Table VI. Estimated Hydrogen to Silver Distances (A)

Ag_1-H_1	2.53	$Ag_n-H_1{}^a$	2.78
Ag_1-H_2	2.54	Ag_n-H_2	2.78
Ag_1-H_3	3.49	Ag_n-H_3	3.26
Ag_1-H_4	3.49	Ag_n-H_4	3.04
Ag_1-H_5	3.40	Ag_n-H_5	2.94
Ag_1-H_6	3.40	Ag_n-H_6	3.15

^{a} Ag_n refers to silver in the normal position estimated at $x/a_1 = 0.850, y/a_2 = 0.289, z/c = 0.187$.

C_3 and C_9 atoms about the C_1-C_2 bond. The dihedral angle between $C_1-C_2-C_3$ and $C_2-C_1-C_9$ is 1.8 ± 2.3°.

That the divergent lobes of the p orbitals are twisted outward from their normal positions (assuming sp² hybridization) is consistent with the argument[24] that in cis-ethylenic systems the π-bonded carbon p orbitals are distorted in order to relieve strain due to bond oppositions. (It is noteworthy that for the *trans* double bond in the humulene–silver nitrate adduct the silver ion is distorted only 5° from the normal position, whereas for the cis double bonds in the norbornadiene adduct, the distortion is approximately 24°.)

Finally, a distortion of the p orbitals could be attributed to a rotation of the p orbitals about the C_1-C_2

(24) P. D. Gardner, R. L. Brandon, and N. J. Nix, *Chem. Ind.* (London), 1363 (1958).

axis affecting a further spreading of the divergent lobes and a congestion of those which are convergent. The driving force for such a distortion would be a stabilization due to increased overlap of the convergent lobes and resulting homoconjugation. It is unlikely that homoconjugation is a very important factor in the bonding of the complex. Homoaromaticity in cyclononatriene itself is expected to be small according to simple LCAO–MO calculations,[3,4] and it would seem reasonable that the silver ion would tend to withdraw electrons during complex formation, thus further decreasing any existing p-orbital overlap. Also, increases in the trigonal carbon angles and a decrease in the tetrahedral angles of the ring, which would be expected to accompany significant homoconjugation, are small and can be explained by the intraannular hydrogen interactions.

Proton and Phosphorus-31 Nuclear Magnetic Resonance Studies of Tetraalkoxyphosphonium Hexachloroantimonates and Related Compounds[1a]

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Abstract: Tetramethoxyphosphonium hexachloroantimonate (Ia) was obtained in moderate yield from the reaction between trimethyl phosphite and methyl hypochlorite in the presence of antimony pentachloride (reaction ii, X = O). Proton and phosphorus-31 nuclear magnetic resonance (nmr) and infrared and conductivity studies support this formulation. Evidence was also obtained for the formation of the triethoxymethoxy- and triphenoxymethoxyphosphonium cations. These results confirm that such salts are intermediates in the reaction between phosphite triesters and alkyl hypochlorites. The control reaction (iii) between trimethyl phosphite and antimony pentachloride gave a minor product which was shown to be trimethoxymethylphosphonium hexachloroantimonate (II), the intermediate from intermolecular transmethylation.

Current advances in the understanding of the mechanisms of phosphorus reactions owe much to the detection and characterization of four- and five-covalent intermediates resulting from valency expansion of phosphorus(III) compounds.[2-11] While stable pentaalkoxy-

phosphoranes[2] and trialkoxyalkylphosphonium salts[3,4] have been isolated, the tetraalkoxyphosphonium salts have only been tentatively identified as transient intermediates. Denney and Relles[12] observed their formation using proton nmr in the reactions between trialkyl phosphites and neopentyl hypochlorite (reaction i).

(1) (a) A preliminary account of this work was given in J. S. Cohen, *Tetrahedron Letters*, 3491 (1965); (b) Department of Pharmacology, Harvard Medical School, Boston, Mass. 02115.

(2) (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, 85, 3252 (1963); (b) F. Ramirez, *Pure Appl. Chem.*, 9, 337 (1966).

(3) K. Dimroth and A. Nurrenbach, *Angew. Chem.*, 70, 26 (1958); *Chem. Ber.*, 93, 1649 (1960).

(4) F. G. Verkade, T. J. Hutteman, M. K. Fung, and R. W. King, *Inorg. Chem.*, 4, 83 (1965).

