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Reaction of Thioxophosphorane Sulfenyl Bromides with Ethyl Vinyl Ether: Mechanistic and Synthetic Aspects

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ABSTRACT

The mechanistic and synthetic aspects of the addition reaction of thioxophosphorane sulfenyl bromide with ethyl vinyl ether were studied in detail by NMR techniques. It has been found that the regiospecific, primary product of the reaction, 1-bromo-1-ethoxy-2S(dialkoxythiophosphoryl)ethane I, is unstable and undergoes slow decomposition to give four compounds. The formation of thiophosphoryl derivatives, vinyl ethers II and III, aldehyde IV, and the symmetrical hemiacetal anhydride V, has been considered in terms of a carbocation intermediate. By choice of the appropriate reaction conditions, the aldehyde IV can be obtained in very high yield.

INTRODUCTION

Derivatives of organo thio and dithiophosphates play an important role in pure and applied chemistry [1, 2, 3, 4]. Significant precursors of this class of compounds are pseudohalogens containing electrophilic centers at dicordinate sulfur attached to a good leaving group: e.g., $(RO)_2P(O)SX$, $(RO)_2P(S)SX$, (X=Br, Cl, OR',NR'_2, $(RO)_2P(O)S$, $(RO)_2P(S)S$) [5].

Recently, such compounds became interesting models for mechanistic studies [6]. Special attention was paid to electrophilic addition of thioxophosphorane sulfenyl halides to unsaturated systems. Addition of oxophosphorane sulfenyl chlorides to enol ethers and esters was first described by Michalski and Musierowicz [7]. Most recently, a similar reaction with enol silyl ethers was employed by Skowronska and Dybowski in a new strategy for Z-olefin synthesis [8].

In the present work, which is a part of our systematic studies, we wish to report the electrophilic addition of thioxophosphorane sulfenyl bromides to ethyl vinyl ether. The simple alkyl\aryl sulfenyl chlorides react with vinyl ethers to form the Markovnikoff adduct. As shown by Toyishima and coworkers [9], the unsaturated ethers undergo an electrophilic attack that results in the formation of regiospecific but nonstereospecific products. This is explained by the formation of a carbocation intermediate. There are no similar detailed studies on the reactivity of more complex sulfenyl halides such as oxo and/or thioxo sulfenyl halides.

RESULTS AND DISCUSSION

The thioxophosphorane sulfenyl bromides react with ethyl vinyl ether giving adduct I in quantitative yield. The primary product of the addition reaction was found to be unstable, and it underwent slow decomposition to form four species (II–V). The distribution of secondary products strongly depends on the reaction conditions. In the rigorous absence of moisture, the formation of products II and III was observed, whereas the presence of traces of water favored the formation of a more complex mixture, which contained four products. The decomposition pathway was monitored by ^{31}P NMR spectroscopy and the instability of adduct I considerably differentiates the class of compounds under discussion

*To whom correspondence should be addressed.
Dedicated to Professor Leopold Horner on the occasion of his eightieth birthday.

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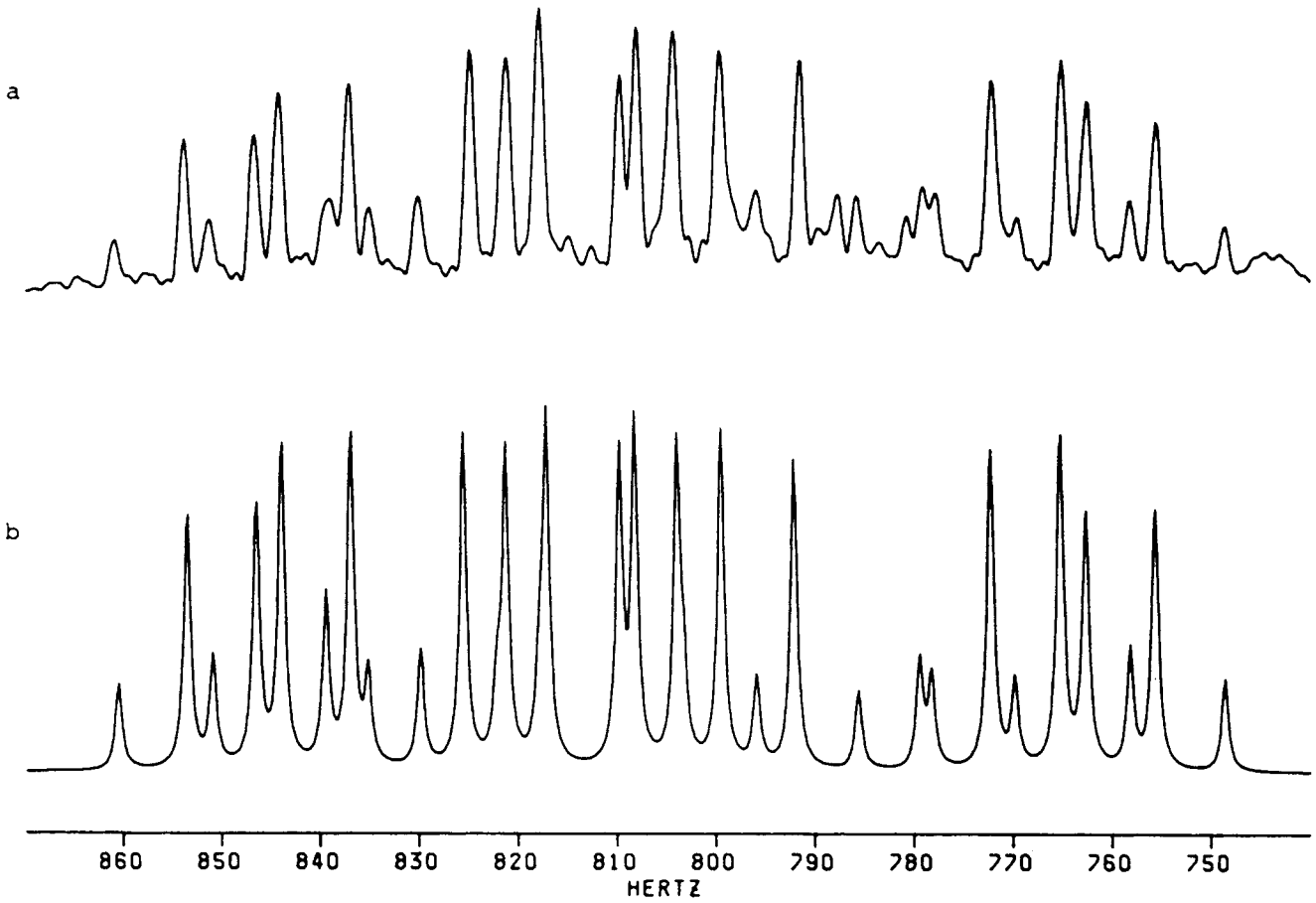


