D$ −11° (*c* 0.9); (2*R*,4*S*,5*S*)-2-ethoxy-3,4-dimethyl-5-phenyl-1,3,2-thiazaphospholidin-2-one (17), m.p. 68—70 °C (from di-isopropyl ether), $[\alpha]_D$ +33° (*c* 1.0); (2*S*,4*S*,5*R*)-2-ethoxy-3,4-dimethyl-5-phenyl-1,3,2-thiazaphospholidin-2-one (22), as a clear oil, $[\alpha]_D$ −76° (*c* 0.5); (2*S*,4*S*,5*S*)-2,5-diphenyl-3,4-dimethyl-1,3,2-thiazaphospholidin-2-one (4), m.p. 164—166 °C (from di-isopropyl ether–benzene), $[\alpha]_D$ −26° (*c* 1.0); (2*S*,4*S*,5*S*)-2-amino-3,4-dimethyl-5-phenyl-1,3,2-thiazaphospholidin-2-one (18), m.p. 184—187 °C (from chloroform–light petroleum), $[\alpha]_D$ +6.3 (*c* 1.1).

1,3,2-*Thiazaphospholidin-2-ones* via *Scheme* 2.—A solution of freshly distilled thionyl bromide (60 g) in benzene (200 ml) was added to a suspension of finely divided (−)-ephedrine hydrochloride (50 g) in benzene (200 ml). After 1 h the mixture was warmed gently, then refluxed until evolution of gas ceased (3 h). Concentration gave a buff solid which was fractionally crystallised from ethanol–methanol to yield (1) (32.4 g, 49%) as white crystals, m.p. 184 °C; δ(in CD_3OD) 1.34 (3 H, d), 2.78 (3 H, s), 3.66 (1 H, dq), and 5.67 (1 H, d); $[\alpha]_D$ −97° (*c* 1.1 in methanol).

Triethylamine (3 ml) was added to a suspension of (1) (1 g) in *O*-methyl phenylphosphonothiochloridate (2) (3 ml). The reaction is exothermic. After 5 min dichloromethane (25 ml) was added and stirring continued for a further 15 min. The solution was filtered, concentrated, and the residue chromatographed [benzene–acetone (7 : 3)] to give the *trans*-aziridine [19] (3) (0.3 g, 54%), (4) (0.2 g, 17%), and (5) (0.2 g, 17%).

Endocyclic P–N *Bond-cleavage Reactions.—Acid-catalysed.* An excess of a dilute solution of anhydrous hydrogen chloride in methanol was added to a solution of (4) (1 g) in methanol. After 15 min the solution was purged with nitrogen and concentrated to give *O*-methyl *S*-[(1*S*,2*S*)-1-phenyl-2-methylaminopropyl] (*S*)-phenylphosphonothioate hydrochloride (35); δ(CD_3OD) 1.19 (3 H, d), 2.72 (3 H, s), 3.76 (3 H, d, *J* 13 Hz), and 4.36 (1 H, dd, *J* 11.8 and 9.0 Hz); $[\alpha]_D$ +81° (*c* 0.9 in methanol). Likewise (20) gave

O-methyl *S*-[(1*R*,2*S*)-1-phenyl-2-methylaminopropyl] (*S*)-methylphosphonothioate hydrochloride (36); δ_H (CD_3OD) 1.39 (3 H, d), 2.76 (3 H, d), 2.83 (3 H, s), 3.57 (3 H, d), and 5.07 (1 H, dd, *J* 11.2 and 4.8 Hz); δ_P −56.4, $[\alpha]_D$ −138° (*c* 1.4); and (17) gave *O*-ethyl *O*-methyl [(1*S*,2*S*)-1-phenyl-2-methylaminopropyl](*R*)-phosphorothioate hydrochloride (37); δ(CD_3OD) 1.09 (3 H, d), 1.20 (3 H, t), 2.78 (3 H, s), 3.60 (3 H, d, *J* 13.2 Hz), and 4.62 (1 H, dd, *J* 13.4 and 8.5 Hz); $[\alpha]_D$ +109° (*c* 1.5).

