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A NOVEL BICYCLIC PHOSPHONIUM YLIDE FROM THE REACTION OF A 1,2-DIHYDROPHOSPHORIN WITH DIMETHYL ACETYLENEDICARBOXYLATE.

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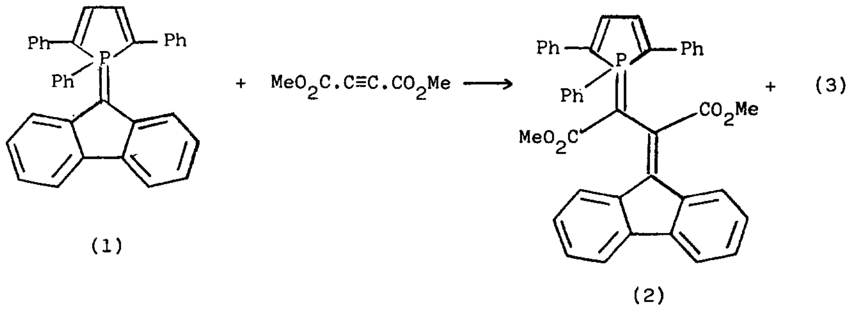
SUMMARY: The reaction of 1,2,5-triphenylphospholium fluorenylide with dimethyl acetylenedicarboxylate gives two 1:1 adducts, one of which is shown by X-ray analysis to have a novel 1-phosphabicyclo[3.2.1]octatriene structure.

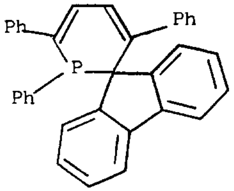
We have recently achieved the synthesis of phosphonium ylide analogues of fulvalenes.[1] Although in general these compounds show the characteristic reactions of phosphonium ylides, the pentafulvalene analogue (1) provided the first authentic example of thermally-induced Stevens rearrangement of a phosphonium ylide.[2]

The reaction of the fulvalene-ylide (1) with dimethyl acetylene dicarboxylate (DMAD) in refluxing dry benzene gives two isomeric 1:1 adducts (2) and (3).[3] The dark red adduct (2), m.p. 244-245°; m/z 618(100, M^+) 329(90) and 165(55); ^1H $\delta(CDCl_3$; at room temperature all resonances are broad) 3.2, 3.6 and 3.8 (bs, 6H) and 6.4-8.1 (m, 25H); λ_{max} ($CDCl_3$) 417 nm (4.30); is clearly analogous to those adducts formed by stabilised ylides[4] and by other fulvalene ylides.[5] The broad resonances are presumably due to restricted rotation about the ylide carbon-carbonyl bond, although restricted rotation about other bonds is clearly possible.[6] In view of the facile Stevens rearrangement of (1) to the phosphine (4),[2] it seemed likely that the pale-yellow adduct (3) was derived from (4) and indeed a reaction of (4) with DMAD gave (3) (77%), m.p. 260-262°(d); m/z 618(28, M^+), 346(15), 272(100) and 165(8); $^1H\delta(CDCl_3)$ 3.39(s, 3H), 3.66(s, 3H), 3.83(dd, J_{HH} = 4.1, $J_{PC=CCH}$ = 20Hz, 1H $\geq$CH), 6.77(d, J_{HH} = 4.1Hz, ½H, half of dd due to =CH), 6.85-7.76(m, together with 6.77, 23H) and 8.47(bd, J = 8.1Hz, 1H). Alkaline hydrolysis of (3) gave a so far unidentified, ring-opened

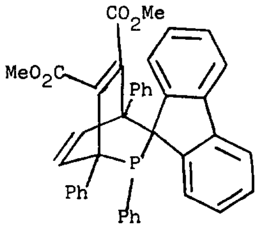


phosphine oxide (5); m.p. 285-286°; ν_{max} (KBr) 1150-1180 cm^{-1}; m/z 636(100, M^{+}), 577(36), 563(40) and 165(44); ^{1}H δ(CDCl$_3$) 3.07(s, 3H), 3.62(s, 3H), 3.95(dd, J_1 = 6.7, J_2= 2.4Hz, 1H), 4.12(d, J = 18.5Hz, 1H), 5.64(d, J = 18.5, 1H), 6.34-7.76(m, 23H) and 8.31(d, J = 7.7Hz, 1H). The fragments at m/z 346 and 272 given by (3) in the mass spectrometer suggested that this adduct might be a simple Diels Alder adduct (6) in spite of the large steric hindrance to this reaction. However, an X-ray analysis has established a novel 1-phosphabicyclo[3.2.1]octatriene structure for (3).

