Reactions of Phosphines with Acetylenes. Part IX.¹ 1,2-Alkylidenediphosphoranes stabilised by Acyl and Ester Groups

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1.2-Alkylidenediphosphoranes stabilised by acyl groups have been prepared quantitatively from the reaction of tertiary phosphines (2 mol.) and diacylacetylenes (1 mol.). The phosphoranes are thermally less stable and more readily hydrolysed than the corresponding phosphoranes stabilised by ester groups. The hydrolyses occur with expulsion of tertiary phosphine and the driving force for the fragmentation is shown not to be derived from the donation of electrons by a phosphoranyl group but probably from the formation of a P=O bond. The diphosphorane derived from diphenylmethylphosphine and dimethyl acetylenedicarboxylate has been synthesised by an alternative route.

IN a previous report ² we described the stable 1,2-alkylidenediphosphoranes (1) and (2) which were prepared by the reactions of the appropriate tertiary phosphine with dimethyl acetylenedicarboxylate. We have extended this reaction to include the preparation of stable 1,2-alkylidenediphosphoranes from diacylacetylenes and have explored alternative synthetic routes to both types of 1,2-diphosphoranes.

¹ Part VIII, E. M. Richards, J. C. Tebby, R. S. Ward, and D. H. Williams, J. Chem. Soc. (C), 1969, 1542.

Horner and Hoffmann³ have reported on the reaction of triphenylphosphine and dibenzoyldiacetylene to give a 2:1-adduct. They have suggested a betaine structure in which the negative charge cannot be stabilised by $p^{\pi}-d^{\pi}$ bonding.

The acyl 1,2-diphosphoranes (3a), (3b), (4a), and (4b) were prepared in almost quantitative yield from the

² M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc.* (C), 1967, 2442.

³ L. Horner and H. Hoffmann, Angew. Chem., 1956, 68, 473.

reactions of an excess of triphenylphosphine or diphenylmethylphosphine with dibenzoyl- or di-p-tolylacetylenes in ether solution. These 1,2-diphosphoranes

Me

(2)

MeO₂C

(4)a;R=Ph

,CO2 Me

PPh₂

Мe

Ph₃P

RĆO

(3)a; R=Ph

b;R=p-tolyl

COR

۱ PPh3

are less stable than their analogues from dimethyl acetylenedicarboxylate, and their ready hydrolysis prevented wholly satisfactory analyses being obtained.

b;R=p-tolyl

TABLE 1

The i.r. spectra of acyl-stabilised alkylidenephosphoranes

		*
Phosphorane	ν(C=O) cm. ⁻¹ (KBr)	Ref.
Ph ₃ P=CHBz	1500	а
Ph ₃ P=CHAc	1529	b
$Ph_3P=C(Cl)Bz$	1470	a
$Ph_3P=C(Br)Bz$	1465	a
$Ph_{3}P=C(I)Bz$	1465	a
∠CH ₂ Bz		
Ph ₃ P=C	1497	C
Bz		
(3a; $R = Ph$)	1478	
(3b; $R = p$ -tolyl)	1475	
(4a; $R = Ph$)	1475	
(4b; $R = p$ -tolyl)	1475	

^a A. J. Speziale and K. W. Ratts, J. Amer. Chem. Soc., 1963, **85**, 2790. ^b F. Ramirez and S. Dershowitz, J. Org. Chem., 1957, **22**, 41. ^c F. Ramirez, O. P. Madan, and C. P. Smith, Tetrahedron, 1968, 22, 567.

The diphosphoranes were characterised, however, by the absence of carbonyl absorptions in the usual region of the i.r. spectrum and the presence of intense bands

J. Chem. Soc. (C), 1970

The n.m.r. spectra of (3b), (4a), and (4b) also indicated that two molecules of phosphine had reacted with one of the acetylenic ketone. The ¹H n.m.r. spectra are summarised in Table 2. The absence of a methine proton in the δ 6-4 p.p.m. region of the spectra determined from trifluoroacetic acid solutions, indicates that the ketonic compounds are weaker bases than the compounds derived from the acetylenic ester. The presence of several conformers such as those identified from the n.m.r. spectra of (1) and (2) was not observed. This is in accordance with those of other workers who have studied acyl-stabilised alkylidenephosphoranes.4,5

The acyl-1,2-diphosphoranes were thermally less stable than their ester analogues and thus satisfactory mass spectra could not be obtained. A molecular ion was observed only in the spectrum of (4a) (at m/e 634), while all the spectra were characterised by intense peaks due to the phosphine and acetylene components and their daughter fragments.

