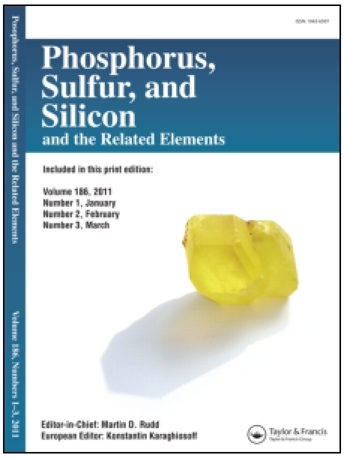

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CONCERNING THE MECHANISM OF THE FORMATION OF PHOSPHORANES FROM THE REACTION OF TRICOORDINATED PHOSPHORUS COMPOUNDS AND ALKYL BENZENESULFENATES

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CONCERNING THE MECHANISM OF THE FORMATION OF PHOSPHORANES FROM THE REACTION OF TRICOORDINATED PHOSPHORUS COMPOUNDS AND ALKYL BENZENESULFENATES

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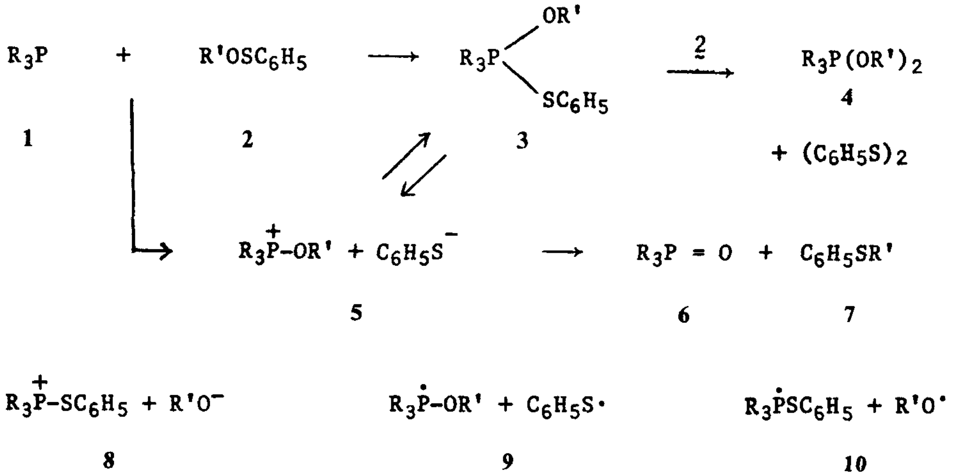
Trimethyl phosphite has been allowed to react with methyl benzenesulfenate, methyl *p*-methoxybenzenesulfenate, methyl *m*-trifluoromethylbenzenesulfenate and methyl *p*-nitrobenzenesulfenate. The first three esters react at virtually the same rate whereas the *p*-nitro compound is considerably less reactive. These data support a mechanism which involves direct insertion of phosphorus into the S—O bond with some donation of lone pairs on sulfur into an orbital on phosphorus in the transition state. Other experiments show that the reaction is irreversible. A dithioaryltrioxyphosphorane has been shown to decompose to a phosphite and a diaryl disulfide.

The reaction of trivalent phosphorus compounds with two moles of alkyl benzenesulfenates often leads to dialkoxy containing phosphoranes and diaryl disulfides.[1] In four cases it has been shown that a mixed thiooxyphosphorane, **3**,



is formed as an intermediate during the course of the reaction.[1b,c,2] It has been assumed that **3** then reacts with another mole of **2** to give the product **4** and diaryl disulfide. Just how this occurs has not been determined. The formation of **3** could occur in a number of ways, and in fact **3** may not be formed in those reactions which do not yield **4**. The other course of the reaction of **1** and **2** yields a phosphoryl compound **6** and an alkyl aryl sulfide. When this path is followed an ion pair, **5**, is implicated. Whether **3** is formed initially and then dissociates to **5** or whether **5** is formed directly from **1** and **2** has not been determined. Alternatively an ion pair **8** might be a precursor of **5** and **3**, as might the radical pairs **9** and **10**. No evidence has ever been found which suggests that **9** and **10** are formed. In particular the usual products of α and β-scission which are generally found from these reactions have not been observed in any system studied so far.[3]

Barton and co-workers[4] have investigated the nature of the reactions of ions **5** and **8** where R was *n*-butyl, R' was methyl and the benzyl group was substituted for phenyl. When tri-*n*-butylphosphine was allowed to react with methyl benzylsulfenate, the only products of the reaction were tri-*n*-butylphosphine oxide and methyl benzyl sulfide. The formation of **5** is clearly implicated. This concept received support from the following experiment; methylation of tributylphosphine oxide with trimethyloxonium fluoroborate followed by reaction with *t*-butyl thiolate yielded only tri-*n*-butylphosphine oxide and methyl *t*-butyl sulfide. This experiment demonstrates beyond doubt that the ions of **5** can react to give **6** and **7**.