FIGURE 1 (a) Experimental and (b) simulated spectra of SCH_2 and OCH_2 fragments of 1-bromo-1-ethoxy-2-S(diisopropoxythiophosphoryl)ethane I. The spectrum was simulated using a commercially available PANIC program on an Aspect 3000 computer.

from those reported by Toyishima and colleagues [9].

The crucial prerequisite for understanding the formation of the secondary products II–V is the structure of the primary product I. Note that, for this case, both linear Markovnikoff and anti-Markovnikoff adducts and/or 1,3,2-dithioxophospholane could be considered as primary products of reaction. Since the hypothetical structures should reveal dramatically different spectral features, in particular proton-phosphorus scalar couplings and chemical shifts, the NMR technique was found to be the method of choice for this work.

Shown in Figure 1a is the 200.13 ^1H NMR spectrum of adduct Ia in the region of methylene groups. Due to the overlapping effect of magnetically nonequivalent protons for both S—CH_2 and O—CH_2 groups, the structure of adduct I could not be unambigously assigned. Therefore, we decided to employ more advanced NMR techniques. In order to ascertain the scalar connectivities and coupling constants, two dimensional phase sensitive and time proportional phase increment (TPPI) experiments have been performed [10]. The most important feature of the cross-peaks in phase sensitive COSY spectra is the splitting that corresponds to the coupling between a pair of spins giving rise to the cross-peak that appears in antiphase along both frequency axes (active coupling), whereas any coupling to side spins appears as additional phase splitting along the appropriate frequency axis (passive coupling).

Figure 2 displays the phase sensitive pure absorption COSY spectrum of adduct I that was monitored in a mixture of solvents (chloroform-d; benzene-d6, v\v 1:1) in order to separate the overlapped multiplets. The cross-peak analysis revealed the connectivities between signals observed at δ= 4.1 and δ = 6.0 corresponding to the S—CH_2—CH— backbone, and the signals at δ = 4.3 and 3.9 originated from diastereotopic O—CH_2 protons of the ethoxy residue. The coupling constants were estimated from phase sign analysis of the individual resonances for appropriate expanded off-diagonals as shown in Figure 3. In particular, this method was found to be invaluable for assignment of the geminal proton–proton coupling constants of the anisochronous SCH_2 and OCH_2 protons. It has been

