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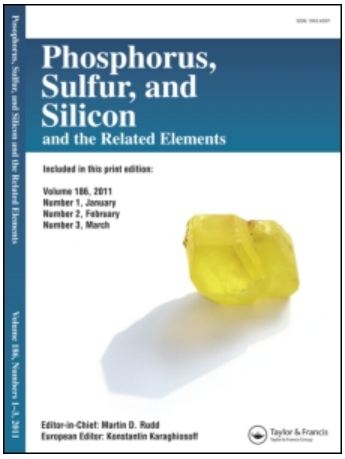

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P-HALOGENYLIDS OF PHOSPHORUS. SYNTHESIS AND PROPERTIES

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P-Halogenylids of phosphorus are new perspective organophosphorus reagents. The first P-halogenylids have been obtained by as[1,2] and then by other chemists.[3]

At present there are several methods of P-halogenylid synthesis. The most general method og P-halogenylid preparation consists in „oxidative ylidation" of CH-acids - derivatives of trivalent phosphorus with tetrahalogenmethanes (CCl_4 or CBr_4) [2, 4]

$$R_2P\text{-}CHR'_2 + CHlg_4 \longrightarrow R_2\overset{Hlg}{\underset{|}{P}} = CR'_2 + CHHlg_3$$

1 2

R = Alk, Ph, AlkO, Alk_2N;

CR'_2 = CH_2, CHAlk, $CHSiMe_3$ CHSMe, CPh_2, $CHSO_2CF_3$, $C(SO_2Ar)_2$, $C(CO_2Alk)_2$

The formation of P-halogenylids is favored by electronoacceptor substituents R' at α-carbon atom in phosphines 1, increasing the activity of hydrogen atom, and by bulky substituents at phosphorus atom. [4]

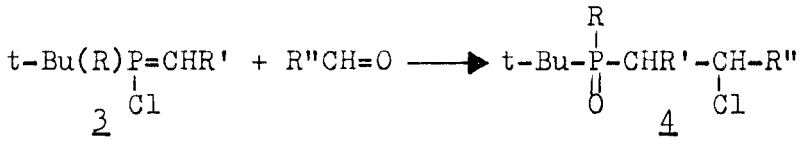
P-Halogenylids are also yielded in the reaction of chlorophosphines with halogensulphonmethanes in the presence of base as a result of α-halogenphosphine- P-halogenylid rearrangement (C, P -halogen shift) [1]

$$R_2PCl + HlgCHR'\text{-}SO_2R'' \xrightarrow{B:} R_2P\text{-}\overset{Hlg}{\underset{|}{C}}R'\text{-}SO_2R'' \longrightarrow R_2\overset{Hlg}{\underset{|}{P}}{=}CR'SO_2R''$$

R= Et, i-Pr, Ph;

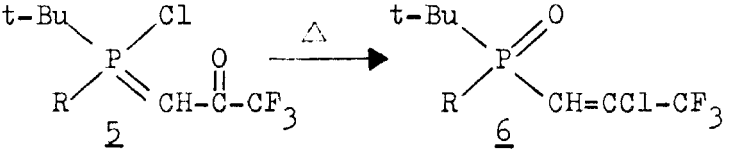
R'= H, SO_2Ar; R"= CF_3, Ar

P-Halogenylids have high reactivity, they contain two reaction centres - electrophilic P-atom and anionic α-carbon atom. The activity of P-halogenylids to electrophiles depends on stabilization of negative charge at ylid C-atom by substituents. „Unstabilized" P-halogenylids react easily with HHlg, Lewis acids, carbonyl compounds, acyl chlorides and so on [4, 5]

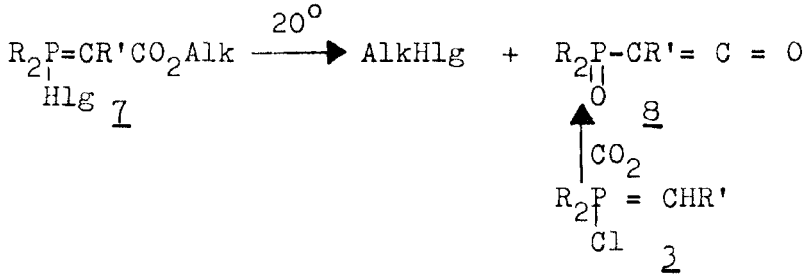


R = Alk, Alk_2N; R'= H, Alk; R"= H, Alk, Ar

Unlike Wittig reaction with triphenylphosphonium ylids, P-halogenylids react with aldehydes withot cleavage C-P bond, to yield β-chloroalkylphosphine oxyde 4. If P-halogenylids contain carbonyl group (compound 5), they rearrange into β-chlorovinylphosphine oxydes 6 [7]



