

PHOSPHOROTHIOATES—III

REACTIONS OF PHOSPHOROTHIONYL DISULPHIDES WITH ORGANOMETALLIC REAGENTS¹

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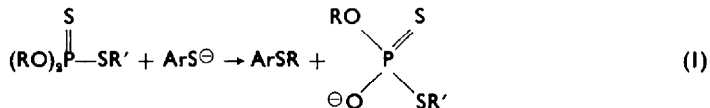
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Abstract—Organometallic reagents attack the S-S bonds of phosphorothionyl disulphides (V) to give high yields of the corresponding S-substituted phosphorodithioates. S-Alkenyl and S-alkynyl phosphorodithioates, previously unknown, were prepared in this manner. No indication of attack at phosphorus atoms, of reduction of S-S bonds, or of benzylic rearrangements of the organometallic reagents were observed.

SINCE the discovery of the value of esters of O,O-dialkyl phosphorodithioic acids (I) as insecticides of low mammalian toxicity² many publications have been devoted to their preparation.



Preparation of S-alkyl esters normally offers little difficulty, since such esters can readily be obtained by addition of the corresponding phosphorodithioic acids to double bonds^{2a,3} or by reaction of salts of the acids with alkyl halides.⁴ S-Aryl esters may, in principal, be prepared by reacting O,O-dialkyl phosphorochloridithioates (II) with thiophenolate salts. Although a German patent⁵ does describe the formation of I (R' = Ar) by this means, this apparently simple reaction suffers from the difficulty that the highly nucleophilic thiol anion often reacts as readily with the product as with the starting material (Eq. 1). We have found, for example, that no more than a 32% yield of I (R = C₂H₅, R' = C₆H₅) could be obtained from the reaction of sodium



thiophenolate with II (R = C₂H₅), although III could be obtained in 80% yield by reaction of sodium phenoxide with II under similar conditions. Ethyl phenyl sulphide

¹ Paper II in this series: B. Miller, *J. Amer. Chem. Soc.* **84**, 403 (1962).

^{2a} G. A. Johnson, J. H. Fletcher, K. G. Nolan and J. T. Cassaday, *J. Econ. Entomol.* **45**, 279 (1952);

^b R. D. O'Brien, *Toxic Phosphorus Esters*. Academic Press, New York (1960).

^{2a} G. R. Norman, W. M. LeSuer and T. W. Mastin, *J. Amer. Chem. Soc.* **74**, 1961 (1952); ^b N. N. Mel'nikov and K. D. Shvetsova-Shilovskaya, *Doklady Akad. Nauk S.S.S.R.* **86**, 543 (1952); ^c T. L. Vladimirova and N. N. Mel'nikov, *Zh. Obshch. Khim.* **26**, 2659 (1956); ^d A. A. Oswald, K. Griesbaum and B. E. Hudson, Jr., *J. Org. Chem.* **28**, 1262 (1963).

⁴ N. N. Mel'nikov, K. D. Shvetsova-Shilovskaya, M. Y. Kagan and I. M. Mil'shtein, *Zh. Obshch. Khim.* **29**, 1612 (1959).

⁵ G. Schrader, *Ger. Patent* 855,176 (1953).

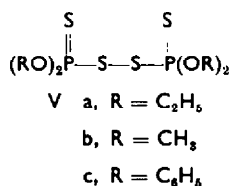


was obtained as the major by-product from reaction of sodium thiophenolate with II. It is not surprising that dealkylation of I (or II) should compete with displacement of a halide ion from II, since the very high nucleophilicities of thiol anions toward alkylating agents are not accompanied by correspondingly high nucleophilicities toward pentavalent phosphorus.¹

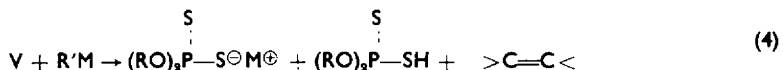
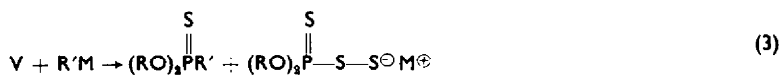
Several highly ingenious syntheses of S-aryl phosphorodithioates have been devised which circumvent the problem of dealkylation during their synthesis.^{6,7} These procedures have not been widely utilized, since they employ intermediates which are rather difficult to prepare.

Preparation of S-alkenyl and S-alkynyl phosphorodithioates offers obvious difficulties. Prior to the publication of the preliminary report of this work,⁸ IV was the only reported example of an S-alkenyl phosphorodithioate ester,⁹ while no S-alkynyl esters had been reported.

