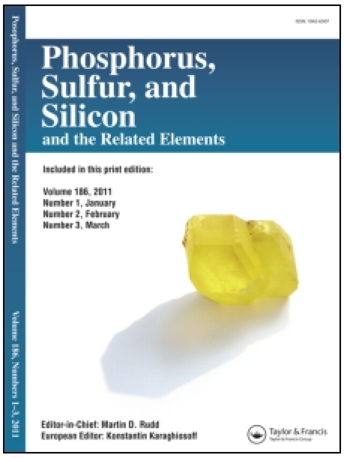

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New Types of Functionally Substituted Methylphosphonites and Their Derivatives

A. A. Prishchenko[a]; M. V. Livantsov[a]; I. F. Lutsenko[a]
[a] M.V. Lomonosov Moscow State University, Moscow, USSR

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NEW TYPES OF FUNCTIONALLY SUBSTITUTED METHYLPHOSPHONITES AND THEIR DERIVATIVES

A.A.PRISHCHENKO, M.V.LIVANTSOV, and I.F.LUTSENKO
M.V.Lomonosov Moscow State University,
Moscow 119899, USSR

Organophosphorus compounds containing a functional group in the α-position of the alkyl radical are of great interest in both theoretical fundamental investigations and for practical applications. Functionally substituted methylphosphonites and their derivatives, belonging to this broad class of organophosphorus compounds, are convenient objects for investigating mutual effects of trivalent phosphorus and a heteroatom, or functional groups attached to it in the α-position. They have also become key substances in obtaining new organophosphorus compounds. Functionally substituted compounds of tetracoordinated phosphorus have been intensively investigated in recent years; rather convenient methods of synthesis of these compounds have been proposed and their properties have been studied in detail[1]. However, the corresponding compounds of tricoordinated phosphorus are not available or difficult to obtain. Recently we reported on the properties of halogen-substituted methylphosphines and their derivatives[2]. The present paper is devoted to the synthesis and investigation of the reactivity of alkoxy-, dialkylamino- and carbonyl substituted methylphosphonites and their derivatives. In synthesis of alkoxymethylphosphonites and their analogs we were the first to use labile alkoxymethylmagnesium chlorides in the reactions with tricoordinated phosphorus acid chlorides[3]. Previously unknown dialkoxymethylphosphonites and their analogs were obtained from hypophosphorous acid and trialkylorthoformates. The process of esterification and dialkoxymethylation of hypophosphorous acid, being dependent on a catalyst, proceeds in different ways and results in the formation of dialkoxymethylphosphonite structures

$(RO)_2PCH(OR)_2$ and $(RO)Me_3SiOPCH(OR)_2$. Di- and trialkoxymethyl(dialkyl)phosphines with bulky alkyl substituents are obtained by the interaction of lithium dialkylphosphides with di- or trialkoxycarbenium tetrafluoroborates.

$$R_2PLi + (RO)_{3-n}H_n\overset{+}{C}\ BF_4^- \xrightarrow[-LiBF_4]{} R_2PCH_n(OR)_{3-n},\quad n = 0,\ 1$$

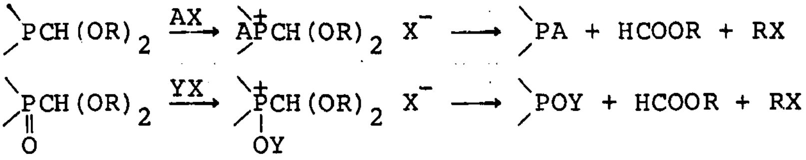
Previously unavailable dialkylaminomethylphosphonites are readily formed in the reaction of dialkoxyphosphines with dialkylaminomethylalkyl ethers.

$$(RO)_2PH + R_2NCH_2OR \longrightarrow (RO)_2PCH_2NR_2 + ROH$$

α-Carbonylphosphonites, containing POSi fragment, were obtained by condensation of pivaloyl chloride with alkoxy(trimethylsiloxy)phosphines in the presence of triethylamine

$$RO(Me_3SiO)PH + t\text{-}BuC(O)Cl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} RO(Me_3SiO)PC(O)Bu\text{-}t$$

