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CYCLIC ORGANOPHOSPHORUS COMPOUNDS—IV*

REACTIONS OF THIONYL CHLORIDE WITH CYCLIC AND OPEN-CHAIN HYDROGEN PHOSPHITES

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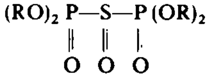
Abstract—Cyclic and open-chain hydrogen phosphites react with thionyl chloride in benzene solution at 35–40°. In addition to the corresponding thiopyrophosphates (symmetrical—in the case of cyclic hydrogen phosphites) a complex mixture of one and two P atom-containing products was produced. Evidence bearing on the mechanism of the reaction, particularly concerning the site of the initial attack and the origin of thiopyrophosphates, is discussed. Previous reports on the course of related reactions are inadequate.

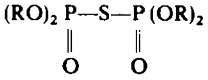
INTRODUCTION

THE reactions of thionyl chloride with dialkyl phosphites and their cyclic structural analogues have not been reported except the possibility of bis/dialkoxyphosphinyl/ sulphoxide (I) formation cited in the patent literature.[1] This reaction was reinvestigated by Schrader *et al.*,[2] who claimed the previous report to be erroneous and found that asym. tetraethyl thiopyrophosphate (III, R = Et) is the only product formed in the reaction between sodium diethyl phosphite and thionyl chloride. The authors suggested the possible transient formation of I, its subsequent reduction by means of sodium diethyl phosphite to the sym. tetraethyl thiopyrophosphate (II, R = Et), and immediate isomerization of the latter affording the thermodynamically stable asymmetrical compound (III, R = Et). However, no evidence concerning the reaction pathway was given.



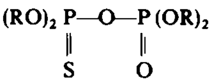
$(RO)_2\underset{\overset{\|}{O}}{P}-\underset{\overset{\|}{O}}{S}-\underset{\overset{|}{O}}{P}(OR)_2$

I



$(RO)_2\underset{\overset{\|}{O}}{P}-S-\underset{\overset{\|}{O}}{P}(OR)_2$

II



$(RO)_2\underset{\overset{\|}{S}}{P}-O-\underset{\overset{\|}{O}}{P}(OR)_2$

III

This work presents an attempt to establish the precursor of tetra-alkyl thiopyrophosphates, which are also formed in the reactions between dialkyl phosphites or their cyclic structural analogues and thionyl chloride. Although the sym. tetra-alkyl

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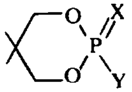
[*] Part III; A. Zwierzak and J. Michalski, *Canad. J. Chem.* 47, 1163 (1969). Paper CIL on organophosphorus compounds.

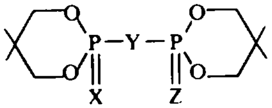
thiopyrophosphates anticipated as intermediates have been described,[3] they are too unstable to be detected or isolated under the reaction conditions. This situation prompted us to choose 2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (IV) as a model compound. Reaction with thionyl chloride was supposed to afford bis(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinanyl) sulphide (V), the only known, perfectly stable sym. thiopyrophosphate.[4] The results, which have been verified for open-chain dialkyl phosphites, are presented below.

RESULTS

2-Oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (IV) reacted with thionyl chloride with evolution of hydrogen chloride and sulphur dioxide. The main product, which separated from benzene in 35–40% yield, was identified as pure sym. cyclic thiopyrophosphate (V) by comparison with an authentic specimen.[4b] In addition, a very complex mixture of compounds was isolated. All components of this mixture were detected qualitatively by means of TLC (R_F values given in Table 1), paper chromatography, and IR spectroscopy. Among the neutral products: 2-chloro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (VI), 2-chloro-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan (VII), cyclic asym. thiopyrophosphate (VIII) and cyclic pyrophosphate (IX) were identified. Acidic products, separated by washing the reaction mixture with sodium bicarbonate solution, consisted of 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (X), 2-hydroxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan (XI) as well as three other unidentified compounds, possibly decyclization products. There was neither chromatographic nor spectroscopic evidence for the formation of any other neutral compound. Distinct changes in the ratio of the reactants (from 1 : 1 to 3 moles of phosphite per 1 mole of thionyl chloride) as well as the reverse mode of mixing the reagents did not affect the total yield of sym. cyclic thiopyrophosphate (V) or the final qualitative result. The use of tertiary amines as hydrogen chloride binding agents also did not influence the reaction course to any serious extent. But considerable difference in the composition of products was observed if the sodium derivative of cyclic phosphite instead of the free ester (IV) was used in the reaction. The yield of cyclic sym. thiopyrophosphate (V) was diminished to 9%, the total amount of acidic products was increased, and a new component, viz. cyclic sym. dithiopyrophosphate (VIIIa) was detected in the reaction mixture. This result can be explained if we consider all the possible transformations which can take place when the sodium derivative of phosphites react with sulphur dioxide formed as a by-product in the reaction. As was demonstrated recently,[5] a complex mixture containing sym. dithiopyrophosphates together with other products is formed under these conditions.