Clearly, a general method for the synthesis of phosphorodithioate esters, and of S-aryl, alkenyl and alkynyl esters in particular, would be highly desirable. One possible such method is the reaction of organometallic reagents with phosphorothionyl disulphides (V). Attack of organic "anions" at a sulphur atom of V should



give the desired phosphorodithioate ester (Eq. 2). At least two other possible reactions must be considered, however: reaction at a phosphorus atom to give O,O-dialkyl phosphonothioate esters (VI; as in Eq. 3) and reduction of the S—S bond (Eq. 4).



In practice, no evidence for reactions (3) or (4) has been found, and excellent yields of esters derived from path (2) have been obtained.

Aryl and alkyl esters. Grignard reagents were found to react much more rapidly with V than with organic disulphides. Reaction mixtures refluxed vigorously and

* N. N. Mel'nikov, A. F. Grapov and K. D. Shvetsova-Shilovskaya, *Zh. Obshch. Khim.* **27**, 1905 (1957).

⁷ J. Michalski, J. Wiczorkowski, J. Wasiak and B. Pliszka, *Rocz. Chem.* **33**, 247 (1959).

⁸ B. Miller, *J. Amer. Chem. Soc.* **82**, 6205 (1960).

⁹ W. R. Dively, A. H. Haubein, A. D. Lohr and P. B. Moseley, *J. Amer. Chem. Soc.* **81**, 139 (1959).

required external cooling when the reactions were carried out on a large scale. The rate at which the disulphides were added to the Grignard reagent usually determined the reaction time since disappearance of the yellow disulphide colour indicated that reaction was complete within a few minutes after addition of the disulphide.

Phenylmagnesium bromide reacted with Va to give O,O-diethyl S-phenyl phosphorodithioate (I, $R = C_2H_5$, $R' = C_6H_5$) in 78% yield. The ester was identical with the product of reaction of sodium thiophenolate with II ($R = C_2H_5$). Vapour phase chromatography of the distilled ester and of the crude reaction mixture afforded no evidence for the presence of VI ($R = C_2H_5$, $R' = C_6H_5$), which would result from attack of the Grignard reagent at a phosphorus atom. Similarly, *n*-butyllithium, *i*-butylmagnesium bromide, and *sec*-butylmagnesium bromide reacted with Va to give the corresponding S-butyl esters in yields of 86 to 99%. The esters were identical with those obtained by reacting potassium O,O-diethyl phosphorodithioate with the appropriate butyl bromides. Again, no evidence could be obtained for reaction of the organo-metallic reagents at phosphorus rather than sulphur atoms.

The high yields obtained, though gratifying, were rather surprising. Since disulphide bonds are quite easily reduced, it was thought that *i*-butylmagnesium bromide, which has often been observed to give reduction rather than addition products on reaction with carbonyl compounds,¹⁰ would give particularly low yields of the desired *i*-butyl ester on reaction with Va. The observed 99% yield, however, left little opportunity for reduction to have occurred.

Reduction of ketones by Grignard reagents is usually attributed to hydride transfer via six-membered cyclic transition states.¹⁰ The complete absence of reduction in the reactions of Grignard reagents with V can be understood if these reactions proceed by direct nucleophilic attack at sulphur atoms rather than by cyclic transition states.

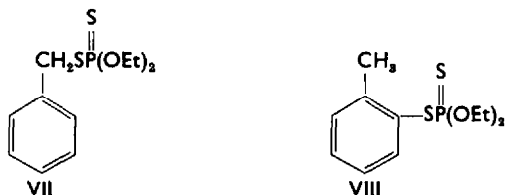
Several factors should decrease the importance of cyclic transition states in the reactions of Grignard reagents with disulphides as compared to their reactions with carbonyl compounds. Grignard reagents should form much weaker complexes with sulphur than with the more basic oxygen atoms of carbonyl groups. Furthermore, six-membered cyclic transition states can be obtained only if the magnesium ion is assumed to complex with sulphur atoms of the disulphide bonds. These atoms are joined to two electron withdrawing groups, and would be far less likely to form complexes than would "thiono" sulphurs, which bear formal negative charges. If a Grignard reagent were to complex with a thiono sulphur, however, transfer of a hydride ion to the disulphide bond would require a seven or eight membered ring in the transition state.

The question of whether the size of a required cyclic transition state or the inherently weak complexing between magnesium and sulphur is responsible for the absence of reduction by Grignard reagents will be considered in the following section.