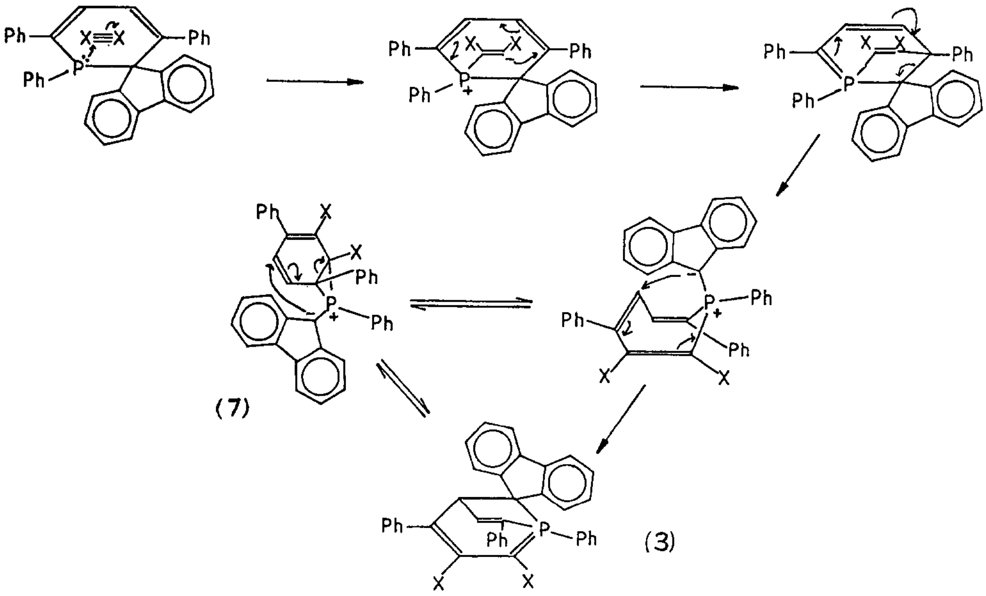
Crystal Data:- $C_{41}H_{31}O_4P$, M = 618.7, Orthorhombic, $\underline{a}$ = 19.927(20), $\underline{b}$ = 19.500(20), $\underline{c}$ = 16.652(17)Å, $\underline{U}$ = 6470.6Å^3, Z = 8, $\underline{Dc}$ = 1.27 g cm^{-3}, F(000) = 2592, space group Pbcn (no.60), Mo-$\underline{K}\alpha$ radiation, λ = 0.71069Å, $\underline{\mu}$(Mo-$\underline{K}\alpha$) = 0.89 cm^{-1}.



(4)



(6)



Scheme

2176 diffraction intensities were recorded on a Stöe STADI-2 diffractometer. The structure was determined by automatic centrosymmetric direct methods (SHELX) and was refined by least squares with allowance for anisotropic temperature factors for all non-hydrogen atoms. Hydrogens were included in the refinement at geometrically determined positions. The final R was 0.090[†] (for 1849 independent reflections with $I > \sigma(I)$). A projection of the molecule is shown in the Figure.

The failure of the phosphine oxide obtained from (4) to react with DMAD suggests that (3) is derived from initial nucleophilic attack[7] of phosphorus on DMAD, presumably followed by cyclisation and rearrangement as shown in the scheme. It is difficult to rationalise the spectroscopic data obtained for the phosphine oxide (5) in terms of a simple hydrolysis product of (3) and we suspect that a rearrangement has occurred in the formation of (5).

The fragments observed at m/z 346 and 272 in the mass spectrum of (3) may be rationalised by involvement of the 7-phosphanorcaradiene valence isomer (7).[8] In this connection it is interesting to note that the reaction of (1) with DMAD in ethyl acetate containing traces of water gives significant amounts (40%) of dimethyl-3,6-diphenylphthalate (8), m/z 346(M^+). However, separate experiments showed that neither of the adducts (2) or (3) form (8) on hydrolysis, thermolysis, or oxidation and it seems likely that, in wet ethyl acetate, (1) hydrolyses to 1,2,5-triphenylphosphole oxide, which is known to react with DMAD to give (8).[9]

[†] The atomic coordinates 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.

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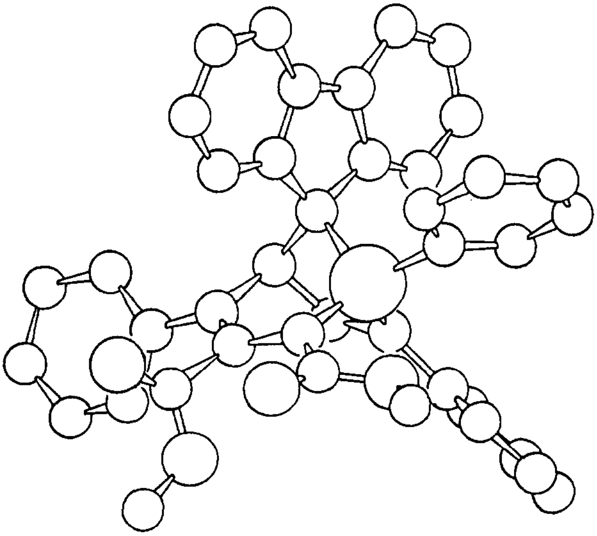

FIGURE

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