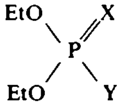
IV: X = O, Y = H
VI: X = O, Y = Cl
VII: X = S, Y = Cl
X: X = O, Y = OH
XI: X = S, Y = OH



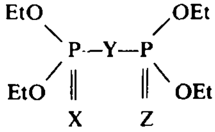
V: X = Z = O, Y = S
VIII: X = Y = O, Z = S
VIIIa: X = Z = S, Y = O
IX: X = Y = Z = O

The complexity of the reaction between 2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (IV) and thionyl chloride precludes any conclusive statements concerning the reaction mechanism. Undoubtedly, the main direction of the process involves the formation of sym. thiopyrophosphate, which can subsequently isomerize to asym. thiopyrophosphate (as observed in the case of open-chain thioanhydrides of this type), the origin of the former, however, seems to be obscure.

Further attempts to elucidate the origin of sym. thiopyrophosphate are focussed on the reaction between thionyl chloride and diethyl phosphite. The complex mixture of compounds formed was partially separated by means of distillation *in vacuo*. The idividual fractions were analyzed qualitatively by TLC. The following compounds were identified by comparison of their R_F values (Table 2) with those of authentic specimens prepared by independent procedures: diethyl phosphite (unreacted starting material, XII), diethyl phosphorochloridate (XIII), diethyl hydrogen phosphate (XIV), diethyl phosphorochloridothionate (XV), diethyl hydrogen phosphorothioate (XVI), tetraethyl pyrophosphate (XVII), and asym. tetraethyl thiopyrophosphate (XVIII). All these compounds correspond to those (V–XI) obtained in the reaction between thionyl chloride and cyclic hydrogen phosphite (IV). Sym. tetraethyl thiopyrophosphate (XIX), which could not be detected, rearranges quantitatively to the asymmetrical isomer (XVIII) under the reaction conditions.[3]



XIII: X = O, Y = H
XIII: X = O, Y = Cl
XIV: X = O, Y = OH
XV: X = S, Y = Cl
XVI: X = S, Y = OH
XX: X = O, Y = SEt
XXI: X = O, Y = SCl



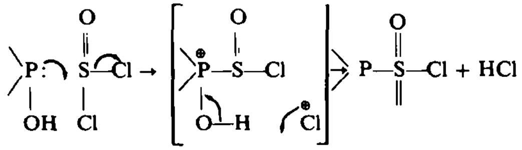
XVII: X = Y = Z = O
XVIII: X = S, Y = Z = O
XVIIIa: X = Z = S, Y = O
XIX: X = Z = O, Y = S

In addition to the products mentioned, considerable amounts of O,O,S,-triethyl phosphorothiolate (XX) were formed during the reaction of diethyl phosphite (XII) with thionyl chloride. This compound was isolated from the mixture by column chromatography on silica gel and identified by comparison of its physical and spectral properties with those of a standard sample.[6] The detection of XX, which could be formed only by dealkylation of a suitable quasi-phosphonium complex, indicates that a conceivable source of such a complex could be the reaction of diethoxyoxophoranesulphenyl chloride (XXI) with diethyl phosphite (XII). The crucial step in the initial reaction appears to be the transient formation of the corresponding sulphenyl chloride (XXI). Full evidence in support of this was provided by a separate experiment in which diethyl phosphite (XII) was added very slowly to a large excess of thionyl chloride. In this particular case diethoxyoxophosphoranesulphenyl chloride (XXI) was detected in the reaction mixture by TLC. Furthermore, it was found that compound XXI, prepared independently in pure state,[7] reacted easily with diethyl phosphite (XII) affording the mixture of asym. tetraethyl thiopyrophosphate (XVIII), diethyl phosphorochloridate (XIII), diethyl hydrogen phosphorothioate (XVI), diethyl phosphorochloridothionate (XV), and O,O,S,-triethyl phosphorothiolate (XX). This reaction was studied by Michalski *et al.*[8], but the formation of the latter two compounds was not observed at 0–5°. When the reaction of XXI with diethyl phosphite (XI) was carried out in presence of diethyl hydrogen phosphate (XIV), in addition to all products mentioned previously, tetraethyl pyrophosphate (XVII) was also produced.

