Reactions of Phosphines with Acetylenes.   Part 18.[1]   The Mechanism of Formation of 1,2-Alkylidenediphosphoranes

By **John C. Tebby** * and **Ian F. Wilson,** Department of Chemistry, North Staffordshire Polytechnic, Stoke-on-Trent ST4 2DE

D. Vaughan Griffiths, Department of Chemistry, University of Keele, Staffordshire ST5 5BG

The reactions of dimethyl acetylenedicarboxylate and dibenzoylacetylene with a variety of tertiary arylphosphines, in excess, have been studied.   Evidence is presented to show that 1,2-alkylidenediphosphoranes are formed *via* zwitterionic intermediates which have the character of nucleophilic carbenes.   1,2-Bismethoxycarbonyl-2-thioxo-ethylidenetriphenylphosphorane and 1,2-dibenzoyl-2-thioxoethylidenetriphenylphosphorane have been isolated by trapping the intermediate with sulphur.

THE reaction of dimethyl acetylenedicarboxylate with excess of triphenylphosphine gives the 1,2-alkylidene-diphosphorane (1) in quantitative yield.[2,3]   No mechanism has been postulated for this reaction.   However, when the acetylenic ester is present in excess, or when electrophilic or protic trapping agents are present,

has been found to be quite sensitive to the nature of the phosphine.   In the reactions with dimethyl acetylene-dicarboxylate a moderate reduction of the nucleophilic properties of the triarylphosphine, *e.g.* Ar $= p$-ClC$_6$H$_4$, could be tolerated but the attachment of electron-donating groups to the aryl rings of the phosphine
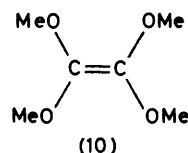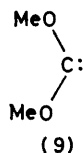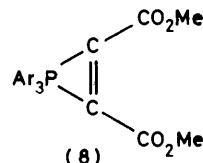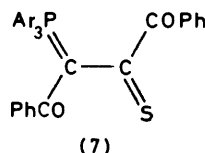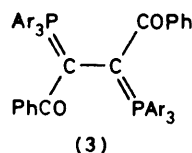

SCHEME
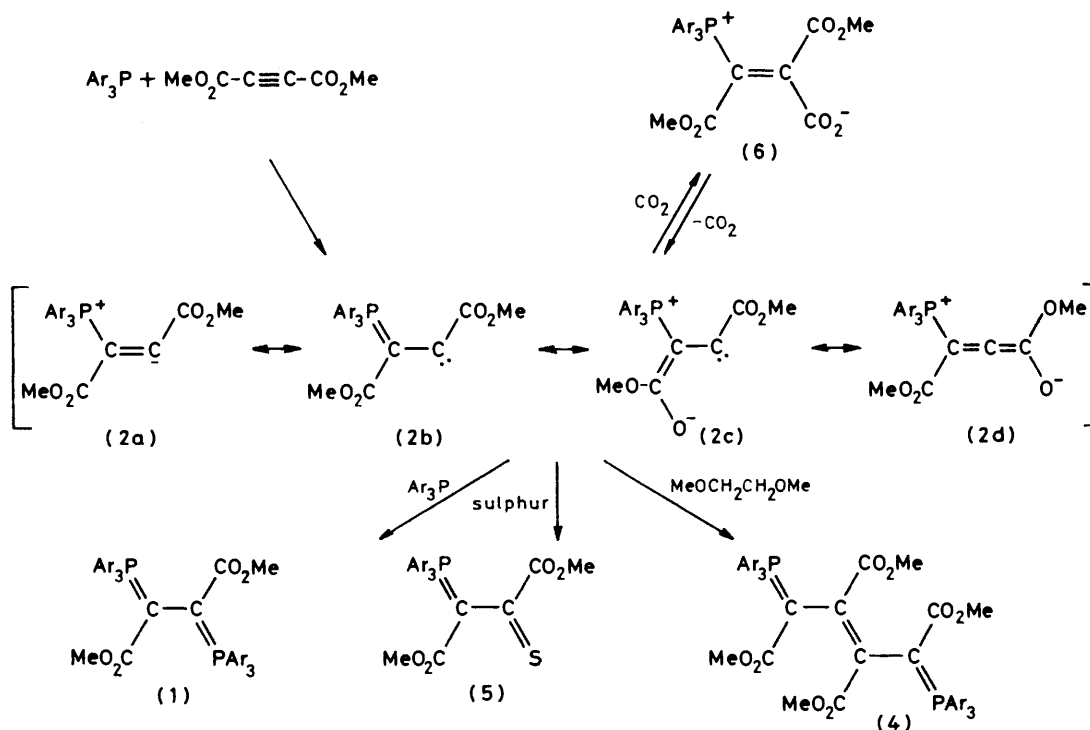
products are formed which are consistent with the initial formation of the zwitterionic intermediate (2a).[4] Phosphines have been shown to react at electron-rich centres [5] such as the oxygen atom of certain carbonyl groups [6] or the nitrogen atom of azide [7] or nitrile groups,[8] but reaction at an electron-rich carbon atom such as the β-carbon atom of the zwitterionic intermediate (2a) would be a novel process.