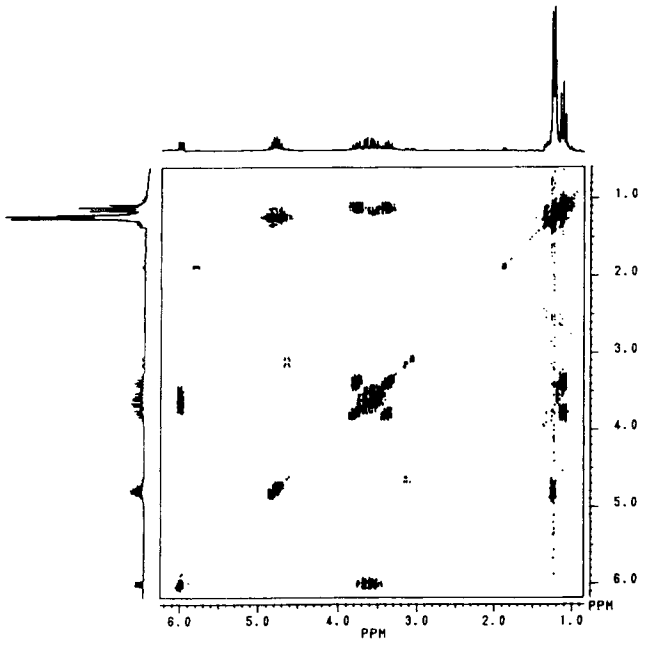
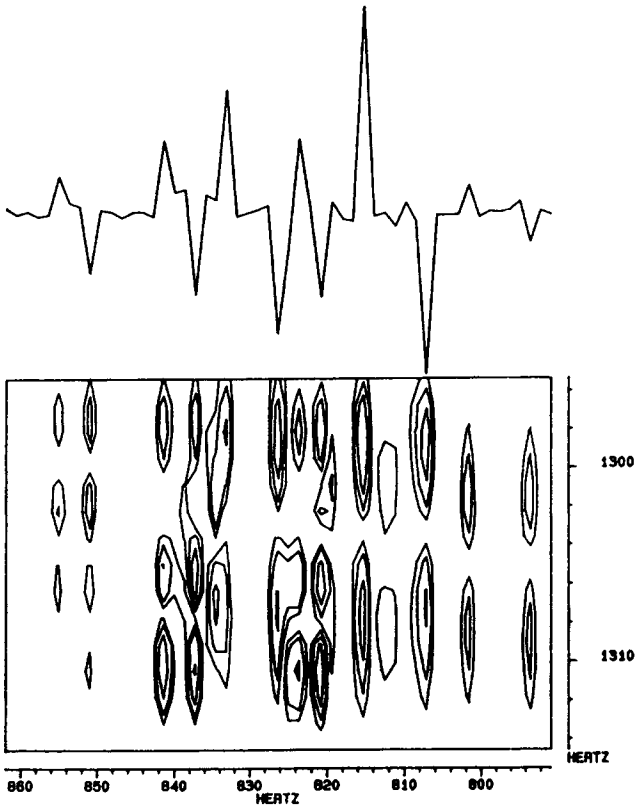


FIGURE 2 The negative contours of two dimensional 200 MHz ^1H—^1H phase sensitive TPPI spectrum of 1-bromo-1-ethoxy-2-S(diisopropoxythiophosphoryl)ethane I. The spectrum was recorded with a spectral width of 1404 Hz in ω_1 and ω_2, 1024 points in t_2 and 512 t_1 increments, zero-filled to 2K–2Kmatrix before Fourier transform.

established from phase sensitive COSY experiments that diastereotopic CH_2 protons attached to sulfur atom are separated by $\Delta\delta$ = 0.1, and the signals were found to be at δ = 4.15 and 4.05. They are coupled with the phosphorus atom, the vicinal coupling constant $^3J_{PH}$ is equal to 18.2 Hz. Those couplings to the adjacent methine proton are equal to $^3J_{HH}$ = 3.2 and 8.4 Hz. The geminal coupling constant was found to be $^2J_{HH}$ = 14.1 Hz. The SCH_2 signals are flanked by O—CH_2 resonances of both protons which are separated by $\Delta\delta$ = 0.4 ppm in the solvent mixtures employed. The appropriate proton–proton vicinal and geminal coupling constants were found to be 7.2 and 9.7 Hz, respectively. Since, as reported elsewhere [11], the phase sensitive COSY spectra demonstrate a larger line separation than the true separation for antiphase lines and a smaller one for in-phase lines, the accuracy of coupling constants had to be verified. Figure 1b shows the simulated spectrum of the S—CH_2 and O—CH_2 region. It has been unambiguously concluded from these NMR data that a linear Markovnikoff adduct is formed as the primary product of the addition reaction.

The structures of the secondary products of the reaction, which were established by NMR techniques, are shown in Scheme 1.

It should be emphasized that by choice of appropriate reaction conditions this reaction can be



