Fulvalene Ylides. A Stevens Rearrangement of 1-Fluoren-9-ylidene-1,2,5-triphenyl-λ⁵-phosphole[1]

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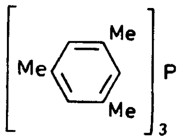
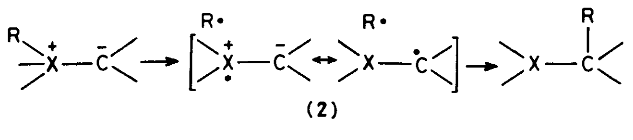
Quantitative, thermal rearrangement of the title ylide provides the first authentic example of a 1,2-Stevens rearrangement of a phosphorus ylide; the structure of the spiro-1,2-dihydrophosphorinine product has been confirmed by *X*-ray analysis.

While both nitrogen[2] and sulphur[3] ylides readily undergo thermally induced Stevens rearrangement to give amines and sulphides, respectively, the only report[4] of a similar reaction of a phosphorus analogue, that of the highly sterically hindered ylide (**1**),† has recently been shown to be in error.[5] Indeed the stability of (**2**, X = N), generally accepted as the intermediate in Stevens rearrangements of nitrogen ylides,[2] would be predicted to be less for (**2**, X = P) since it depends to some extent on pπ-bonding with the heteroatom. We now report the first authentic example of a Stevens rearrangement of a phosphorus ylide which, together with reactions of the product,[6] leads to novel phosphorus heterocycles.

On refluxing in toluene, 1-fluoren-9-ylidene-1,2,5-triphenyl-λ⁵-phosphole (**3**)[7] undergoes virtually quantitative conversion into an isomeric product (**4**),‡ m.p. 200—203 °C; *m/z* 476 (100%) and 399 (12); ^{1}H n.m.r. δ ($CDCl_3$) 5.41 (dd, 1H, J_1 7.7 Hz, J_2 0.7 Hz), 6.5—7.6 (m, 22H), 7.85 (d, 1H, *J* 7.4 Hz), and 7.96 (d, 1H, *J* 7.7 Hz); $^{31}P\{^1H\}$ n.m.r. δ ($CDCl_3$) −27.6 p.p.m. (relative to external 85% H_3PO_4); $\lambda_{max.}$ (MeCN) 353 nm (log ε 4.20) and 261 nm (log ε 4.38), which was identified as a phosphine on the basis of its ^{31}P n.m.r. chemical shift and its oxidation to the phosphine oxide (**5**),‡ m.p. 297—298 °C; $\nu_{max.}$ 1180 cm^{-1}; *m/z* 492 (100%; M^+); $^{31}P\{^1H\}$ n.m.r. δ ($CDCl_3$) +28.4 p.p.m. The u.v. spectrum of (**4**) [1,4-diphenylcyclohexa-1,3-diene has $\lambda_{max.}$ 345 nm (log ε = 4.1)][8] and the low intensity of the *m/z* 165 (fluorenyl) fragment suggest a spiro-1,2-dihydrophosphorinine structure



(**1**)



(**2**)

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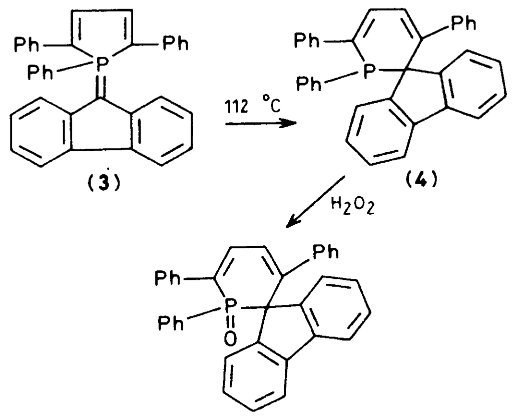
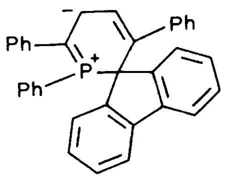
† The formation of a 1,4-Stevens rearrangement product from rearrangement of diphenyl-3-methylbut-2-enyl-3-methylbut-2-enylidenephosphorane has been reported, but not designated as such (C. H. Armstrong and J. E. Baldwin, *Chem. Commun.*, 1970, 631).