The last two experiments can be considered as simplified model sequences for studying the reactions between thionyl chloride and open-chain or cyclic phosphites, proving that oxophosphoranesulphenyl chloride is an intermediate. On this basis all the essential steps in the reaction can be, at least partially, interpreted in terms of interactions between phosphites and the corresponding oxophosphoranesulphenyl chlorides. The final results of all reactions studied are in full accord with this assumption. Although there is no conclusive evidence that at least some of the reaction products cannot be formed by different ways.

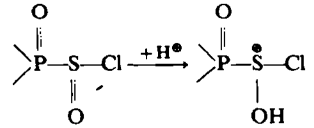
DISCUSSION

The foregoing experimental results are consistent with a mechanistic scheme involving transient formation of the corresponding oxophosphoranesulphenyl chlorides. The following interpretation of the formation of these intermediates may be offered. The reaction of thionyl chloride with phosphites is a stepwise process in which the initial attack of the ester in its tervalent form[9] may occur at various points of the thionyl chloride molecule. At least two of the three possible directions can lead to the expected oxophosphoranesulphenyl chloride: (A) Initial attack of the phosphite molecule may occur at the S atom as a simple nucleophilic displacement of a chloride anion giving rise to the formation of a sulphinyl type intermediate (XXII):

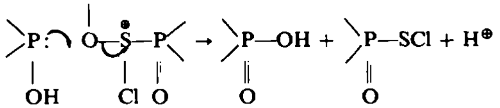


XXII

The latter is subsequently deoxygenated by another molecule of phosphite to provide oxophosphoranesulphenyl chloride (XXIII). It seems reasonable to assume that acid-catalysis plays an important role in this step:

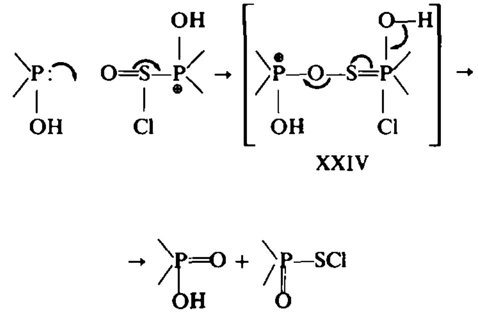


XXII



XXIII

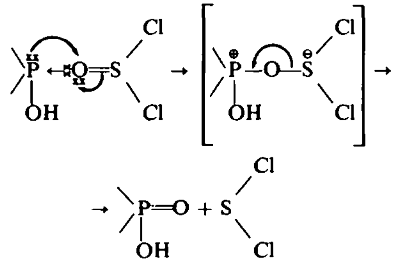
Protonation may take place at the phosphoryl O atom as well. If this is the case, the oxidation of phosphite can be mechanistically envisioned as a two-step process involving a pentacovalent phosphorus intermediate (XXIV):



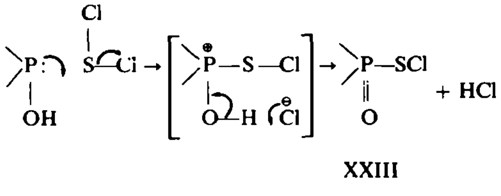
XXIV

XXIII

(B) Deoxygenation of thionyl chloride, possibly in a two-stage process, in which the phosphite molecule acts predominantly as a nucleophile should be considered:



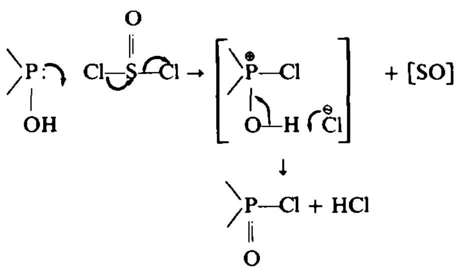
The transition state for this attack on doubly bonded oxygen is stabilized by back donation of lone pair electrons into the vacant 3d orbitals of phosphorus. A biphilic attack of this type, widely recognized in tervalent phosphorus chemistry,[10] would result in the formation of sulphur dichloride which, in turn, can react with another molecule of phosphite, affording the expected oxophosphoranesulphenyl chloride (XXIII):



XXIII

A similar interpretation of the reaction between thionyl chloride and trialkyl phosphites has been suggested by Poshkus and Herweh.[11] There is, however, no evidence to favour this mechanism over a nucleophilic attack on sulphur (path A).