Further evidence on the reaction pathway leading to the 1,2-alkylidenediphosphoranes was sought by varying the nature of the phosphine, the acetylene, the solvent, and by the addition of trapping reagents.   The reaction

inhibited the formation of the diphosphorane.   Suitable modification of the structure of the electrophilic acetylene increases the upper limit of the nucleophilic properties of the phosphines.   Thus, unlike the acetylenic ester, dibenzoylacetylene gave the 1,2-alkylidenediphos-phoranes (3) when reacted with excess of tri-*p*-tolyl-phosphine or tris-*p*-methoxyphenylphosphine.   A further increase in nucleophilic properties could not be tolerated and di-*p*-tolylmethylphosphine failed to give the diphosphorane.   The reactions were not markedly affected by the use of alternative non-polar solvents to the usual solvent, diethyl ether, except that the 1,4-

alkylidenediphosphorane (4) was produced when dimethoxyethane was the solvent. In alcohol a completely different reaction occurs [9] with the alcohol participating as a reactant.

of the acetylenic and phosphorus substituents. A common route to alkylidenephosphoranes is the reaction of a carbene intermediate with tertiary phosphines.[12,13] Dimethoxycarbene (9) also has other properties in com-

Although the use of nucleophilic trapping agents is made difficult by the presence of excess of phosphine it was possible to trap the intermediate by adding two equivalents of triphenylphosphine to dimethyl acetylenedicarboxylate in the presence of five equivalents of sulphur in benzene. The product is 1,2-dimethoxycarbonyl-2-thioxoethylidenetriphenylphosphorane (5; Ar = Ph). The same compound may be obtained by trapping the intermediate produced from the fragmentation of the carboxylate betaine (6; Ar = Ph) which is prepared by the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate in the presence of carbon dioxide. The intermediate produced by the reaction of triphenylphosphine with dibenzoylacetylene can also be trapped with sulphur to give 1,2-dibenzoyl-2-thioxoethylidenetriphenylphosphorane (7; Ar = Ph). The corresponding carboxylate derivative cannot be prepared from dibenzoylacetylene and its decomposition in the presence of sulphur cannot therefore be studied.

The mechanisms of nucleophilic and electrophilic attack of acetylenes has been considered theoretically.[10] Hückel MO calculations indicate that whilst electrophilic attack of an acetylene favours the formation of a cyclic intermediate, a zwitterionic structure such as (2) will generally be more stable than a cyclic structure when the reaction involves nucleophilic attack. Thus, although it is quite feasible that a cyclic intermediate such as the phosphiren (8) would react with a second molecule of phosphine to give an alkylidenediphosphorane, the formation of such an intermediate is not expected. Furthermore, the requirement that the phosphine must have a middle range of nucleophilic character, that the reaction is sensitive to moderately small changes in the nature of the groups bound to the acetylenic carbon atoms, and that sulphur can react in place of the tertiary phosphine are in better accord with the intermediacy of a zwitterion which has some carbene character.

