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THE REACTIONS OF TRIALKYLSILYL-CONTAINING PHOSPHITES WITH ELECTROPHILIC ORGANIC COMPOUNDS

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The reactions of silyl-containing phosphites with electrophilic alkynes and various carbonyl compounds have been investigated. The higher nucleophilicity of silyl phosphites, relative to the analogous trialkyl phosphites, and the ease with which transfer of a silyl group occurs from the initially formed quasi-phosphonium intermediates, has a significant impact both on the nature of the products formed and the conditions needed to bring about the reaction.

SCHEME 1

Both characteristics are clearly shown in the reaction of $TmsOP(OR)_2$ (R = alkyl or Tms) with phthalic anhydride. Reaction with trialkyl phosphites, which requires high temperatures and long reaction times, gives the bisphthalide (1) whereas reaction with $(TmsO)_3P$ occurs at room temperature in a few minutes to give the novel phosphonate (2).

SCHEME 2

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Rapid transfer of the silyl group also is well illustrated in the reactions of electrophilic alkynes where the initially formed 1:1 intermediates (3; W = H or CO_2Et , R = alkyl or Tms) rearrange to give the corresponding silylated systems (4) before further intermolecular reactions can occur.