P-Halogenylids 7 with alkoxycarbonyl group produce halogen alkyl and phosphorylated Ketens 8 above 20° C [8]



Phosphorylated ketens are also formed in reactions of „unstabilized" ylids with carbon dioxyde. [5]

P-Halogenylids react with a number of electrophiles to yield new ylids (transylidation reaction) [4]

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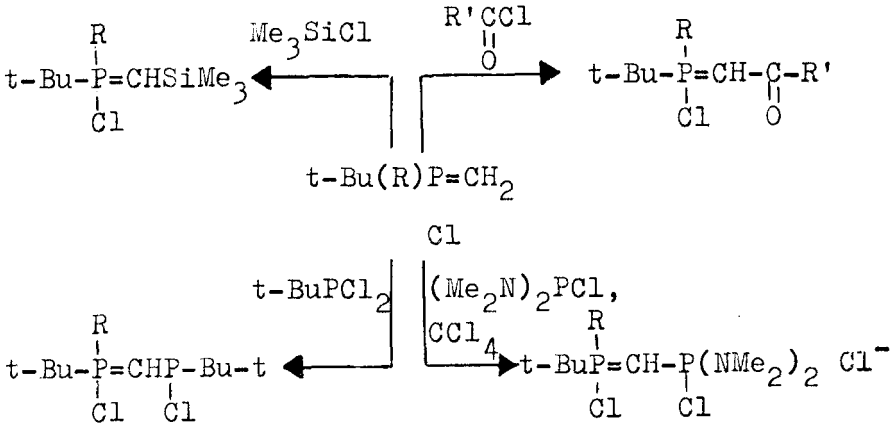
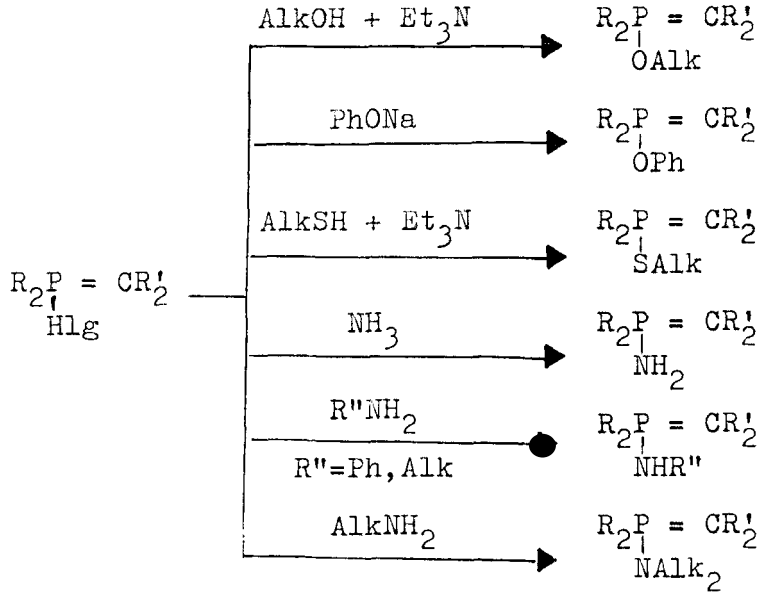


„Stabilized" P-halogenylids react with nucleophyles by usual scheme yielding new P-substituded ylids[1,2]



R' = SO_2Ph, SO_2CF_3, CO_2Me, CO_2Et, $SiMe_3$

„Unstabilized" P-halogenylids add compounds containing mobile hydrogen to give phosphonium salts [9]

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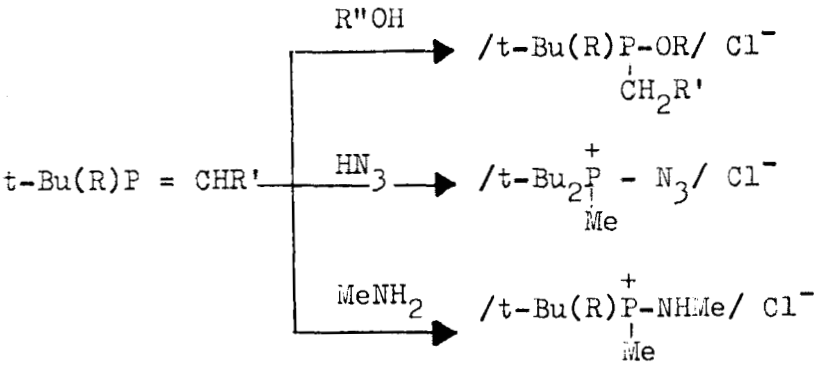

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