(5) D. B. Denney and H. M. Relles, *J. Am. Chem. Soc.*, 86, 3897 (1964); 87, 138 (1965); 88, 1839 (1966).

(6) R. G. Harvey and E. R. DeSombre, "Topics in Phosphorus

Chemistry," Vol. 1, Interscience Publishers, New York, N. Y., 1964, p 57.

(7) B. Miller, ref 6, Vol. 2, 1965, p 133.

(8) G. M. Blackburn and J. S. Cohen, ref 6, Vol. 6, in press.

(9) H. N. Rydon, Special Publication No. 8, The Chemical Society, London, 1957, p 61; H. N. Rydon and B. L. Tonge, *J. Chem. Soc.*, 3043 (1956).
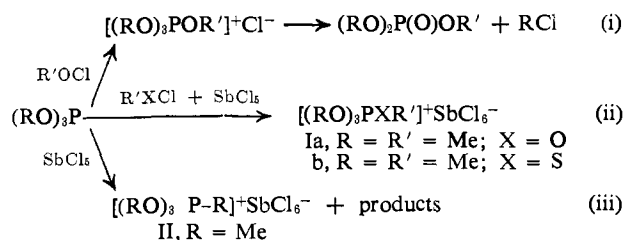
(10) O. Mitsunobu, T. Obata, and T. Mukaiyama, *J. Org. Chem.*, 30, 101, 1071 (1965).

(11) B. Miller, *J. Am. Chem. Soc.*, 88, 1841 (1966).

(12) D. B. Denney and H. M. Relles, *Tetrahedron Letters*, 573 (1964).

Antimony pentafluoride and related compounds have been used extensively in the now classical work of Olah and co-workers[13] for the isolation of salts of relatively unstable carbonium ions. Hilgetag and Teichmann[14] applied this technique to the reaction between trialkyl phosphites and alkyl sulfenyl chlorides (reaction ii, X = S) to give isolable tetralkyloxythiolphosphonium salts (I, X = S). The present work describes a similar application of the technique to the trialkyl phosphite-alkyl hypochlorite reaction (ii, X = O) leading to the first isolation and characterization of a tetraalkoxyphosphonium salt (Ia).

Investigation of the control reaction (iii) between trimethyl phosphite and antimony pentachloride led to the isolation of the minor product trimethoxymethylphosphonium hexachloroantimonate (II),[15] which was shown to be the intermediate for intermolecular transmethylation.

$$[(RO)_3POR']^+Cl^- \longrightarrow (RO)_2P(O)OR' + RCl \quad (i)$$

$$(RO)_3P \xrightarrow[]{R'XCl + SbCl_5} [(RO)_3PXR']^+SbCl_6^- \quad (ii)$$

with R'OCl branch above and SbCl₅ branch below:

Ia, R = R' = Me; X = O
b, R = R' = Me; X = S

$$[(RO)_3\,P\text{-}R]^+SbCl_6^- + products \quad (iii)$$

II, R = Me

Experimental Section

All phosphites were distilled and stored in a desiccator (sodium drying is not recommended). Antimony pentachloride (90%) was obtained from the Baker and Adamson Co., Morristown, N. J. The methylene dichloride used was analytical grade and was dried over calcium chloride. All melting points are corrected.

Nuclear Magnetic Resonance Spectroscopy. Proton nmr data were obtained using a Varian Associates A-60 spectrometer. Chemical shifts are quoted in τ values relative to tetramethylsilane (τ 10) as external reference.

Phosphorus-31 nmr data were obtained using a Varian Associates 4300B spectrometer operating at 24.3 Mcps with 5- or 15-mm nonspinning sample tubes. Chemical shifts are quoted in δ ppm relative to 85% H_3PO_4 as external reference. Unstable materials were stored and manipulated in nmr tubes at liquid nitrogen temperature.