Reaction with benzyl grignards. Two isomers might be obtained from the reaction of Va with a benzyl Grignard reagent: the "normal" product (VII) or the "rearranged" isomer (VIII). Both isomers were independently synthesized—VII by reaction of potassium O,O-diethyl phosphorodithioate with benzyl chloride and VIII by reaction of *o*-tolyl magnesium bromide with Va—in order to detect any allylic rearrangement.

¹⁰ M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Non-metallic Substances*, Chap. VI. Prentice-Hall, New York (1960).

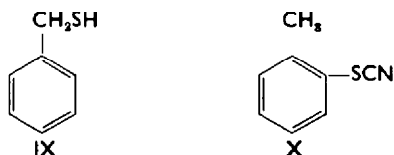
The two isomers could easily be separated on a polyethylene glycol VPC column, and less than $\frac{1}{2}$ of 1% of VIII could readily be detected in a sample of VII.



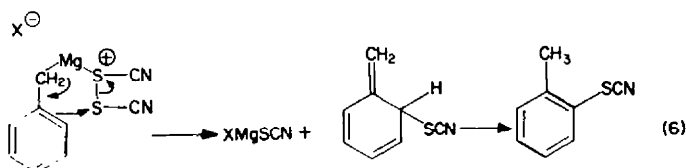
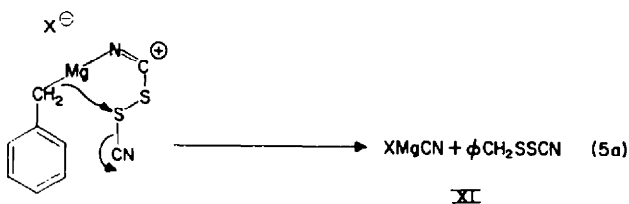
Reaction of Va with benzylmagnesium chloride gave a 93% yield of VII. Neither the crude reaction mixture nor the distilled product contained detectable amounts of VIII.

To determine whether the absence of allylic rearrangement was characteristic only of disulphides of phosphorodithioic acids, benzylmagnesium chloride was reacted with phenyl disulphide. VPC analysis of the benzyl phenyl sulphide produced disclosed no phenyl *o*-tolyl sulphide.

In contrast to the reactions with the two disulphides described above, Eastham and Cannon¹¹ have reported that reaction of benzylmagnesium chloride with thiocyanogen gives the "normal" mercaptan (IX) and the "rearranged" thiocyanate (X) in a 3:1 ratio.



To rationalize the formation of the normal isomer as the mercaptan and the "abnormal" isomer as the thiocyanate, the authors suggested that two different paths were followed (Eqs 5 and 6):¹¹

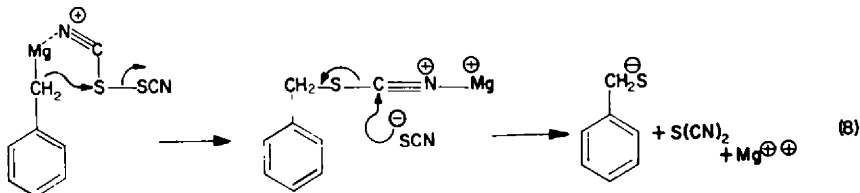
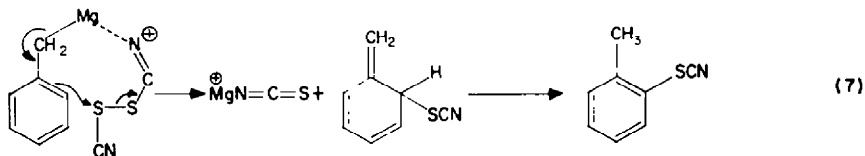


¹¹ J. F. Eastham and D. Y. Cannon, *J. Org. Chem.* **25**, 1504 (1960).

In support of their proposed mechanism for the formation of benzyl mercaptan, Eastham and Cannon cited the work of Lecher and Wittmer,¹² who reported that thiothiocyanates such as XI are very easily hydrolyzed. Lecher and Wittmer's studies, however, clearly show that XI would hydrolyze by nucleophilic attack at the sulphur attached to the organic radical, to give the more stable thiocyanate ion rather than a benzyl mercaptide anion.¹³ This is in accord with expectations from other cleavage reactions of disulphides.¹⁴ It seems quite unlikely, therefore, that benzyl mercaptan could be formed by reaction (5b).

