A New Bicyclic Phosphorane

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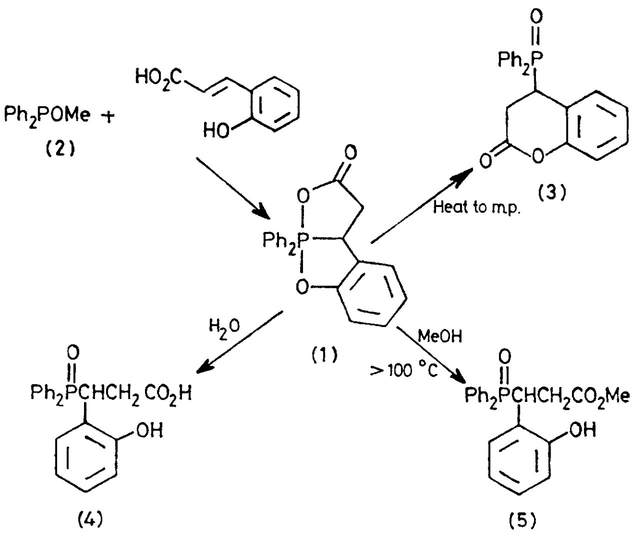
Summary Reaction of 2-hydroxycinnamic acid with methyl diphenylphosphinite (**2**) yields an unusual bicyclic acyloxyphosphorane (**1**).

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 ^1H 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.

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[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.