Tetramethoxyphosphonium Hexachloroantimonate (Ia). A methylene dichloride solution of methyl hypochlorite was prepared by carefully controlled (to pH 8.0) addition of 1 N acetic acid to sodium hypochlorite solution (4–6%, 90 ml) and methanol (2.8 ml).[16] The methyl hypochlorite was extracted with methylene dichloride (five 5-ml portions) until no more yellow coloration was obtained. The extracts were dried (calcium chloride) and filtered into a four-necked flask, fitted with a reflux condenser and a calcium chloride tube, and cooled to −70° in an acetone–Dry Ice bath. Methylene dichloride solutions (15 ml) of trimethyl phosphite (3.5 ml, 1 mole) and antimony pentachloride (3.8 ml, 1 mole) were added dropwise under dry nitrogen with stirring. After the addition was completed (15–30 min), the flask was allowed to warm slowly up to 10°. Ether or petroleum ether (sodium dried) was added, and a white solid precipitated. This was separated by filtration using a sintered glass disk, washed with ether, and dried in a desiccator. Tetramethoxyphosphonium hexachloroantimonate (Ia) was recrystallized three times from methylene dichloride-ether and had mp 139° dec; 5.6 g (38%).

Anal. Calcd for $C_4H_{12}O_4Cl_6PSb$: P, 6.3; Cl, 43.5. Found: P, 6.5; Cl, 43.6.

(13) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, 86, 1360 (1964), and others in the series.
(14) G. Hilgetag and H. Teichmann, *Chem. Ber.*, 96, 1465 (1963).
(15) *Cf.* D. H. Brown, G. W. Fraser, A. McAuley, and D. W. A. Sharp, *Chem. Ind.* (London), 2098 (1965).
(16) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1094, 1105 (1954).

The solid slowly decomposed during several weeks in an evacuated desiccator.

Proton Nmr Studies on Ia. (i) The solutions of methyl hypochlorite extracted into methylene dichloride and deuteriochloroform solvents showed only one product peak, τ 6.02, in the proton nmr spectrum.

(ii) The spectrum of the crude product Ia in methylene dichloride solution contained only a doublet centered at τ 5.70 (J_{PH} = 11.2 cps). Impurities were less than 5%. To a solution of a recrystallized sample of Ia at −50° a solution of trimethyl phosphite (10%) in methylene dichloride was added dropwise. An exothermic reaction ensued, and the nmr spectrum of the solution now contained ten major peaks including a doublet at τ 8.5 (J_{PH} = 17 cps).

(iii) There was no change in the spectrum of a solution of Ia in methylene dichloride after standing at 23° for 24 hr. On heating at 50° for 2 hr, the following doublets were observed: τ 5.80, 5.85, and 7.82 (the latter two in a ratio of 3–3.5:1) with coupling constants J_{PH} of 11.5, 11.5, and 17.2 cps, respectively. Ia was almost insoluble in $CHCl_3$ and $CDCl_3$.

Infrared Studies on Ia. An infrared absorption spectrum was recorded using a Beckman IR-7 spectrophotometer on a 4% methylene dichloride solution of Ia in a 0.5-mm cell. The bands shown in Table I were observed.

Table I

Band, cm⁻¹	Assignment
874 (m)	Sym P—(OC)₄ stretching
1088 (s)	Asym P—(OC)₄ stretching
1189 (m)	C—OP stretching
1270 (m)	P=O stretching
1454 (w)	CH₃ asym bending
2310 (w)	2 × 1189 cm⁻¹
2990 (s)	CH₃ sym C—H stretching
3055 (vs)	CH₃ asym C—H stretching

A spectrum was also recorded using a Perkin-Elmer Infracord spectrophotometer on a KBr disk of Ia. This showed no band corresponding to P=O stretching. All other bands were as given in Table I.

Conductivity Studies. Measurements were taken on a Barnstead PM3A conductivity meter operating at 60 cycles and 23°. The following values were recorded for the specific conductivities of 10^{-4} M solutions in methylene dichloride of compounds Ia and II; 1.08×10^{-6} and 1.22×10^{-6} ohm⁻¹ cm⁻¹, respectively. Pure methanol gave a value of 7.4×10^{-7} ohm⁻¹ cm⁻¹, methylene dichloride was nonconducting, and a number of tetraalkylammonium salts gave values in the range 2.0–2.3×10^{-6} ohm⁻¹ cm⁻¹.

Trimethoxymethylphosphonium Hexachloroantimonate (II). (i) Using the same conditions as described above, methylene dichloride solutions of trimethyl phosphite (1.75 ml, 1 mole) and antimony pentachloride (1.9 ml, 1 mole) were dripped into a flask containing methylene dichloride (20 ml). Addition of ether gave a white precipitate of trimethoxymethylphosphonium hexachloroantimonate, 0.8 g (12%), which on recrystallization from methylene dichloride-ether had mp 153° dec.

