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P^{31} AND H^1 N.M.R. STUDIES OF TETRAMETHOXYPHOSPHONIUM HEXACHLORANTIMONATE AND RELATED COMPOUNDS

by

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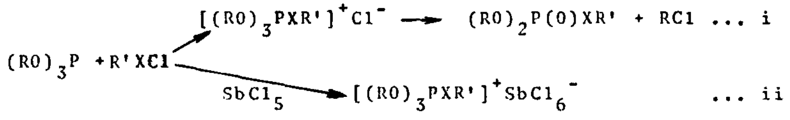
Recently Denney and Relles (1) have shown, using proton n.m.r. spectroscopy, that tetraalkoxyphosphonium salts are formed as intermediates in the reactions of trialkyl phosphites with alkyl hypochlorites (reaction i, X = O). Antimony pentachloride has now been used to trap such intermediates (reaction ii, X = O), following the method of Hilgetag and Teichmann (2) for the reaction of trialkyl phosphites with alkyl sulphenyl chlorides (reaction ii, X = S). Antimony pentafluoride has also been extensively used by Olah and his associates (3) in the preparation of relatively stable carbonium and acylium salts.



I a, R = R' = Me, X = O
b, R = R' = Me, X = S

Crystalline tetramethoxyphosphonium hexachlorantimonate

(Ia) was obtained in 38% yield (recryst. x 3 methylene dichloride/ether, m.p. 139^{o}d. Found: P, 6.5; Cl, 43.6. $C_4H_{12}O_4Cl_6PSb$ requires P, 6.3; Cl, 43.5%) on the simultaneous addition of methylene dichloride solutions of trimethyl phosphite and antimony pentachloride to a methylene dichloride solution of methyl hypochlorite (4).

The proton n.m.r. spectrum of this compound consists of a doublet centred at τ = 5.70 (J_{PH} = 11.2 cps.). The value quoted by Denney and Relles (1) for the chemical shift of the α-protons of the transient tetraneopentyloxyphosphonium chloride ($t_{1/2}$ = 3 mins.) was 5.69. By comparison with trimethyl phosphite (τ = 7.0), trimethyl phosphate (6.5), and pentamethoxyphosphorus (5) (6.3), such a value for the tetramethoxyphosphonium cation is consistent with less electron shielding at the α-hydrogen atoms.

The I.R. spectrum of Ia contained the following bands:

cm^{-1}	Assignment
874(m)	Sym. P-$(OC)_4$ stretching
1088(s)	anti-sym. P-$(OC)_4$ stretching
1189(m)	C-OP stretching
1454(w)	CH_3 bending
2990(s)	CH_3 sym. C-H stretching
3055(vs)	CH_3 anti-sym. C-H stretching

These were observed for a 4% solution in methylene dichloride, in which some P=O absorption was also found (1280 cm^{-1}). However, the spectrum obtained on using a KBr plate of Ia had no such absorption. The I.R. spectrum quote by Hilgetag and Teichmann (6) for compound Ib shows absorption for P-SC vibrations, but, the apparent absence of strong absorption corresponding to P-OC vibrations is a puzzling feature of their spectrum.

P^{31} n.m.r. studies were carried out on a number of reaction mixtures. Comparison of the results were made when trimethyl and triethyl phosphites were treated with antimony pentachloride alone, or with antimony pentachloride and methyl hypochlorite in methylene dichloride solution. Results (Table I) indicated the formation of an additional product in the latter case with chemical shift (relative to 85% H_3PO_4) of about -50 ppm. That this peak corresponded to the tetraalkoxyphosphonium cation was confirmed by the fact that pure Ia had a P^{31} chemical shift of -51.5 ($\pm$ 1) ppm in methylene dichloride solution. This value confirms the recent qualitative prediction of Ramirez and Desai (7) 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 (not always observed) with a chemical shift of -56 ppm in the control reaction for trimethyl phosphite was further investigated. Addition of ether to the reaction mixture in methylene dichloride solution resulted in the precipitation of a material which was not Ia. This had melting point 153°d, and a proton n.m.r. spectrum containing two doublets, τ = 5.87 (J_{PH} = 11.5 cps) and 7.85 (J_{PH} = 17.2 cps). The latter corresponds reasonably well to the chemical shifts and coupling constants recorded for tetraalkyl phosphonium salts (8). The ratio of the areas of these two doublets was of the order of 3 or 4 to 1 respectively. Thus, while a compound of the type $[(MeO)_3P\text{-}R]^+$ $SbCl_6^-$ is definitely indicated by this evidence (a chemical shift of -56 ppm has been assigned to a transient trialkoxyalkylphosphonium salt (9)), it cannot, as yet, be concluded whether R here is CH_3 or CH_2Cl. The latter would indicate interaction with the solvent, methylene dichloride, and the formation of the Arbuzov-Michaelis intermediate in 9% yield. This might account for the only moderate yields obtained of the desired product Ia (cf. 2). However, one would expect

TABLE I

P^{31} Chemical Shifts Relative to 85% H_3PO_4, in ppm (± 1).[a]

$(MeO)_4PSbCl_6$ in CH_2Cl_2 -51.5

Phosphite	$+SbCl_5$	$+SbCl_5$ $+MeOCl$	Formulation	Ref.
$(MeO)_3P$	+1	+1	$(MeO)_3PO$	
	-8	-8	$(MeO)_2P(O)Cl$	
	-28	-27		
	-36	-34	$(MeO)_2P(O)CH_3$	10
	--	-53	$(MeO)_4P^+$	
	-56[b]	--	$(MeO)_3P^+-R$	
$(EtO)_3P$	+16	--	$(EtO)_2PO_2O$	13
	+10	+8		
	--	+5		
	+1.5	+1	$(EtO)_3PO$	
	-4	-3	$(EtO)_2P(O)Cl$	13
	-16	-14		
	-22	-23		
	--	-50	$MeOP^+(OEt)_3$	

(a) Spectra recorded on a Varian 4300B spectrometer at 24.3 Mc/s using non-spinning 1 mm. sample tubes.
Only major and consistent peaks are recorded. Relative proportions were variable.

(b) This component not always observed (R = CH_2Cl or CH_3).

to observe the presence of a P^{31} chemical shift corresponding to the Arbuzov-Michaelis product $(MeO)_2P(O)CH_2Cl$, with a quoted value of -18.5 ppm (10). In fact no such value was obtained, although there was a component at -27 ppm as yet unassigned.

The proton n.m.r. spectrum of Ia was unchanged after standing in methylene dichloride solution for 24 hours. On heating at 50° for 2 hours doublets of the following τ values were observed, 5.80, 5.85, 7.82, with coupling constants J_{PH} 11.5, 11.5 and 17.2 cps respectively. The latter two were in a ratio of approximately 3:1. It would appear that the product in this case is the same as that from the reaction of trimethyl phosphite with antimony pentachloride (see above). Further evidence as to its structure is hampered by the difficulty of finding a truly inert solvent for Ia.

Apart from the intrinsic value of such phosphonium compounds, it would be of interest to compare their P^{31} chemical shifts with a five-membered cyclic homologue (cf. 11,12). Work is progressing in this direction.

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