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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Dipiiosphoniomethanes with Hydrogen Atom, OH- And SH-Groups at Phosphorus

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DIPHOSPHONIOMETHANES WITH HYDROGEN ATOM, OH- AND SH--GROUPS AT PHOSPHORUS

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Recently it has been shown that the interaction of equimolar amount of HHlg with phosphinosubstituted ylides (I) and phosphoryl- and thiophosphorylsubstituted ylides (II) leads to monoprotonation products: at the carbon or phosphorus of (I) and at the carbon or oxygen (sulfur) of (II) 1. We have found that products of double protonation, diphosphoniomethanes with P-H (III) and P-OH (IV) bonds respectively, are formed by the action of excess acid  $(HSO_3F, HHlg)$ .

$$\begin{array}{lll} R_{2}^{P-C(Y)=PPh_{3}} & \text{(I)} & + & 2H^{+} & \rightarrow & R_{2}^{\frac{1}{p}}(H)-CH(Y)-\frac{1}{p}Ph_{3} & \text{(III)} \\ R_{2}^{P}(X)-C(Y)=PPh_{3} & \text{(II)} & + & 2H^{+} & \rightarrow & R_{2}^{\frac{1}{p}}(XH)-CH(Y)\frac{1}{p}Ph_{3} & \text{(IV)} \\ R & = & Bu, & Ph, & PhO; & X & = & O, & S; & Y & = & COOEt, & Ts, & Ph_{3}. \end{array}$$

Diprotonation of ylides (V) and (VI) with acyl groups at the carbon proceeds at the phosphorus atom and the C=O of (V), or at the PO and CO groups of (VI), and gives two geometric isomers of the enolic form of diphosphoniosubstituted acetone and acetophenone (VII, VIII).

$$Ph_{2}P-C(COR')=PPh_{3}$$
 (V) +  $2H^{+} \rightarrow Ph_{3}^{\dagger}P(Ph_{2}^{\dagger}H)C=C(OH)R'$  (VII)  
 $Ph_{2}P(X)-C(COR')=PPh_{3}$  (VI) +  $2H^{+} \rightarrow Ph_{3}^{\dagger}P(Ph_{2}^{\dagger}XH)C=C(OH)R'$  (VIII)  
 $R'=Me$ ,  $Ph$ ;  $X=O$ ,  $S$ .

Compound  $Ph_3^{\frac{1}{p}}(Ph_2^{\frac{1}{p}}OH)C=C(OH)Me$  23r was isolated in crystalline form. According to X-ray analysis, OH- and POH-groups are in trans-position and form strong H-bonds with Br.

1. T.A.Mastryukova, M.I.Kabachnik, Usp. Khim., 1383, 52, 1751.