Anal. Cacld for $C_4H_{12}O_3Cl_6PSb$: Cl, 44.9. Found: Cl, 44.7.

The proton nmr spectrum in methylene dichloride solution showed two doublets centered at τ 5.87 (J_{PH} = 11.5 cps) and 7.85 (J_{PH} = 17.2).

(ii) 1,1-Dichloroethane (distilled) was used as solvent for a reaction carried out as in part i. The product (3.0 g, 21% yield) was the same as in part i; the ratio of the doublets in the nmr spectrum in methylene dichloride solution was 3:1 (1,1-dichloroethane was not a useful solvent for the product since the low-field doublet was partially covered).

Phosphorus-31 Nmr Studies. (i) Reactions were carried out on a small scale, using proportionately one-quarter of the amounts of the reactants given above, but with smaller volumes of methylene dichloride (2–5 ml). The reaction solutions were quickly transferred from the cooled flask into a 5-mm nmr tube and scanned in the spectrometer. Chemical shifts for the major and consistent peaks are given in Table II. The minor component at −56 ppm in the control reaction (iii) could not always be observed.

(ii) A saturated methylene dichloride solution of Ia was prepared. The mean value for the chemical shift obtained, using a 15-mm

Table II. P³¹ Chemical Shifts (ppm) Relative to 85% H_3PO_4[a]
[(MeO)₄PSbCl₆ in CH₂Cl₂, −51.5]

Phosphite	+SbCl₅ Chem shifts	+SbCl₅ Peak areas, %	+SbCl₅ + MeOCl Chem shifts	+SbCl₅ + MeOCl Peak areas, %	Formulation	Ref
(MeO)₃P	+1	25	+1	40	(MeO)₃PO	
	−8	30	−8	40	(MeO)₂P(O)Cl	
	−28	15	−27	7	(MeO)₂P(O)CH₂Cl	b
	−36	25	−34	3	(MeO)₂P(O)Me	c
	...	..	−53	10	(MeO)₄P⁺	
	−56[d]	3	...	..	(MeO)₃P⁺Me	
(EtO)₃P	+16	5	...	..	[(EtO)₂PO]₂O	e
	+10	5	+8	5		
	...	..	+5	5		
	+1.5	45	+1	35	(EtO)₃PO	
	−4	30	−3	35	(EtO)₂P(O)Cl	c
	−16	5	−14	3		
	−22	5	−23	5	(EtO)₂P(O)CH₂Cl	b
	...	..	−50	5	(MeO)P⁺(OEt)₃	
(CH₂O)₂POEt	+18	10	+14	25	[RO)₂PO]₂O	
	+4	25	+3	25	Acyclic phosphate	
	−3	30	−3	5	Acyclic P(O)Cl	
	−17	15	−18	10	(CH₂O)₂P(O)OR	17
	−25	15	−27	25	Acyclic P(O)CH₂Cl	b
	...	..	−39	5		
	...	..	−53	3	(CH₂O)₂P(O)R (R = Me, Et)	f

[a] Spectra recorded on a Varian 4300B spectrometer at 24.3 Mcps using nonspinning 5-mm sample tubes. Only major and consistent peaks are recorded. Relative peak areas were variable, values are approximate (±1). [b] This work. [c] K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, 7, 307 (1962). [d] This component not always observed. [e] R. A. Y. Jones and A. R. Katritzky, *Angew. Chem. Intern. Ed. Engl.*, 1, 32 (1962). [f] G. M. Blackburn, personal communication.

nonspinning sample tube, was −51.5 ppm. Attempts to observe the splitting pattern were unsuccessful.

(iii) Trimethyl phosphite was refluxed in methylene dichloride solution. Evolution of gas was observed. After 4 hr the solution was concentrated under vacuum, and the product showed the following chemical shifts: +3 (phosphate), −25, and −32 [(MeO)₂-P(O)Me] ppm in a ratio of 8:10:1 (also some residual phosphite, −140 ppm).

