Exceptionally Stable Oxyphosphoranes. Intramolecular Nucleophilic Attack by a Phosphine Oxide on a Carboxylic Carbonyl Group

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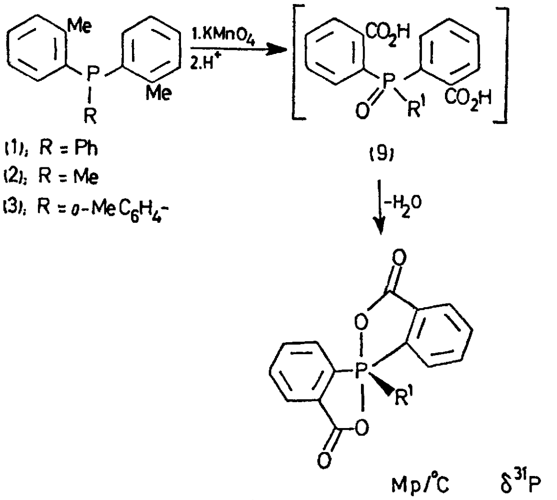
Summary Exceptionally stable spirocyclic oxyphosphoranes were prepared by potassium permanganate oxidation of bis-*o*-tolylarylphosphine oxides followed by acidification, probably involving nucleophilic attack by a phosphine oxide oxygen atom on a carboxylic carbonyl group.

NUCLEOPHILIC attack of a phosphine oxide oxygen atom on the carbonyl group of acetic anhydride, followed by formation of an unstable oxyphosphorane has been postulated to account for the racemization of optically active phosphine oxides.[1,2] Relatively stable spirocyclic oxyphosphoranes have recently been reported.[3] We report a novel synthesis of exceptionally stable spirocyclic oxyphosphoranes (4)—(6) (Scheme) possibly involving a similar mechanism.[1]

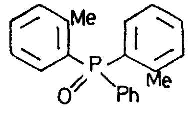


	Mp/°C	δ ^{31}P
(4); R^1 = Ph	225	+60·8 (CDCl$_3$)
(5); R^1 = Me	165	+51·0 (CDCl$_3$)
(6); R^1 = o-HO$_2$CC$_6$H$_4$-	256	+46·5 (CF$_3$CO$_2$H)

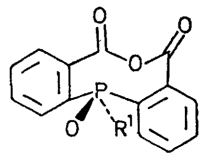
SCHEME

Condensation of *o*-tolylmagnesium bromide with phenylphosphonous dichloride yielded bis-*o*-tolylphenylphosphine (1). Potassium permanganate oxidation of (1) followed by acidification, produced (4) directly. Alternatively, (1) was converted into (7) by H_2O_2, then further oxidized as above again giving (4).

Structure elucidation† of (4)—(6) was achieved mainly from the ^{31}P n.m.r. spectra which distinguish (4)—(6) from an alternative phosphine oxide structure, such as (8). The ^{31}P chemical shifts of tertiary phosphine oxides[4] generally occur within the range 0—55 p.p.m. downfield from an 85% H_3PO_4 reference. These data are consistent with the oxyphosphorane structures,[5] for which the ^{31}P chemical shifts are usually observed upfield from an 85% H_3PO_4 reference.



(7)



(8)

The stability of the new oxyphosphoranes is reflected in their instantaneous formation from the precursor dicarboxylic acids (9) which could not be isolated. Equally, (4) survived heating for 30 min at 340 ° C, refluxing for 30 min with 2 M aq. NaOH, or refluxing for 1 h with LiAlH$_4$ in ether. However, the disodium salt of (9) (R^1 = Ph) was obtained on heating (4) with 2 mol of solid NaOH for 20 min at 250 °C. This salt was again transformed to (4) on dissolution in water and acidification.

In contrast to their thermal stability, (4) and (5), being cyclic anhydrides,[6] easily lose CO_2 under electron impact, giving negligible intensity for the molecular ions and abundant $(M - CO_2)^{+\cdot}$ ions. For (6), this process was accompanied by a further ready CO_2 elimination, probably originating from the carboxy group.

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† Consistent elemental analyses were obtained for all new compounds.

[1] L. Horner and H. Winkler, *Tetrahedron Letters*, 1964, 3271.

[2] D. B. Denney, A. K. Tsolis, and K. Mislow, *J. Amer. Chem. Soc.*, 1964, **86**, 4486.

[3] D. Hellvinkel and W. Krapp, *Angew. Chem. Internat. Edn.*, 1974, **13**, 542, and references therein.

[4] H. R. Hays and D. J. Peterson, in 'Organic Phosphorous Compounds,' Vol. **3**, ed. G. M. Kosolapoff and L. Maier, Wiley, New York, 1972, p. 423.

[5] D. Hellvinkel, in 'Organic Phosphorus Compounds,' Vol. **3**, ed. G. M. Kosolapoff and L. Maier, Wiley, New York, 1972, p. 185; an *X*-ray structure analysis is planned in collaboration with Dr. Olga Kennard and her co-workers.

[6] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 222.