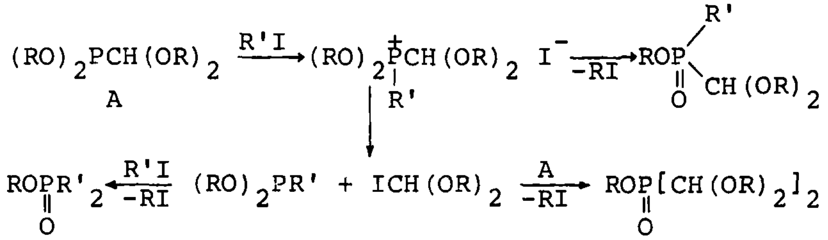
Thus, some practical synthesis methods of new functionally substituted methylphosphonites on the basis of available compounds were found. Studies of the properties of dialkoxy-, trialkoxy-, dialkylaminomethyl- and α-carbonylphosphonites revealed a unique reactivity of these compounds in various transformations connected with a high lability of P-C bond at the stage of quasiphosphonium compounds formation. Quasiphosphonium compounds with dialkoxymethyl fragments, obtained from dialkoxymethylcompounds of tri- and tetracoordinated phosphorus, are unstable and form tricoordinated phosphorus compounds, alkylformates and alkylhalogenides



$$>PCH(OR)_2 \xrightarrow{AX} >A\overset{+}{P}CH(OR)_2\ X^- \longrightarrow >PA + HCOOR + RX$$

$$>\underset{\overset{\|}{O}}{P}CH(OR)_2 \xrightarrow{YX} >\underset{\overset{|}{OY}}{\overset{+}{P}}CH(OR)_2\ X^- \longrightarrow >POY + HCOOR + RX$$

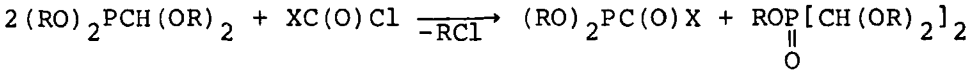
Presence of a labile P-C bond in dialkoxymethylphosphonites rises question about their participipitation in the Arbuzov reaction. Dialkoxymethylphosphonites form with alkyl iodide under moderate conditions with the usual products of the classical rearrangement (phosphinates of non-symmetrical structure) phosphinates of symmetrical structure, their amount in the mixture being about 10-20%.



$$\underset{A}{(RO)_2PCH(OR)_2} \xrightarrow{R'I} (RO)_2\overset{+}{P}(R')CH(OR)_2\ I^- \xrightarrow[-RI]{} RO\overset{O}{\overset{\|}{P}}(R')CH(OR)_2$$

$$RO\overset{O}{\overset{\|}{P}}R'_2 \xleftarrow[-RI]{R'I} (RO)_2PR' + ICH(OR)_2 \xrightarrow[-RI]{A} RO\overset{O}{\overset{\|}{P}}[CH(OR)_2]_2$$

The unusual direction of the Arbuzov reaction is due to the rupture of the P-C bond under the attack of the iodine anion of the electrophilic central carbon atom of dialkoxymethyl group in the intermediate quasiphosphonium compound. Cleavage of the P-C bond is the only possible direction of the reaction between dialkoxymethylphosphonites and acyl chlorides, some new or difficult to obtain α-carbonylphosphonites and bis(dialkoxymethyl)phosphinates were obtained that way



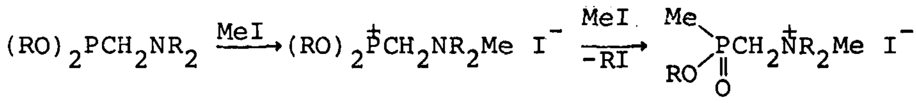
$$2(RO)_2PCH(OR)_2 + XC(O)Cl \xrightarrow[-RCl]{} (RO)_2PC(O)X + RO\overset{O}{\overset{\|}{P}}[CH(OR)_2]_2$$

X = Alk, AlkO.