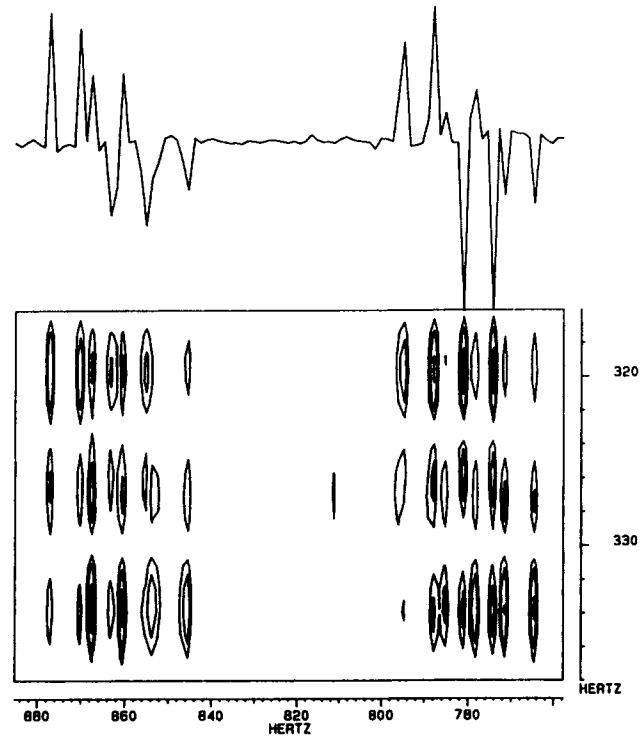
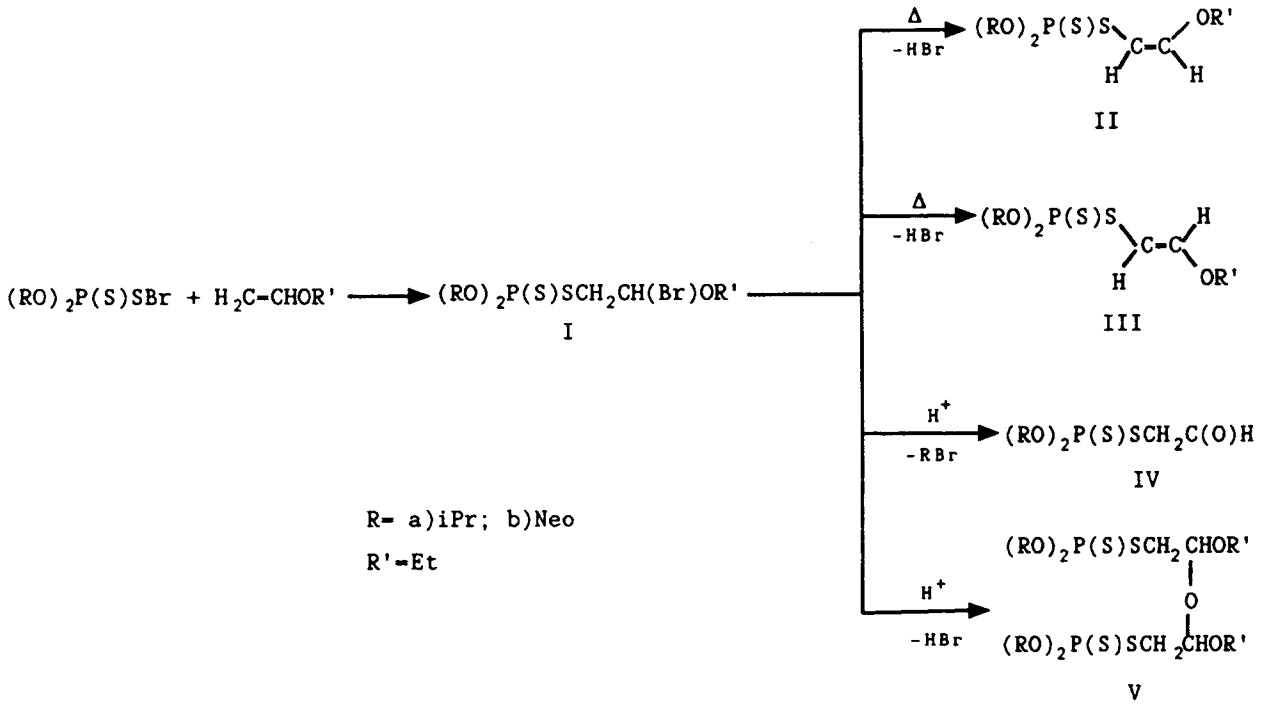


FIGURE 3 Expanded positive and negative cross peaks from Figure 2(**a**) S—Ch_2 resonances and (**b**) O—CH_2 resonances of ethoxy group. The upper cross-section projections show the sign of the appropriate signals.

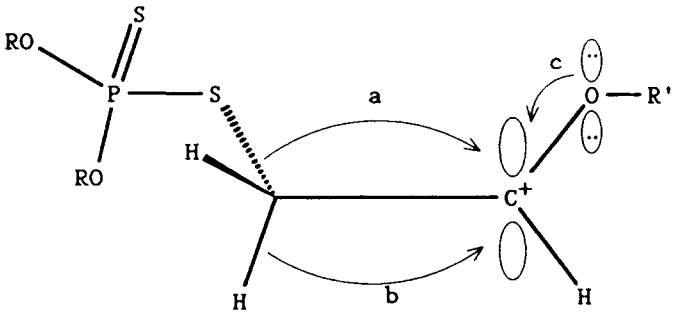


SCHEME 1

driven to give a single product. With a catalytic amount of dilute hydrochloric acid, the hemiacetal anhydride V is formed in a yield of 80%. In the presence of 2N HCl dialkoxythiophosphoryl-S-acetaldehyde IV is obtained in 90% yield. Hence, the decomposition of the adduct I can be considered as a simple, highly efficient method of synthesis of products IV and/or V. The hemiacetal anhydride V was found to be unstable, and, in acidic environment, further decomposed to the aldehyde IV. The vinyl isomers II and III were distilled and separated by chromatography from the crude mixture obtained via decomposition of I in the absence of moisture.

The instability of adducts I, compared to their structural analogs obtained in the reaction of alkyl\aryl sulfenyl halides with vinyl ethers, can be thought of as a unique feature of dithiophosphate derivatives. It seems most likely that the products of decomposition are formed via a carbocationic intermediate, as shown in Scheme 2.