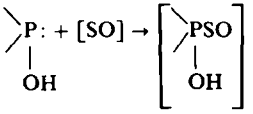
(C) The reaction between a phosphite and thionyl chloride can be also assumed to proceed by initial attack on "positive" chlorine. In this case two bonds from chlorine to sulphur are broken and an unstable molecule of sulphur monoxide displaced:



The chlorophosphonium cation can then react with the chloride anion to give the corresponding phosphorochloridate. The formation of sulphur dioxide, always observed in the reactions between phosphites and thionyl chloride, can be accounted for by assuming some consecutive processes involving sulphur monoxide. It can disproportionate spontaneously:[12]

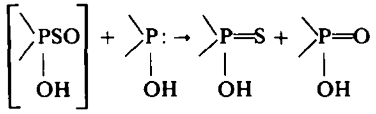
$$2[SO] \rightarrow SO_2 + 1/8\,S_8$$

or react with the available phosphite to form a sulphoxide (XXV):



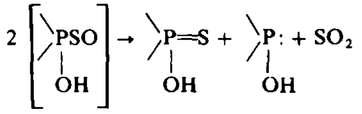
XXV

The latter can disappear by oxygen transfer to another molecule of phosphite thus accounting for the formation of the corresponding acids:

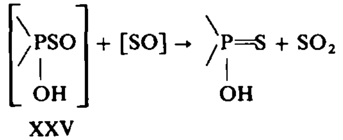


XXV

Disproportionation of the sulphur monoxide adduct (XXV) and/or the reaction of this adduct with another molecule of sulphur monoxide should be also considered:



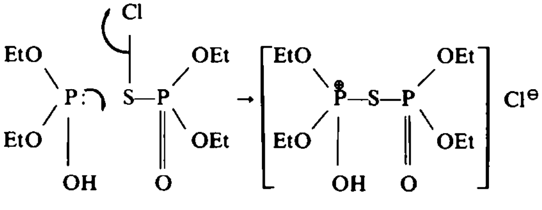
XXV



XXV

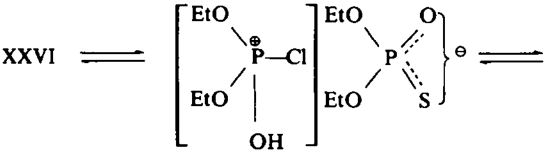
Consecutive reactions of sulphur monoxide formed *in situ*, which have been discussed above, were also proposed by Poshkus and Herweh[11] as an adequate interpretation for the reactions between trialkyl phosphites and thionyl chloride.

The formation of final products obtained in the reactions between thionyl chloride and open-chain or cyclic hydrogen phosphites can be explained plausibly in terms of the consecutive reactions of the latter and the corresponding oxophosphoranesulphenyl chlorides formed as reactive intermediates. As suggested previously,[8] the quasiphosphonium complex (XXVI), characteristic for Arbuzov type reactions, is formed in the first step of the reaction between diethyl phosphite and diethoxyoxophosphoranesulphenyl chloride. This reaction was chosen to illustrate all possibilities of decomposition of the intermediate complex. In the case of cyclic hydrogen phosphites the overall reaction is simpler because no dealkylation due to C—O bond fission can occur.

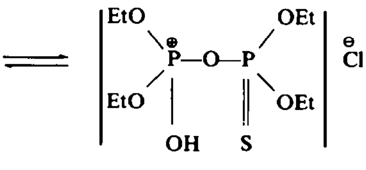


XXVI

It is reasonable to assume a dynamic equilibrium between the ion-pair (XXVI) and two other phosphonium complexes (XXVII and XXVIII), which can be derived from XXVI by stepwise nucleophilic displacements:



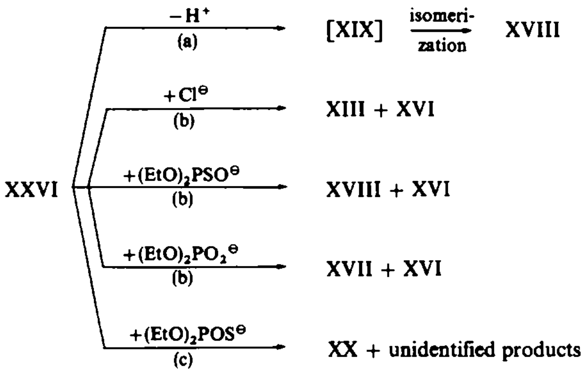
XXVII



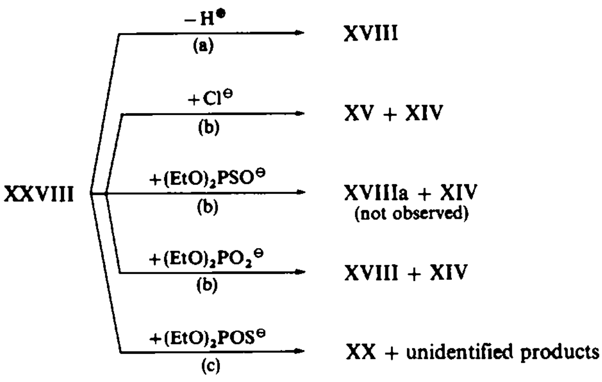
XXVIII

A similar equilibration of quasi-phosphonium complexes has been postulated[13] to account for the formation of triphenylphosphine oxide and bis(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinanyl) oxide in the reaction between triphenylphosphine and di(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) disulphide. The equilibrium between the complexes of type XXVI and XXVII has been claimed[14] to account for the formation of diethyl phosphorochloridate and O,O,S-triethyl phosphorodithioate in the reaction between diethoxythionophosphoranesulphenyl chloride and triethyl phosphite.

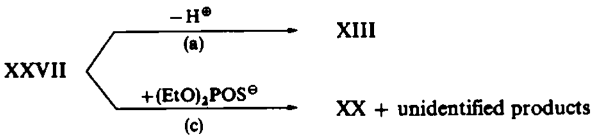
The cationic part of XXVI can collapse by various different ways: (a) proton transfer, (b) sulphur-phosphinyl bond fission, and (c) alkyl-oxygen bond fission:



Similar decomposition of the phosphonium cation of XXVIII seems to be responsible for the formation of diethyl phosphorochloridothionate (XV) among the spectrum of other products:



The cation of XXVII can decompose only by proton transfer (a) or alkyl-oxygen bond fission (c):



According to general principles of the concept of hard and soft acids and bases[15] route (c) seems the most likely dealkylation possibility. In fact, neither triethyl phosphorothionate nor triethyl phosphate were detected among the reaction products.

TABLE 1. THE R_F VALUES OF SOME CYCLIC ORGANOPHOSPHORUS COMPOUNDS CONTAINING NEOPENTYL GLYCOL SKELETON.*

Compound No.	R_F (solvent system: benzene-acetone, 4:1) (A)	Remarks†
IV	0·23	orange spot, strong "tailing effect"
VI	0·62	pale-violet, round spot
VII	0·80	orange, round spot
V	0·30	yellow spot, strong "tailing effect"
VIII	0·56	yellow, round spot
IX	0·31	yellow spot, strong "tailing effect"
VIIIa	0·80	orange spot, weak "tailing effect"

* Kieselgel G (E. Merck) (0·25 mm) was used as adsorbent.

† Chromatograms were developed by spraying with 5% $AgNO_3$ aq. followed by 2% ethanolic bromothymol blue.

TABLE 2. THE R_F VALUES OF SOME ETHYL ESTERS OF ORGANOPHOSPHORUS ACIDS.*

Formula (No)	R_F values		
	Solvent system (B) C_6H_6—$CH_3COOC_2H_5$ (5:4)	Solvent system (C) C_6H_6—CH_3COCH_3—$CHCl_3$ (20:10:3)	Solvent system benzene
XII	0·28	0·37	0·00
XIII	0·65	0·68	0·00
XV	0·78	0·80	0·72
XX	0·49	0·53	0·00
XXI	0·34	0·52	0·00
$(EtO)_3P{=}S$	—	0·77	0·52
XIX	0·30	0·38	0·00
XVIII	0·64	0·62	0·00
XVII	0·20	0·28	0·00

* Silica Gel Woelm (0·25 mm) was used as adsorbent. Chromatograms were developed by spraying with 5% $AgNO_3$ aq. followed by 2% ethanolic bromothymol blue.