The acyl 1,2-diphosphoranes were readily hydrolysed by water to the corresponding phosphine oxides and diaroylethanes. The reaction proceeded via the expulsion of tertiary phosphine. This was shown by the hydrolysis of (4a) in wet iodomethane which resulted in the formation of dimethyldiphenylphosphonium iodide, diphenylmethylphosphine oxide, and dibenzoylethylene. Scheme 1 shows two paths which were considered for the hydrolysis. Path (a) involves the addition of water followed by the expulsion of the tertiary phosphine and path (b) involves the addition of two equivalents of water before expulsion of the phosphine.

The very low basicity of the acyl-stabilised diphosphoranes (3) and the similarity of the fragmentation to analogous reactions in the literature ⁶ led us to favour path (a). We reconsidered path (b) at the suggestion of a referee, who also suggested that the two paths might be distinguished by treating the disalt of (3) with 1 mol. of base under anhydrous conditions. It was not

TABLE 2

N.m.r. parameters for the 1,2-diphosphoranes (3) and (4)

Phosphorane	Solvent	Assignment	δ (p.p.m.)	$J(P-CH_3)$	Proton ratios		
(3a; R = Ph)	CDCl ₃	Ar	$8 \cdot 4 - 6 \cdot 8(m)$				
(3b; $R = p$ -tolyl)	CDCl ₃	Ar	$8 \cdot 2 - 6 \cdot 5(m)$		38		
	Ar-CH ₃	2.23(s)		6			
(4a; $R = Ph$)	CF_3CO_2H	Ar	8.4 - 6.9(m)		30		
		P-CH ₃	$2 \cdot 14(d)$	13 Hz	6		
(4b; $R = p$ -tolyl) $CDCl_3$	Ar	8·48·0(d)		4			
			7.6-6.9(m)		24		
	Ar–CH ₃	2·36(s)		6			
		$P-CH_3$	1.70(d)	12 Hz	6		
(4b; $R = p$ -tolyl) CF_3CO_2H	CF ₃ CO ₂ H	Ar	8.3 - 6.9(m)		30		
	Ar-CH ₃	2.53(s)		6			
		$P-CH_3$	$2 \cdot 13(d)$	13 Hz	6		
	PCH ₃ °	$2 \cdot 13(d)$	13 Hz	6			

in the 1475-1480 cm.⁻¹ region, characteristic of acyl groups in conjugation with alkylidenephosphorane groups (see Table 1).

⁴ F. J. Randall and A. W. Johnson, Tetrahedron Letters, 1968,

possible to do this for the acyl diphosphoranes since a salt could not be isolated. However disalts of the diphosphorane stabilised by carboxylic ester groups

⁶ G. Wittig, H. Eggers, and P. Duffner, Annalen, 1958, **619**, 10; J. A. Ford and C. V. Wilson, J. Org. Chem., 1961, **26**, 1433; J. A. Elix and M. V. Sargent, J. Amer. Chem. Soc., 1968, **90**, 1631.



Ph₃F

MeO₂C

Ph₂

Me

RCO

 $\{1\}$

CO_Me

PPh3

COR

PPh2

Мe

^{2841.} ⁵ H. J. Bestmann and J. P. Snyder, J. Amer. Chem. Soc., 1967, 89, 3936.

Org. are isolable and therefore the test was carried out on

one of these salts. Treatment of the dihydrochloride of (2) with one equivalent of sodium methoxide in methanol gave a cream-coloured solid the i.r. spectrum of which contained



phosphoranyl-phosphonium salt (5; $R^1 = Me$, $R^2 = OMe$). The salt (5) would be expected to consist of a mixture of interconverting conformers resulting from restricted rotation.² It was not surprising, therefore, that the n.m.r. spectrum of the cream-coloured solid in deuteriochloroform was fairly complex in the methoxy-group and *P*-methyl regions. Although it was not possible to make assignments, there was no evidence for the presence of the diphosphorane or its disalt. Phosphine could be isolated neither by ether extraction nor after the product had been left in dichloromethane solution for 1 week. Addition of further sodium methoxide led to the formation of the 1,2-diphosphorane.

