Reactions of Phosphines with Acetylenes. Part VI.[1] 2-Phosphonia-ethanesulphonate Betaines. The Sulphonation of Vinyl Phosphonium Salts

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Dimethyl acetylenedicarboxylate, triphenylphosphine, sulphur dioxide, and water react to give the betaine 1,2-dimethoxycarbonyl-2-triphenylphosphoniaethane sulphonate(4a). The n.m.r. spectra show that only the threo-diastereoisomer crystallises from the reaction mixture, and retains a cyclic conformation in solution. The betaine readily fragments on heating and forms a stable phosphorane on treatment with alkali. Similar betaines (4b) and (4c) are formed using methyl propiolate and methyl phenylpropiolate. It has been shown that the betaines are formed *via* sulphonation of vinyl phosphonium salts. The previously reported 1,2-dimethoxycarbonylvinylphosphonium bromide was in error and has now been prepared.

THE reactions of tertiary phosphines with electrophilic acetylenes have been shown to give products of widely differing structures which depend upon the reactants and the ratio of reactants used.[1-3] The formation of all the products is consistent with reaction pathways which involve a 1 : 1-phosphine–acetylene dipolar intermediate in the first step. With triphenylphosphine and dimethyl

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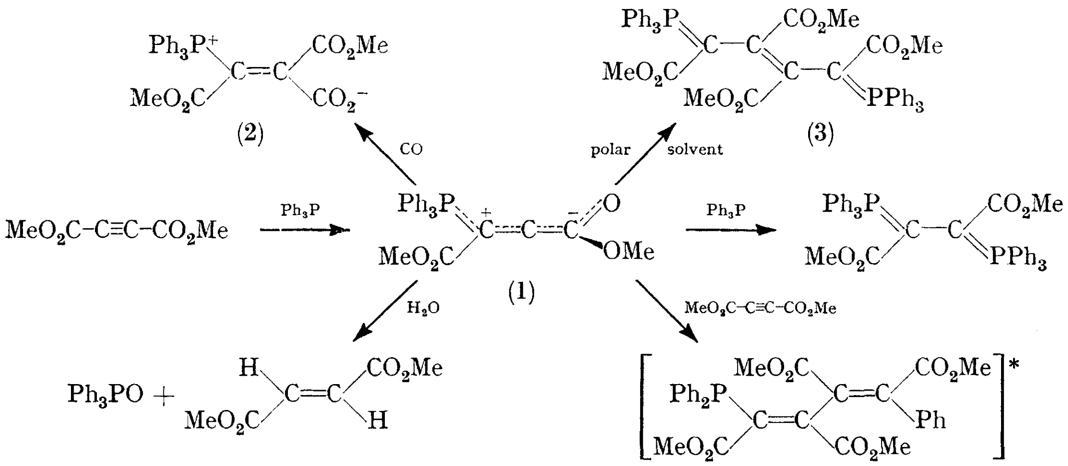
[1] Part V, M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc.* (*C*), 1968, 1609.

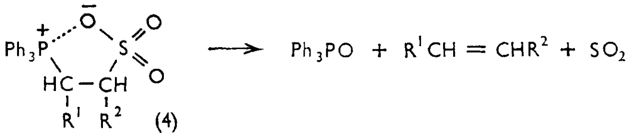
[2] (*a*) A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 1961, 2126; (*b*) M. A. Shaw, J. C. Tebby, J. Ronayne, and D. H. Williams, *J. Chem. Soc.* (*C*), 1967, 944; (*c*) M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc.* (*C*), 1967, 2442.

[3] D. W. Allen, J. C. Tebby, and D. H. Williams, *Tetrahedron Letters*, 1965, 2361; D. W. Allen and J. C. Tebby, *Tetrahedron*, 1967, **23**, 2795.

acetylenedicarboxylate the 1 : 1 intermediate (1) has been trapped as (2) using carbon dioxide.[2b] This particular intermediate behaves in a versatile manner and, in addition to reacting with carbon dioxide, it dimerises to the 1,4-diphosphorane (3) in polar solvents,[4] forms a 1,2-diphosphorane with excess phosphine,[2c] and gives 1 : 2 adducts in the presence of an excess of acetylenic ester.[2a] If water is present the 1 : 1 intermediate hydrates and fragments to give triphenylphosphine oxide and dimethyl fumarate. With monosubstituted acetylenes the last step is aryl migration.[3] We now show that if sulphur dioxide is present in addition to water, fragmentation or aryl migration is avoided and adducts are formed which are triphenylphosphoniaethanesulphonates (4).