Nucleophilic carbenes have been previously described [11] and several resonance structures (2b—d) which have carbenoid or allenic structures can be envisaged for the zwitterion. The contribution made by these canonical structures would clearly be dependent on the nature

mon with the reactive intermediate from the reaction of phosphines and acetylenes.[14] Both react with sulphur to give thiocarbonyl compounds, both react with dimethyl acetylenedicarboxylate, and both dimerise, dimethoxycarbene to give the ethylene (10), and the intermediate (2) to give the 1,4-alkylidenediphosphorane (4).[15] This latter reaction was previously formulated as involving the carboxylate betaine (6) but the above evidence and its formation directly from the phosphine and acetylene when the reaction is carried out in dimethoxyethane lead us to believe that the 1,4-alkylidenediphosphorane (4) is formed by the dimerisation of the intermediate (2).

In conclusion, we have shown that the reactions of electrophilic acetylenes with tertiary phosphines can proceed *via* very versatile 1 : 1 intermediates. Although their nucleophilic character is normally predominant, in the absence of electrophilic substances the intermediates may exhibit carbenoid characteristics and react in the manner shown in the Scheme.

EXPERIMENTAL

Reactions of Acetylenes with Excess of Tertiary Phosphines. —The reactions were carried out by the method previously described.[2] The 1,2-alkylidenediphosphoranes (1; Ar = p-ClC$_6$H$_4$), m.p. 132—139°, (3; Ar = p-MeC$_6$H$_4$), m.p. 192° (decomp.), and (3; Ar = p-MeOC$_6$H$_4$), m.p. 141—144°, gave satisfactory elemental analyses and appropriate i.r. and [1]H n.m.r. spectra.[16] Dibenzoylacetylene was prepared by oxidation [17] of 1,4-diphenylbut-2-yne-1,4-diol which was obtained by the reaction [18] of benzaldehyde with acetylenedimagnesium bromide.[19]

1,2-Bismethoxycarbonyl-2-thioxoethylidenetriphenylphosphorane (5; Ar = Ph).—(a) 1,2-Bismethoxycarbonyltriphenylphosphonium carboxylate [2] (1 g) was added to a suspension of sulphur (flowers; 2 g) in dry benzene (5 cm³). After 1 h at 50° the undissolved sulphur was removed and the solution evaporated. The orange oil was dissolved in hot ethyl acetate and cooled to give the *product* (0.2 g),

m.p. 183—183.5°, as bright yellow crystals (Found: C, 65.6; H, 4.8. $C_{24}H_{21}O_4PS$ requires C, 66.0; H, 4.8%), $\nu_{max.}$(KBr) 695, 750, 1 040, 1 110, 1 245br, 1 395, 1 680, and 1 715 cm^{-1}, δ_H(CDCl$_3$) 7.95—7.26 (15 H, m), 3.85 (3 H, s), and 3.28 (3 H, s), δ_P(CDCl$_3$) 11.26, δ_P (C$_6$H$_6$) 9.84 p.p.m., δ_C (Table), m/e 436 (M^+), 421, 408, 377, 299, 294, 262, 185, and 183br.

(b) Triphenylphosphine (0.26 g) in dry benzene (1 cm^3) was rapidly added with shaking to dimethyl acetylene-dicarboxylate (0.08 g) and sulphur (flowers; 0.15 g) in dry benzene (1 cm^3). A reaction occurred instantaneously. The excess of sulphur and precipitated triphenylphosphine sulphide were separated. The orange solution gave δ_P(C$_6$H$_6$) 9.84 (5; Ar = Ph), and 42.11 p.p.m. (Ph$_3$PS) with an intensity ratio of 1:2. The ^{13}C n.m.r. spectrum of the product showed signals identical with those from the product from (a) (Table).

