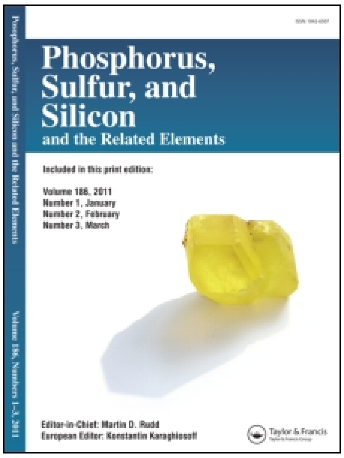

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New Aspects of the Chemistry of Quasiphosphonium Intermediates

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NEW ASPECTS OF THE CHEMISTRY OF QUASIPHOSPHONIUM INTERMEDIATES

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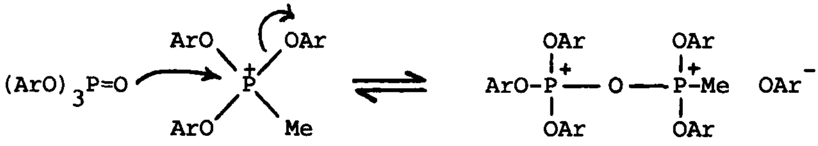
Abstract Information is presented on the thermal decomposition and disproportionation of triaryl phosphite-methyl halide adducts and on the preparation, structure, and properties of some novel, highly stable alkoxyphosphonium halides.

The formation of alkyltriaryloxyphosphonium halides and their thermal decomposition to aryl halides and diaryl alkylphosphonates is well known.[1] We observed, however, in the course of preparing methyltriphenoxyphosphonium bromide that the isolated product on a number of occasions was the unexpected dimethyldiphenoxyphosphonium salt. Further investigations have now shown that disproportionation may occur as a competitive process to Arbuzov cleavage on heating methyltriaryloxyphosphonium halides at 175°C or higher. All species of the type $(ArO)_nP^+Me_{4-n}$ may be formed, although the tetraphenoxyphosphonium halides are not normally detected as they decompose readily to triphenyl phosphate. The redistribution of aryloxy and methyl groups cannot be accounted for by a simple process of anion exchange such as that which occurs for species of the type derived from triaryl phosphites and the halogens.[2] The mechanism proposed in the present studies is shown in Scheme 1, involving initial

$$
\begin{aligned}
(ArO)_3\overset{+}{P}Me\ X^- &\rightleftharpoons (ArO)_3P + MeX \\
(ArO)_3\overset{+}{P}Me\ X^- &\rightleftharpoons (ArO)_2\overset{+}{P}(Me)X\ OAr^- \\
(ArO)_2\overset{+}{P}(Me)X + (ArO)_3P &\rightleftharpoons (ArO)_3PMe + (ArO)_3\overset{+}{P}X \\
(ArO)_2PMe + (ArO)_3\overset{+}{P}Me &\rightleftharpoons (ArO)_2\overset{+}{P}Me_2 + (ArO)_3P \\
(ArO)_3\overset{+}{P}X + OAr^- &\rightleftharpoons (ArO)_4\overset{+}{P}\ X^- \longrightarrow ArX + (ArO)_3PO
\end{aligned}
$$

SCHEME 1

displacement of phenoxide by halide, followed by positive halogen transfer and subsequent alkylation of the newly-formed phosphorus (III) species. A similar mechanism may account for an earlier report that the thermal decomposition of the iodomethane adducts of diphenyl phenylphosphonite and phenyl diphenylphosphinite yields phosphonates devoid of methyl substituents.[3] ^1H and ^{31}P nmr studies of the reaction media during decomposition of the methyltriaryloxyphosphonium halides in $CDCl_3$ at 125°C show that reversible formation of quasiphosphonium intermediates containing P-O-P bonds may also occur. The combined evidence suggests that these intermediates are formed by the interaction of triaryl phosphate with the methyltriaryloxyphosphonium halide to give a dipositive quasiphosphonium ion as shown (Scheme 2).



δ_P, Ar = phenyl: 34.0 (d) 77.4 (dq)

δ_P, Ar = o-tolyl: 32.3 (d) 77.0 (dq)

(J_{POP} 30 - 32 Hz; J_{PCH} 15 - 16 Hz)

SCHEME 2

Trineopentyl phosphite has been shown[1] to yield intermediates sufficiently stable for isolation in certain examples of the Michaelis-Arbuzov reaction. We now report the reactions of more highly hindered phosphorus(III) esters derived from 2,2,2-triphenylethanol, 2,2-diethylbutan-1-ol, and 1-norbornyl alcohol. The first of these has the disadvantage that it readily undergoes elimination; the phosphite could not be isolated, although the diphenylphosphinite was prepared and gave a stable intermediate (δ_P 72 ppm) on reaction with iodomethane. A stable intermediate was previously obtained in the reaction of the alcohol with tributylphosphine dibromide.[4] The phosphite derived from 2,2-diethylbutan-1-ol reacted in a similar manner to trineopentyl phosphite,[5] giving the ketophosphonium bromide (δ_P 41 ppm) from α-bromoacetophenone but only the vinyl phosphate (δ_P -6 ppm) (and no identifiable intermediate) from α-chloroacetophenone. Little additional stabilisation was achieved in these cases. The stabilising effect of the 1-norbornyl group in 1-norbornyloxytriphenylphosphonium chloride[6] prompted us to prepare tri-(1-norbornyl) phosphite and to study its reactions. The ester afforded quasiphosphonium halides of unusually high stability (Table I), including a stable Perkow intermediate in its reaction with p-nitro-α-chloroacetophenone. ^{31}P chemical shifts for the trinornornyloxyphosphonium salts, for their Arbuzov cleavage products when formed, and also for trinorbornyl phosphate (δ_P -10 ppm) were at higher field than for the corresponding acyclic analogues by ca. 10 - 15 ppm in each case.

