Tetrahedron Letters No.20, pp. 1263-1266, 1964. Pergamon Press Ltd.
Printed in Great Britain.

PHOSPHACYCLOBUTENES AS INTERMEDIATES IN ADDITION OF PHOSPHORANES TO ACETYLENES

G.W.Brown, R.C.Cookson and I.D.R.Stevens,

The University, Southampton.

(Received 27 February 1964)

PHOSPHINIMINES (I) react with dimethyl acetylenedicarboxylate to form 1:1 adducts II, the structure of IIb having been proved by X-ray analysis (1) [IIa, m.p. 197-8°, longest λ_{max}313 mμ (ε 8300); IIb, 180°, 321 mμ (11100); IIc, 243°, 340 mμ (10500); IId, 235°, 346 mμ (16600); IIe, 244°, 377 mμ (16000)]. Reaction must proceed through the intermediate III, which then breaks the P-N bond. Even the imine IV, which might have undergone Michael addition to give V, reacted in the same way to give an adduct [m.p. 170°, longest λ_{max}289 mμ (ε 5000)] with structure VI, assigned on the basis of the NH band at 3380 cm.$^{-1}$ and the similarity of its spectra and those of its salts with those of IIa and its salts. When the nitrogen atom was made less nucleophilic than in Ie, as in the N-2,4-dinitrophenyl-, -benzoyl-, -ethoxycarbonyl- or -p-toluenesulphonyl-imines addition to the acetylene ester no longer occurred. VII, R= Ph, COPh and p-$SO_2C_6H_4CH_3$ also failed to react.

Phosphoranes with no α-hydrogen atom added to dimethyl acetylenedicarboxylate in the same way. Thus pentaphenylphosphorane (VIII) gave IX [m.p. 257°, longest λ_{max} 365 mμ (ε 3000) presumably *via* X, and the fluorenylidene analogue gave a similar adduct [m.p. 211°, 427 mμ (10000)]. Hendrickson (2) has just described the addition of C-benzoyl-methylene-triphenylphosphorane to dimethyl acetylenedicarboxylate both by Michael addition and through the phosphacyclobutene.

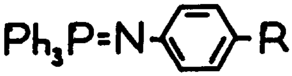
In methylene chloride or dry ether at 0° the phosphazines (XI) gave adducts with dimethyl acetylenedicarboxylate [XIIa, m.p. 126-7°, λ_{max} 368 mμ (13800); XIIb, 140°, 366 mμ (14000)] formed by Michael addition. In warm ethyl acetate these adducts (XII) decomposed to triphenylphosphine and the pyrazole-triester (XIII). The single proton that appears at τ 3.45 ($CDCl_3$ solution) in the N.M.R. spectrum of XIIa is evidence against addition to the P=N bond (the parent phosphazine, XIa, has no olefinic proton at higher field than the aromatic ones). On the other hand the phosphazine XIV, with no α-hydrogen atoms, added *via* the phosphazacyclobutene to give the adduct XV [m.p. 225°, 417 m (18000)].

This facile opening of the phosphacyclobutene and phosphazacyclobutene rings is reminiscent of the isomerisation of the cyclobutene systems (3) from addition of dimethyl acetylenedicarboxylate to enamines.

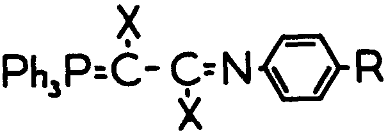
G.W.B. acknowledges a D.S.I.R. Research Studentship.

1. G. W. Brown, R.C. Cookson, I.D.R. Stevens, T.C.W. Mak and J. Trotter, *Proc. Chem. Soc.*, 1964, in press.
2. J.B. Hendrickson, R. Rees and J.F. Templeton, *J. Amer. Chem. Soc.*, 1964, **86**, 107.
3. G.A. Berchtold and G.F. Uhlig, *J. Org. Chem.*, 1963, **28**, 1459,

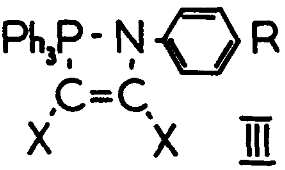
K.C. Brannock, R.D. Burpitt, V.W. Goodlett and J.G. Thweatt, *ibid.*, p. 1464; C.F. Huebner, E. Donoghue *et al.*, *ibid.*, pp. 1732 and 3134.



I R = H (a) $COOCH_3$ (c) Br (b) $COCH_3$ (d) NO_2 (e)



II X = $COOCH_3$



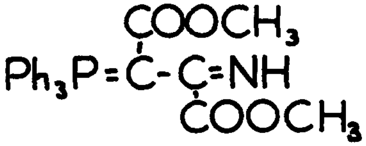
III

$Ph_3P{=}NH$

IV

$Ph_3P{=}N{-}\underset{COOCH_3}{C}{=}CHCOOCH_3$

V



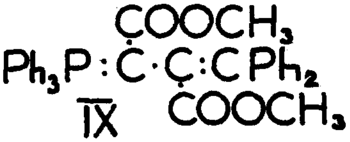
$Ph_3P{=}\overset{COOCH_3}{C}{-}\underset{COOCH_3}{C}{=}NH$

$(EtO)_3P{=}NR$

VI VII

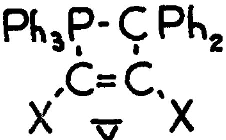
$Ph_3P{:}CPh_2$

VIII



$Ph_3P{:}\overset{COOCH_3}{C}{\cdot}\underset{COOCH_3}{C}{:}CPh_2$

IX

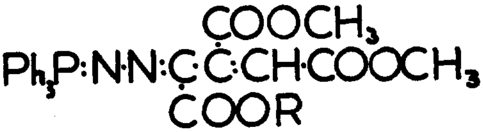


X

$Ph_3P{=}N{\cdot}N{=}CHCOOR$

XI R = CH_3 (a)

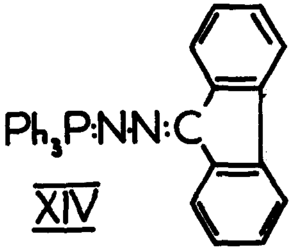
C_2H_5 (b)



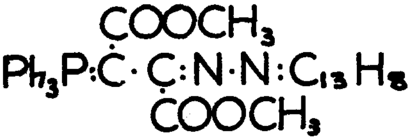
$Ph_3P{:}N{\cdot}N{:}\underset{COOR}{C}{\cdot}\overset{COOCH_3}{C}{:}CH{\cdot}COOCH_3$

XII

XIII



XIV



$Ph_3P{:}\overset{COOCH_3}{C}{\cdot}\underset{COOCH_3}{C}{:}N{\cdot}N{:}C_{13}H_8$

XV