Base-catalysed. Direct ^{31}P monitoring of the reaction of a solution of (4) in methanol with a dilute solution of sodium methoxide in methanol revealed a smooth (5 min) reaction to give a single product (38) which on storage (1 h) was converted to dimethyl phenylphosphonate. Compound (38) was spectroscopically identical to the compound generated by treatment of (35) above, with dilute base. Conversely treatment of (38) with dilute methanolic hydrogen chloride gave (35).

Similarly treatment of (17) with sodium methoxide in methanol followed by acidification with hydrogen chloride gave (37) above.

(+)-(S)-*Ethyl Methyl Phenylphosphonate* (26) (*Scheme* 6).—An excess of a dilute solution of anhydrous hydrogen chloride in ethanol was added to a solution of (4) (1 g) in ethanol. After 15 min the solution was concentrated and the residue dissolved in chloroform and washed with dilute sodium carbonate solution. The solution was again concentrated and the residue dissolved in a dilute solution of sodium methoxide in methanol. After 12 h the mixture was poured into water and extracted with chloroform. Concentration of the chloroform solution and chromatography of the residue, eluting with ethyl acetate–light petroleum (4 : 1), gave (26) (0.34 g, 52%) $[\alpha]_D$ +2.9° (*c* 2.0) [11] and dimethyl phenylphosphonate (0.09 g, 15%).

Endocyclic P–S Bond Cleavage by Grignard Reagents.—An excess of a solution of methylmagnesium iodide in benzene was carefully added to a solution of (4) (0.5 g) in benzene (25 ml). After 30 min the mixture was poured into an aqueous solution of ammonium chloride and extracted with benzene. The solution was concentrated and the residue crystallised to give (27) (0.5 g, 95%), m.p. 136—137 °C (from chloroform–light petroleum); δ_H 1.06 (3 H, d), 1.94 (3 H, d, *J* 13.4 Hz), and 2.48 (3 H, d, *J* 11.0 Hz); δ_P −38.1; $[\alpha]_D$ +113° (*c* 0.6). Storage of a solution of (27) (0.5 g) in pyridine–acetic anhydride (2 : 1; 15 ml) for 3 h followed by conventional processing gave the acetate (28) (0.5 g, 88%); δ_H 0.97 (3 H, d), 1.75 (3 H, d, *J* 13.8 Hz), 2.16 (3 H, s), 2.34 (3 H, d, *J* 10.2 Hz), 4.30 (1 H, m), and 4.74 (1 H, d, *J* 11.2 Hz); $[\alpha]_D$ +164 (*c* 0.5).

Similar treatment of (17) with methylmagnesium iodide followed by acetylation of the crude reaction mixture gave a mixture of (31) (75%); δ_H 0.95 (3 H, d), 1.30 (3 H, t), 1.42 (3 H, d, *J* 15.7 Hz), 2.24 (3 H, s), 2.49 (3 H, d, *J* 9.8 Hz), and 4.71 (1 H, d, *J* 11.1 Hz); $[\alpha]_D$ +141° (*c* 1.8), and its dimethyl phosphinamidate analogue (15%); δ_H 1.00 (3 H, d), 1.47 and 1.51 (3 H, d, *J* 13.4 Hz), 2.25 (3 H, s), 2.48 (3 H, d, *J* 10.4 Hz), and 4.68 (1 H, d, *J* 11.2 Hz); $[\alpha]_D$ +219° (*c* 0.7).

(+)-(R)-*Methyl Methylphenylphosphinate* (29) (*Scheme* 7).—A solution of (28) (1.2 g) and trifluoromethanesulphonic acid (1.5 ml) in methanol (25 ml) was stored for 30 min, then poured into water and extracted with chloroform. The solution was concentrated and the residue chromatographed, eluting with benzene–acetone–methanol (8 : 1 : 1), and distilled to give (29) [10] (0.55 g, 86%), $[\alpha]_D$ +51° (*c* 2.3). Likewise methanolyses using (27) as precursor, or anhydrous hydrogen chloride as acid, gave similar results.

(−)-(S)-*Ethyl Methyl Methylphosphonate* (32) (*Scheme* 7).—A solution of (31) (0.5 g) and trifluoromethanesulphonic acid (0.75 ml) in methanol (20 ml) was stored for 20 h, then processed as above to give (32) [8] (0.15 g, 71%), $[\alpha]_D$ −1.9° (*c* 1.5).

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