* *Note added in proof:* This structure [2a] is now believed to be incorrect.[2d] The revised structure will be the subject of a separate communication.



(4)

$Ph_3PO + R^1CH=CHR^2 + SO_2$

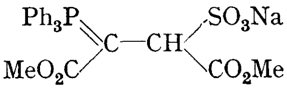
	R¹	R²
a;	CO_2Me	CO_2Me
b;	H	CO_2Me
c;	Ph	CO_2Me

The structures of these betaines were established from their physical and chemical properties and from a comparison with model compounds. The structures were confirmed by the synthesis of two of the adducts.

The adducts readily fragment in boiling toluene, the adduct from dimethyl acetylenedicarboxylate giving sulphur dioxide, triphenylphosphine oxide, and dimethyl fumarate. Extrusion reactions are common in sulphur chemistry and sulphite esters and γ-sultones may be desulphonated upon heating.[5] In this case all three fragments are stable molecules which have been extruded in their own right. The fragmentation indicates that in the adducts, the original phosphine and sulphur dioxide entities each become bonded to one of the acetylenic carbon atoms as do the two protons derived from the water.

The i.r. spectra of the adducts showed absorptions at 1100 cm.$^{-1}$ which indicate the presence of a phosphonium centre and absorptions in the 1225—1220 and 1035—1038 cm.$^{-1}$ regions which indicate the presence of a sulphonate grouping. A sulphite grouping can not be rigorously excluded on i.r. evidence alone due to the lack of suitable models.

The adduct from dimethyl acetylenedicarboxylate was shown to possess a P^+–CH grouping when it gave the stable phosphorane (5) on treatment with dilute sodium hydroxide solution. The phosphorane was a sodium salt and gave the original adduct on treatment with acid. In addition to absorptions at 1200 and 1040 cm.$^{-1}$ due to the sulphonate grouping, the i.r. spectrum of (5) showed



(5)

an intense carbonyl absorption at 1622 cm.$^{-1}$ which is characteristic of phosphoranes stabilised by carboxylic ester groups.[2c] The adducts from methyl propiolate and methyl phenylpropiolate did not form phosphoranes and triphenylphosphine was the only isolable product. This was probably due to preferential removal of the β-proton when an activating group is absent from the α-carbon atom, and indicates that the methoxycarbonyl-groups are at the β-position as shown in (4b) and (4c).

The ^{31}P n.m.r. spectra in trifluoroacetic acid confirm the presence of a phosphonium centre.[2b] The chemical shifts observed were (4a) —28 p.p.m., (4b) —22 p.p.m., and (4c) —27 p.p.m. relative to 85% phosphoric acid.

The 100 Mc. ^{1}H n.m.r. spectrum of (4a) in trifluoroacetic acid contains a 15H resonance in the δ 7·7—8·1 region which corresponds to three phenyl rings; a 1H pair of doublets (J 11 and 13·5 c./sec.) centred at

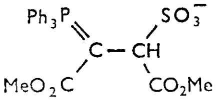
[4] M. A. Shaw, N. E. Waite, and J. C. Tebby, unpublished results.

[5] J. L. Kice, in 'Chemistry of Organo-Sulphur Compounds,' ed. N. Karasch, Pergamon Press, 1966, vol. 2.

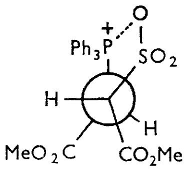
δ 5·65 and a second 1H pair of doublets (J 11 and 2 c./sec.) centred at δ 5·22 which correspond to two methine protons coupled to each other and to the phosphorus atom; and two 3H singlets at δ 3·41 and 3·30 p.p.m. which correspond to two ester methoxy-groups. The fairly large H–H vicinal coupling constant of 11 c./sec. indicates that the two protons are being held in an approximate *trans*-conformation. Also notable is the low P–H coupling constant of 2 c./sec.