The paths a and b in Scheme 2 lead to vinyl isomers (II and III), whereas path c in Scheme 2 leads to formation of thiophosphoryl aceticaldehyde IV. The absence in the mixture of products of an anti-Markovnikoff addition, which would be obtained by direct attack of sulfur on carbon and cyclic rearrangement, does not provide evidence against the existence of a carbocationic intermediate. It can only be concluded from these results that spontaneous elimination of hydrogen bromide and\or dealkylation are kinetically and thermodynamically



SCHEME 2

favorable processes compared with a thiophosphoryl group migration that requires the breaking of a sulfur-carbon bond.

CONCLUSION

From the proposed reaction pathway, it can be speculated that a carbocation intermediate plays an important role in the distribution of the secondary products of the reaction. Three main factors seem to be responsible for the formation of a carbocation intermediate. First, the higher electronegativity of the thiophosphoryl residue compared to alkyl\aryl substituents can contribute significantly to the decomposition of adduct I. Second, the adjacent thiono sulfur in the neighboring-group mechanism may facilitate the leaving of a bromide ion. Third, the weak C—Br bond is more suscep-

tible for breaking than an analogous C—Cl bond. Finally, the synthetic use of the addition reaction should be stressed. In a strongly acidic environment, the dialkoxythiophosphoryl S-acetaldehydes IV can be obtained in a one-pot reaction in excellent yield.

EXPERIMENTAL

NMR spectra were recorded using a Bruker MSL 300 and Bruker AC 200 spectrometer equipped with multinuclear and QNP probeheads, respectively. ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane as external standard, and the ^{31}P chemical shifts were measured relative to 85% phosphoric acid as external standard. Mass spectra were determined with an LKB mass spectrometer at an ionizing voltage of 15 and 70 eV. The ethyl vinyl ether was purchased from Fluka and used without further purification. The thioxophosphorane sulfenyl halides were prepared by direct bromination of the suitable disulfides according to our procedure described elsewhere [12].

1-Brom-1-Ethoxy-2S(Dialkoxythiophosphoryl) Ethane I

The freshly prepared thioxaphosphorane sulfenyl bromide (0.02 m) in 10 cm^3 of dry dichloromethane was added slowly to a solution of 2.9 g(0.04 m) of ethyl vinyl ether at a temperature of −10 °C. After the mixture had been stirred for 1 h at −10 °C and for a further 30 min at room temperature, the yellow-red color disappeared. The reaction was monitored by ^{31}P NMR spectroscopy and showed that product I was obtained with quantitative yield. The excess of the ethyl vinyl ether was removed under reduced pressure at −5 °C. Then, 100 mg of residual yellow oil was dissolved in a mixture of benzene(d6)-chloroform(d) and taken for NMR studies. Ia; 200 MHz ^1H NMR, δ = 1.15 [t CH_3—], δ = 1.42[d $(CH_3)_2CH$—, $^3J_{HH}$ = 6.2/Hz], δ = 1.44 [d$(CH_3)_2CH$—, $^3J_{HH}$ = 6.2 Hz], δ = 4.88[n=CH— $^3J_{HP}$ = 12.3 Hz], δ = 4.05 [q S—CH_2—$^2J_{HH}$ = 14.1 Hz, $^3J_{HP}$ = 18.2 Hz], δ = 4.15 [q S—CH_2—, $^2J_{HH}$ = 14.1 Hz, $^3J_{HP}$ = 18.2 Hz] δ = 3.85 [o O—CH_2— $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 7.2 Hz], δ= 4.25 [o O—CH_2—], δ = 6.01 [dd —CHBr,$^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 8.1 Hz]; 50.32MHz ^{13}C NMR, δ = 14.8 [(CH_3—) δ = 23.2[$(CH_3)_2CH$—,$^3J_{CP}$ = 4.8 Hz], δ = 23.8 [$(CH_3)_2CH$—$^3J_{CP}$ = 4.8 Hz], δ = 42.3 [S—CH_2—,$^2J_{CP}$ = 3.2 Hz], δ = 61.3 [O—CH_2—,$^2J_{CP}$ = 4.2 Hz] δ = 74.9 [—CH—,$^2J_{CP}$ = 6.42 Hz], δ = 91.8 [—CHBr—$^3J_{CP}$ = 5.8 Hz]; 80.96 MHz ^{31}P NMR δ = 90.6.

Ib; 200 MHz ^1H NMR, δ = 0.99 [s $(CH_3)_3C$—], δ = 1.15[t CH_3—], δ = 3.73 [—CH_2—, $^2J_{HP}$ = 6.8Hz;], δ = 4.05 [q S—CH_2— $^2J_{HH}$ = 14.1 Hz,$^3J_{HP}$ = 18.2 Hz], δ = 4.15 [q S—CH_2—,$^2J_{HH}$ = 14.1 Hz, $^3J_{HP}$ = 18.2 Hz], δ= 3.85 [o O—CH_2— $^2J_{HH}$ = 9.7 Hz,$^3J_{HH}$ = 7.2 Hz], δ = 4.25 [o O—CH_2—], δ= 6.01 [dd —CHBr, $^3J_{HH}$ = 3.2 Hz,$^3J_{HH}$ = 8.1 Hz]; 50.32 MHz ^{13}C NMR, δ = 14.8[(CH_3—)], δ = 26.3 [$(CH_3)_3C$—], δ = 32.1 [—C— $^3J_{CP}$ = 9.64 Hz], δ = 42.3 [S—CH_2—,$^2J_{CP}$ = 3.2 Hz], δ = 61.3 [O—CH_2—,$^2J_{CP}$ = 4.2 Hz], δ = 77.7 [—$CH_2$$^2J_{CP}$ = 6.42 Hz], δ = 91.8 [—CHBr—$^3J_{CP}$ = 5.8 Hz]; 80.96 MHz ^{31}P NMR δ = 94.2.

