A New Bicyclic Phosphorane

By J. Allen Miller* and Denis Stewart

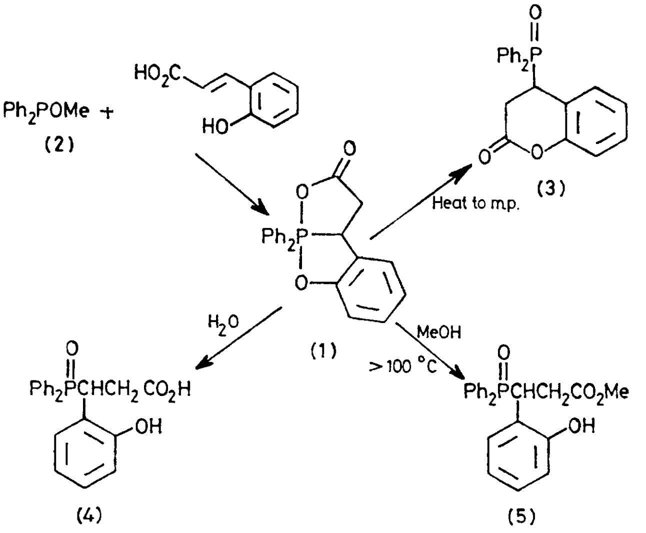
(*Department of Chemistry, The University, Dundee* DD1 4HN)

Summary Reaction of 2-hydroxycinnamic acid with methyl diphenylphosphinite (**2**) yields an unusual bicyclic acyloxyphosphorane (**1**).

Despite the vast literature on pentacovalent phosphorus compounds, acyloxyphosphoranes are comparatively rare species, with only a few substantiated examples.[1] All of these have been described in recent years, and have been found to possess a spirocyclic structure, in which the acyloxy group is generally, but not always,[1a] part of a heterocyclic ring incorporating phosphorus. We now report the isolation of the acyloxyphosphorane (**1**), which has a hetero bicyclo[3.3.0]octane structure of a type not previously described in the phosphorane field.[2]

The phosphorane (**1**) is best prepared by heating at 90 °C a chloroform solution of equimolar amounts of methyl diphenylphosphinite (**2**) and 2-hydroxycinnamic acid. Methanol is the other product, and evaporation of this and the solvent yields an oil, from which (**1**), m.p. 139—141 °C, may be obtained by crystallization from dry benzene–light petroleum (b.p. 40—60 °C). Structure (**1**) follows from microanalytical and spectroscopic evidence. In particular, the product showed δ + 18·8 p.p.m. (upfield from 85% H_3PO_4), a typical ^{31}P shift for a phosphorane,[3] and its i.r. spectrum showed ν_{max} 1715 cm^{-1}, but no band for a P=O group. The ^{1}H n.m.r. spectrum is extremely complex in the δ 5·0—2·5 region, although the line shape is not inconsistent with the P–CH–CH_2 unit in (**1**).

By comparison with spirocyclic acyloxyphosphoranes, the adduct (**1**) is not very stable, and rearranges at its m.p. to form the diphenylphosphinoylcoumarin derivative (**3**). The lactone ring of (**1**) is also sensitive to water, and other protic species such as methanol (above 100 °C). Thus recrystallization of (**1**) in the presence of traces of water yields the phosphine oxide (**4**), while prolonged heating of the methyl diphenylphosphinite (**2**) reaction mixture at over 100 °C produces the ester (**5**). Each of the oxides (**3**)—(**5**) has been prepared by an independent route, and has been subject to standard analytical and spectroscopic procedures, which confirmed their structures.



It is envisaged that synthesis of analogues of (**1**), in which the *P*-phenyl groups are replaced by other ligands, will permit a study of some of the factors which influence structural and permutational features of phosphoranes in the bicyclic series.

(*Received*, 20*th December* 1976; *Com.* 1385.)

---

[1] D. Bernard and R. Burgada, *Tetrahedron Letters*, 1973, 3455; (b) Y. Segall, I. Granoth, A. Kalir, and E. D. Bergmann, *J.C.S. Chem. Comm.*, 1975, 399; (c) T.Saegusa, S. Kobayashi, and Y. Kimura, *J.C.S. Chem. Comm.*, 1976, 443.

[2] Examples of different bicyclo[3.3.0]phosphoranes are described by: D. Hellwinkel and W. Krapp, *Angew. Chem. Internat. Edn.*, 1974, **13**, 542; W. S. Sheldrick, A. Schmidpeter, and J. H. Weinmaier, *ibid.*, 1976, **14**, 490; D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Amer. Chem. Soc.*, 1972, **94**, 245; D. Houalla, J. F. Brazier, M. Sanchez, and R. Wolf, *Tetrahedron Letters*, 1972, 2969.

[3] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, 'Topics in Phosphorus Chemistry,' Vol. 5, Interscience, New York, 1967, p. 47.