

Formation of Alkyl Phosphenites from Alkyl Phosphinates

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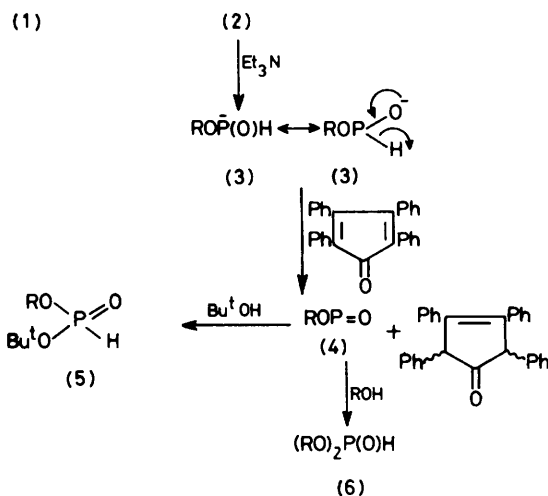
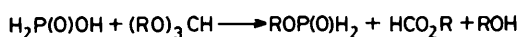
Summary Mild oxidation, in the presence of *t*-butyl alcohol, of the anions formed by treatment of alkyl phosphinates, ROP(O)H_2 , with triethylamine affords the mixed phosphonate diesters $\text{RO}(\text{Bu}^t\text{O})\text{P(O)H}$; this reaction may be interpreted by assuming the intermediate formation of alkyl phosphenites, ROP=O .

PHOSPHENOUS ACID (HO-P=O) and its esters are unknown;¹ this communication describes the formation of alkyl phosphenites by mild oxidation of the anion obtained by treating alkyl phosphinates with base.

Alkyl phosphinates (**2**) may be prepared by dissolving anhydrous phosphinic acid (**1**) in trialkyl orthoformates.² The esters so obtained cannot be conveniently purified, and

though the crude mixture may be used in Michael additions to acrylic acid derivatives,^{3,4} base-induced decomposition is the major reaction in the presence of less active substrates such as alkyl halides. When this decomposition is allowed to proceed in the presence of a hydride ion acceptor, such as tetraphenylcyclopentadienone, the phosphinate ester is converted into the corresponding phosphonate diester in good yield.⁵ This sequence is accommodated by the pathway shown in the Scheme⁵ and in support of this we now report that in the presence of *t*-butyl alcohol the mixed diester (**5**) is formed.

Freshly prepared methyl phosphinate was diluted with 20 times its volume of dry benzene and the solution concentrated at room temperature to remove as much methanol as possible. The ester was then decomposed by adding it to



a; R = Me
b; R = Et

SCHEME 1

a dilute benzene solution containing tetraphenylcyclopentadienone (1 mol. equiv.), triethylamine (0.25 mol. equiv.), and Bu^tOH (3 mol. equiv.). When the colour of the dienone was discharged (1 h) solvents were removed at room temperature and the residue heated rapidly, but briefly, *in vacuo*. The distillate consisted of a mixture of dimethyl phosphonate (**6a**),⁶ methyl t-butyl phosphonate (**5a**),⁶ and di-t-butyl phosphonate (**5**; R = Bu^t).^{6,7} All

† A major product of the non-oxidative decomposition of (**2a**) or (**2b**) is an insoluble, infusible, brown solid which, when thoroughly washed with dilute HCl, has a phosphorus content in reasonable agreement with the formula (HP=O). This may arise by loss of RO^- from (**3**), giving oxophosphine (HP=O) which could polymerise in concentrated solution but revert to the ester (**2**) in the presence of an alcohol. Significantly, the formation of this material is virtually eliminated by dilution with methanol or ethanol and decomposition does not occur with (**2**, R = Bu^t). However, our attempts to trap oxophosphine have been ambiguous as yet.

‡ We have assumed that the reactivity of $\text{P}^{\text{III}}=\text{O}$ will parallel that of $\text{P}^{\text{IV}}=\text{O}$ in such species as metaphosphates. This parallel holds for $\text{P}=\text{N}$ in an analogous system (ref. 1).

¹ Nitrogen analogues ($\text{RN}=\text{PNR}_2$) carrying bulky substituents are known: E. Niecke and W. Flick, *Angew. Chem. Internat. Edn.*, 1973, **12**, 585.

² S. Fitch, *J. Amer. Chem. Soc.*, 1964, **86**, 61. The ester is formed in about 80% yield; for the other products see: M. J. Gallagher and H. Honegger, *Tetrahedron Letters*, 1977, 2987.

³ L. Maier, *Helv. Chim. Acta*, 1973, **56**, 489.

⁴ M. J. Gallagher and J. Sussman, *Phosphorus*, 1975, **5**, 91.

⁵ C. J. R. Fookes and M. J. Gallagher, *J.C.S. Perkin I*, 1975, 1876.

⁶ Identified by n.m.r. (³¹P, ¹H) and gas chromatographic comparison with authentic samples: V. Mark and J. R. Van Wazer, *J. Org. Chem.*, 1964, **29**, 1006; 1967, **32**, 1187; A. Zwierzak and M. Kluba, *Tetrahedron*, 1973, **29**, 1089.

⁷ This is formed from the oxidation of t-butyl phosphinate (**2**, R = Bu^t), which arises by transesterification of the alkyl phosphinate (**2**) and Bu^tOH (ref. 8): M. J. Gallagher and H. Honegger, *J.C.S. Chem. Comm.*, 1978, 54.

⁸ K. A. Petrov and R. G. Goltsova, *Russian Chem. Rev.*, 1966, **35**, 622.

⁹ A. J. Kirby, *Chem. and Ind.*, 1963, 1877.

three compounds could be shown (³¹P n.m.r.) to be present in the reaction mixture before distillation. Similar treatment of ethyl phosphinate (**2b**), affords diethyl phosphonate (**6b**),⁶ ethyl t-butyl phosphonate (**5b**),⁶ and di-t-butyl phosphonate.^{6,7} The overall yield of isolated phosphonates is ca. 70%; the mixed ester is the major component (50–60%) and di-t-butyl phosphonate the minor (ca. 5%). The formation of (**6**) is attributed to the difficulty of completely freeing the heat-sensitive ester (**2**) of the alcohol formed in its preparation. The primary alcohols would be expected to compete very efficiently with Bu^tOH for (**4**).

The mixed ester (**5**) cannot arise by transesterification of dimethyl or diethyl phosphonate with Bu^tOH ⁸ and, in the absence of a hydride ion acceptor, the phosphinate is destroyed without the formation of substantial amounts of phosphonates.† The most reasonable explanation for the formation of (**5**) is the intermediacy of an alkyl phosphenite (**4**) formed from the phosphinate esters under basic conditions.‡ The mode of formation is analogous to the oxidative generation of metaphosphate ion from phosphonate monoanion.⁹

The distillation residues consist largely of cyclopentenones but also contain small amounts of hydroxycyclopentenones which may arise as a result of cycloaddition of the phosphenite ester to tetraphenylcyclopentadienone.⁶ Attempts to trap the ester (**4**) with 2,3-dimethylbuta-1,3-diene or with benzil have been unsuccessful but we are continuing our efforts in this direction.

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