1-Ethoxy-2S(Dialkoxythiophosphoryl) Ethene II and III

The 1-brom-1-ethoxy-2S(dialkoxythiophosphoryl)-ethane I (ca 1 g) was dissolved in 30 cm^3 of dichloromethane and was kept at room temperature for one week. After completion of the decomposition, the solvent was removed, and the residual mixture was distilled under reduced pressure, bp-87,90 °C/0.15 mmHg. The crude mixture contained 60% of vinyl products. *Cis* and *trans* isomers were separated by chromatography on silica gel (benzene-carbon tetrachloride 1:1) IIa; 200 MHz ^1H NMR, δ= 1.15 [t CH_3—], δ = 1.42 [d $(CH_3)_2CH$—$^3J_{HH}$ = 6.2 Hz], δ = 1.44 [d $(CH_3)_2CH$—,$^3J_{HH}$ = 6.2 Hz], δ = 3.85 [q O—CH_2—$^3J_{HH}$ = 7.2 Hz], δ = 4.88 [n =CH—$^3J_{HP}$ = 12.3 Hz], δ = 4.93 [dd S—CH=$^3J_{HH}$ = 5.3 Hz, $^3J_{HP}$ = 5.4 Hz], δ =6.31 [dd =CH—OR, $^4J_{HP}$ = 3.1 Hz]; 50.32 MHz ^{13}CNMR, δ = 14.5 [(CH_3—)], δ = 23.2 [$(CH_3)_2CH$—$^3J_{CP}$ = 4.8 Hz], δ = 23.8 [$(CH_3)_2CH$—$^3J_{CP}$ = 4.8 Hz], δ = 61.3 [O—CH_2—$^2J_{CP}$ = 4.2 Hz], δ = 74.9 [—CH—$^2J_{CP}$ = 6.4 Hz] δ = 89.5 [S—CH=$^2J_{CP}$ = 8.3 Hz], δ = 149.8 [=CHOR—$^3J_{CP}$ = 10.2 Hz]; 80.96 MHz ^{31}P NMR δ = 87.0.

IIb; 200 MHz ^1H NMR, δ = 0.99 [s $(CH_3)_3C$—], δ = 1.15[t CH_3—] δ = 3.73 [—CH_2— $^3J_{HP}$ = 6.8Hz;], δ = 3.88 [—CH_2— $^3J_{HP}$ = 6.4 Hz;], δ= 4.15 [q O—CH_2— $^3J_{HH}$ = 7.2 Hz], δ = 4.93[dd S—CH= $^3J_{HH}$ = 5.3 Hz, $^3J_{HP}$ = 5.4 Hz], δ = 6.31 [dd =CH—OR $^4J_{HP}$ = 3.1 Hz];50.32 MHz ^{13}C NMR, δ = 14.3 [(CH_3—)], δ = 26.3[$(CH_3)_3C$—], δ = 32.1 [—C— $^3J_{CP}$ = 9.6Hz], δ = 61.3 [O—CH_2— $^2J_{CP}$ = 4.2 Hz], δ= 77.7 [—CH_2— $^2J_{CP}$ = 6.4 Hz], δ = 89.5[S—CH= $^2J_{CP}$ = 8.3 Hz], δ = 149.8 [=CHOR$^3J_{CP}$ = 10.2 Hz]; 80.96 MHz ^{31}P NMR δ = 90.7; m/e = 340, Anal.: Found; C, 49.21; H, 8.72; P, 9.61; S, 17.98; calcd C,49.41; H, 8.53; P, 9.12; S, 18.82.

IIIa 200 MHz ^1H NMR, δ = 1.15 [t CH_3—], δ = 1.42 [d$(CH_3)_2CH$— $^3J_{HH}$ = 6.2 Hz], δ = 1.44 [d$(CH_3)_2CH$— $^3J_{HH}$ = 6.2 Hz], δ = 3.85 [q O—CH_2— $^3J_{HH}$ = 7.2 Hz], δ = 4.88 [n =CH—$^3J_{HP}$ = 12.3 Hz], δ = 6.63 [dd S—CH=$^3J_{HH}$ = 12.4 Hz, $^3J_{HP}$ = 9.3 Hz], δ= 5.06 [dd =CH—OR $^4J_{HP}$ = 3.1 Hz]; 50.32 MHz^{13}C NMR, δ = 14.6 [(CH_3—)], δ = 23.2 [$(CH_3)_2CH$—$^3J_{CP}$ = 4.8 Hz], δ = 23.8 [$(CH_3)_2CH$—$^3J_{CP}$ = 4.8 Hz], δ = 61.3 [O—CH_2—$^2J_{CP}$ = 4.2 Hz], δ = 74.90 [—CH—$^2J_{CP}$ = 6.4 Hz], δ = 157.5 [S—CH=$^2J_{CP}$ = 9.3 Hz], δ = 91.8 [=CHOR,$^3J_{CP}$ = 6.5 Hz]; 80.96 MHz ^{31}P NMR δ = 89.4.