These results show that path (a) does not operate for the diester and that the phosphoranyl group does not provide the driving force for the expulsion of the tertiary phosphine. It seems reasonable to conclude that the formation of a P=O bond provides the driving force for the fragmentation. Path (b) is an example of such a fragmentation.⁷ However, considering that the n.m.r. spectra of the acyl diphosphoranes in trifluoroacetic acid show no evidence of protonation, a mechanism which avoids the protonation of the diphosphoranes by water would be preferred.

It should be noted that the stabilised diphosphoranes already have extensively developed phosphonium centres and that protonation is not essential for the formation of a phosphine leaving group. Thus, two molecules of water may not be essential for fragmentation. When the diphosphorane is dissolved in water it is likely to be solvated as shown in Scheme 2 and a fragmentation such as that shown would be quite feasible.



The acyl-1,2-diphosphoranes also decomposed in chloroform solution at room temperature as indicated by changes in their i.r. spectra. The carbonyl absorption bands at 1475 cm.⁻¹ slowly decreased while the bands at 1685 cm.⁻¹ (corresponding to carbonyl absorption of the diaroylethanes) slowly increased in intensity. The final products were the phosphine oxides and diaroylethanes. (Note that the diaroylethylenes are reduced by diphenylmethylphosphine and triphenyl-phosphine in the presence of water, whereas dimethyl-fumarate is reduced only by diphenylmethylphosphine and water.²)

An attempt was made to synthesise the 1,2-diphosphorane (1) via the bis-phosphonium salt (6). It was proposed to quaternise 2 mol. of triphenylphosphine with 1 mol. of methyl dibromosuccinate in order to obtain the required bis-phosphonium salt (6). However this mode of reaction could not be achieved.



When the reaction was carried out in ethanol-free chloroform dibromotriphenylphosphorane as a white deliquescent solid which fumed in air was formed; its identity was established by comparison of its i.r. spectrum with that of an authentic specimen prepared from triphenylphosphine and bromine in chloroform. The mother liquors from the reaction were found to contain dimethyl fumarate.

In methanol solution a different reaction was observed; the salt which was formed gave the stable alkylidenephosphorane (7) when treated with aqueous sodium hydrogen carbonate solution. Triphenylphosphine oxide was also obtained from the methanolic solution.

⁷ A. M. Aguiar and H. Aguiar, J. Amer. Chem. Soc., 1966, **88**, 4090; J. J. Brophy and M. J. Gallagher, Chem. Comm., 1967, 344.

J. Chem. Soc. (C), 1970

Convincing evidence has been put forward⁸ that phosphines will attack a halogen atom directly when the carbon atom to which it is bonded bears one or more electron-withdrawing groups. Both of the above reactions are readily explained by such a mechanism. Attack of triphenylphosphine on the ' positive ' bromine atom of the bromosuccinic ester produces an ion-pair which gives dimethyl fumarate in the aprotic solvent, but undergoes solvolysis in the protic media to give triphenylphosphine oxide, methyl bromide, and methyl bromosuccinate (see Scheme 3). (12) which were characterised as their respective oxides. Hoffmann and Diehr¹² obtained the vinyl phosphine (11) by addition of diphenylphosphine to phenylacetylene.

Thus it seemed reasonable to expect that diphenylphosphine would react readily with dimethyl acetylenedicarboxylic ester. Accordingly two equivalents of diphenylphosphine were added to one equivalent of the acetylenic ester in ether. No attempt was made to isolate the resulting bis-phosphine but the solution was treated directly with iodomethane to give the bisphosphonium salt (13). On treatment of the salt with



In the last-mentioned case the methyl bromosuccinate can react further * with a second mol. of triphenylphosphine to give the salt (8) first obtained by Osuch, Franz, and Zienty⁹ from triphenylphosphine hydrobromide and dimethyl fumarate.

Borowitz and Virkhaus¹⁰ have proposed that triphenylphosphine and phenacyl bromide gives the ion-pair (9), which in aprotic solvents gives the quaternary phosphonium salt (10). In protic solvents the ionpair undergoes solvolysis to acetophenone, triphenylphosphine oxide, and an alkyl bromide (RBr from solvent ROH).

$$Ph_{3}\overset{-}{P}Br \quad CH_{2}COPh \qquad Ph_{3}\overset{-}{P}CH_{2}COPh \quad Br^{-}$$
(9) (10)

A different route to the 1,2-diphosphorane (2) was then explored. Aguiar and Archibald¹¹ treated lithium diphenylphosphide with phenylacetylene and obtained both the vinyl phosphine (11) and the bis-phosphine



* A sample of methyl bromosuccinate was prepared and treated with triphenylphosphine in methanol. A salt was formed, which gave (7) on treatment with base.

