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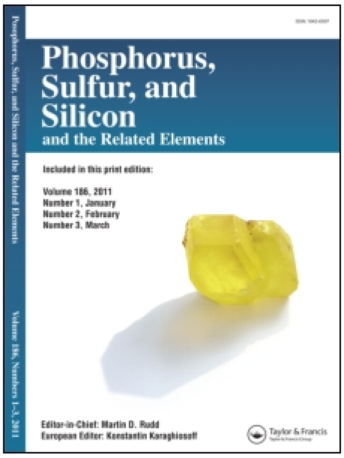

Phosphorus, Sulfur, and Silicon and the Related Elements

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The Interaction of Phosphite Esters with α-Iodoketones in the Presence of Silver Ion

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THE INTERACTION OF PHOSPHITE ESTERS WITH α-IODOKETONES IN THE PRESENCE OF SILVER ION.

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<u>Abstract</u> The reactions of trialkyl phosphites with α-iodoketones in the presence of silver perchlorate or silver tetrafluoroborate yield the corresponding trialkyl phosphates and tetra-alkyl pyrophosphates. Under certain conditions, CIDNP effects indicate the involvement of radical-pairs in the formation of unstable betaine intermediates.

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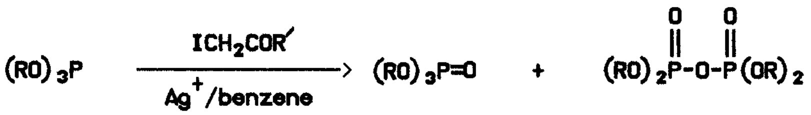
We have reported the formation of trimethyl phosphate and tetramethyl pyrophosphate as the exclusive phosphorus-containing products in the interaction of trimethyl phosphite with iodoacetone or with α-iodoacetophenone in the presence of silver perchlorate in benzene solution.[1] Further investigations of this type of reaction have now shown that similar results are obtained for a range of phosphite esters $(RO)_3P$ (R = Me, i-Bu, neopentyl) (Scheme 1) and we now discuss possible mechanisms for these reactions. In no case was the ketophosphonium perchlorate[2] obtained, nor was there any detectable trace of the Arbuzov or Perkow products which are normally formed in the reactions of α-halogenoketones with phosphorus(III) esters.[2] The possibility that phosphate may originate from the oxidising action of perchlorate is excluded as silver tetrafluoroborate gives rise to the same products (Table I). The reaction rate appeared to be sensitive to traces of



$$(RO)_3P \xrightarrow[Ag^+/\text{benzene}]{ICH_2COR'} (RO)_3P{=}O \quad + \quad (RO)_2\overset{\overset{O}{\|}}{P}-O-\overset{\overset{O}{\|}}{P}(OR)_2$$

(R = Me, i-Bu, neopentyl; R′ = Me, Ph)

SCHEME 1

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Table I Products of the interaction of trialkyl phosphites with α-iodoketones in the presence of silver ion in $C_6H_6/C_6D_6(1:1)$

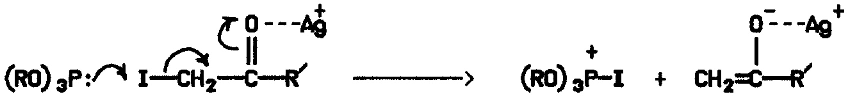
R in $(RO)_3P$	R′ in ICH_2COR'	Ag^+ salt	time (min)[b]	$(RO)_3PO$[a] δ_P	$(RO)_2P(O)OP(O)(OR)_2$ δ_P
Me	Me	ClO_4^-	65	2.2	-10.3
Me	Me	ClO_4^-	30	1.8	-10.5
Me	Ph	BF_4^-	30	2.6	-10.2
Bu^i	Ph	ClO_4^-	19	0.4, -1	-12.9
Pe^{neo}	Me	ClO_4^-	16	-0.9, -2	-13.6
Pe^{neo}	Ph	ClO_4^-	16	-0.03, -2	-12.7

[a] Where two figures are given, one is assigned to the dialkyl phosphate, which is formed from dialkyl phosphite present in the starting material. [b] Reaction not necessarily complete.

moisture. Although the same products (phosphate and pyrophosphate) were obtained under rigorously anhydrous conditions, the reactions proceeded more slowly than with "normally" dried laboratory reagents.