TABLE I Reactions of tri-(1-norbornyl) phosphite

Halogeno compound	Product[a]	δ_P	m/z(%)[b]
MeI	$(RO)_3\overset{+}{P}Me\ I^-$	+ 37	379(100)
$PhCOCH_2Br$	$(RO)_3\overset{+}{P}CH_2COPh\ Br^-$	+ 27	483(100)
$p\text{-}BrC_6H_4COCH_2Br$	$(RO)_3\overset{+}{P}CH_2COC_6H_4NO_2\text{-}p\ Br^-$	+ 26	561/3(55)
$PhCOCH_2Cl$	$(RO)_3\overset{+}{P}CH_2COPh\ Cl^-$	+ 27	
$p\text{-}O_2NC_6H_4COCH_2Cl$	$(RO)_3\overset{+}{P}OC(:CH_2)C_6H_4NO_2\text{-}p\ Cl^-$	- 17	528 (11)
$p\text{-}O_2NC_6H_4COCH_2Br$	$(RO)_3\overset{+}{P}OC(:CH_2)C_6H_4NO_2\text{-}p\ Br^-$	- 17	528 (11)
	$(RO)_3\overset{+}{P}CH_2COC_6H_4NO_2\text{-}p\ Br^-$	+ 25	

[a] Phosphonium salt isolated (R = 1-norbornyl). [b] FAB (P^+ ion)

Unusual features of the reactivity of tri-(1-norbornyl) phosphite were its complete lack of reactivity at room temperature with either chloroacetone or phenacyl chloride (which give vinyl phosphates readily with trialkyl phosphites in general) and the unexpected formation of the ketophosphonium chloride, together with tri-(1-norbornyl) phosphate on heating with phenacyl chloride at 70°C. Steric factors do not appear to be involved in view of the observed reactions with phenacyl bromide and with p-nitrophenacyl chloride (Table I). The tri-(1-norbornyloxy)phosphonium salts showed high thermal stability, the methiodide undergoing only slow decomposition at 150°C. No evidence of disproportionation as reported above for the phenoxy analogues was however found. The ketophosphonium bromides yielded the expected Arbuzov products slowly at 150°C, whereas the Perkow intermediate underwent abnormal cleavage of the vinyloxy group to yield trinorbornyl phosphate and an acetylene, and a number of unidentified by-products were also obtained.

X-ray crystallographic data for a number of quasiphosphonium salts are given in Table II and in all cases show the tetrahedral configuration, with minimum $P^+....X^-$ distances of between 4.05 and 4.99 Å, the distance being shortest in the case of the triphenoxy derivative for which the positive charge on phosphorus can be assumed to be the most intense. Measured P-O bond lengths are significantly less than the calculated single P-O bond length (ca. 1.75 Å) and reveal significant double bond character. The decreasing stability of quasiphosphonium salts with increasing numbers of alkoxy ligands shows, however, the greater importance of the inductive (-I) effect of oxygen in determining reactivity. Nitrogen ligands, however, have a markedly stabilising effect and

d_π-p_π interaction is clearly shown, not only by measured bond lengths of 1.581 - 1.609 (calculated 1.718 for a single P-N bond) but also by the adoption of a planar sp^2 configuration at nitrogen.

TABLE II X-ray crystallographic data

Phosphonium salt[a]	Mean P-O (Å)	$P^+...X^-$ (Å)
$Ph\overset{+}{P}(OCH_2CMe_3)_2Me\ Br^-$	1.549(5)	4.43
$Ph_2\overset{+}{P}(OCH_2CMe_3)Me\ Br^-$	1.568(4)	4.61
$Ph_2\overset{+}{P}(OCH_2CMe_3)CH_2COPh\ Br^-$	1.573(8)	4.23
$(Me_2N)_2\overset{+}{P}(OCH_2CMe_3)Me\ I^-$	1.546(7)	4.99
$(PhO)_3\overset{+}{P}Me\ Br^-$	1.55(4)	4.05
$(RO)_3\overset{+}{P}CH_2COPh\ Br^-$	1.527(13)	4.58
$(RO)_3\overset{+}{P}O(:CH_2)C_6H_4NO_2\text{-}p\ Cl^-$	1.540(23)	4.71

[a] R = 1-norbornyl

Fast atom bombardment mass spectrometry has been found to be a useful additional tool in the characterisation of quasiphosphonium salts. In the positive ion spectrum the phosphonium ion appears, sometimes as the base peak, and fragments by pathways analogous to those observed during thermal decomposition.

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