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The Effect of Silver Perchlorate of the Reaction of Trialkyl Phosphite with α -Halogenoketones

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THE EFFECT OF SILVER PERCHLORATE OF THE REACTION OF TRIALKYL PHOSPHITE WITH α -HALOGENOKETONES

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Trialkyl phosphites are known to react with α -halogenoketones to yield β -ketophosphonates (Arbuzov product) or vinyl phosphates (Perkow product) according to conditions.¹ α -Hydroxyphosphonate may be formed in addition, in protic media.² We have now shown that none of these products is formed in the presence of silver perchlorate (in benzene solution); nor could we detect the ketophosphonium perchlorate reported previously.¹ Phosphorus-31 nmr showed the formation of trimethyl phosphate and tetramethyl pyrophosphate as the exclusive phosphorus - containing products. The sequence of possible reaction is complex and the overall stoichiometry may vary somewhat according to the rate and order of mixing. Trialkyl phosphate could be formed by elimination of alkyne from vinyloxyphosphonium intermediate produced together with silver iodine in first stage of the interaction. Pyrophosphate formation would then result from nucleophilic attack of trimethyl phosphate on the trimethoxy(1-methylvinyloxy)phosphonium ion, which may be formed as a reactive intermediate. Evidence for formation of methyl perchlorate in the final dealkylation of the quasiphosphonium intermediate is provided by proton nmr spectroscopy and by the formation of the N-methylquinolinium salt on addition of quinoline. No change in the ³¹P nmr spectrum occurs at this stage. Other by-products of the main reactions include the dehalogenated ketone (acetone from iodoacetone or acetophenone from α -iodoacetophenone).

1. P.A.Chopard, V.M.Clark, R.F.Hudson and A.J.Kirby: *Tetrahedron*, 21, 1961 (1965)

2. Gy.Keglevich, I.Petneházy, L.Tőke and H.R.Hudson: *Phosphorus Sulfur*, 29, 341 (1987) and cited references.