

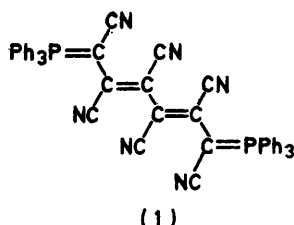
Reactions of Phosphines with Acetylenes. Part 17.¹ Formation and Stereochemistry of 1,2-Dicyano-2-phosphoniaethanesulphonate Betaines

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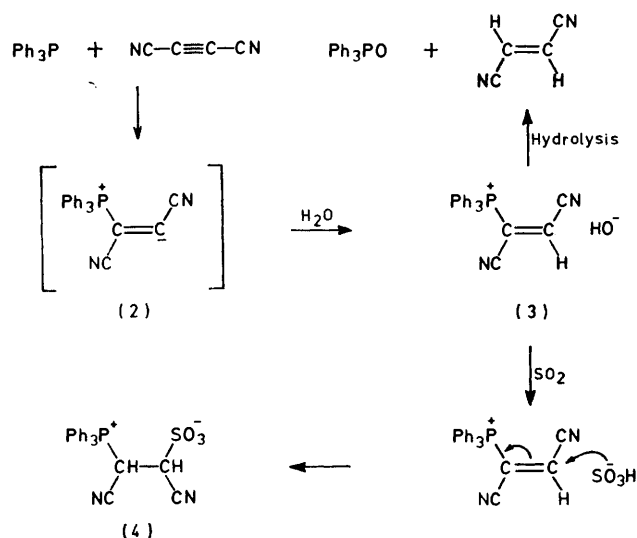
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The initial intermediate in the reaction of triarylphosphines with cyanoacetylenes may be trapped as an adduct with water and sulphur dioxide. The structures of the adducts are shown to be phosphoniaethanesulphonate betaines. Vicinal n.m.r. coupling constants show that in trifluoroacetic acid solution the betaines from dicyanoacetylene are held in a rigid conformation of the *threo* configuration. However, in dimethyl sulphoxide solution the coupling is removed by a slow proton exchange process.

THE mechanism of the reaction of triphenylphosphine and dimethyl acylenedicarboxylate has been studied in some detail² and the 1 : 1 intermediate has been trapped using carbon dioxide³ and water and sulphur dioxide.⁴ Dicyanoacetylene is much more reactive than the acetylenic ester and its reactions with triphenylphosphine gives polymerised acetylene in addition to the stable alkylidene-1,6-diphosphorane (1)⁵ (an ylide of quite different structure to those obtained from the acetylenic ester). Furthermore, attempts to trap the initial intermediates of the reaction with carbon dioxide have failed.⁵



The reaction of triphenylphosphine and dicyanoacetylene in the presence of water gives triphenyl-



phosphine oxide and fumaronitrile. We consider that these products arise from the hydrolysis of the polar 1 : 1

intermediate (2) as shown in the Scheme. Fragmentation is avoided if sulphur dioxide is also present. The product is the phosphoniaethanesulphonate betaine (4) which we believe is formed by sulphonation of the protonated intermediate (3) as shown in the Scheme. The structure of the betaine (4) is evident from (a) its fragmentation in boiling toluene to give triphenylphosphine oxide, sulphur dioxide, and fumaronitrile; (b) i.r. bands at 1 220, 1 100, and 1 042 cm⁻¹ (SO₃⁻), and the shift of ν(CH) 2 835 upon deuterium exchange to ν(CD) 2 100 cm⁻¹; (c) its ³¹P n.m.r. resonance at 26.0 p.p.m.;† and (d) the similarity of its ¹³C n.m.r. spectrum (Table 1)

TABLE 1

¹³ C N.m.r. parameters ^a of phosphoniaethanesulphonate betaines				
Aromatics	(4)	(5)	(6)	(7)
P-C	114.83(87)	118.29(87)	117.64(88)	117.98(88)
o-C	135.95(10)	136.59(10)	135.49(11)	134.69(10)
m-C	133.25(13)	131.89(13)	132.71(13)	131.89(13)
p-C	139.46(2)	137.66(2)	138.25	137.13
Others				
α-C	31.82(51) ^b	45.10(33)	25.22(55)	25.48(55)
β-C	50.58	68.31(2)	48.10(5)	62.22
CN	112.54		114.61	
CN	112.91			
Me		55.50		
Me		55.70		55.62
CO		168.66(4)		168.53
CO		169.87(2)		

