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A New Approach to P-C Bond Formation by Using Tri-Methylsilyl Phosphites

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A NEW APPROACH TO P-C BOND FORMATION BY USING TRI-METHYLSILYL PHOSPHITES

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The in situ silylation of phosphorous acid diesters to phosphorous acid triesters by hexamethyldisilazane and trimethylsilyl halides under conditions of Michaelis-Arbuzov reaction was found as an efficient and facile reaction principle for P-C bond formation.

In general the method can be applied also to Michaelis-Arbuzov reactions of phosphonous and hypophosphorous acid esters, to Tavs reaction of phosphorous and phosphonous acid esters as well as to photochemical conversions of arylhalides with trimethylsilyl phosphites. In any case described the observed yield is nearly quantitative. The industrial production of trisodium phosphonoformate via mono- and bis-trimethylsilylphosphite is an example for the practical use of P-C bond formation by in situ silylation.

$$H_3PO_3 \xrightarrow{HMDS \atop -H_2O} Me_3SiO-P \xrightarrow{OH \atop H} \xrightarrow{HMDZ \atop H} H-P(OSiMe_3)_2 + P(OSiMe_3)_3$$

2 + 3
$$\frac{\text{HMDZ}}{\text{C1-COOR}}$$
 RO-C-P(OSiMe₃)₂ $\frac{\text{NaOH}}{\text{Na}_3}$ Na₃[PO₃CO₂] x 6H₂O

Starting from phosphorous acid or phosphorus trichloride or phosphorus trioxide, respectively, the viricidal agent can be obtained in a quasi one-pot procedure in nearly quantitative yield. (1)

(1) K. Issleib et al., DD 215085, 218101, 243497, 243498