Triethoxymethoxyphosphonium Hexachloroantimonate. Methylene dichloride solutions of triethyl phosphite (5.0 ml, 1 mole) and antimony pentachloride (3.8 ml, 1 mole) were added dropwise to a solution of methyl hypochlorite. After completion of the reaction, petroleum ether (bp 30–40°) was added, and a yellow oil separated, which could not be crystallized. Some of this was pipetted into a cooled proton nmr tube and diluted with methylene dichloride. The spectrum obtained (see Figure 1) showed the following characteristics (apart from solvent peaks): multiplet centered at τ 5.32, 5.75 doublet ($J_{PH} = 11.5$ cps), and 8.37 distorted triplet ($J_{HH} = 7$ cps). An estimate of the areas under the multiplet and doublet (by weighing peaks) gave a ratio of 4:1, respectively. Heating the sample to 50 and then to 80° produced no systematic diminution in the splitting pattern of the multiplet.

Triphenyl Phosphite–Methyl Hypochlorite Reaction. Triphenyl phosphite (7.7 ml, 1 mole) and antimony pentachloride (3.8 ml, 1 mole) solutions were added dropwise to a solution of methyl hypochlorite in methylene dichloride. An unstable red precipitate was formed. A sample of the solution was quickly transferred to a cooled nmr tube. The spectrum showed a doublet centered at τ 5.38 ($J_{PH} = 12.2$ cps); an approximate ratio relative to the total broad phenyl proton multiplet was 1:10.

Addition of ether to half of the reaction mixture while still cold produced a copious brown precipitate (6 g, mp 137° dec after recrystallization of methylene dichloride–ether). The proton nmr spectrum showed a triplet at τ 8.16 ($J_{HH} = 7$ cps), a singlet at 5.46 (ratio 1:1.8, respectively), and a quartet at 4.98 (7 cps.). Addition of ether resulted in the reprecipitation of the solid. On redissolving in methylene dichloride the nmr spectrum now showed two sets of triplets (τ 8.80, 8.20) and quartets (6.47, 5.00), as well as the singlet (4.50).
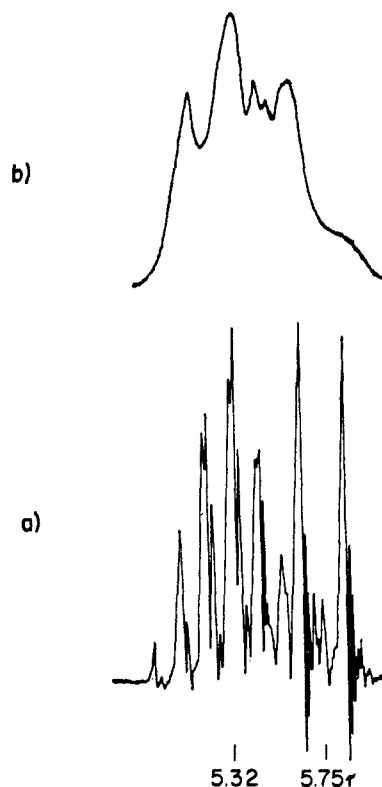

Figure 1. Section of proton nmr spectrum of triethoxymethoxyphosphonium hexachloroantimonate showing (a) multiplet of ethyl methylene protons and doublet of methoxy protons and (b) central peak of multiplet at higher resolution.

5.32   5.75τ

Ethyl Ethylene Phosphite Reactions. Ethyl ethylene phosphite was prepared by transesterification between triethyl phosphite and ethylene glycol.[17] A reaction was carried out as described for Ia using this phosphite but gave no useful result.

Phosphorus-31 nmr studies were carried out as described above, and the results are detailed in Table II.

Perkow Reaction with Antimony Pentachloride. Trimethyl phosphite (3.6 ml, 1 mole) and antimony pentachloride (3.8 ml, 1 mole) were added simultaneously to a solution of α-chloroacetone (2.4 ml, 1 mole) in dichloromethane (15 ml). Addition of ether or petroleum ether to the reaction solution gave a yellow oil, the nmr spectra of which gave no consistent result.

The control reaction between α-chloroacetone and antimony pentachloride in methylene dichloride solution gave a precipitate while still cold, which was filtered onto a sintered-glass disk. The proton nmr spectrum in methylene dichloride solution showed two singlets at τ 6.97 and 5.34 (ratio 3:2). On addition of aliquots of a solution of α-chloroacetone in methylene dichloride, these peaks were observed to shift upfield in a stepwise manner. The solid was very unstable.