Randall and Johnson[6] have studied the low geminal coupling constants for some stable oxomethylene-phosphoranes and report J_{PCH} for these compounds to be usually above 20 c./sec. when pure, but that an exchange reaction with 1—3% of the corresponding phosphonium salt will drastically reduce the splitting. The splitting may be reduced to the order of 7 c./sec. at room temperature and will broaden and coalesce to a singlet upon warming. This situation would not be expected for (4a) in strongly acidic media since very little of the conjugate base (6) (a phosphorane) should be present. The absence of an exchange reaction was confirmed when the spectrum of (4a) in deuteriotrifluoroacetic acid was unchanged relative to that in trifluoroacetic acid.

A low vicinal P–H coupling constant would be expected if the sulphonate and phosphonium groups were held close together in the cyclic conformation (7), in which case the PCCH dihedral angle will approach right angles and reduce $^3J_{\mathrm{PH}}$ to a low value.[7] The alternate conformer with the β-methoxycarbonyl group at right angles to the bulky triphenylphosphonium group is expected to be less favourable than (7). This conclusion precludes the existence of the erythro-form (8) in trifluoroacetic acid solution.



(6)



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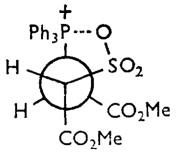
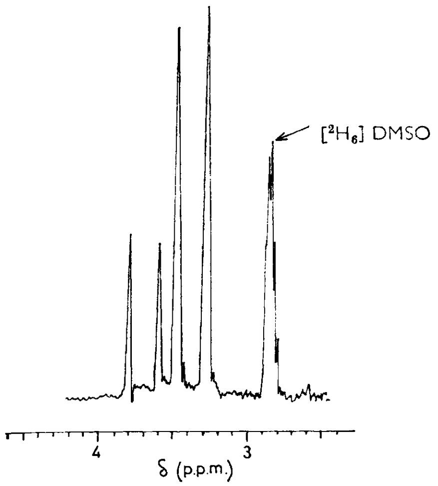


(8)

The 100 Mc. n.m.r. spectrum of (4a) is more complex in $[^2H_6]$-dimethyl sulphoxide solution but can be rationalised as a 2 : 1 mixture of threo- and erythro-diastereoisomers (7) and (8) (see methoxy-resonances in Figure). If this is so, either the erythro-form is converted into the less crowded threo-form in acidic solution or the threo-form is partially converted into the erythro-form in dimethyl sulphoxide. That the latter is the case is indicated by the lack of H–D exchange in deuteriotrifluoroacetic acid and was confirmed when the spectrum of (4a) in dimethyl sulphoxide was considerably changed by the addition of deuterium oxide. Two H–D exchange reactions could be discerned, one much faster than the other. The fast exchange reaction, which was complete in 3 min., involved the exchange of the α-methine proton of the less-stable erythro-diastereoisomer, as was shown by the disappearance of the quartet at δ 5·96 p.p.m. ($^2J_{\mathrm{PH}}$ 13 and $^3J_{\mathrm{HH}}$ 8 c./sec.) and the collapse of the quartet at δ 4·36 p.p.m. ($^3J_{\mathrm{PH}}$ 14 and $^3J_{\mathrm{HH}}$ 8 c./sec.) to a doublet (J 14 c./sec.). The slower exchange reaction (*ca.* 30% completed after 3 min.) involved the exchange of the α-methine of the predominent threo-diasteoisomer as shown by the continued presence of quartets at δ 5·65 p.p.m. ($^2J_{\mathrm{PH}}$ 14 and $^3J_{\mathrm{HH}}$ 10 c./sec.) and δ 4·56 p.p.m. ($^3J_{\mathrm{PH}}$ 2 and $^3J_{\mathrm{HH}}$ 10 c./sec.) due to the α- and β-methine protons of the non-deuteriated diastereoisomer, with an additional doublet (J 2 c./sec.) piercing the centre of the quartet at δ 4·56 p.p.m. When the H–D exchange reaction was complete only two doublets remained in the methine region.