^{13}C N.m.r. parameters for thiones (5; Ar = Ph) and (7; Ar = Ph

Ph$_3$P Aromatics	(5; Ar = Ph)	(7; Ar = Ph)
P–C	122.91 (94)	123.21 (93)
o-C	133.37 (10)	133.42 (11)
m-C	128.86 (12)	128.94 (13)
p-C	132.45 (2)	132.41 (3)
Others		
α-C	91.60 (115)	106.21 (101)
C=S	200.92 (11)	204.38 (7)
C=O	164.95 (17)	191.83 (12)
C=O	169.72 (17)	192.32 (9)
Me	51.20	
Me	52.60	

Non-assigned resonance lines

139.83; 139.56
135.20; 135.08
132.27; 132.03
129.97; 129.54
127.67

Spectra were run in CDCl$_3$. Resonance positions are in p.p.m. relative to Me$_4$Si as internal reference and are accurate to ±0.7 Hz. Values in parentheses are those for coupling to phosphorus

1,2-Dibenzoyl-2-thioxoethylidenetriphenylphosphorane (7; Ar = Ph).—Triphenylphosphine (0.26 g) in dry benzene (1 cm^3) was rapidly added with shaking to dibenzoyl-acetylene (0.12 g) and sulphur (flowers; 0.15 g) in dry benzene (1 cm^3). The products from five such reactions

were pooled and ^{31}P n.m.r. indicated the mixture to contain Ph$_3$PS and (7; Ar = Ph) in the ratio of 4:1. Chromatography on alumina (activity 4) (column 10 × 1.5 cm) with chloroform as eluant removed a number of minor coloured impurities and then the major components were separated on a silica column (15 × 1.5 cm) using the same solvent. Removal of the solvent from the appropriate fractions gave an orange oil. Addition of ethyl acetate and its subsequent removal under reduced pressure gave orange crystals of (7; Ar = Ph) as the monohydrate (Found: C, 74.3; H, 4.7. $C_{34}H_{27}O_3PS$ requires C, 74.7; H, 4.9%), δ_P(CDCl$_3$) 10.95 p.p.m., δ_C (Table).

REFERENCES

[1] Part 17, P. J. Butterfield, J. C. Tebby, and D. V. Griffiths, J.C.S. Perkin II, 1979, 1189.
[2] A. W. Johnson and J. C. Tebby, J. Chem. Soc., 1961, 2126.
[3] M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, J. Chem. Soc. (C), 1967, 2442.
[4] N. E. White, D. W. Allen, and J. C. Tebby, Phosphorus, 1971, 1, 139.
[5] H. Hoffman and H. J. Diehr, Angew. Chem. Internat. Edn., 1964, 3, 737.
[6] F. Ramirez, Accounts Chem. Research, 1968, 1, 168.
[7] B. H. Freeman, D. Lloyd, and M. C. Singer, Tetrahedron, 1974, 30, 211; A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966.
[8] P. J. Butterfield, J. C. Tebby, and T. J. King, J.C.S. Perkin II, 1978, 1237.
[9] I. F. Wilson and J. C. Tebby, J.C.S. Perkin I, 1972, 2830.
[10] S. I. Miller and R. Tanaka, 'Selective Organic Transformations,' Wiley, New York, vol. 1, 1970.
[11] T. R. Oaks, H. G. Davies, and F. J. Nagel, J. Amer. Chem. Soc., 1969, 91, 4761; W. M. Jones and C. L. Ennis, ibid., 1967, 89, 3069.
[12] A. J. Speziale and R. W. Ratts, J. Amer. Chem. Soc., 1960, 82, 1260.
[13] D. M. Lemal and E. H. Banitt, Tetrahedron Letters, 1964, 245.
[14] R. W. Hoffmann, Angew. Chem. Internat. Edn., 1971, 10, 529.
[15] M. A. Shaw, J. C. Tebby, J. Ronayne, and D. H. Williams, J. Chem. Soc. (C), 1967, 944.
[16] I. F. Wilson, Ph.D. Thesis, North Staffordshire Polytechnic, 1972.
[17] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, J. Chem. Soc., 1946, 39.
[18] G. Dupont, Ann. Chim., 1913, 30, 507.
[19] I. M. Heilbron, E. R. H. Jones, and R. A. Raphael, J. Chem. Soc., 1944, 136.