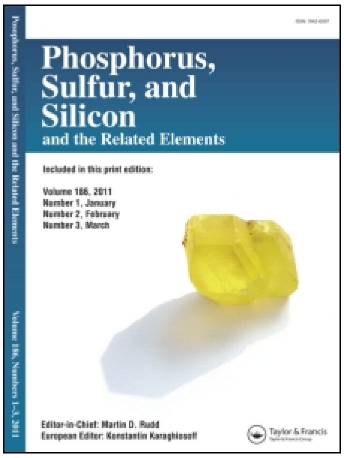

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The Quest for Metaphosphate Species. Phosphoric Chlorides and Anhydrides as Reactive Precursors

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THE QUEST FOR METAPHOSPHATE SPECIES. PHOSPHORIC CHLORIDES AND ANHYDRIDES AS REACTIVE PRECURSORS

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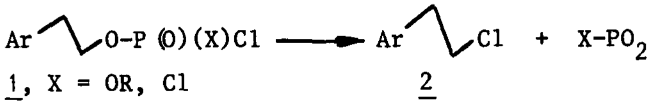
Abstract (β-Arylethyl)phosphorochloridates decompose easily yielding 1-chloro-2-arylethanes *via* the concerted P-Cl fission and the expulsion of metaphosphate species. Mixed anhydrides derived from carboxylic and amidophosphoric acids undergo unimolecular fragmentation to carboxyamides and metaphosphate esters.

The metaphosphate ion, PO_3^- was postulated thirty years ago[1] as a reactive intermediate involved in the hydrolysis of phosphate monoesters, and its existence in the monomeric form in the gas phase has recently been demonstrated by NICI mass spectrometry.[2] Participation of the metaphosphate type species attracts unceasing attention,[3] and recent reports[4] show that a variety of neutral, phosphorus-containing systems can function as precursors for the metaphosphate derivatives of the general formula $X\text{-}PO_2$. Theoretical calculations suggest[5] that it is not the intrinsic instability but rather high electrophilicity of the metaphosphate monomer that makes it such an elusive reaction intermediate.

We report here on two organophosphorus systems which can be considered as derivatives of the metaphosphate XPO_2, "inserted" into the molecular framework, and which undergo facile fragmentation releasing the metaphosphate species and forming simple phosphorus-free products.

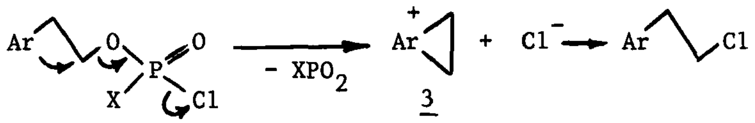
PHOSPHOROCHLORIDATES

We have found[6] that (2-arylethyl)phosphorochloridates (1) are highly unstable and are easily converted into the corresponding 1-chloro-2-arylethanes (2).



(1)

Reaction (1) is a specific example of the collapse of a phosphate RO-P(O)(X)Y proceeding with expulsion of the metaphosphate XPO_2 and with formation of an alkyl derivative R-Y. Our results show that such a collapse is strongly facilitated by the β-aryl substituent in the ester group (and by the electron-releasing substituents in the aryl group), and hence indicate the participation of the benzenonium intermediate (3).



(2)

Experiments with substrates containing poorer leaving groups at phosphorus (*e.g.* p-nitrophenoxy) carried out under solvolytic conditions demonstrated that the fission of the O-P and the P-Cl bonds occurs in a synchronous manner and that the driving force for the expulsion of the metaphosphate is the nucleophilic assistance by the β-aryl group, coupled together with the departure of the good leaving group from the phosphoryl center.

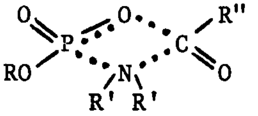
MIXED ANHYDRIDES

Upon gentle heating (or at room temperature) mixed anhydrides (4) derived from carboxylic and amidophosphoric acids undergo fragmentation yielding carboxyamides and metaphosphate esters.[7]

$$\underset{\underline{4}}{(RO)(R'_2N)P(O)OC(O)R''} \longrightarrow R'_2N\text{-}C(O)R'' + RO\text{-}PO_2 \qquad (3)$$

Reaction (3) is highly selective in terms of the group migrating from phosphorus to carbon, *i.e.* no carboxylic esters (products of the RO group migration) were observed in fragmentations of substrates 4. The kinetics, solvent effects and activation parameters, as well as substituent effects determined for reaction (3) demonstrated that the fragmentation is a unimolecular process with little (if any) charge development in the transition state :

$\underline{4}$ →



→ products (4)

The effects of solvents and Lewis acids on the reaction rate and on the activation parameters can be explained best by postulating stabilizing interactions with either carboxyamide or metaphosphate fragments being formed in the course of the reaction.

Current MO calculations[8] confirm the concerted nature of the fragmentation and explain the observed selectivity in terms of stereoelectronic effects.

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