Methylation of tri-*n*-butylphosphine sulfide with trimethyl oxonium fluoroborate followed by reaction with lithium benzyloxide yielded only tri-*n*-butyl-phosphine oxide and methyl benzyl sulfide. It was concluded that a pair of ions analogous to **8** was formed, but that they reacted to give **5** via **3**. These interesting results provide some insight into the nature of the reactions when $R = n - C_4H_9$.

The major goal of this work has been to study the formation of phosphoranes from the reactions of alkyl benzenesulfenates with phosphites and mixed alkoxy thiophosphites. The initial goal has been to try to decide between a direct insertion reaction as the means of forming **3** and the alternative ionic paths. The possibility that **1** and **2** form some sort of a complex prior to reaction cannot be discounted and no evidence concerning this point has been obtained.

During the course of developing the chemistry of phosphorane production from these reagents, several observations have been made which bear on the mechanism of the initial reaction. In the case of the reaction of trimethyl phosphite with methyl benzenesulfenate, it has been found that the highest yield of pentamethoxyphosphorane is achieved when the reaction is conducted in pentane at −78°C and when the concentration of the reagents is as high as possible.[5] In methylene chloride the yield of pentamethoxyphosphorane is substantially less. The fact that the reaction proceeds so smoothly in pentane at −78°C favors a nonionic process for the production of **3**. If **3** is formed directly and reaction with more **2** to give **4** is in competition with ionization to **5**, then the higher the concentration of **2** the lower the yield of **6** and **7**. On the other hand, if **5** is formed first and it then reacts to give **3**, a higher concentration of **2** will yield more **4** only if the equilibrium between **3** and **5** is set up more rapidly than the destruction of **5** to give **6** and **7**. This latter possibility certainly cannot be ignored.

If production of **5** is the rate controlling step, then varying the stability of ArS^- should have an affect on the rate of the production of **5** and on the rate of disappearance of **1**. It was the purpose of this study to investigate the reactions of various methyl arylsulfenates with trimethyl phosphite. Some other mechanistic work related to this reaction also is reported.

RESULTS AND DISCUSSION

Four methyl arylsulfenates have been prepared and allowed to react with trimethyl phosphite in toluene at −70°C. The sulfenates were phenyl, **11**, *p*-methoxyphenyl,

12, *m*-trifluoromethylphenyl, **13**, and *p*-nitrophenyl, **14**. The course of the reactions was followed by ^{31}P NMR spectroscopy. Compounds **11**, **12** and **13** reacted with trimethyl phosphite at essentially the same rate, i.e. ca. 70% of the trimethyl phosphite was consumed after 60 min. Interestingly only 10% of the trimethyl phosphite had reacted with **14** after 60 min. Ethyl 2,4-dinitrobenzenesulfenate did not react with triethyl phosphite at room temperature. One might expect the rates of production of the ion pairs **5** to follow the pKa's of the thiophenols. These are: *p*-methoxythiophenol, 9.76, phenylthiophenol, 9.32, and *p*-nitrothiophenol, 6.42.[6] The pKa of *m*-trifluoromethylthiophenol was calculated to be 8.07 using the Hammett equation with $\rho = +2.91$ and $\sigma_m = +0.43$.[7] Clearly the results of this study do not favor the production of **5** as the first product of the reaction of the methyl arylsulfenates with trimethyl phosphite. Parker and Kharasch[8] have studied the reactions of nitro-substituted diphenyl disulfides with a variety of nucleophiles. They found that the order of reactivity was 2,4-dinitrophenyl > *p*-nitrophenyl > *o*-nitrophenyl > phenyl. Their results support the contention that if **5** is formed in the rate determining step then the 2,4-dinitro compound should have been the most reactive.