Reaction (6) also seems to be an unlikely path. A magnesium ion would certainly form a coordinate bond with the trivalent nitrogen atom in preference to the sulphur of a thiocyanogen molecule. Furthermore, if path (6) were followed, there would seem to be no reason why phosphorothionyl disulphides should not react with benzyl Grignard reagents to give "abnormal" products by the same path.

The essentially complete formation of *o*-tolunitrile from the reaction of benzylmagnesium chloride with cyanogen¹⁵ shows that coordination of a nitrile nitrogen with a magnesium ion can lead to products of the "abnormal" type. It therefore seems that the most probable mechanisms for the formation of IX and X, are those given in Eqs (7) and (8).



Hydrolysis of the benzyl but not the *o*-tolyl thiocyanate results directly from the nature of the initial products of each reaction.

Since an eight membered ring is the most probable transition state for formation of the "rearranged" isomer X, the lack of formation of a "rearranged" product from the reaction of benzylmagnesium chloride with phosphorothionyl disulphides does not seem to be due to the unfavorable size of the cyclic transition states. The explanation for the sole formation of the "normal" benzylic ester, therefore, seems to be

¹² H. Lecher and M. Wittmer, *Chem. Ber.* **55**, 1474 (1922).

¹³ Organic thiothiocyanates gave thiocyanic acid on hydrolysis or alcoholysis. Mercaptans were not isolated. Reaction of mercaptans with thiothiocyanates gave mixed organic disulphides.¹³

¹⁴ A. J. Parker and N. Kharasch, *J. Amer. Chem. Soc.* **82**, 3071 (1960).

¹⁵ V. F. Raaen and J. F. Eastham, *J. Amer. Chem. Soc.* **82**, 1349 (1960).

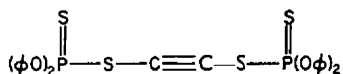
that coordination of the magnesium ion with a sulphur atom plays little part in the reaction, which may be regarded as a direct attack of the benzylic "anion" on a sulphur atom.

In accordance with the discussion above, it seems probable that the lack of reduction of sulphur-sulphur bonds of disulphides by Grignard reagents is also due to absence of coordination of the magnesium ion with sulphur atoms, rather than the unfavorable size of the required cyclic transition states.

Alkenyl and alkynyl esters. In addition to the difficulties which might be encountered in the reaction of phosphorodithionyl disulphides with alkyl and aryl Grignard reagents, the possibility existed that the unknown S-alkenyl and S-alkynyl phosphorodithioates might prove to be intrinsically unstable. Vinylmagnesium bromide and monosubstituted lithium acetylides, however, reacted smoothly with V to give the corresponding S-alkenyl and S-alkynyl phosphorodithioates in yields of 57 to 79%. These yields are appreciably lower than those obtained using alkyl Grignard reagents, but the lower yields are due, at least in part, to purification of the vinyl and alkynyl esters by distillation through a short fractionating column, while the alkyl esters were isolated by molecular distillation. Some decomposition of the unsaturated esters occurs during distillation.

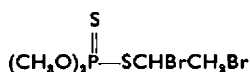
S-alkenyl and S-alkynyl phosphorodithioates are mobile yellow liquids which discolour slowly on standing at room temperature for several weeks. Their structures were confirmed by the presence of double bond stretching peaks at 6.3μ and triple bond stretching peaks at 4.6μ in the infrared spectra of the vinyl and alkynyl phosphorodithioates respectively.

Several attempts to prepare esters containing terminal acetylene groups (I, $R' = -C \equiv CH$) failed. The reactions were quite sluggish, due to the insolubility of dilithium acetylide in ether or hydrocarbons. Although the terminal acetylene could not be prepared, in one attempt using disulphide Vc a very small amount of a yellow solid, m.p. $111-112^\circ$, was obtained. Its analysis agreed with that required for the diphosphorodithioylacetylene XII. The product decomposed on standing at room temperature, however, and could not be obtained from subsequent runs.

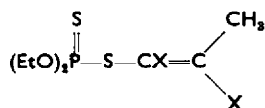


XII

Both the S-vinyl and S-alkynyl esters added bromine readily in carbon tetrachloride solution to give the corresponding S-1,2-dibromoethyl (XIII) and S-1,2-dibromopropenyl esters. The structure of XIII was shown by the absence of double bond absorption in the $6-6.5 \mu$ region, and of XIVa by the absence of triple bond absorption and the appearance of a double bond peak at 6.2μ . The dibromides were reasonably stable in the refrigerator, but decomposed after a few weeks at room temperature.