EXPERIMENTAL

Solvents were purified by conventional methods. Commercial $SOCl_2$ was purified as described.[16] Benzene was dried over NaH and freshly distilled before use. All extracts were dried over $MgSO_4$ and evaporated under reduced press. B.ps and m.ps (taken in capillaries) are uncorrected. IR spectra were recorded for nujol mulls on a Perkin–Elmer Infracord. TLC was carried out on standard glass plates covered with 0·25 mm of Kieselgel G (E. Merck) or Silica Gel Woelm. Samples were analysed as ca. 5% solns in benzene or acetone. Four solvent systems were employed: (A) benzene-acetone (4:1), (B) benzene-ethyl acetate (5:4), (C) benzene-acetone-chloroform (20:10:3), (D) t-butanol-acetone-water-NH_3 aq. (5:4:1:1).[17] All chromatograms were developed by spraying them with 5% $AgNO_3$ aq followed by 2% ethanolic bromothymol blue soln unless otherwise stated.

2-Oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (IV) was obtained by hydrolysis of the corresponding chlorophosphite in presence of triethylamine.[18]

Bis 2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinanyl sulphide (V), m.p. 186–188° was obtained by the action of sulphur dichloride on IV in presence of Et_3N.[4b]

Compounds VI, VII, IX and VIIIa were prepared as described in the previous paper of this series. Compounds VIII, X, XI (Et_3N salt), XII, XIII, XIV, XV, XVI, XVII, XVIII and XVIIIa were prepared by conventional methods.

Compound XIX (n_D^{20} – 1·4605) was obtained as described.[3]

O,O,S-*Triethyl phosphorothiolate* (XX). The compound was obtained by a modification of the procedure described.[6] Diethyl phosphite (29·0 g, 0·21 mole) was added to the soln of NaOEt prepared by dissolving Na (4·6 g, 0·2 mole) in EtOH (80 ml). Finely powdered S (8·0 g, 0·25 mole) was then added portionwise with stirring and cooling (15–20°). EtBr (27·3 g, 0·25 mole) was added when the S had dissolved, and the mixture was refluxed gently for 4 hr. NaCl was filtered off, the filtrate evaporated, the residue dissolved in benzene (150 ml), and washed with water (2 × 50 ml). Chromatographically pure (TLC) O,O,S-triethyl phosphorothiolate (30·8 g, 78%) was obtained on distillation *in vacuo*, B.p. 94–95°/4 mm, n_D^{20} – 1·4576/Lit.[6]: b.p. 122·5–123°/20 mm, n_D^{20} – 1·4578.

Triethyl phosphorothionate. Finely powdered S (24·0 g, 0·75 mole) was added portionwise with stirring and occasional cooling to triethyl phosphite (116·2 g, 0·7 mole) at 80–90°. Stirring was continued for ½ hr at this temp. The mixture was then cooled to room temp, filtered, and distilled *in vacuo* to give 111·3 g (80%) of chromatographically pure (TLC, solvent systems: (C) and benzene) triethyl phosphorothionate, b.p. 117–118°/35 mm, n_D^{20} – 1·4482. (Lit.[19]: b.p. 88·5°/8 mm, n_D^{20} – 1·4480).

Compound XXI was prepared according to Michalski *et al.*[7] starting from chromatographically pure triethyl phosphorothionate, yield—85%, b.p. 53–55°/0·2 mm, n_D^{20} – 1·4692 (Lit:[7] b.p. 45–46° 0·12 mm, n_D^{20} – 1·4668. The product was chromatographically pure (TLC, solvent systems: (B), (C) and benzene).