^a All spectra were run in TFA [plus trace of (CD₃)₂CO for locking] and assignments were confirmed by 'off-resonance' experiments. Resonance positions are in p.p.m. with respect to T.M.S. as internal reference and are accurate to ±0.6 Hz. Values in parentheses are those for coupling to phosphorus.
^b C-H exchanges in [²H]TFA.

with that of the corresponding betaine (5) from dimethyl acylenedicarboxylate. Although the basic structure of the betaines (4) and (5) are the same, the ¹H n.m.r. spectra (Table 2) show that the conformations which they adopt in trifluoroacetic acid are quite different. Thus in trifluoroacetic acid solution the ester betaine (5) gives a spectrum with *J*_{PCCH} 2 and *J*_{HCCH} 11 Hz which corresponds to the conformation (5a) whilst the dicyano betaine (4) gives a spectrum with *J*_{PCCH} 11 and *J*_{HCCH}

† Positive shifts are downfield of 85% phosphoric acid.

1 Hz which corresponds to the conformation (4a). The very low HCCH vicinal coupling constant for the latter

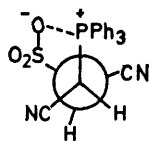
TABLE 2

¹H N.m.r. parameters of phosphoniaethanesulphonate betaines

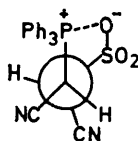
Compound	Solvent	δ(PCH)	J _{PCH}	δ(PCCH)	J _{PCCH}	J _{HCCH}
(4)	TFA	6.2 (dd)	16	5.0 (dd)	11	0.97 ^a
(4)	DMSO	4.0–5.2		4.87 (d)	13	
(5)	TFA	5.65 (dd)	13.5	5.22 (dd)	2	11
(6)	TFA	4.1 (m)	11 ^b	4.8 (m)		
(8)	TFA	5.77 (dd)	16	4.92 (dd)	11	<1 ^a
(8)	CDCl ₃			4.59	12	
(9)	TFA	6.13 (dd)	16	4.52 (dd)	11	<1 ^a

^a The very small vicinal HCCH coupling was not observed in the continuous wave spectra from the MH 100 but was detectable in the FX 100 pulsed spectrum of (4). ^b Measured from the spectrum of the betaine which was prepared using D₂O.

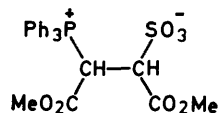
betaine indicates that conformer (4b) does not make a significant contribution to the structure.⁶ Both be-



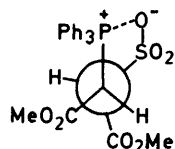
(4a)



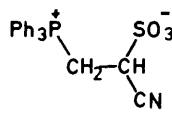
(4b)



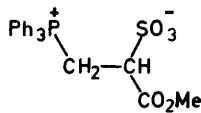
(5)



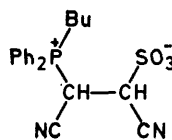
(5a)



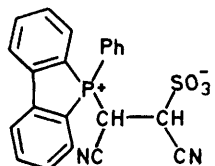
(6)



(7)



(8)



(9)

taines (4) and (5) have a *threo* configuration because the *erythro* conformations could not explain the observed vicinal coupling constants and the fact that decomposition of the betaines in boiling toluene gives fumaronitrile and dimethyl fumarate, respectively, and none of the maleic compounds.

The rigidity of the conformations of the dicyanobetaines is also reflected by the close similarity of the vicinal coupling constants when the groups attached to phosphorus are varied through the series triphenyl,

butyldiphenyl, biphenyl-2,2'-ylenephenyl (Table 2). That this is due to the presence of a strong attractive force between the sulphonate and phosphonium groups is confirmed by the inertness of the sulphonate group to alkylation by triethyloxoniumtetrafluoroborate in liquid sulphur dioxide or dichloromethane.* The strong preference for conformation (4a) in which there is maximum separation of the cyano-groups compared to the less crowded conformer (4b) or either of the staggered conformations of the *erythro* form indicates that there is also a significant dipolar repulsion between adjacent cyano-groups.

The ¹H n.m.r. spectrum of a freshly prepared solution of the dicyanobetaine (4) in deuteriotrifluoroacetic acid shows no α -proton resonance. Thus there is exchange of the α -proton in trifluoroacetic acid which, although very slow relative to the n.m.r. time scale, means that it is not possible to be completely confident that the solid has the same stereochemistry as occurs in solution. It should be remembered, however, that decomposition of the dicyanobetaine (4) in boiling toluene gives fumaronitrile and it is unlikely that α -proton exchange would occur in these circumstances.