⁸ H. Hoffmann and H. J. Diehr, Angew. Chem. Internat. Edn., 1965, 4, 737.

aqueous sodium hydrogen carbonate solution the 1,2-diphosphorane (2) was obtained.



The above synthesis could not be extended to the 1,2-diphosphoranes (4a) and (4b) since it appeared that diphenylphosphine added to the carbonyl group in preference to the acetylenic bond.

EXPERIMENTAL

The spectra were determined on a Perkin-Elmer 60 MHz n.m.r. spectrometer, an A.E.I. MS9 double-focusing

- ⁹ C. Osuch, J. E. Franz, and F. H. Zienty, J. Org. Chem., 1964, 29, 3721.
 ¹⁰ I. J. Borowitz and R. Virkhaus, J. Amer. Chem. Soc., 1963,
- Solution and T. G. Archibald, Tetrahedron Letters,
 ¹¹ A. M. Aguiar and T. G. Archibald, Tetrahedron Letters,
- 1966, 5471. ¹² H. Hoffmann and H. J. Diehr, Chem. Ber., 1965, **98**, 363.

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mass spectrometer, and a Unicam SP 200 i.r. spectrometer.

1, 2-Dibenzoyl-1, 2-bistriphenylphosphoranylideneethane-

(3a).—Triphenylphosphine (2.6 g.), dissolved in dry ether (15 ml.), was stirred and cooled to 0° while a solution of dibenzoylacetylene (1.2 g.) in ether (60 ml.) was added dropwise to give a cream-coloured precipitate. The mixture was stirred 15 min. after the addition and then the solid was collected. The *product* (3a) (3.7 g., 97%), crystallised from chloroform-ether, had m.p. 199—200° (Found: C, 79.95; H, 5.35; P, 7.45. $C_{52}H_{30}O_2P_2,H_2O$ requires C, 80.4; H, 5.4; P, 8.0).

1,2-Di-p-toloyl-1,2-bistriphenylphosphoranylidene-ethane (3b).—Prepared in a similar manner to (3a) from triphenylphosphine (2.6 g.) and di-p-toluoylacetylene (1.3 g.), the *product* (3b) was obtained in 95% yield and had m.p. 179—180° (Found: C, 81.7; H, 5.85; P, 8.1. $C_{54}H_{44}O_2P_2$ requires C, 82.4; H, 5.6; P, 7.9%).

 $1, 2\mbox{-}Dibenzoyl\mbox{-}1, 2\mbox{-}bisdiphenylmethylphosphoranylidene-}$

ethane (4a).—Prepared in a similar manner to (3a) from diphenylmethylphosphine (2.0 g.), the product (4a) was obtained in 100% yield and had m.p. 188—189° (Found: C, 78.6; H, 6.0; P, 9.65. $C_{42}H_{36}O_2P_2$ requires C, 79.5; H, 5.7; P, 9.8%).

1,2-Di-p-toluoyl-1,2-bisdiphenylmethylphosphoranylideneethane (4b).—Prepared in a similar manner to (3a) from diphenylmethylphosphine (2.0 g.) and di-p-toluoylacetylene (1.3 g.), the *product* (4b) was obtained in 97% yield and had m.p. 201—202° (Found: C, 78.6; H, 6.2; P, 9.4. $C_{44}H_{40}O_2P_2$ requires C, 79.6; H, 6.05; P, 9.35%).

Hydrolysis of the 1,2-Diphosphorane (4a).—(a) The diphosphorane (50 mg.) was dissolved in chloroform (5 ml.) and the i.r. spectrum of the solution was recorded at intervals. The intensity of the absorption at 1475 cm.⁻¹ slowly decreased whilst that at 1685 cm.⁻¹ slowly increased. The solution was examined by t.l.c. on silica with ethyl acetate as eluant. Two components were observed which corresponded to dibenzoylethane and diphenylmethyl-phosphine oxide.

(b) The diphosphorane (250 mg.) was heated under reflux with water (10 ml.) for 4 hr. The mixture was cooled and extracted with chloroform. The extracts were dried and chromatographed through a silica column. With ether as eluant dibenzoylethane was obtained, m.p. and mixed m.p. 144—146°. Elution of the column with methanol gave diphenylmethylphosphine oxide (135 mg., 79%), a sample of which from ether had m.p. and mixed m.p. 107—108°.