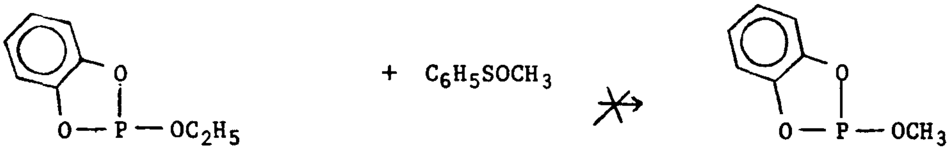
The relative reactivities of **11–14** might be construed as favoring the formation of **8**. In fact Brown and Hogg[9] have studied the reactions of *p*-substituted *o*-nitrobenzenesulfenyl bromides and chlorides with cyclohexane. They found for the bromides the following relative reactivity order: *p*-CH_3, 5; *p*-Cl, 4.5; H, 3.5, *p*-CF_3, 1.4 and *p*-nitro, 1. Except for the *p*-chloro the order is that predicted for nucleophilic displacement on sulfur and follows that found in this work.

The formation of **8** in pentane at −78°C seems very unlikely indeed. A more likely explanation involves direct insertion into the S—O bond. This process can certainly be subject to the availability of the electrons on sulphur, particularly if sulfur is acting as the donor and oxygen as the acceptor in the three-membered ring transition state. In such a transition state sulfur will take on a partial positive charge.

During the course of studying the reaction of methyl *m*-trifluoromethylbenzenesulfenate with trimethyl phosphite, a resonance at δ +3.65 was observed in the ^{31}P NMR spectrum. This absorption is assigned to the tetramethoxyphosphonium cation. For reference tetramethoxyphosphonium tetrafluoroborate absorbs at δ +1.95.[10]

The interpretation of the experiments outlined above requires that the reaction of trimethyl phosphite and the methyl arenesulfenates be irreversible. In order to demonstrate that this is the case, triethyl phosphite, in excess, was allowed to react with methyl benzenesulfenate and the reaction mixture was investigated for the presence of mixed methyl ethyl phosphites by ^{31}P NMR spectroscopy. Only one resonance was found at δ 138.9. The mixed phosphites absorb at δ +139.6, diethyl methyl phosphite, δ 140.4 dimethyl ethyl phosphite and δ +141.2, trimethyl phosphite.

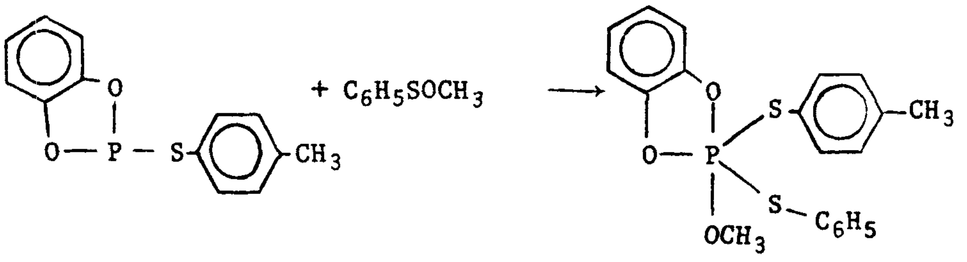
In another experiment, the phosphite, **15**, was allowed to react with an



15 **16**

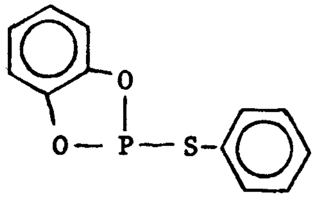
insufficient amount of methyl benzenesulfenate. After the reaction was completed, only one resonance in the phosphite region was present, δ 127.7. Addition of authentic methyl phosphite, **16**, which is a product of the reverse reaction, led to the appearance of a new resonance at δ 127.9. Both of these experiments argue that the initial reaction is irreversible.

In an attempt to prepare a phosphorane containing two arylthio groups, compound **17** was allowed to react with an equimolar amount of methyl benzenesulfenate.

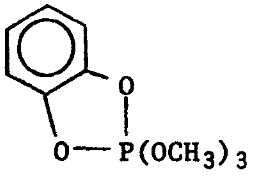


17 **18**

The products of this reaction were recovered, **17**, 6%, **19**, 5%, **16**, 52%, **20**, 11% and acyclic phosphates, 26%. There seems to be little doubt that **18** was formed



19



20

and that it lost the elements of phenyl *p*-tolyl disulfide rapidly to give **16** which reacted to a small extent with more methyl benzenesulfenate to give **20**. The presence of **19** might be construed as evidence for reversal of the formation of **18**. However it was found that **19** and di-*p*-tolyl disulfide react to give **17** and thus the formation of **19** can be accounted for without invoking a reversal of the formation of **18**.

The results reported support direct formation of **3** when **1** is a phosphite.