Reaction of 2-*oxo*-5,5-*dimethyl*-1,3,2-*dioxaphosphorinan* (IV) *with thionyl chloride*. $SOCl_2$ (2·4 g, 0·02 mole) in benzene (10 ml) was added dropwise with stirring and occasional cooling to a soln of IV (6·0 g, 0·04 mole) in benzene (75 ml) at 35–40°. Evolution of HCl and SO_2 was observed. Stirring was continued for 2 hr at 35–40°; the mixture was then left overnight at room temp, degassed, and partially evaporated. Colourless crystals (A), which separated (2·4 g, 36·5%, m.p. 184–186°), were filtered off and washed with benzene. On recrystallization from benzene-chloroform (1:1) A melted at 186–187° and was identified (m.m.p., IR) as V by comparison with an authentic sample. The filtrate was diluted with benzene (100 ml), washed successively with 5% $NaHCO_3$aq. (2 × 30 ml) and water (3 × 30 ml), dried, and evaporated to yield the solid (B) – 1·6 g. The combined washings were acidified (dil HCl) and evaporated (room temp). The oily residue was dissolved in acetone (30 ml), dried, and evaporated to give colourless, partially crystallizing syrup C, 1·9 g.

The solid (B) was shown to contain (TLC, solvent system A): (XVI, VII, VIII, V and/or IX). Chromatographic detection of IX in presence of V was impossible. Therefore, a sample of B (1·65 g in 50 ml benzene) was heated in presence of Et_3N (1·1 g) for 4 hr at 35–40° and then analysed. Compound V isomerized under these conditions quantitatively (as proven independently) to VIII and a characteristic spot of IX could be sun on the chromatogram. The presence of IX in the solid B was also confirmed by IR spectral analysis before and after isomerization. Strong absorptions at 1292 and 772 cm^{-1}, characteristic of V, were absent from the spectrum of the isomerized sample, which exhibited strong bands at 788 and 733 cm^{-1}, indicating the presence of IX and VIII respectively. Phosphoryl absorption was found only at 1315 cm^{-1}, a region characteristic for P═O in IX and VIII as well.

Syrup C was analysed by ascending paper chromatography [Whatman paper No. 1; solvent system: propanol-aq. ammonia-water (12:3:1)]. The chromatogram was developed by spraying with Hanes and Isherwood[20] reagent. Five spots (R_F: 0·05, 0·25, 0·54, 0·58 and 0·66) were detected, two of which were identified as derived from X and XI. Authentic samples of X and XI have R_F values 0·54 and 0·66 respectively.

Only slight variations in the yield of V (30–40%) were observed when the molar ratio of IV to $SOCl_2$ was changed from 1:1 to 3:1. Compound V was also formed in 30% yield when a benzene soln of IV was added to $SOCl_2$ at 35–40°. In all cases mentioned, the reaction mixtures were worked-up and analysed as described in the previous experiment. The same qualitative results were obtained.

Reaction of 2-*oxo*-5,5-*dimethyl*-1,3,2-*dioxaphosphorinan* (IV) *with thionyl chloride in presence of triethylamine*. To the soln of IV (6·0 g, 0·04 mole) and Et_3N (4·05 g, 0·04 mole) in benzene (75 ml), $SOCl_2$ (2·4 g, 0·02 mole) was added dropwise with stirring and cooling at 35–40°. Stirring was continued for 2 hr at this temp, and the mixture was left overnight at room temp. The ppt was filtered off and washed successively with benzene (3 × 15 ml) and water (3 × 25 ml). The insoluble solid (2·0 g, 30%), m.p. 179–180°, was dried and crystallized from benzene-$CHCl_3$ (1:1) to give pure V, m.p. 184–186°, identical (m.m.p, IR) with an authentic specimen of V. A benzene soln, worked-up and analysed as described, revealed the presence of all compounds detected in the experiment carried out in the absence of amine. The yield of V dropped to 26%, when the reaction was performed in presence of pyridine, and even to 11%—in presence of 2,6-lutidine.

The reaction of sodium salt of cyclic phosphite IV *with thionyl chloride.* NaH (0·95 g, 0·04 mole) was suspended in benzene (30 ml) and the soln of IV (6·0 g, 0·04 mole) in benzene (40 ml) was added with stirring. Stirring was continued for 1 hr at room temp; the soln was then heated to 35–40° and $SOCl_2$ (2·4 g, 0·02 mole) added at this temp with stirring and cooling. After the mixture had been stirred for 2 hr at 35–40°, it was filtered and the ppt washed with water (2 × 50 ml). The insoluble residue (0·6 g, 9%), m.p. 160–163° was crystallized from benzene-$CHCl_3$ (1:1) to give pure V, m.p. 183–185°, undepressed on admixture with an authentic specimen. A benzene soln was found to contain VIIIa in addition to the components mentioned in the previous experiments.