Dialkoxymethylphosphines are easily splitted by acyl chlorides, unstable chloroformal cannot compete in this case with acyl chloride and decomposes according to the scheme:

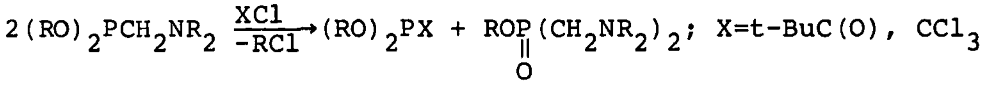
$$R_2PCH(OR)_2 + XC(O)Cl \longrightarrow R_2PC(O)X + ClCH(OR)_2 \longrightarrow RCl + HCOOR$$

Similar transformations were also carried out with dialkylaminomethylphosphonites containing a labile P-C bond. Dialkylaminomethylphosphonite can be easily quaternized at the nitrogen atom by the first equivalent of methyl iodide, an intermediate phosphonite is formed which gives an ordinary product of Arbuzov reaction with the excess methyl iodide.



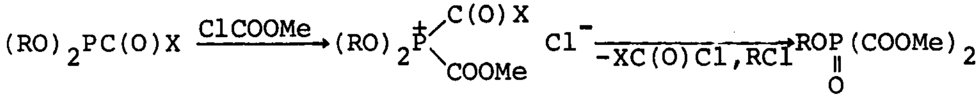
$$(RO)_2PCH_2NR_2 \xrightarrow{MeI} (RO)_2\overset{+}{P}CH_2NR_2Me\ I^- \xrightarrow[-RI]{MeI} (Me)(RO)\overset{O}{\overset{\|}{P}}CH_2\overset{+}{N}R_2Me\ I^-$$

On the other hand, the interaction of dialkylaminomethylphosphonite with pivaloyl chloride and carbon tetrachloride is phosphorus atom oriented and is accompanied by the rupture of P-C bond.



$$2(RO)_2PCH_2NR_2 \xrightarrow[-RCl]{XCl} (RO)_2PX + RO\underset{\underset{O}{\|}}{P}(CH_2NR_2)_2;\ X=t\text{-}BuC(O),\ CCl_3$$

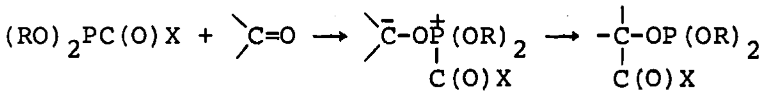
Most striking is the lability of P-C bond in α-carbonylphosphonites. Thus the reaction of pivaloylphosphonite with an excess of methoxycarbonylchloride leads to bis(methoxycarbonyl)phosphinate, i.e. it proceeds with the rupture of P-C bond and formation of pivaloyl chloride.



$$(RO)_2PC(O)X \xrightarrow{ClCOOMe} (RO)_2\overset{+}{P}\begin{smallmatrix}C(O)X\\ COOMe\end{smallmatrix}\ Cl^- \xrightarrow[-XC(O)Cl,RCl]{} RO\underset{\underset{O}{\|}}{P}(COOMe)_2$$

X = t-Bu

The unique reactivity of α-carbonylphosphonites made it possible to use these compounds as new organophosphorus synthons for the development of a selective method of C-C formation. Under mild conditions α-carbonylphosphonites can be easily added to the carbonyl group of a number of aldehydes, ketones, α-ketophosphonates forming functionally substituted phosphites of various structures.



$$(RO)_2PC(O)X + \rangle C=O \longrightarrow \rangle\bar{C}\text{-}O\underset{\underset{C(O)X}{|}}{\overset{+}{P}}(OR)_2 \longrightarrow -\overset{|}{\underset{\underset{C(O)X}{|}}{C}}\text{-}OP(OR)_2$$

X = Alk, AlkO

Evidently the addition begins with the tricoordinated phosphorus attack at the carbonyl group; the bipolar intermediate stabilization is accompanied by the rupture of P-C bond and the acylium-cation migration. Likewise the functionally substituted methylphosphonites investigated by us interact with the classical reagents of organophosphorus chemistry in a new direction via the P-C bond rupture and retention of tricoordinated phosphorus.

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