IIIb 200 MHz ^1H NMR, δ = 0.99 [s $(CH_3)_3C$—], δ = 1.15[t CH_3—], δ = 3.73 [—CH_2— $^3J_{HP}$ = 6.7Hz],

δ = 3.88 [—CH_2— $^3J_{HP}$ = 6.4 Hz], δ= 4.05 [q O—CH_2— $^3J_{HH}$ = 7.2 Hz], δ = 6.63[dd S—CH=, $^3J_{HH}$ = 12.4 Hz, $^3J_{HP}$ =9.3 Hz], δ = 5.06 [dd =CH—OR, $^4J_{HP}$ = 3.1Hz]; 50.32 MHz ^{13}C NMR, δ = 14.5 [(CH_3—)], δ = 26.3[$(CH_3)_3$C—], δ = 32.1 [—C— $^3J_{CP}$ = 9.6Hz], δ = 61.3 [O—CH_2—, $^2J_{CP}$ = 4.2 Hz], δ= 77.7 [—CH_2— $^2J_{CP}$ = 6.4 Hz], [S—CH=$^2J_{CP}$ = 9.3 Hz], δ = 91.8 [=CHOR$^3J_{CP}$ = 6.5 Hz]; 80.96 MHz ^{31}P NMR δ = 91.9,m/e = 340. Anal.: Found; C, 48.90; H, 8.48; S, 17.98; Calcd C, 49.41; H,8.53; S, 18.82.

bis(*Dialkoxythiophosphoryl*) *-S-Hemiacetal Anhydride V*

The thioxophosphorane sulfenyl bromide (0.02 m) in 10 cm^3 of drydichloromethane was added slowly to a solution of 2.9 q (0.04 m) of ethyl vinyl ether at −10 °C. After the mixture had been stirred for 1 h at −10 °C and for a further 30 min at room temperature, the yellow-red color disappeared. Then 10 cm^3 of acetone containing 0.2 cm^3 of 0.1 N hydrochloric acid was added. The mixture was stirred for 30 min at ambient temperature, then dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residual oil containing 85% of V and 15% of IV was subjected to NMR studies without further purification.

Va 200 MHz ^{1}H NMR, δ = 1.15 [t CH_3—], δ = 1.42 [d$(CH_3)_2$CH— $^3J_{HH}$ = 6.2 Hz], δ = 1.44 [d$(CH_3)_2$CH— $^3J_{HH}$ = 6.2 Hz], δ = 2.98 [dd S—CH_2 $^3J_{HH}$ = 5.6 Hz, $^3J_{HP}$ = 15.4 Hz],δ = 3.85 [q O—CH_2— $^3J_{HH}$ = 7.2 Hz], δ =4.55 [CH—OR], δ = 4.88 [n =CH— $^3J_{HP}$ = 12.3Hz]; 50.32 MHz ^{13}C NMR, δ = 14.5 [(CH_3—)], δ = 23.2[$(CH_3)_2$CH— $^3J_{CP}$ = 4.8 Hz], δ = 23.8[$(CH_3)_2$CH— $^3J_{CP}$ = 4.8 Hz], δ = 74.9 [—CH— $^2J_{CP}$ = 6.4 Hz], δ = 36.9 [S—$CH_2{}^2J_{CP}$ = 3.6 Hz], δ = 61.3 [O—CH_2—$^2J_{CP}$ = 4.2 Hz], δ = 102.0 [—CHOR$^3J_{CP}$ = 5.8 Hz]; 80.96 MHz ^{31}P NMR δ = 92.3.

Vb 200 MHz ^{1}H NMR, δ = 0.99 [s $(CH_3)_3$C—], δ = 1.15[t CH_3—], δ = 3.73 [—CH_2— $^3J_{HP}$ = 6.8Hz], δ = 2.98 [dd S—CH_2 $^3J_{HH}$ = 5.6 Hz,$^3J_{HP}$ = 15.4 Hz], δ = 3.88 [—CH_2—$^3J_{HP}$ = 6.4 Hz], δ = 4.05 [q O—CH_2—$^3J_{HH}$ = 7.2 Hz], δ = 4.55 [CH—OR]; 50.32 MHz^{13}C NMR, δ = 14.8 [(CH_3—)], δ = 26.3 [$(CH_3)_3$C—], δ = 32.1 [—C—, $^3J_{CP}$ = 9.6 Hz], δ =61.3 [O—CH_2— $^2J_{CP}$ = 4.2 Hz] δ = 77.7 [—CH_2— $^2J_{CP}$ = 6.4 Hz], δ = 36.9 [S—$CH_2{}^2J_{CP}$ = 3.6 Hz], δ = 102.0 [—CHOR$^3J_{CP}$ = 5.8 Hz]; 80.96 MHz ^{31}P NMR δ = 95.8.

