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On the Reactions of Trithiophosphites with Alcohols in the Presence of Transition Metal Halides

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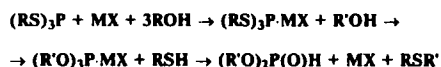
ELVIRA S. BATYEVA, LIDIYA I. KURSHEVA, LILIYA V. FROLOVA,
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Recently we have established that triphenyl- and trialkyltrithiophosphites react with copper(I) halides with the formation of different types of complexes depending on substituents in the thioalkylgroup and on the conditions. These complexes readily react with alcohols resulting in dialkylphosphorous acid [1]. We have assumed that the analogous phosphorylation of alcohols by $(\text{PhS})_3\text{P}$ and $(\text{AlkS})_3\text{P}$ must be conducted in the presence of transition metal halides (CuCl , CuBr , CdCl_2 , CdI_2 , ZnCl_2 , HgCl_2 , HgBr_2) as well.

Actually we have found that $(\text{RS})_3\text{P}$ reacts with EtOH , MeOH in the presence of CuCl , CuBr with the formation of dialkylphosphites. Reaction in the presence of CdCl_2 , CdI_2 , ZnCl_2 , HgCl_2 and HgBr_2 proceed analogously. In the reaction of $(\text{AlkS})_3\text{P}$ with ethanol the quantity of CdCl_2 has been varied from equimolecular to 15%. In this case $(\text{EtO})_2\text{P}(\text{O})\text{H}$ is formed in high yield and purity.

We assume that the complex of $(\text{AlkS})_3\text{P}$ or $(\text{PhS})_3\text{P}$ with the transition metal halide is formed first and then the substitution of the thiol-group by the alkoxy-group occurs with the elimination of AlkSH or PhSH with the following interaction of the latter, with the trialkylphosphite complex resulting in dialkylphosphorous acid.



$\text{R} = \text{Et}, \text{C}_5\text{H}_{11}, \text{Ph}$ $\text{R}' = \text{Et}, \text{Me}$ $\text{X} = \text{Cl}, \text{Br}, \text{J}$ $\text{M} = \text{Cu(I)}, \text{Zn}, \text{Cd}, \text{Hg(II)}$

The phosphorylation of alcohols by trialkyltrithiophosphites in the presence of transition metal halides, in our opinion is an alternative method for obtaining dialkylphosphorous acids from white phosphorus and disulfides according to the nonchloroanhydride technology.

References

- [1] Kursheva L.I.; Frolova L.V.; Bykova M.V.; Batyeva E.S. Zh.Obshch.Khim.1996. 66. 1458.