Results and Discussion

(a) Trimethyl Phosphite Reactions. The simultaneous addition of trimethyl phosphite and antimony pentachloride to a solution of methyl hypochlorite[16] in methylene dichloride at −70° resulted in the formation of tetramethoxyphosphonium hexachloroantimonate (Ia) (38% yield). The proton nmr spectrum of this compound in methylene dichloride solution consisted of a doublet centered at τ 5.70 ($J_{PH} = 11.2$ cps). The value quoted by Denney and Relles[12] for the chemical shift of the α protons of tetraneopentyloxyphosphonium chloride, with half-life at room temperature of 3 min, was τ 5.69. By comparison with trimethyl phosphite (τ 7.0), trimethyl phosphate (τ 6.5), and penta-

(17) G. M. Blackburn, J. S. Cohen, and A. R. Todd, *Tetrahedron Letters*, 2873 (1964).

methoxyphosphorus[5] (τ 6.3) such a value for the tetramethoxyphosphonium cation is consistent with less electron shielding at the α-hydrogen atoms. The product was shown not to be a molecular complex between trimethyl phosphite and antimony pentachloride since addition of a methylene dichloride solution of trimethyl phosphate resulted in an exothermic reaction.

Comparative phosphorus-31 nmr studies were carried out on a number of reaction mixtures. Results (Table I) when trimethyl phosphite was treated with antimony pentachloride and methyl hypochlorite (reaction ii, X = O) or with antimony pentachloride alone (reaction iii) indicated the formation in the former case of an additional product with a chemical shift (relative to 85% phosphoric acid) of about −50 ppm. That this peak corresponded to the tetramethoxyphosphonium cation was confirmed by the fact that pure Ia had a mean P^{31} chemical shift of −51.5 (±1) ppm in methylene dichloride solution. This value confirms the recent qualitative prediction of Ramirez and Desai[2a] that a tetraalkoxyphosphonium cation would have a chemical shift of the order of −60 ppm, with shielding at phosphorus intermediate between that of phosphites and phosphates.

The formation of a minor component with a chemical shift of −56 ppm in the control reaction of trimethyl phosphite with antimony pentachloride was investigated. Addition of ether to the reaction mixture resulted in the precipitation of a small amount of material. The proton nmr spectrum contained two doublets at τ 5.87 (J_{PH} = 11.5 cps) and 7.85 (J_{PH} = 17.2 cps) in a ratio of 3:1. The latter doublet corresponds reasonably well in chemical shift and coupling constant to those recorded for tetraalkylphosphonium salts.[18,19] Together with the chlorine analysis, this evidence indicated a formulation [(MeO)₃P⁺Me]SbCl₆⁻ (II) for the product (12% yield). While this work was in progress, the isolation of the corresponding hexafluoroantimonate was reported by Brown, et al.,[15] from the reaction between trimethyl phosphite and antimony pentafluoride. A chemical shift of −56 ppm has been assigned to a transient trialkoxyalkylphosphonium salt.[2b]

The trimethoxymethylphosphonium ion is the intermediate for the Arbuzov–Michaelis reaction[6]

(MeO)₃P + MeCl ⟶ [(MeO)₃PMe]⁺Cl⁻ ⟶

(MeO)₂P(O)Me + MeCl
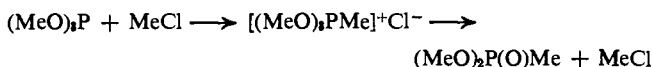
Previous preparations of trialkoxyalkylphosphonium salts (as opposed to triphenoxyalkylphosphonium derivatives[20]) have been carried out by alkylation of phosphites with oxonium or carbonium salts.[3,4]

A reaction carried out in 1,1-dichloroethane solution gave the same product II in roughly the same yield, confirming that II was not in fact an Arbuzov–Michaelis intermediate derived by reaction with the solvent. This minor component is presumably an intermediate in the formation of dimethyl methylphosphonate as one of the major products of the reaction. The intermolecular reaction would account for the moderate yields of the desired tetraalkoxyphosphonium salt Ia obtained in reaction ii (cf. ref 14). As expected, the

peak of dimethyl methylphosphonate shows a marked relative decrease when comparing reaction ii with iii (see Table II).

