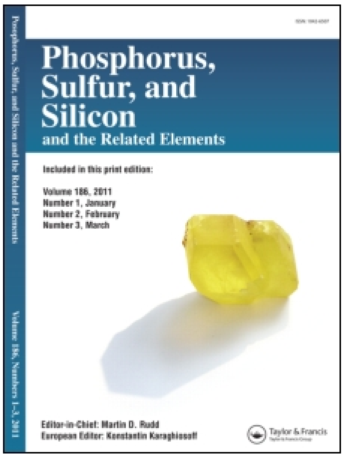

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New Types of Functionally Substituted Cyclic Phosphoranes

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NEW TYPES OF FUNCTIONALLY SUBSTITUTED CYCLIC PHOSPHORANES

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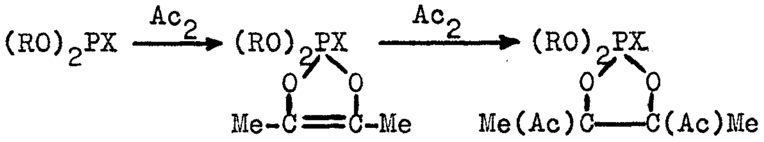
Abstract Dialkoxymethyl- and α-carbonylphosphonites are the key compounds for the synthesis of new types of functionally substituted cyclic phosphoranes.

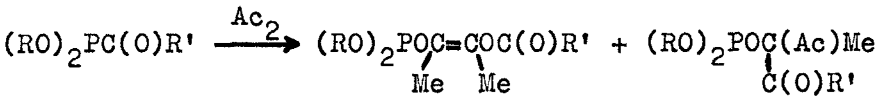
Functionally substituted methylphosphonites and their derivatives are convenient objects for the investigation of mutual effect of tricoordinated phosphorus with a functional group or heteroatoms in the α-position. They are also key compounds for synthesis of new types of organophosphorus compounds of various structure.[1] Dialkoxymethyl- and alkoxycarbonylphosphonites react with diacetyl according to a classic scheme to give phospholenes, 1,2 and phospholanes, 3.



1, 2 3

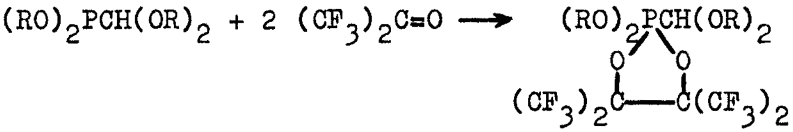
R=Et; X= CH(OEt)$_2$: 1,3; COOMe : 2.

By contrast, at the same conditions acylphosphonites are added to diacetyl by P-C bond rupture yielding the mixture of 1,2- and 1,4-adducts.



$$(RO)_2PC(O)R' \xrightarrow{Ac_2} (RO)_2POC(Me){=}C(Me)OC(O)R' + (RO)_2POC(Ac)Me(C(O)R')$$

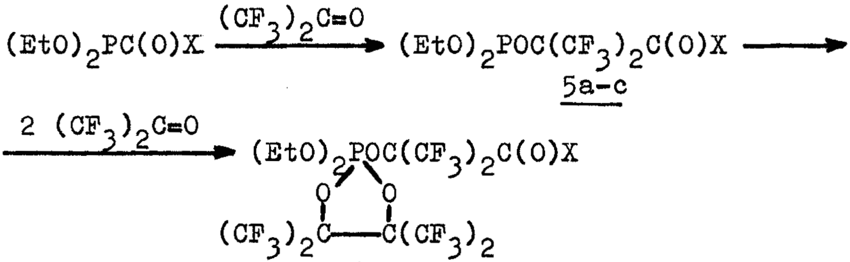
Hexafluoroacetone reacts according to a classic scheme only with dialkoxymethylphosphonites giving phospholane, 4.



R=Et : 4.

4

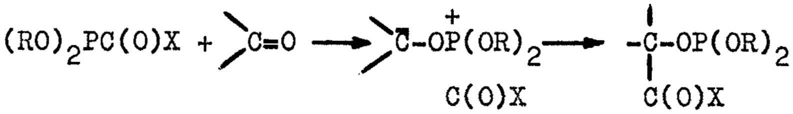
α-Carbonylphosphonites containing the most labile P-C bond react with the first equivalent of hexafluoroacetone forming the insertion products, 5 **which** in the presence of excess of hexafluoroacetone give the functionally substituted phosphoranes, 6.



6a-c

X= i-Pr : 5a, 6a; t-Bu : 5b,6b; MeO : 5c,6c.

Evidently the formation of phosphites, 5 begins with the tricoordinated phosphorus attack at the carbonyl group; the bipolar intermediate stabilization is accompanied by the rupture of P-C bond and acylium-cation migration.



X = Alk, AlkO.

The unique lability of the P-C bond in the functionally substituted methylphosphonites may be widely used for various synthetic purposes. [2,3]

Some physical data of compounds 1-6 are given in Table I. ^{31}P nmr spectra were recorded on a JEOL FX-100 spectrometer in C_6D_6 solvent with an 85% solution of H_3PO_4 in D_2O as external standard (^{31}P, 42.26 MHz). The positive chemical shifts are given in the downfield from standard.

TABLE I Some physical data of compounds, 1-6.

Compound no.	Yield (%)	b.p. (^{o}C, 1 mm)	n_D^{20}	δ_P (s, ppm)
1	90	85	1.4428	-42.6
2	63	95	1.4491	-49.3
3	34	130	1.4480	-45.7
4	96	66	1.3770	-39.4
5a	88	41	1.3875	133.8[a]
5b	90	52	1.3970	140.9[b]
5c	81	39	1.3785	137.1[c]
6a	75	73	1.3675	-57.6
6b	80	96	1.3750	-57.9
6c	78	90	1.3630	-58.6

a $^4J_{PF}$ 24.4 Hz; [b] $^4J_{PF}$ 44 Hz; [c] $^4J_{PF}$ 14 Hz;
s - singlet.

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