When the ¹H n.m.r. spectrum is run on a solution of the dicyanobetaine (4) in [²H₆]dimethyl sulphoxide, the α -proton resonance is barely visible since it is extensively broadened. Additions of small amounts of trifluoroacetic acid lessen the broadening and shift the signal downfield which is in accordance with the participation of the trifluoroacetic acid in the α -proton exchange process. The exchange of the α -proton can also be monitored by observing the 'proton-decoupled' and 'undecoupled' ¹³C n.m.r. signal of the α -carbon under similar conditions. In [²H₆]dimethyl sulphoxide the 'proton-decoupled' α -carbon signal is observed clearly as a doublet due to the phosphorus coupling, but in the 'undecoupled' spectrum the signal broadens extensively to give an unresolved signal. In comparison, the same resonance with trifluoroacetic acid as solvent gives a clearly visible proton coupling indicating a slower exchange rate of the α -proton in the trifluoroacetic acid. Thus in the dicyanobetaines the usual role of dimethyl sulphoxide, which is to slow proton exchange processes, appears to be reversed. This is presumably due to the higher basicity of dimethyl sulphoxide relative to trifluoroacetic acid.

The reaction of monocyanoacetylene with triphenylphosphine, water, and sulphur dioxide gives the cyanobetaine (6) which is similar to the ester betaine (7) obtained from methyl propiolate. The n.m.r. parameters are given in Tables 1 and 2. In particular it is interesting to note the similarity of the chemical shift and the phosphorus coupling of the α -carbons in these two compounds. The ¹H n.m.r. resonances for the methylene and methine groups were observed as separate signals in the cyanobetaine (6) only when trifluoroacetic

* The prepared reagent gave a high yield of ethyl benzenesulphonate when treated with sodium benzenesulphonate under the same reaction conditions.

acid was the solvent and even then the resonances were complex. The geminal PCH coupling was, however, obtained from the spectrum of the dideuteriated betaine which was prepared in the presence of D₂O rather than H₂O. Under these conditions the methine proton and one of the methylene protons are replaced by deuterium leaving the remaining methylene proton resonance clearly visible in the spectrum as a doublet at δ 4.1 (J_{PCH} 11 Hz). The variations in J_{PCH} (Table 2) reflect the effects of substitution at the α -carbon.

EXPERIMENTAL

¹H and ¹³C n.m.r. spectra were determined on JEOL MH 100 and FX 100 spectrometers. ³¹P N.m.r. spectra were determined on a Perkin-Elmer R10 instrument. Compounds were either available from previous work or were prepared as indicated.

1,2-Dicyano-2-triphenylphosphoniaethanesulphonate (4).⁷—Freshly prepared dicyanoacetylene⁸ in dry diethyl ether (20% solution) was added dropwise at 0 °C to an equimolar quantity of triphenylphosphine dissolved in moist diethyl ether saturated with sulphur dioxide. The precipitate was separated, washed with ether, and dried to give the betaine, m.p. 167–168° (Found: C, 62.5; H, 4.1; N, 6.65; *M*, 450 (Rast). C₂₂H₁₇N₂O₃PS requires C, 62.8; H, 4.09; N, 6.65%; *M*, 420), δ_{P} (TFA) 26.0 p.p.m. The mass spectrum contained ions from thermal decomposition products only.

The betaine (0.5 g) was thermally decomposed in boiling toluene (50 cm³) for 2 h whilst pure nitrogen was bubbled through the solution. The evolved sulphur dioxide was removed from the stream of nitrogen by a cooled standardised iodine solution and estimated by back-titration against

sodium thiosulphate. The quantity of sulphur dioxide (average of three runs) corresponded to a molecular formula of C₂₂H₁₇N₂O₃PS. G.l.c. (10% Apiezon L) of the non-volatile products showed the presence of fumaronitrile and the absence of maleonitrile. Evaporation of the solution gave triphenylphosphine oxide.

1-Cyano-2-triphenylphosphoniaethanesulphonate (6).—Cyanoacetylene⁹ (3.0 g) in dry ether (50 cm³) was cooled to –50 °C and added over 30 min to a stirred solution at 0 °C of triphenylphosphine (15 g) in moist ether (250 cm³) which was saturated with sulphur dioxide. The red solid (13.5 g, 57%) was separated, washed with ether, and dried to give the betaine, m.p. 117–119° (Found: C, 63.65; H, 4.45; N, 3.4. C₂₁H₁₈NO₃PS requires C, 63.8; H, 4.56; N, 3.54%), δ_{P} (CHCl₃) 18 p.p.m.

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