Methoxy-region in the 100 Mc. n.m.r. spectrum of the adduct (2a) ($[^2H_6]$-dimethylsulphoxide solution)

The low value of $^3J_{\mathrm{PH}}$ (2 c./sec.) has been rationalised in terms of the conformation (7). However, in the erythro-diastereoisomer the interaction of the two methoxy-carbonyl groups will reduce the PCCH dihedral angle. The rise in $^3J_{\mathrm{PH}}$ to 14 c./sec. is attributed to a decrease in the dihedral angle to approximately 60° as shown in (8). Similar increases in vicinal coupling constants for a relatively small change in dihedral angle has been reported for steroidal phosphonates.[8] The exchange reactions in dimethyl sulphoxide are attributed to the formation of small amounts of the conjugate phosphorane (6), which would lead to H–D exchange of the α-proton. This is confirmed by the lack of diastereoisomer interconversion in the less acidic adducts (4b) and (4c) as discussed later. The absence of free rotation about the αβ-carbon–carbon bond is also confirmed since the deuteriated diastereoisomers show different vicinal coupling constants.

The presence of only one non-labile diastereoisomer in trifluoroacetic acid shows that it must be this form (the

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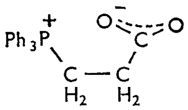
[6] F. J. Randall and A. W. Johnson, *Tetrahedron Letters*, 1968, 2841.

[7] P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Amer. Chem. Soc.*, 1968, **90**, 715.

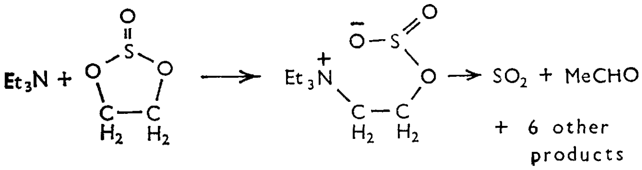
[8] C. Benezra and G. Ourisson, *Bull. Soc. chim. France*, 1966, 1825.

threo-diastereoisomer) which crystallises from the reaction mixture. The strong attraction between the phosphonium and sulphonate groups is probably an important factor for this phenomenon. It is well recognised that anionic oxygen is usually strongly attracted to phosphonium centres and many examples of phosphoranes with P–O bonds are known. But it is wholly reasonable that the very stable sulphonate grouping should be reluctant to form a phosphorane preferring to make an electrostatic bond. Denney and Smith[9] observed that the betaine (9) does not exist in the phosphorane form and suggested similar reasons. A cyclic conformation may also apply to (9) but this would be more difficult to prove in this instance. An example of such bonding with a triphenylphosphonium group has been claimed by Chopard.[10] The ^{31}P n.m.r. spectrum of a tris(dimethylamino)phosphonium betaine indicates[11] that this type of compound exists as an equilibrium mixture of the betaine and phosphorane.

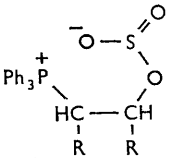

(9)

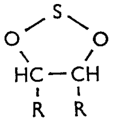
The 100 Mc. n.m.r. spectra of (4b) (in $[^2H_6]$dimethyl sulphoxide or trifluoroacetic acid solution) and (4*c*) (in deuteriochloroform, $[^2H_6]$dimethyl sulphoxide, or trifluoroacetic acid solution) did not show evidence of important amounts (>10%) of isomer forms (due to erythro- and threo-diastereoisomers). The methine and methylene proton resonances of (4c) were amenable to analysis in $[^2H_6]$dimethyl sulphoxide solution and showed a one-proton pair of doublets ($^3J_{HH}$ 11 c./sec. and $^2J_{PH}$ 13 c./sec.) centred at δ 6·05 and a one-proton triplet ($^3J_{HH} \bumpeq {}^3J_{PH} \bumpeq$ 11 c./sec.) centred at δ 4·77 p.p.m.

