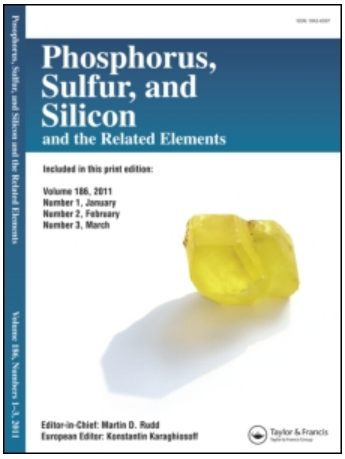

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Products in the Reactions of Trialkyl Phosphites with α-Halogeno-acetophenones in Alcoholic Media

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Products in the Reactions of Trialkyl Phosphites with α–Halogeno-acetophenones in Alcoholic Media

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α-Hydroxyphosphonates are formed, in addition to vinyl phosphates and dehalogenated ketones, in the reactions of trimethyl phosphite (in methanol) or triethyl phosphite (in ethanol) with variously substituted α-chloro, α-bromo, and α,α,-dichloro-acetophenones. Tri-isopropyl phosphite in propan-2-ol gives only the vinyl phosphate. Ketophosphonates are not detectable amongst the reaction products under the conditions used. Trends in product composition can be correlated with the leaving ability of halogen, substituent effects, structure of the phosphite, and reaction temperature. Reactant ratios may also influence the product composition. The reactions of trimethyl phosphite in methanol with 4-nitro-α-chloroacetophenone, or α,α-dichloroacetophenones yield the dehalogenated α-hydrogxyphosphonates in addition. In the case of the 4-nitro derivative, this product cannot be accounted for by reaction of the phosphite with dehalogenated ketone (4-nitroacetophenone). Dehalogenation of the first-formed α-hydroxyphosphonate was, however, shown to occur under reaction conditions and appears to require the removal of positive chlorine, followed by protonation. Reactions of the α,α-dichloroacetophenones were similar to those of the α-chloroacetophenones, giving the corresponding chlorovinyl phosphate, α,α-dichloro-α-hydroxyphosphonate, and monodehalogenated ketone(i.e. α-chloroacetophenone); the latter was not however detected as it reacted further with excess phosphite to give the expected products as described above. Possible mechanisms for the various reactions are discussed. The ^{1}H and ^{13}C nmr spectra of the α-hydroxy-phosphonates show magnetic non-equivalence of the two alkoxy groups, attributed to restricted rotation about the P-C bond as a result of intramolecular hydrogen-bonding.