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SILYL PHOSPHITES. II.

REACTIONS OF TRIS(TRIMETHYLSILYL) PHOSPHITE WITH ALKYL HALIDES

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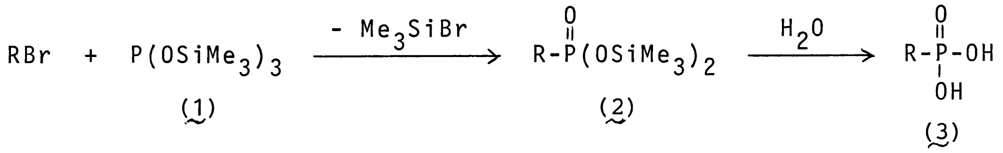
Alkylphosphonic acids and phenacyl enol-phosphate were obtained in high yields by the reactions of alkyl bromides or phenacyl bromide with tris(trimethylsilyl) phosphite followed by hydrolysis under very mild conditions.

One of the most useful reactions in organo-phosphorus chemistry is the reaction of trialkyl phosphites with alkyl halides. This is known as the Arbusov reaction, and the reactivity of various phosphites has been investigated in detail.[1] It has been demonstrated in a previous paper[2] that silyl phosphites reacted smoothly with diphenyl disulfide to give the corresponding S-phenyl phosphorothioates in almost quantitative yields. In view of the high reactivity of the silyl phosphites toward electrophiles, the reactions of tris(trimethylsilyl) phosphite (1) with alkyl halides were tried.[3]

When a mixture of tris(trimethylsilyl) phosphite (1) (17 mmol) and n-butyl bromide (34.8 mmol) was heated at 110°C for 7 hr without using solvent, bis(trimethylsilyl) butylphosphonate (2a) (bp 122-123°C/19 mmHg) was obtained in 89% yield. When n-butyl iodide was used in place of n-butyl bromide, several by-products were formed together with 2a. On the other hand, when n-butyl chloride was employed, no reaction was observed under the same condition.

Similarly, bis(trimethylsilyl) benzylphosphonate (2b) was obtained in 91% yield when the reaction of benzyl bromide (16.8 mmol) with 1 (6.04 mmol) was carried out at 160°C for 6 hr. When benzyl chloride was used in place of benzyl bromide, 2b (bp 118°C/1.3 mmHg) was obtained in 80% yield. Benzyl iodide, however, could be used in this reaction, but side reactions were also observed.



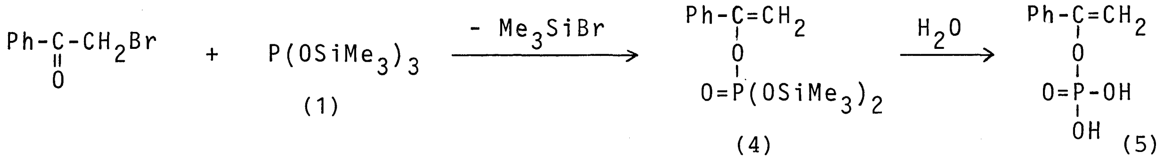
$$\mathrm{RBr} + \underset{(1)}{\mathrm{P(OSiMe_3)_3}} \xrightarrow{-\mathrm{Me_3SiBr}} \underset{(2)}{\mathrm{R\text{-}\overset{O}{\overset{\|}{P}}(OSiMe_3)_2}} \xrightarrow{\mathrm{H_2O}} \underset{(3)}{\mathrm{R\text{-}\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}\text{-}OH}}$$

2a, 3a: $R = n\text{-}C_4H_9$; 2b, 3b: $R = C_6H_5CH_2$

Bis(trimethylsilyl) phosphonates (2) prepared in the present experiments could be easily hydrolyzed by simple treatment with water at room temperature to the corresponding phosphonic acids (3), whereas dialkyl phosphonates, in general, hydrolyzed by treating with hydrochloric acid under reflux. Butylphosphonic acid (3a) (mp 101-102°C) and benzylphosphonic acid (3b) (mp 172-173°C) were obtained in almost quantitative yields from 2a and 2b, respectively.

It is known that trialkyl phosphites react with α-halogenated carbonyl compounds to give enol-phosphates with elimination of a molecule of alkyl halide (the Perkow reaction). The direct displacement of halide ion to give the isomeric 2-oxoalkylphosphonates (the Arbusov reaction) can also occur, and the properties of the carbonyl compounds and the phosphites may result in the formation of either one of the isomers or a mixture of the two. In consideration of the above facts, the reaction of 1 with phenacyl bromide was examined.

When phenacyl bromide (36.2 mmol) was treated with 1 (90.6 mmol) in dry benzene at room temperature for 3 hr, only phenacyl bis(trimethylsilyl) enol-phosphate (4) (bp 131-132°C/0.25 mmHg) was obtained in 66% yield.4) Compound 4 was hydrolyzed smoothly by a simple addition of water at room temperature to afford phenacyl enol-phosphate (5) (mp 166-168°C).5)



In a similar manner, isopropenyl bis(trimethylsilyl) phosphate (bp 127-130°C/0.55 mmHg) was obtained in 47% yield by the reaction of bromoacetone with 1 under the same condition.4)

The authors heartily thank Professor Teruaki Mukaiyama for his encouragement and discussion throughout the investigation.

References and Notes

1) A.J.Kirby and S.G.Warren, "The Organic Chemistry of Phosphorus", Elsevier Publishers, Amsterdam (1967), p.37.
2) T.Hata and M.Sekine, J.Amer.Chem.Soc.,96,7363(1974).
3) Little attention has been paid to the utility of silyl phosphites except the only example reported by Russian workers involving some reactions with alkyl halides: N.F.Orlov, M.A.Belokrinitskii, B.L.Kaufman, and E.V.Sudakova, Chem.Abstr.,72, 90571a(1970).
4) The structure was confirmed by IR and NMR spectra. In this reaction, no phosphonate derivative could be detected.
5) Compound 5 was obtained in 68% yield as a pyridinium salt from the reaction of 1 with phenacyl bromide without isolation of 4. Compound 5 is relatively unstable and the most favorable procedure for isolation of 5 is the subject for a future study.

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