XIII

XIVa, X = Br
b, X = Cl

Addition of chlorine to either the vinyl or alkynyl esters apparently resulted in appreciable oxidation of the thiono sulphur, since strong P=O peaks at 7.9μ appeared in the IR spectra of the crude products. Although XIVb could be isolated by chromatography on alumina, it darkened rapidly, even in the refrigerator, and decomposed completely in less than a week.

EXPERIMENTAL¹⁶

*O,O-Diethyl phosphorothionyl disulphide (Va) and O,O-dimethyl phosphorothionyl disulphide (Vb)*¹⁷

The O,O-dialkyl phosphorodithioic acid (6 moles) was stirred in 1 l. water and the solution brought to pH 8 by the addition of KOH aq. Any non-ionic impurities were extracted with methylene chloride and KNO₃ (6.8 moles) added. Conc. H₂SO₄ (6.8 moles) was dropped into the rapidly stirred solution over a 3 hr period. The disulphide was extracted with methylene chloride, washed several times with water and dried (MgSO₄). Evaporation of the solvent left ca. 60% of the disulphide. O,O-Diethyl phosphorothionyl disulphide¹⁸ had n_D^{25} 1.555. O,O-Dimethyl phosphorothionyl disulphide had m.p. 49–51° (reported,¹⁹ m.p. 51–52°).

O,O-Diphenyl phosphorothionyl disulphide (Vc)

O,O-Diphenyl phosphorodithioic acid (60.0 g, 0.22 mole) was oxidized as described for the preparation of Va and Vb. The product was recrystallized from heptane to give 38.2 g (64%) white needles, m.p. 74.6–75.0°. (Found: C, 51.4, 51.2; H, 4.0, 3.8; P, 11.3, 11.1; S, 23.0, 22.8. Calc. for C₂₄H₂₀O₄P₂S₄: C, 51.3; H, 3.6; P, 11.0; S, 22.8%).

Preparation of phosphorothioate esters.

The reactions of Va with phenylmagnesium bromide and n-butyllithium are described in detail. Reactions with other organometallic reagents were all run in a similar manner.

O,O-Diethyl S-phenyl phosphorodithioate

(a) *Reaction of Va with phenyl magnesium bromide.* Va (7.90 g, 0.0213 mole) was dissolved in 25 ml anhydrous ether. A 0.850N solution of phenylmagnesium bromide (27 ml, 0.023 mole) was added drop by drop, over a 15 min period, to the stirred solution. Stirring was continued at room temp for 50 min. The reaction mixture was poured onto ice, washed with dil. HCl aq, dil. NaHCO₃ aq and water, and dried (MgSO₄). Evaporation of the solvent left 5.95 g yellow oil which was distilled in a molecular still at 0.01 mm Hg at 88–95° to give 4.36 g (0.0166 mole, 78%) O,O-diethyl S-phenyl phosphorodithioate (n_D^{25} 1.558), identical in IR spectrum and VPC retention time with the product of method (b).

(b) *Reaction of potassium thiophenolate and O,O-diethyl phosphorochloridithioate.* A solution of potassium thiophenolate (0.096 mole) in 200 ml of t-butyl alcohol was heated to 50° and a solution of O,O-diethyl phosphorochloridithioate (19.72 g, 0.105 mole) in 35 ml t-butyl alcohol was added rapidly. The temp rose to 60° and was maintained for 2.25 hr. The mixture was then cooled, extracted with 3N KOH aq, washed with water and evaporated *in vacuo*. The residue was dissolved in ether, dried (CaCl₂) and evaporated to give 17.4 g yellow oil, which was distilled at 1.4 mm Hg to give 8.17 g (0.0312 mole, 32%) Ia, b.p. 140–145°, n_D^{25} 1.557 (reported,⁸ b.p. 0.1 mm, 102.5–104.5°, n_D^{20} 1.563). A 21% yield of ethyl phenyl sulphide was obtained by redistillation of lower boiling fractions.

¹⁶ Microanalyses were by Dr. Julius Kuck and his group at the Research Laboratories, American Cyanamid Co., Stamford, Conn., and by Galbraith Microanalytical Laboratories, Knoxville, Tenn. VPC analyses were carried out using a 6 ft. 20% polyethylene glycol on 60-80 Mesh Chrom W Column, in Aerograph A-100 or F & M 500 vapor phase chromatography instruments.