Dialkoxythiophosphoryl-S-Acetaldehyde IV

One-Pot Synthesis. The freshly prepared thioxophosphoranesulfenyl bromide (0.04 m) in 20 cm^3 of dry dichloromethane was added slowly to a solution of 5.8 g (0.08 m) of ethyl vinyl ether at a temperature of −10 °C. After the mixture had been stirred for 1 h at −10 °C and for a further 30 min at room temperature, the yellow-red color disappeared. The excess of ethyl vinyl ether was removed under reduced pressure at −5 °C. The residual crude oil (I) was dissolved in 30 cm^3 of acetone, and 2 cm^3 of 3N hydrochloric acid was added. The mixture was stirred at room temperature for over 30 min. The acetone was removed under reduced pressure. The residue was treated with chloroform, the organic phase was dried over $MgSO_4$ and the filtrate concentrated by rotary evaporation. The yield was determined by ^{31}P NMR spectroscopy and found to be 95%. The product obtained was distilled under reduced pressure (bp 70–72 °C/0.15 mmHg) giving IV in 90% yield.

Synthesis via Hemiacetal Anhydride V. The 1 g of crude oil of V was dissolved in 30 cm^3 of acetone, and 2 cm^3 of 3N hydrochloric acid was added. The mixture was stirred at room temperature for over 30 min. The acetone was removed under reduced pressure. The residue was treated with chloroform, and the organic phase was dried over $MgSO_4$, then the filtrate was concentrated by rotary evaporation. The product obtained was distilled under reduced pressure (bp 70–72 °C/0.15 mmHg) giving 90% yield.

IVa; 200 MHz ^{1}H NMR, δ = 1.42 [d $(CH_3)_2$CH—$^3J_{HH}$ = 6.2 Hz], δ = 1.44 [d $(CH_3)_2$CH—$^3J_{HH}$ = 6.2 Hz], δ = 3.52 [dd S—$CH_2{}^3J_{HH}$ = 2.2 Hz, $^3J_{HP}$ = 19.5 Hz], δ= 4.88 [n =CH— $^3J_{HP}$ = 12.3 Hz], δ = 9.56[t CH(O)]; 50.32 MHz ^{13}C NMR, δ = 23.2 [$(CH_3)_2$CH—$^3J_{CP}$ = 4.8 Hz], δ = 23.8 [$(CH_3)_2$CH—$^3J_{CP}$ = 4.8 Hz], δ = 74.9 [—CH—$^2J_{CP}$ = 6.4 Hz], δ = 42.7 [S—$CH_2{}^2J_{CP}$ = 3.6 Hz], δ = 193.5 [—CH(O)$^3J_{CP}$ = 3.3 Hz]; 80.96 MHz ^{31}P NMR δ = 90.0.

IVb; 200 MHz ^{2}H NMR, δ = 0.99 [s $(CH_3)_3$C—], δ = 3.52[dd S—CH_2, $^3J_{HH}$ = 2.2 Hz, $^3J_{HP}$ =19.5 Hz], δ = 3.73 [—CH_2— $^3J_{HP}$ = 6.8 Hz],δ = 3.88 [—CH_2— $^3J_{HP}$ = 6.4 Hz], δ = 9.56[t CH(O)]; 50.32 MHz ^{13}C NMR, δ = 26.3 [$(CH_3)_3$C—], δ= 32.1 [—C— $^3J_{CP}$ = 9.6 Hz], δ = 77.7 [—CH_2— $^2J_{CP}$ = 6.4 Hz], δ = 42.7 [S—$CH_2{}^2J_{CP}$ = 3.6 Hz], δ = 193.5 [—CH(O),$^3J_{CP}$ = 3.3 Hz]; 80.96 MHz ^{31}P NMR δ = 93.7,m/e = 313, 314, 315.

REFERENCES

[1] C. Fest, K. J. Schmidt, *The Chemistry of Organophosphorus Pesticides*, 2nd ed., Springer, Berlin, New York,1982.

[2] M. Eto, Organophosphorus Pesticides; *Organic and Biological Chemistry*, CRC Press, Inc., Cleveland, 1974.

[3] P. H. Molyneux: Chap. 3, E. R. Braithwaite (ed): in *Lubrication and Lubricants*, Elsevier, Amsterdam (1967).

[4] D. E. C. Corbridge, *Phosphorus, An Outline of its-Chemistry, Biochemistry and Technology*, 3rd ed., Elsevier, Amsterdam, 1985.

[5] J. Michalski, A. Skowrońska, A. Łopusinski, *Phosphorus and Sulfur, 58*, 1991, 61.

[6] A. Łopusinski, J. Michalski, M. Potrzebowski, *J. Chem. Soc. Chem. Commun.*, 1982, 1362.
[7] J. Michalski, S. Musierowicz, *Chem. and Industry*, 1959, 565.
[8] P. Dybowski, A. Skowrońska, *Synthesis*, *7*, 1990, 609.
[9] K. Toyishima, T. Okuyama, T. Fueno, *J. Org. Chem.*, *43*, 1978, 2789.
[10] G. Bodenhausen, H. Kogler, R. R. Ernst, *J. Magn. Res. 50*, 1984, 370.
[11] D. Neuhaus, G. Wagner, M. Vasak, J. H. R. Kagi, K. Wutrich, *Eur. J. Biochem.*, *151*, 1987, 257.
[12] A. Łopusinski, M. Potrzebowski, *Phosphorus and Sulfur*, *32*, 1987, 55.