Hydrolysis of (4a) in the Presence of Iodomethane.—The diphosphorane (100 mg.) was heated under reflux with wet iodomethane (5 ml.) for 72 hr. Dimethyldiphenylphosphonium iodide (34 mg., 43%) was collected and, after crystallisation from ethanol, had m.p. and mixed m.p. 252—253°. The iodomethane was evaporated off from the filtrate and the residue was crystallised from alcohol to give yellow flakes of dibenzoylethylene (18 mg., 38%), m.p. and mixed m.p. 107—110°. The filtrate was evaporated to give a yellow gum which was extracted with hot ether (5 ml.). The extract was evaporated to dryness and the residue was triturated with light petroleum. Diphenylmethylphosphine oxide (20 mg., 46%) was obtained which, after crystallisation from ether, had m.p. and mixed m.p. 105—108°.

Hydrolysis of the 1,2-Diphosphoranes (3a), (3b), and (4b).-

The hydrolyses were carried out by method (b) above. The corresponding phosphine oxides and diaroylethanes were obtained.

Reaction of Triphenylphosphine with Methyl Dibromosuccinate.---(a) In chloroform. Triphenylphosphine (2.6 g.) and methyl dibromosuccinate (1.5 g.) were heated under reflux with ethanol-free chloroform (10 ml.) for 10 min. The solution was cooled and dibromotriphenylphosphorane (1.9 g., 90%) was collected. It had an i.r. spectrum superimposable on that of an authentic sample. The chloroform was evaporated from the filtrate and the residual oil was heated under reflux with iodomethane (10 ml.) for 1 hr. A colourless solid was collected and identified as triphenylmethylphosphonium iodide (1.7 g., 85%), m.p. and mixed m.p. 180-182°. The iodomethane was evaporated off from the filtrate and the residual oil was crystallised from methanol to give plates of dimethyl fumarate (0.3 g., 43%), m.p. and mixed m.p. 103-104°.

(b) In methanol. Triphenylphosphine (1.3 g.) and methyl dibromosuccinate (0.8 g.) dissolved in dry methanol (10 ml.) were set aside overnight. The methanol was evaporated off and the residue was extracted with several portions of hot ether. The extracts were evaporated to dryness and the residue of triphenylphosphine oxide (0.6 g., 85%) crystallised from aqueous methanol; it had m.p. and mixed m.p. $155-156^{\circ}$.

The residue, after extraction with ether, was treated with aqueous sodium hydrogen carbonate. After the gas evolution had ceased the phosphorane (7) (0.5 g., 50%) was collected. It had m.p. and mixed m.p. $158-159^{\circ}$ after crystallisation from chloroform-light petroleum, and had an i.r. spectrum superimposed on that of an authentic sample.¹⁰

Reaction of Diphenylphosphine with Dimethyl Acetylenedicarboxylate.—Diphenylphosphine (3.8 g.) and dimethyl acetylenedicarboxylate (1.4 g.) dissolved in dry ether (70 ml.) were kept under a nitrogen atmosphere for 4 days. The buff-coloured precipitate was filtered off under nitrogen. Iodomethane (10 ml.) was added to the filtrate and the mixture was set aside for 24 hr.; a buff-coloured solid was collected and crystallised from chloroform to give (1,2-dicarbomethoxyethane-1,2-bisdiphenylmethylphosphonium diiodide (13) (3.2 g., 42%), m.p. 132—133° (Found: C, 47.9; H, 4.6%; equiv. wt.,¹³ 398. $C_{32}H_{34}I_2O_4P_2$ requires C, 48.1; H, 4.3%; equiv. wt., 399).

The bis-phosphonium iodide (13) (0.5 g.) dissolved in chloroform (2 ml.) was shaken with aqueous sodium hydrogen carbonate (5 ml.) for 30 min. The chloroform layer was washed with water, dried, and evaporated. The residual gum was triturated with ether to give the 1,2-diphosphorane (2) (0.3 g., 88%) the i.r. and n.m.r. spectra of which were superimposable on that of an authentic sample.² A sample was crystallised from chloroform-ether and had m.p. and mixed m.p. $215-217^{\circ}$.

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¹³ S. T. Ross and D. B. Denney, Analyt. Chem., 1960, **32**, 1896.