Although interaction with the solvent might have been anticipated, the absence of a peak in the phosphorus-31 nmr spectrum at −18.5 ppm, the value assigned for (MeO)₂P(O)CH₂Cl,[21] appeared to show otherwise. A methylene dichloride solution of trimethyl phosphite was refluxed and then showed two major peaks at +3 (trimethyl phosphate) and −25 ppm. The latter value could only correspond to (MeO)₂P(O)CH₂Cl and is the same as the only hitherto unassigned value[1a] obtained for the reactions between trimethyl phosphite and antimony pentachloride.

The proton nmr spectrum of Ia was unchanged after standing in methylene dichloride solution for 24 hr. On heating at 50° for 2 hr doublets at the following τ values were observed: 5.80, 5.85, and 7.82, with coupling constants J_{PH} = 11.5, 11.5, and 17.2, respectively. The latter two doublets were found to be consistently in a ratio of 3:1. It appears that the product is the same as that (II) obtained from the reaction (iii) between trimethyl phosphite and antimony pentachloride. The anticipated formation of dimethyl methylphosphonate is ruled out by the ratio of areas of the POCH₃ and PCH₃ doublets.

The infrared spectrum of Ia in solution in methylene dichloride (4%) showed some absorption at 1270 cm⁻¹, due to P=O stretching. However, the spectrum obtained on a potassium bromide pellet of Ia had no such absorption. The infrared spectrum quoted by Hilgetag and Teichmann[14] for compound Ib shows a band at 583 cm⁻¹ corresponding to P-SC stretching but the apparent absence of strong absorption for P-OC stretching (at about 1000 cm⁻¹) is surprising.

That the symmetrical P-(OCH₃)₄ stretching of Ia absorbs as low as 874 cm⁻¹, compared with about 970 cm⁻¹ for triethyl phosphate,[22] is analogous to the situation in trimethyl phosphate which shows this band at 850 cm⁻¹.[23] The corresponding antisymmetrical P-(OCH₃)₄ bands for Ia and trimethyl phosphate are at 1088 and 1042 cm⁻¹, respectively. The C-OP stretching band at 1189 cm⁻¹ is also analogous to that of trimethyl phosphate at 1171 cm⁻¹.

It is interesting to note that both for compound Ia and trimethyl phosphate only the antisymmetrical CH₃ bending gives rise to appreciable bands (at 1454 and 1447 cm⁻¹, respectively), while the symmetrical CH₃ bending (which usually shows a significant band at 1380 cm⁻¹) seems to be practically inactive. This may possibly result from the high symmetry in these cases.

The very high C-H stretching frequencies of Ia (2990 and 3055 cm⁻¹) are not, however, shared by trimethyl phosphate, which absorbs almost normally (at 2833 and 2933 cm⁻¹). The increase in the stretching frequency of the hydrogen atoms is unusual and might be connected with some kind of interaction between these atoms and the anionic chlorine atoms, which increases the energy needed for this stretching.

Conductivity measurements confirmed that Ia and II were salts.

(18) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 40, 449 (1964).

(19) See also C. E. Griffin and M. Gordon, *J. Organometal. Chem.*, 3, 414 (1965).

(20) R. F. Hudson and P. A. Chopard, *Helv. Chim. Acta*, 45, 1137 (1962); 48, 1983 (1965).

(21) See footnote c, Table II.

(22) E. D. Gergman, U. Z. Littauer, and S. Pinchas, *J. Chem. Soc.*, 847 (1952).

(23) Documentation of Molecular Spectroscopy Catalogue, Compound Card No. 5176.

(b) Reactions with Other Phosphites. Evidence for the formation of a new P–O bond was obtained when methyl hypochlorite was treated with triethyl phosphite and antimony pentachloride (reaction ii, X = O, R = Et, R' = Me). Although no solid could be isolated in this case, addition of petroleum ether to the reaction mixture in methylene dichloride resulted in the separation of an oil. The proton nmr spectrum of this showed a doublet (Figure 1) with characteristic splitting (J_{PH} = 11.5 cps) for the P–OCH$_3$ group, and with a chemical shift (τ 5.75) expected for the presence of a positive charge at phosphorus. An additional peak was also observed at −50 ppm in the phosphorus-31 nmr spectrum compared to the control reaction iii (Table I).