Reaction of diethyl phosphite with thionyl chloride. A soln of $SOCl_2$ (23·8 g, 0·2 mole) in benzene (50 ml) was added dropwise with stirring and occasional cooling (35–40°) to a soln of diethyl phosphite (55·2 g, 0·4 mole) in benzene (250 ml). After the addition was complete, stirring was continued for 4 hr at 35–40°. Evolution of HCl and SO_2 was observed. The resulting mixture was degassed, evaporated, and flash distilled *in vacuo* to give two fractions: (a) 30·5 g, b.p. 30–45°/0·01 mm (bath temp, 65–75°), n_D^{20} – 1·4216 and (b) 24·4 g, b.p. 90–105°/0·05 mm (bath temp 130–145°) n_D^{20} – 1·4455. Fraction (a) was redistilled to afford: fraction (a′) 15·6 g, b.p. 38–40°/0·8 mm (bath temp 65–75°), n_D^{20} 1·4180, identified (TLC, solvent systems (B) and (C)) as XIII contaminated with some amounts of unreacted XII, and fraction (a″) 12·1 g, b.p. 40–45°/0·8 mm (bath temp 70–80°), n_D^{20} – 1·4205, identified (TLC, solvent systems (B), (C) and benzene) as a mixture of XII, XIII and XV. Fraction (b) was dissolved in $CHCl_3$ (200 ml) and extracted with 5% $NaHCO_3$aq (3 × 75 ml). The organic layer was washed with water (50 ml), dried, and distilled *in vacuo* to give two fractions: (b′) 7·1 g, b.p. 50–60°/0·1 mm (bath temp 100–130°), n_D^{20} – 1·4382 and (b″) 9·8 g, b.p. 60–100°/0·1 mm (bath temp 130–140°), n_D^{20}, 1·4432. Fraction (b′) was identified (TLC, solvent systems (B) and (C)) as XX, contaminated with XVII and XVIII; fraction (b″) was found to contain mainly the anhydrides XVII and XVIII contaminated with XX. Compound XX was isolated from the fraction (b′) by column chromatography. Fraction (b′) (5·0 g) was chromatographed on 150 g of silicagel (Grace, 50–100 mesh). The material was eluted with benzene-acetone (5:4) and 30 fractions (ca. 20 ml each) were collected. Fractions 13–24 contained pure XX, 1·9 g, b.p. 49°/0·1 mm, n_D^{20} – 1·4580, identical (TLC, IR) with an authentic specimen of this compound.

The water layer was evaporated *in vacuo* and acidified with conc HCl (15 ml). The acidic products were extracted with $CHCl_3$ (5 × 30 ml), dried, and the solvent evaporated *in vacuo* (0·1 mm) to give an oily residue (4·4 g, n_D^{20} – 1·4650), identified (TLC, solvent system (D), chromatograms developed with iodine vapours) as a mixture of XVI and XIV.

The detection of diethoxyoxophosphoranesulphenyl chloride in the reaction between diethyl phosphite and thionyl chloride. A soln of diethyl phosphite (2·8 g, 0·02 mole) in benzene (5 ml) was added dropwise over ½ hr to a soln of $SOCl_2$ (2·4 g, 0·02 mole) in benzene (10 ml) at 35–40°. After the addition was complete, stirring was continued for ½ hr at 35–40° and the resulting soln degassed, and partially evaporated *in vacuo*. The residue analysed by TLC (solvent system (B)) was found to contain XXI as the main component, contaminated with some XII, XIII and XV.

The reaction of diethoxyoxophosphoranesulphenyl chloride XXI *with diethyl phosphite.* A soln of XXI (40·9 g, 0·2 mole) in benzene (50 ml) was added with stirring and occasional cooling (35–40°) to a soln of diethyl phosphite (27·6 g, 0·2 mole) in benzene (100 ml). Stirring was continued for 2 hr at 35–40° (evolution of HCl); the soln was then degassed and distilled *in vacuo* to give two fractions: (a) 7·7 g, b.p. 40–45°/0·2 mm (bath temp 70–80°), n_D^{20} – 1·4272 and (b) 48·5 g, b.p. 80–120°/0·05 mm (bath temp 130–145°), n_D^{20} – 1·4498. Both fractions were worked-up and analysed as described in the previous experiment. Compounds XII, XIII and XV were detected in the fraction (a). Fraction (b) was found to be composed of XVIII, XX and XVI. When the experiment was carried out in presence of XIV, compound XVII was formed in addition to the products mentioned.

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