

Ligand Rearrangement in a Spirophosphorane *via* a Catalysed Dissociation–Association Mechanism

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The spirobicyclic bisethylenedioxyphosphorane (**1**) undergoes ligand isomerization in the presence of methyl trifluoromethanesulphonate; this is an example of an irregular exchange involving a phosphonium ion intermediate.

Ligand isomerizations at pentaco-ordinated phosphorus normally occur through some rearrangement within the P^V compound, such as a Berry pseudorotation or a turnstile

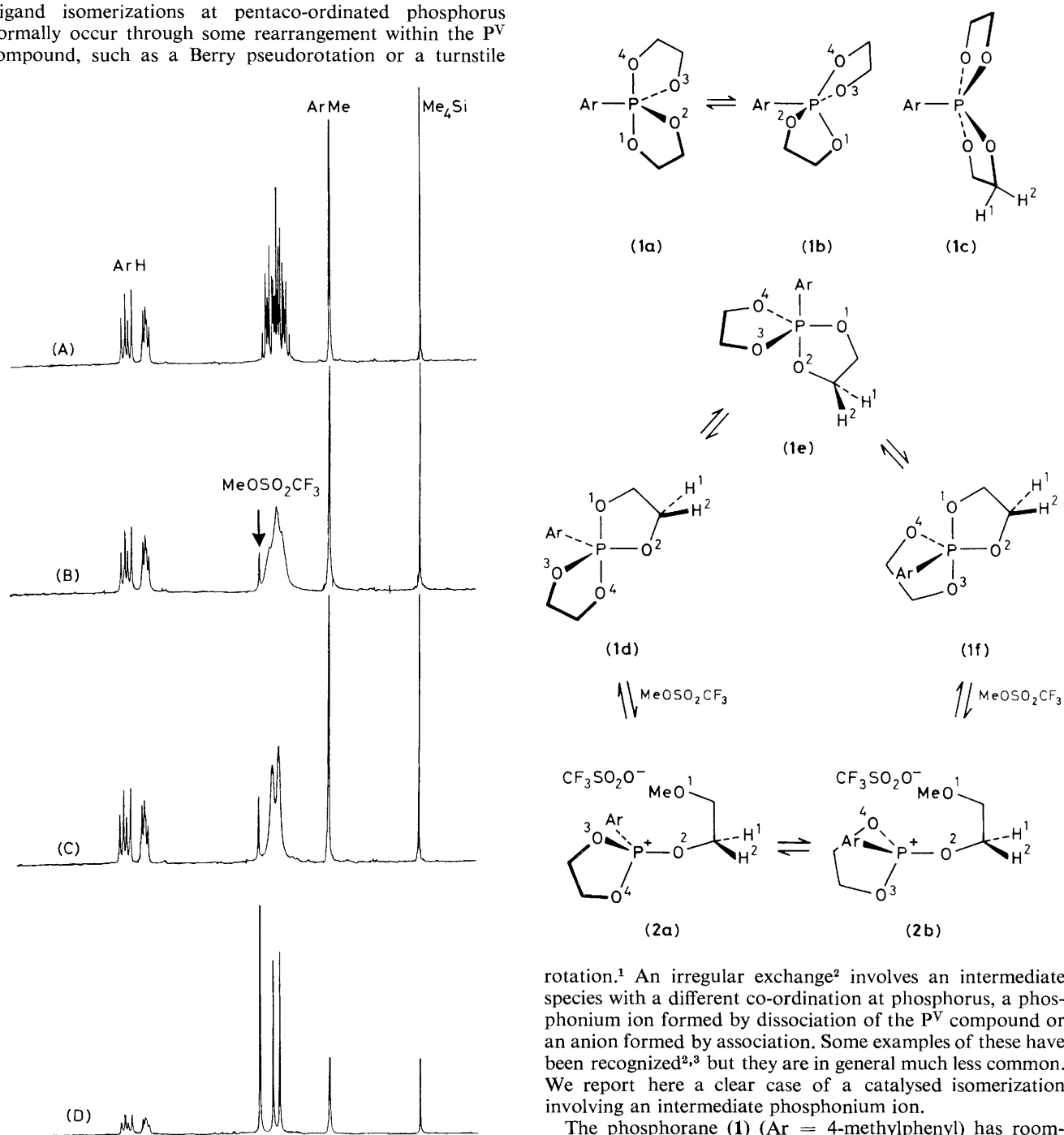


Figure 1. 80 MHz ¹H n.m.r. spectra of the phosphorane (**1**) (Ar = 4-methylphenyl) (0.1 M in CDCl₃) in the presence of (A) 0, (B) 0.1, (C) 0.2, and (D) 2.7 equiv. of methyl trifluoromethanesulphonate.

rotation.¹ An irregular exchange² involves an intermediate species with a different co-ordination at phosphorus, a phosphonium ion formed by dissociation of the P^V compound or an anion formed by association. Some examples of these have been recognized^{2,3} but they are in general much less common. We report here a clear case of a catalysed isomerization involving an intermediate phosphonium ion.

The phosphorane (**1**) (Ar = 4-methylphenyl) has room-temperature n.m.r. spectra showing a complex multiplet for the methylene protons [Figure 1(A)] but a single ¹³C resonance for the methylene carbons. The latter can be attributed to a rapid Berry pseudorotation involving axial-equatorial ex-

change of oxygen atoms (**1a**) \rightleftharpoons (**1b**). However, as is best seen in the tetragonal pyramid (**1c**) which represents the transition state for (**1a**) \rightleftharpoons (**1b**), there remain two sets of non-equivalent hydrogens.⁴ These could become equivalent through a pair of pseudorotations (**1d**) \rightleftharpoons (**1e**) \rightleftharpoons (**1f**), but this does not occur even at temperatures as high as 180 °C⁵ because of the high energy of (**1e**) which has an apical phenyl and one five-membered ring spanning equatorial positions.

In attempting to generate the cyclic phosphonium ion (**2**), we have added methyl trifluoromethanesulphonate to (**1**). This results in coalescence of the methylene signals (Figure 1), with no discernible difference in the remainder of the spectrum. This includes the ³¹P chemical shift which only changes from -19.2 with no MeOSO₂CF₃ to -19.0 with 2.7 equiv. The coalescence can be explained by the irregular exchange involving the phosphonium ion (**2**). The equilibrium concentration of this ion must be very small, as is shown in particular by the ³¹P chemical shift. The coalescence does require a rotation in the phosphonium ion. A simple possibility is shown by the sequence (**1d**) \rightleftharpoons (**2a**) \rightleftharpoons (**2b**) \rightleftharpoons (**1f**), with the P-O-2 bond in the cation undergoing a 120° rotation before ring closing.

The irregular exchange reported here requires the alkylating agent as a catalyst, and is therefore somewhat different from other examples^{2,3} where ionization is spontaneous, producing a zwitterionic intermediate. The present observation requires a system where the phosphonium ion must form with a five-atom ring. With phosphoranes which produce a phosphonium

ion which is acyclic³ or contains a six-atom ring,⁶ the addition of a strong acid³ or MeOSO₂CF₃⁶ results in the quantitative generation of the ion. The implication is that a phosphonium ion with a five-atom ring is considerably less stable than one with a six-atom ring or one which is acyclic (or conversely the five-membered ring phosphoranes are more stable). This closely parallels the well recognized situation which exists with phosphate esters.⁷

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