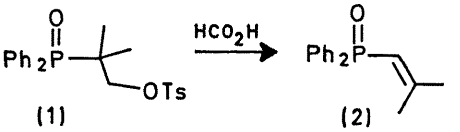
Carbonium Ion Rearrangements: Migration of an Electronegative Group

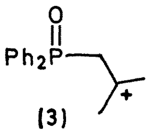
By P. F. CANN, D. HOWELLS, and STUART WARREN*
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary 2-Diphenylphosphinylethyl cations, generated in a variety of ways, rearrange by diphenylphosphinyl migration, even when the resulting cation has an identical structure to the unrearranged cation.

WE have previously reported rearrangements in which a diphenylphosphinyl group migrated from a tertiary to a primary cationic site.[1] The driving force for such a rearrangement is clearly the greater stability of the tertiary cation. These rearrangements were initiated by the deamination of a primary amine, but we have now found that solvolysis of suitable derivatives gives similar results: thus the tosylate of the primary alcohol (**1**) gives the olefin (**2**) on solvolysis in formic acid.

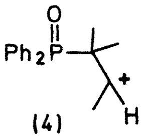


(**1**) (**2**)

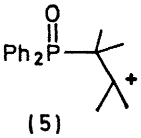


(**3**)

The stable cation (**3**) is presumably an intermediate in this reaction, but although it is clear that σ-participation by the P–C bond must occur at some stage in the reaction, very little information can be gained on the nature of the participation process as the rearrangement itself is probably the fastest step in the overall reaction. We have therefore studied the cations (**4**) and (**5**) in which the driving force for the rearrangement of a diphenylphosphinyl group is progressively less: indeed in (**5**) it is zero.

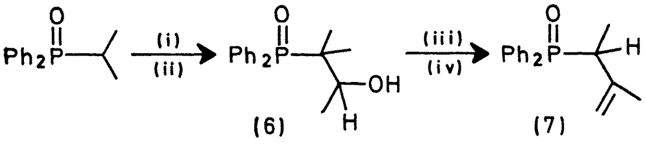


(**4**)



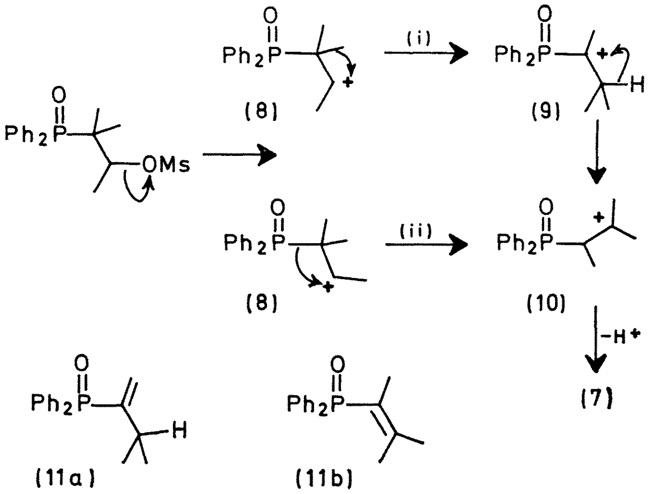
(**5**)

The alcohol (**6**) was prepared by Horner's method[2] from the lithium derivative of diphenylisopropylphosphine oxide and acetaldehyde. Treatment with methanesulphonyl chloride and triethylamine in dichloromethane gave the crystalline mesylate which was dissolved in acetic acid containing sodium acetate at room temperature. The olefin (**7**) was formed in 95% yield together with a small amount of an unidentified product.



(**6**) (**7**)

i: BuLi. ii: MeCHO. iii: MeSO$_2$Cl, Et$_3$N. iv: HOAc, NaOAc.

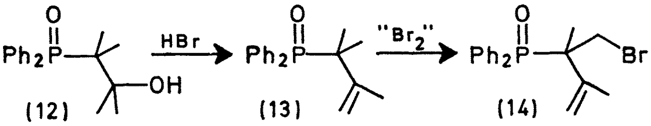


(**8**) (**9**) (**8**) (**10**) (**7**) (**11a**) (**11b**)

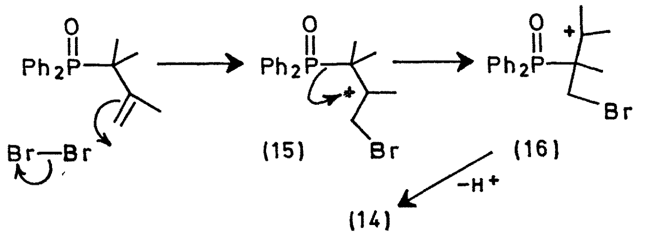
i: Methyl migration. ii: Diphenylphosphinyl migration.

The olefin (**7**) could in principle be formed either by methyl migration followed by a hydride shift (**8**→**9**→**10**) or by diphenylphosphinyl migration (**8**→**10**). We have never observed methyl migration in any of these systems and prefer the simpler, latter route. In any case, if cation (**9**) were an intermediate, the loss of a proton to give olefins (**11a**) or (**11b**) would be expected to occur at least as easily as the hydride shift.

The fully methylated alcohol (**12**) was synthesised from diphenylisopropylphosphine oxide and acetone by Horner's method, but no derivatives suitable for solvolysis could be made. Treatment with methanesulphonyl chloride, HBr (or any other strong acid), or tosyl chloride in pyridine simply gave the olefin (**13**), and we decided to use this as a source of cations by attacking it with suitable electrophiles. Treatment with bromine gave a mixture of at least four products, but pyridinium bromide perbromide[3] or phenyl trimethylammonium perbromide[4] each gave a quantitative yield of a single olefinic bromide identified as (**14**) from its n.m.r. and mass spectra.

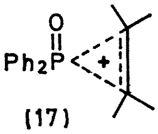


(**12**) (**13**) (**14**)



(**15**) (**16**) (**14**)

This product can arise reasonably only by a diphenylphosphinyl migration (**15**→**16**) in which there is very little driving force: cation (**16**) is more stable than (**15**) only by the reduced inductive effect from a slightly more remote bromine atom. This result suggested to us that a similar migration might occur under even less favourable circumstances if a deuteron was used instead of bromine in electrophilic attack on the olefin (**13**). A solution of (**13**) in CF_3CO_2D was accordingly observed by n.m.r. spectroscopy at 34°. Rapid deuteriation of the olefinic and allylic methyl protons (half-life *ca.* 5 h) was followed by a slower exchange of the protons in the other two methyl groups (half-life 70 h); the aromatic protons did not exchange. Incorporation of deuterium into the methyl groups of the olefin is best explained by the sequence of events described above for the bromination, Br being replaced by D. There is now no difference at all in stability between the cations (**15**-D) and (**16**-D) and it is surprising in view of the electronegativity of the diphenylphosphinyl group and the supposed instability of intermediates (or transition states) such as (**17**) that the rearrangement still occurs. That diphenylphosphinyl migration always occurs in preference to methyl migration is not part of this argument and is simply a consequence of the very unstable cations produced by methyl migration.



(17)

All new compounds gave satisfactory n.m.r. and mass spectra.

We thank the S.R.C. for grants (to P.F.C. and D.H.) and Trinity College for support.

(*Received, July 8th,* 1971; *Com.* 1177.)

---

[1] P. F. Cann and S. Warren, *Chem. Comm.*, 1970, 1026.

[2] L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, 1959, **92**, 2499.

[3] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, 1967, p. 967.

[4] A. Marquet, J. Jacques, and B. Tchoubar, *Bull. Soc. chim. France*, 1965, 511.