For the presumed product [(EtO)$_3$P+OMe]SbCl$_6^-$ it was not possible to accurately integrate the area of the doublet relative to that of the multiplet of the ethyl methylene protons (Figure 1) partly due to the fine splitting. However, an estimate of the ratio was obtained and was smaller than that required for the pure compound. Such a value would tend to indicate that no transesterification had occurred to produce, say, diethyl methyl phosphite.
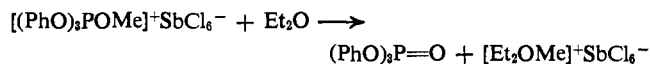
The multiplet of the ethyl methylene group (Figure 1) and the distorted triplet of the ethyl methyl protons were both noted to contain a large degree of fine splitting. Some splitting in the latter case must result from the γ-phosphorus atom. Fine splitting has also previously been described for the methylene proton multiplet of triethyl phosphite and phosphate.[24] The splitting in these cases has now been found to persist in methylene dichloride solution. The observation of doubled resonances in a series of phosphate and other esters, in which the ester groupings were bulky, has been interpreted in terms of rotational isomerism.[25] It is possible to assign peaks in the multiplet (Figure 1) in such a way as to distinguish at least four quartets, with separations of 2 and 6 cps, as well as the splitting due to phosphorus of 8.5 cps. However, the splittings were not found to decrease on heating the sample up to 80°.

On treating methyl hypochlorite with triphenyl phosphite and antimony pentachloride (reaction ii, X = O, R = Ph, R' = Me), a doublet was again observed in the proton nmr spectrum of the reaction solution. This corresponded in splitting (J_{PH} = 12.2 cps) and chemical shift (τ 5.38) to the values expected for the presence of the +P–OCH$_3$ group. However, it was not found possible to isolate the unstable red solid formed. Addition of ether to the reaction mixture while still cold

resulted in the formation of a stable precipitate with an nmr spectrum corresponding to the oxonium salt [Et$_2$O+Me]SbCl$_6^-$.[26]

$$[(PhO)_3POMe]^+SbCl_6^- + Et_2O \longrightarrow$$
$$(PhO)_3P{=}O + [Et_2OMe]^+SbCl_6^-$$

Addition of ether to the solution of this product resulted in the presence of *two* sets of triplets and quartets in the spectrum. This clearly indicated that the solid was not the well-known complex Et$_2$O·SbCl$_5$,[27] which was often formed as a side product in these reactions.

A number of reactions were repeatedly attempted using a variety of other reagents, e.g., *t*-butyl hypochlorite, but without success. The reaction of ethyl ethylene phosphite with methyl hypochlorite and antimony pentachloride and the control reaction without hypochlorite were scanned for their P^{31} nmr spectra (Table II). A peak at low field (−53) was attributed to ethylene methylphosphonate.[28] The value for the intermediate cyclic tetraalkoxyphosphonium cation III would have been of interest for comparative purposes since it is a close analog of cyclic phosphate, but without dπ–pπ bonding.[17] That complete ring opening had not occurred was evidenced by the presence of a major peak (−18 ppm) corresponding to the cyclic phosphate, which must be formed *via* III.

III
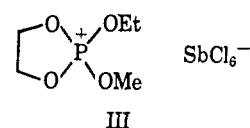
A number of unsuccessful attempts were also made to trap the phosphonium intermediate in the Perkow reaction between α-chloroacetone and trimethyl phosphite using antimony pentachloride.

It is concluded that while this work represents the first isolation of a stable tetraalkoxyphosphonium salt and confirms that these compounds are intermediates in the trialkyl phosphite–alkyl hypochlorite reaction (i), the use of antimony pentachloride does not appear to provide a general technique for the scavenging of such intermediates.

(24) W. E. Shuler and R. C. Axtman, Atomic Energy Commission Research and Development Report No. DP 474, 1960; see also J. R. Ferraro and D. F. Peppard, *J. Phys. Chem.,* 67, 2689 (1963).

(25) T. H. Siddall and C. A. Prohaska, *J. Am. Chem. Soc.,* 84, 2502 (1962).

(26) G. Hilgetag and H. Teichmann, *Angew. Chem. Intern. Ed. Engl.,* 4, 914 (1965).

(27) M. Webster, *Chem. Rev.,* 66, 87 (1966).

(28) See footnote *f*, Table II.