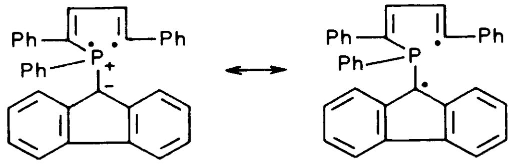
‡ Satisfactory microanalytical data were obtained for all new compounds.



(3) (4) (5)



(6)



(7)

for (**4**) and this has been confirmed by an *X*-ray structure analysis of the corresponding phosphine oxide (**5**).

Crystal data: $C_{35}H_{25}OP{\cdot}CHCl_3$, $M = 611.9$, triclinic, $a = 11.069(9)$, $b = 14.351(11)$, $c = 10.148(8)$ Å, $\alpha = 90.70(7)$, $\beta = 107.28(9)$, $\gamma = 88.83(7)°$, $U = 1538.9$ Å^3, $Z = 2$, $D_c = 1.32$ g cm^{-3}, $F(000) = 632$, space group $P\bar{1}$ (No. 2), Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 3.28$ cm^{-1}.

2309 Diffraction intensities were recorded on a Stoe STADI-2 diffractometer. The structure was determined by the direct phasing routines of MULTAN 78 and was refined by the program SHELX, using 1360 reflections with $I > 3\sigma(I)$, to a final R of 0.084.§ The three phenyl groups were refined as rigid groups and all hydrogen atoms were included with idealised geometries. A projection of the molecule is shown in Figure 1.

The highly shielded olefinic proton at δ 5.41 in the n.m.r. spectrum of (**4**) is presumably due to contributions from (**6**), in spite of the reluctance of tervalent phosphorus to participate in pπ-bonding, since this proton absorbs at greater than δ 6.46 in the phosphine oxide (**5**).

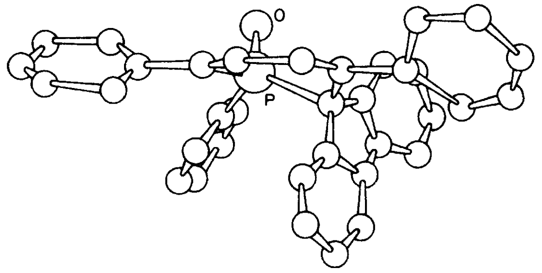
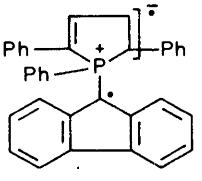
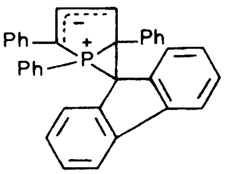


Figure 1. The structure of phosphine oxide (**5**).



(8)



(9)

CIDNP has been observed in Stevens rearrangements of nitrogen ylides[2] and the results support the involvement of (**2**, X = N) as an intermediate. The analogous intermediate in the rearrangement of (**3**) would be (**7**), where the CIDNP phenomenon might be conveniently observed by ^{31}P n.m.r. spectroscopy. However, we have been unable to observe any polarisation effects by either ^{1}H or ^{31}P n.m.r. spectroscopy during the rearrangement of (**3**) under a variety of conditions. Although these results do not exclude the involvement of free radicals, equally they provide no support for either the accepted Stevens rearrangement mechanism or the alternative electron-transfer mechanism, involving (**8**), analogous to that suggested[9] for the base-initiated cyclisation of certain vinyl bromides. A further alternative is an ionic mechanism which at one extreme would involve the cyclic ylide (**9**).

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References

1 Part of this work was presented at the International Conference on Phosphorus Chemistry, Nice, France, September 1983.
2 W. D. Ollis, M. Rey, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1,* 1983, 1009, and references therein.
3 *E.g.* G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith, and I. O. Sutherland, *Chem. Commun.,* 1968, 186; J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *ibid.,* 1970, 576.
4 F. Heydenreich, A. Molbach, G. Wilke, H. Dreeskamp, E. G. Hoffman, G. Schroth, K. Seevogel, and W. Stempfle, *Isr. J. Chem.,* 1972, **10**, 293.
5 H. Schmidbaur and S. Schnatterer, *Chem. Ber.,* 1983, **116**, 1947.
6 D. G. Gilheany, D. A. Kennedy, J. F. Malone, and B. J. Walker, unpublished work.
7 D. G. Gilheany and B. J. Walker, unpublished work.
8 J. Dale and P. O. Kristiansen, *Acta Chem. Scand.,* 1971, **25**, 359.
9 R. Grigg and P. Stevenson, personal communication.

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.