ACKNOWLEDGMENTS

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EXPERIMENTAL

All solvents were carefully dried and distilled before use. All reactions were carried out under an inert atmosphere of either nitrogen or argon. Mass spectra were measured on a Perkin-Elmer Hitachi RMU-7 spectrometer. ^1H NMR spectra were run on a Varian model T-60 spectrometer. All chemical shifts are reported relative to tetramethylsilane. ^{13}C and ^{31}P NMR spectra were run on a Varian model CFT-20 spectrometer, ^{31}P chemical shifts are reported relative to 85% phosphoric acid (external) and a positive sign indicates a shift which is downfield from the standard. ^{13}C chemical shifts are reported relative to tetramethylsilane. All spectra were obtained using a 30° flip angle, a repetition rate of 2 sec. and full proton decoupling. See Table I for NMR and analytical data.

Benzenesulphenyl Chloride

The general procedure used was that of Lecher *et al.*,[11] with some modifications described by Kharash *et al.*[12] The product was purified by distillation (bp 40–42°/0.25 mm) and obtained in a 96.5% yield.

3-Trifluoromethylphenylsulphenyl Chloride

3-Trifluoromethylthiophenol was converted, as above, into 3-trifluoromethylphenylsulphenyl chloride. The red liquid was purified by distillation; bp 31°/0.1 mm (yield 97%).

4-Methoxyphenylsulphenyl Chloride

4-Methoxythiophenol was converted, as above, into 4-methoxyphenylsulphenyl chloride. After removing the volatiles under reduced pressure at ambient temperature, the product was reacted with no further purification.

4-Nitrophenylsulphenyl Chloride

4-Nitrophenylthiophenol was converted, as above, into 4-nitrophenylsulphenyl chloride. After the volatiles were removed under reduced pressure, the product was used without further purification.

Methyl Benzenesulphenate (**11**)

Methyl benzenesulphenate, **11**, was prepared by the method of Langford and Kharash[13] as modified by Denney *et al.*[14] It was purified by distillation; bp 33°/0.25 mm (yield 91%). The ^1H and ^{13}C NMR spectra were identical to those reported.[14]

Methyl 4-methoxyphenylsulphenate (**12**)

The procedure was the same as that used in the preparation of **11**. The product, **12**, was obtained as a slightly yellow oil (bp 66°/0.1 mm) in a 75% yield.

Methyl 4-nitrophenylsulphenate (**14**)

The procedure was the same as that used in the preparation of **11**. The crude product was recrystallized from *n*-heptane to yield 17% of **14** (mp 45–46°).

Methyl 3-trifluoromethylphenylsulphenate (**13**)

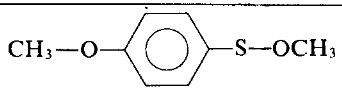
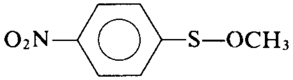
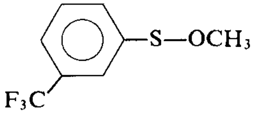
The procedure was the same as that used in the preparation of **11**. The product, **13**, was obtained as a yellow oil; bp 30°/0.1 mm (yield 86%).

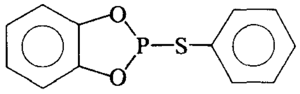
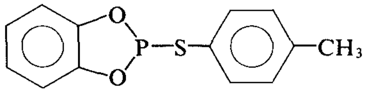
2-Phenylthio-1,3,2-benzodioxaphosphole (**19**)

To a stirred solution of 17.4 g (0.1 mol) of 2-chloro-1,3,2-benzodioxaphosphole in 100 ml of benzene, under nitrogen, was added a mixture of 11.0 g (0.1 mol) of thiophenol and 11.0 g (0.1 mol) of triethylamine in 25 ml of benzene. The reaction mixture was stirred for two hrs at r.t. The triethylamine hy-