¹⁷ These disulphides have usually been prepared by oxidation of the corresponding O,O-dialkyl phosphorodithioic acids with halogens.^{18,19} We have found that the procedure given above is more convenient for large scale preparation, and usually gives a purer product.

¹⁸ L. Malatesta and F. Laverone, *Gazz. Chim. Ital.* **81**, 596 (1951).

¹⁹ M. I. Kabachnik and T. A. Mastryukova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 121 (1955).

O,O-Diethyl O-phenyl phosphorothioate (III)

Reaction of sodium phenoxide and *O,O*-diethyl phosphorochloridate in *t*-butyl alcohol, as described for method b, above, gave a 77% yield of III, b.p. 120–127° (1.4 mm), n_D^{25} 1.513 [reported²⁰ b.p. 140° (7 mm)].

O,O-Diethyl S-n-butyl phosphorodithioate

(a) *Reaction of Va with n-butyllithium.* To a solution of Va (10.45 g, 0.0282 mole) in 20 ml ethyl ether was added a 3.03N solution of butyllithium in hexane (10 ml, 0.0303 mole). The rate of addition was controlled by the vigorous refluxing of the solution and the addition required 15 min. The mixture was stirred 10 min more, washed with water, dried ($MgSO_4$), evaporated and distilled in a molecular still at 60–70° and 0.01 mm Hg, to give 5.85 g (0.0241 mole, 86%) *O,O*-diethyl *S*-*n*-butyl phosphorodithioate, n_D^{25} 1.497. (Found: C, 39.5; H, 7.7; P, 13.0; S, 26.3. Calc. for $C_8H_{16}O_2PS_2$: C, 39.7; H, 7.8; P, 12.8; S, 26.4%.)

(b) *Reaction of potassium O,O-diethyl phosphorodithioate with 1-bromobutane.* A solution of potassium *O,O*-diethyl phosphorodithioate (10.81 g, 0.050 mole) and 1-bromobutane (7.31 g, 0.053 mole) in 50 ml of acetone was refluxed 16 hr. The mixture was cooled, the acetone evaporated and the residue taken up in methylene chloride. The methylene chloride solution was washed with water, dried ($MgSO_4$) and evaporated to give 9.01 g (0.0372 mole, 75%) *O,O*-diethyl *S*-*n*-butyl phosphorodithioate. n_D^{25} 1.495. The IR spectrum and VPC retention times were identical with those of the product from method (a).

O,O-Diethyl S-2,2-dimethylethyl phosphorodithioate

Reaction of Va with *i*-butylmagnesium bromide on a 0.0322 mole scale gave a 99% yield (after molecular distillation) of the ester as a light yellow liquid, n_D^{25} 1.496. (Found: C, 39.9; H, 7.95; P, 13.1; S, 26.6. Calc. for $C_8H_{16}O_2PS_2$: C, 39.7; H, 7.8; P, 12.8; S, 26.4%). Reaction of potassium *O,O*-diethyl phosphorodithioate and *i*-butyl bromide as described for the reaction with 1-bromobutane gave a 41% yield of the ester, which was identical in IR spectrum and VPC retention time with the product of the reaction above.

S-2-Butyl O,O-diethyl phosphorodithioate

Reaction of Va with *sec*-butylmagnesium chloride on a 0.0263 mole scale gave an 88% yield (after molecular distillation) of the ester, n_D^{25} 1.499. (Found: C, 39.9; H, 7.9; P, 12.9; S, 26.5. Calc. for $C_8H_{16}O_2PS_2$: C, 39.7; H, 7.8; P, 12.8; S, 26.4%). Reaction of potassium *O,O*-diethyl phosphorodithioate with 2-bromobutane gave a 38% yield of the ester as a brown liquid, which was identical in IR spectrum and VPC retention time with the previous product.

S-Benzyl O,O-diethyl phosphorodithioate (VII)

Reaction of Va with benzylmagnesium chloride on a 0.0277 mole scale gave a 92.5% yield of VII (after molecular distillation) as a pale yellow liquid, n_D^{25} 1.555 (reported,⁴ n_D^{20} 1.560). The product was identical in IR spectrum and VPC retention time with the product of reaction of *O,O*-diethyl phosphorodithioate and benzyl chloride.²¹

Phenyl o-tolyl sulphide

A solution of phenyl disulphide (16.7 g, 0.077 mole) in 150 ml ether was added to a solution of *o*-tolylmagnesium bromide in ether and the mixture refluxed 1 hr and worked up as usual to give 10.90 g (0.0544 mole, 71%), phenyl *o*-tolyl sulphide, b.p. 120–125° (1.25 mm) (reported²² b.p. 164.5° at 11 mm).

