

Approved For Release 1999/09/10 : CIA-RDP83-00423R001200820006-2
Reaction of diethyl phosphite with esters of phosphorous acid with esters of halogen substituted aliphatic acids.

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The reaction of $(\text{MeO})_3\text{P}$ with $\text{MeO}_2\text{CCHClCH}_2\text{Cl}$ yields mainly $(\text{MeO})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{Cl})\text{CO}_2\text{Me}$, $b_2 106-8^\circ$, $d_4^{20} 1.2691$, $n_D^{20} 1.4535$. The similar reaction of $(\text{EtO})_3\text{P}$ at $110-20^\circ$ yields mainly $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CH}_2\text{Cl})\text{CO}_2\text{Me}$, $b_4 131-2^\circ$, $d_4^{20} 1.1882$, $d_4^{20} 1.1670$, $n_D^{20} 1.4460$, along with some ~~unknown~~ Me 1,2(bis-diethylphosphono)propanoate. The reaction of $\text{MeO}_2\text{CCHClCH}_2\text{Cl}$ with $(\text{EtO})_2\text{P}(\text{O})\text{Na}$ gave exclusively the latter product, $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Me})\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$, $b_3 162-3^\circ$, $d_4^{20} 1.1970$, $d_4^{20} 1.1309$, $n_D^{20} 1.4474$. The above described reaction with $(\text{EtO})_3\text{P}$ run at $140-70^\circ$ proceeds rather complexly: the phosphite dehydrochlorinates the carboxylic esters and the resulting Me 1-chloroacrylate polymerizes in situ; EtCl is also evolved with formation of $(\text{EtO})_2\text{POH}$. The reaction of $(\text{iso-PrO})_3\text{P}$ is similar. A quantitative study of this reaction showed that the amount of $(\text{RO})_2\text{POH}$ formed is considerable smaller than the theoretical, while the amount of evolved RCl is considerable greater. The explanation of this fact lies in that at elevated temp. $(\text{EtO})_2\text{POH}$ reacts with the dihalocarboxylic esters also by the dehydrochlorination route, yielding the polymeric chloroacrylate and $\text{EtOH}(\text{O})(\text{OH})\text{H}$ with evolution of EtCl . Such a reaction of $(\text{EtO})_2\text{POH}$ was also tested by heating the ester with $\text{EtO}_2\text{CCH}_2\text{Br}$ to 150° , when EtBr was evolved and the residue formed an undistillable liquid. The latter on hydrolysis gave $\text{HO}_2\text{CCH}_2\text{PO}_3\text{H}_2$. Of the various possible reaction schemes the most probable is: $(\text{EtO})_2\text{POH} + \text{BrCH}_2\text{CO}_2\text{Et} \rightarrow (\text{EtO})_2\text{P}(\text{OH})(\text{CH}_2\text{CO}_2\text{Et})\text{Br} \rightarrow \text{EtBr} + \text{EtOP}(\text{O})(\text{OH})\text{CH}_2\text{CO}_2\text{Et}$, with the original phosphite reacting in the enolic form. The same reaction was tried with addn. of $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$; the latter ester returned unchanged, which was held as a proof of the above scheme, since a reaction scheme: $(\text{EtO})_2\text{P}(\text{O})\text{H} + \text{BrCH}_2\text{CO}_2\text{Et} \rightarrow (\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et} + \text{HBr} \rightarrow \text{EtBr} + (\text{EtO})\text{P}(\text{O})(\text{OH})\text{CH}_2\text{CO}_2\text{Et}$, should have resulted in some reaction of the allyl ester with HBr . The result is held a confirmation of the enol-keto equil. in dialkyl phosphites,

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the factors of elevated temp. and the solvent (Et bromoacetate) being responsible for the shift toward the enol form.

Cf. V.S.Vinogradova, Uchen.Zapiski Kazan. Gos.Univ.110,5(1950) and T.G.Shavsha, *ibid.* 110-83(1950).