TABLE I

NMR and Analytical Data

Compound	Analysis[a]				^{31}P[b]	^{1}H[b]		^{13}C[b]	
	Calcd.		Found						
	C	H	C	H					
 12	56.44	5.92	56.52	6.08		3.50 s 3.70 s 6.85 d(9) 7.45 d(9)	$\mathrm{SOC}\mathit{H}_3$ $\mathrm{OC}\mathit{H}_3$ $\mathrm{C}\mathit{H}$ $\mathrm{C}\mathit{H}$	55.3 64.0 114.5 129.0 133.5 160.9	$\mathrm{O}\mathit{C}\mathrm{H}_3$ $\mathrm{SO}\mathit{C}\mathrm{H}_3$ $\mathit{C}\mathrm{H}$ $\mathit{C}\mathrm{S}$ $\mathit{C}\mathrm{H}$ $\mathit{C}\mathrm{O}$
 14	45.40	3.81	45.33	3.67		3.80 s 7.65 m	$\mathrm{SOC}\mathit{H}_3$		
 13	46.15	3.39	46.16	3.46		3.78 s 7.40 m	$\mathrm{SOC}\mathit{H}_3$	67.9 119.4 q(3.8) 123.0 q(3.7) 124.2 q(272.6) 125.8 q(1.0) 129.7 131.9 q(32.8) 142.6	$\mathrm{SO}\mathit{C}\mathrm{H}_3$ $\mathit{C}\mathrm{H}$ $\mathit{C}\mathrm{H}$ $\mathit{C}\mathrm{F}_3$ $\mathit{C}\mathrm{H}$ $\mathit{C}\mathrm{H}$ $\mathit{C}\mathrm{CF}_3$ $\mathit{C}\mathrm{S}$

 19	58.06	3.65	57.64	3.70	209.1	7.40 m		113.4 d(0.7)	*C*H
								123.3	*C*H
								127.6 d(15.2)	*C*SP
								128.4 d(1.4)	*C*H
								129.3	*C*H
								135.2 d(4.9)	*C*H
								145.7 d(7.3)	*C*OP
 17					209.5	2.35 s	C*H*$_3$	20.9 s	*C*H$_3$
						7.25 m		113.2 d(0.7)	*C*H
								123.0 s	*C*H
								123.1 d(15.7)	*C*SP
								130.0 s	*C*H
								135.1 d(4.6)	*C*H
								138.5 d(1.5)	*C*H
								145.7 d(7.3)	*C*OP

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[a] In all cases a parent ion was found in the mass spectrum.

[b] The solvent is $CDCl_3$ and the temp. is 30°C. The number in parenthesis is the coupling constant in Hz.

drochloride was separated by forcing the solution through a sintered disk with nitrogen. After having removed the solvent by distillation at atm. pressure the residual oil was distilled (bp 130°/0.02 mm) to yield 7.0 g (28.2%) of **19**. This material solidified upon standing.

2-(4′-Methylphenylthio)-1,3,2-benzodioxaphosphole (**17**)

The same procedure as for the preparation of **19** was used except *p*-thiocresol was substituted for thiophenol. The product, **17**, was obtained as a colorless oil (bp 132–134°/0.01 mm) which solidified upon standing.

Reaction of Trimethyl Phosphite with Sulphenate Esters **11**, **12**, **13** *and* **14**

To a solution of 0.0774 g (0.6 mMol) of trimethyl phosphite in 1.0 ml of toluene-d_8 in an NMR tube, cooled to $-78°$ and under an atmosphere of argon, was added 1.2 mMol of the sulphenate ester dissolved in an equal amount of the same solvent. The NMR tube was capped and quickly transferred to the probe which had been precooled to $-70°$. This temp. was maintained during the course of the experiment. The progress of the reaction was monitored by observing the changes in the relative heights of the ^{31}P NMR absorptions.

Reaction of Triethyl Phosphite with Methyl Benzenesulphenate

Triethyl phosphite, 1.66 g (10 mMol), was allowed to react with 0.7 g (5 mMol) of methyl benzenesulphenate in 2 ml of toluene-d_8 at $-78°$. This mixture was allowed to come to room temp. slowly. The ^{31}P NMR spectrum had absorptions at δ -67.1, $+0.3$ and at $+138.9$.

Reaction of 2-Ethoxy-1,3,2-benzodioxaphosphole (**15**) *with Methyl Benzenesulphenate*

A mixture of 1.84 g (10 mMol) of **15** and 1.4 g (10 mMol) of methyl benzenesulphenate in 3.0 ml of toluene-d_8 was allowed to stand at r.t. for two months. The ^{31}P NMR spectrum was monitored over this period of time. The only downfield absorption ever seen was at δ 127.7.

Reaction of 2-(4′-Methylphenylthio)-1,3,2-benzodioxaphosphole (**17**) *with Methyl Benzenesulphenate*

To a stirred solution of 1.3 g (5 mMol) of phosphite **17** in 3 ml of pentane, at 10° and under an atmosphere of nitrogen, was added 0.7 g (5 mMol) of methyl benzenesulphenate in 2 ml of pentane. This mixture was allowed to stand for 3 days at rt. The ^{31}P NMR spectrum showed absorptions at δ -47.6 (11%), -2.8 (26%), $+127.0$ (52%), $+209.1$ (5%) and $+209.5$ (6%).

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