Reaction of benzylmagnesium chloride with phenyl disulphide

A solution of phenyl disulphide (9.0 g, 0.041 mole) in 50 ml ether was added to benzylmagnesium chloride (0.05 mole) in 150 ml ether and worked up as usual. VPC analysis showed the product to consist of benzyl phenyl sulphide²³ and a small amount of a material with a lower retention time, presumably dibenzyl. No phenyl *o*-tolyl sulphide was present.

²⁰ J. K. Eaton and R. G. Davies, *Ann. Appl. Biol.* **37**, 92 (1950).

²¹ I wish to thank Dr. D. E. Ailman of these laboratories for a sample of VII prepared by this method.

²² E. Bourgeois, *Ber. Dtsch. Chem. Ges.* **28**, 2312 (1895).

²³ T. Carlson, *Ber. Dtsch. Chem. Ges.* **40**, 4191 (1907).

O,O-Diethyl S-vinyl phosphorodithioate

To a solution of Va (10.0 g, 0.0270 mole) in 10 ml ether was added a solution of vinylmagnesium bromide (0.0373 mole) in 25 ml tetrahydrofuran. The reaction was apparently complete in 2 min, and was worked up as usual after 10 min to give 6.13 brown fluid, which was distilled to give 3.55 g (0.0167 mole, 62%) O,O-diethyl S-vinyl phosphorodithioate, b.p. 108–112° (0.70 mm), n_D^{25} 1.512. (Found: C, 33.9; H, 5.5; P, 14.9; S, 29.7. Calc. for $C_4H_{13}O_2PS_2$: C, 33.9; H, 6.1; P, 14.6; S, 30.2%.)

O,O-Dimethyl S-vinyl phosphorodithioate

To a solution of Vb (9.50 g, 0.0302 mole) in 25 ml ether was added a solution of vinylmagnesium bromide (0.0373 mole) in 25 ml tetrahydrofuran. The mixture was worked up as usual after 5 min to give 3.21 g (0.0174 mole, 58%) O,O-dimethyl S-vinyl phosphorodithioate, b.p. 74–77° (2.0 mm), n_D^{25} 1.533. (Found: C, 26.4; H, 5.2; P, 17.1; S, 35.0. Calc. for $C_4H_9O_2PS_2$: C, 26.1; H, 4.9; P, 16.9; S, 34.8%.)

O,O-Diethyl S- β -styryl phosphorodithioate

To a solution of Va (10.0 g, 0.0270 mole) in 10 ml ether was added a solution of β -styrylmagnesium bromide (0.0345 mole) in 50 ml tetrahydrofuran. The reaction was worked up as usual and distilled at 0.01 mm in a molecular still at 110–122° to give 4.62 g (0.0160 mole, 59%) O,O-diethyl S- β -styryl phosphorodithioate, n_D^{25} 1.582. (Found: C, 50.4; H, 6.2; P, 11.0; S, 22.5. Calc. for $C_{11}H_{17}O_2PS_2$: C, 50.0; H, 5.9; P, 10.8; S, 22.2%.)

O,O-Dimethyl S-1,2-dibromoethyl phosphorodithioate (XIII)

To 1.31 g O,O-dimethyl S-vinyl phosphorodithioate (0.00714 mole) in 25 ml CCl_4 were slowly added 1.14 g Br_2 (0.00713 mole) in 10 ml CCl_4 . Evaporation of the solvent left 2.46 g red liquid which was chromatographed on Woelm neutral alumina to give 2.24 g (0.00650 mole, 91%) O,O-dimethyl S-1,2-dibromoethyl phosphorodithioate as a colorless liquid, n_D^{25} 1.590. (Found: Br, 45.1; S, 18.9. Calc. for $C_4H_8Br_2O_2PS_2$: Br, 46.5; S, 18.6%.)

O,O-Diethyl S-1-propynyl phosphorodithioate

A rapid stream of 1-propyne was passed over a stirred solution of *n*-butyl lithium (0.0758 mole) in 150 ml ether at 0° until precipitation of lithium methylacetylide was complete. Va (25 g, 0.0626 mole) in 50 ml ether was added, the mixture stirred for $\frac{1}{2}$ hr, refluxed 15 min and worked up as usual to give 11.1 g (0.0495 mole, 79%) O,O-diethyl S-1-propynyl phosphorodithioate, b.p. 95–99° (0.80 mm), n_D^{25} 1.524. (Found: C, 37.6; H, 6.1; P, 13.8; S, 28.9. Calc. for $C_7H_{13}O_2PS_2$: C, 37.5; H, 5.8; P, 13.8; S, 28.6%.)