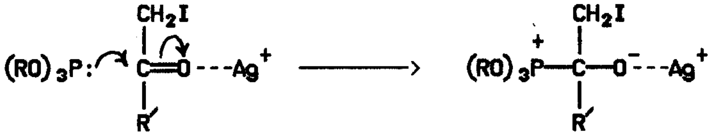
Silver salts form complexes $[(RO)_3P]_nAg^+ X^-$ (n = 1 - 4) with trialkyl phosphites.[3] We found that a 1:1 mixture of the two reagents in benzene exhibited a ^{31}P chemical shift of 127 ppm, due to an equilibrium between the various species. The presence of traces of moisture caused rapid hydrolysis to the dialkyl phosphite, which appeared to interact with the iodoketone in the presence of silver ion to give the corresponding dialkyl phosphate. Addition of iodoketone to the phosphite-Ag^+ solution gave a rapid initial precipitation of silver iodide, followed by further more gradual precipitation as the reaction proceeded to completion. There were no detectable signals at any stage which corresponded to the normal Arbuzov product (δ_P *ca.* 20), Perkow product (δ_P *ca.* -5), or their corresponding precursors.[4] Possible variations of chemical shifts in the presence of silver ion were investigated. In general the ^{31}P signals of phosphonates moved downfield by a maximum of 4 - 5 ppm according to concentration whereas that of the vinyl phosphate was little affected.

The initial interaction of the trialkyl phosphite with the α-iodoketone could occur by nucleophilic attack of phosphorus at the halogen atom (Scheme 2),[5] or the carbonyl carbon atom (Scheme 3). In either case, the reaction may be assisted by coordination of the carbonyl oxygen atom to Ag^+.



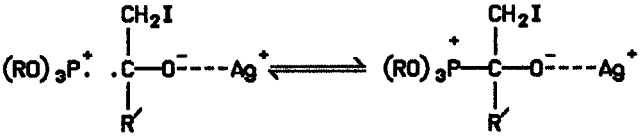
SCHEME 2

Coordination to Ag^+ may also provide some stabilisation for the betaine



SCHEME 3

(shown complexed with Ag^+ in Scheme 3). The betaine is thought to occur in reactions leading to the formation of Perkow products[2] but has never been positively identified. Although we found no direct evidence for such a species during monitoring of the reaction mixture by ^{31}P nmr, we observed strong CIDNP effects (with negative polarisation) in the region δ_P 35 - 40 ppm. The effect was observed for all the phosphites studied but was not always reproducible. No product appeared with a corresponding chemical shift but it is the region in which a trialkyloxyphosphonium ion may be expected to appear. It is tentatively suggested, therefore, that the betaine may be formed transiently *via* a free radical route which involves an initial single-electron transfer from the phosphite to the carbonyl compound (possibly silver-catalysed), followed by a diffusion controlled encounter between the phosphenium radical cation and the carbonyl radical anion (SCHEME 4). Multiplicity of the ^{31}P emission signal suggested coupling to ^{107}Ag and ^{109}Ag,[3(b)] an effect which may be possible in view of the fact that



SCHEME 4

the O-Ag bond is expected to have significant covalent character.[6]

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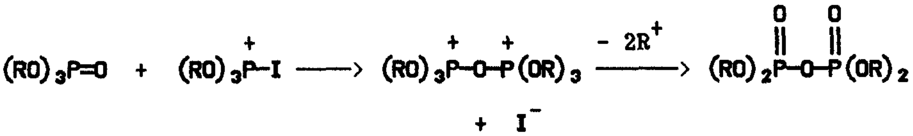
In the presence of moisture, the iodophosphonium enolate (formed as in Scheme 2) would be expected to undergo hydrolysis to yield trialkyl phosphate, together with the hydrodehalogenated ketone CH$_3$COR$'$.[2] Further reaction of the phosphate with an iodophosphonium ion would then account for the formation of tetra-alkyl pyrophosphate, via a doubly charged phosphonium species, formed as shown (Scheme 5).



$$(RO)_3P{=}O + (RO)_3\overset{+}{P}{-}I \longrightarrow (RO)_3\overset{+}{P}{-}O{-}\overset{+}{P}(OR)_3 + I^- \xrightarrow{-\,2R^+} (RO)_2\overset{O}{\overset{\|}{P}}{-}O{-}\overset{O}{\overset{\|}{P}}(OR)_2$$

SCHEME 5

Under anhydrous conditions, however, the overall stoichiometry requires that an alkyne (or related product) should be obtained, in addition to the hydrodehalogenated ketone. An alkyne could in principle be obtained by the elimination of trialkyl phosphate from a vinyloxyphosphonium species, (RO)$_2$P(O)OC(:CH$_2$)R$'$, obtained by rearrangement of the iodophosphonium enolate or the betaine, although such eliminations normally occur only at higher temperatures. Gc-ms of the products obtained by the interaction of trimethyl phosphite with α-iodoacetophenone in the presence of silver tetrafluoroborate did not detect phenylethyne but revealed a complex mixture containing acetophenone, 1- or 3-methyl-1-phenylethene, methyl benzoate, ethyl benzoate, diphenyl ketone, penatdeuterodiphenylketone (derived from C$_6$D$_6$ of the medium), and 2,4-diphenylbut-2-enal. It is likely that a complex combination of heterolytic and homolytic processes is involved.

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