O,O-Diethyl S-phenylethynyl phosphorodithioate

n-Butyllithium in hexane (10 ml 0.0303 mole) was added very slowly to a solution of phenylacetylene (3.81 g, 0.0373 mole) in 15 ml ether at 0°. The reaction was vigorous, with a strong exotherm. More ether was added to dissolve the precipitate which formed, and the solution was added over a 10 min period to a solution of 10 g Va (0.0270 mole) in ether. The mixture was stirred for 1 hr and worked up as usual to give 7.32 g light brown liquid, of which 6.60 g were distilled at 0.01 mm in a molecular still at 85–89°. The yield of O,O-diethyl S-phenylethynyl phosphorodithioate was 4.92 g (0.0172 mole, 71% based on the amount distilled), n_D^{25} 1.592. (Found: C, 50.8; H, 5.5; P, 10.3; S, 22.7. Calc. for $C_{11}H_{13}O_2PS_2$: C, 50.4; H, 5.1; P, 10.8; S, 22.4%.)

O,O-Dimethyl S-1-propynyl phosphorodithioate

A solution of Vb (15.4 g, 0.0490 mole) in 50 ml ether was added to a suspension of 0.0663 mole lithium methylacetylide (prepared as above) in 150 ml ether. The mixture was stirred 1 hr and worked up as usual to give 5.59 g (0.0285 mole, 58%) O,O-dimethyl S-1-propynyl phosphorodithioate, b.p. 115–117° (2.3 mm), n_D^{25} 1.539. (Found: C, 30.7; H, 4.9; S, 32.5; P, 16.1. Calc. for $C_6H_9O_2PS_2$: C, 30.6; H, 4.6; S, 32.7; P, 15.8%.)

Reaction of lithium acetylide with Vc

A stream of acetylene was passed over an ice cooled solution of butyl lithium (0.069 mole) in 250 ml ether until reaction was complete. A solution of Vc (19.0 g, 0.0296 mole) in 150 ml ether was added and the mixture was refluxed 2 hr. and worked up as usual to give 6.8 g dark oil. This was chromatographed on Woelm neutral alumina (activity 1) to give 0.85 g yellow solid, m.p. 111–112°. Its analysis corresponded to that of bis(O,O-diphenyl phosphorodithionyl) acetylene (XII). (Found: C, 53.4; 53.3; H, 3.2, 3.2; P, 10.8, 10.9; S, 22.3, 22.0. Calc. for $C_{26}H_{40}O_4P_2S_4$: C, 53.3; H, 3.4; P, 10.6; S, 21.8%).

O,O-Diethyl S-1,2-dibromo-1-propenyl phosphorodithioate (XIVa)

To a solution of O,O-diethyl S-1-propynyl phosphorodithioate (4.0 g, 0.0178 mole) in 25 ml $CHCl_3$ was slowly added a solution of 2.86 g Br_2 (0.0178 mole) in 15 ml $CHCl_3$. After standing for $\frac{1}{2}$ hr, the solvent was evaporated to give 6.70 g deep red liquid, which was chromatographed on neutral alumina to give 3.71 g (0.0096 mole, 54%) light yellow liquid, n_D^{25} 1.562, whose IR spectrum was almost identical with that of the crude product. (Found: P, 8.3; S, 16.7. Calc. for $C_7H_{13}Br_2O_2PS_2$: P, 8.1; S, 16.7%).

O,O-Diethyl S-1,2-dichloro-1-propenyl phosphorodithioate (XIVb)

Chlorine (0.405 ml, 0.0895 mole) was condensed in a dry ice-acetone bath. The receiver was slowly warmed and the vapors passed into a solution of 2.0 g (0.0895 mole) O,O-diethyl S-1-propynyl phosphorodithioate in 20 ml CCl_4 cooled to -20° . After all the chlorine was added, the reaction mixture was warmed to room temp and the solvent evaporated to give 2.09 g dark red liquid, whose IR spectrum showed a strong band at 7.9μ . Chromatography on alumina gave 0.771 g (0.0262 mole, 29%) yellow liquid, whose IR spectrum showed a strong peak at 6.2μ , but no absorption at 4.6 or 7.9μ . The product darkened and finally set to a black tar on standing in the refrigerator for one week.