A route to the phosphoniaethanesulphite betaine (10) was explored. The reaction of triethylamine with ethane-1,2-sulphite has been described in terms of nucleophilic attack at an α-carbon atom of the cyclic sulphite to give a triethylammonioethanesulphite which then fragments.[12]

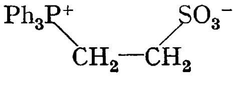


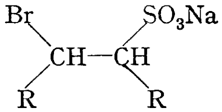
Triphenylphosphine and ethane-1,2-sulphite (11a) in diglyme at 160° were converted almost quantitatively into triphenylphosphine oxide, ethylene, and sulphur dioxide. Thus the reaction proceeded in accordance with the intervention of the phosphoniaethanesulphite (10a). However 1,2-dimethoxycarbonylethane-1,2-sulphite (11b) and triphenylphosphine in diglyme at 160° charred and evolved sulphur dioxide. Very little triphenylphosphine oxide was obtained, in fact most of the triphenylphosphine was recovered and no dimethyl maleate or fumarate could be detected. No reaction occurred under milder conditions.


(10)


(11)

a; R = H
b; R = CO_2Me


(12)


(13)

a; R = H
b; R = CO_2Me

Next, the preparation of triphenylphosphoniaethanesulphonate (12) was attempted by the quaternisation of triphenylphosphine with sodium 2-bromoethanesulphonate (13a). Although there was no reaction in several solvents, a white solid was obtained when the reactants were heated together in the absence of solvent at 120° for one week. Elemental analysis and the n.m.r. spectrum of the product was in accordance with structure (12). The i.r. spectrum possessed bands at 1100, 1200, and 1035 cm.$^{-1}$ which resembled closely the corresponding bands in the adducts. Vigorous conditions were required to promote fragmentation and when the compound melted sulphur dioxide, ethylene, and triphenylphosphine oxide were detected together with some triphenylphosphine. This reduced reactivity may be due to the lack of withdrawing groups which could facilitate the movement of electrons in the fragmentation reaction of the adducts. The sulphonate (12) also resembled the adduct (4a) in that they both dissolved in a mixture of perchloric acid and acetic acid and gave a white solid on addition of ether. The i.r. spectra of both solids showed the presence of perchlorate ions but no reaction occurred with diazomethane under conditions which converted toluene-*p*-sulphonic acid quantitatively into its methyl ester. Upon crystallisation from a neutral solvent the original compounds were obtained in both cases.

An attempt to synthesise the betaine (4a) by a similar route as used for (12) *via* sulphonation of methyl dibromosuccinate was abandoned when sodium sulphite and methyl dibromosuccinate failed to react. However the adducts (4a) and (4c) were readily prepared by mixing aqueous solutions of sodium bisulphite and the appropriate vinylphosphonium salt. The methoxycarbonylstyrylphosphonium bromide (14b) was prepared by the method of Hoffmann and Diehr.[13] These workers also report the preparation of 1,2-dimethoxycarbonyl-

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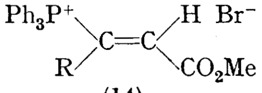
[9] D. B. Denney and L. C. Smith, *J. Org. Chem.*, 1962, **27**, 3404.
[10] P. A. Chopard, *Helv. Chim. Acta*, 1967, **50**, 1016.
[11] F. Ramirez, A. V. Patwardhan, H. J. Kugler, and P. C. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 6276.
[12] R. G. Gillis, *J. Org. Chem.*, 1960, **25**, 651.
[13] H. Hoffmann and H. J. Diehr, *Chem. Ber.*, 1965, **98**, 363.

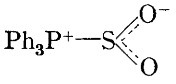
vinylphosphonium bromide (14a) but the product of m.p. 143° was found to be the dihydrobromide of the 1,4-diphosphorane (3).[2b] Although this phosphorane was originally prepared from the carbon dioxide-trapped 1 : 1 intermediate (2) we find [4] that many polar solvents (*e.g.* acetone, acetonitrile, dimethoxyethane, and ethyl acetate) will cause direct dimerisation of the 1 : 1 intermediate (1). The desired vinylphosphonium salt (14a) was prepared in chloroform solution. The salt, which can be precipitated from solution with ether, is extremely deliquescent and a satisfactory analysis was not obtained. The salt was characterised by hydrolysis in cold water when phosphine oxide and fumaric and maleic esters were obtained. The formation of the betaine (4a) in 60% yield when the salt was dissolved in aqueous sodium bisulphite also served to characterise the vinyl salt.



(14)

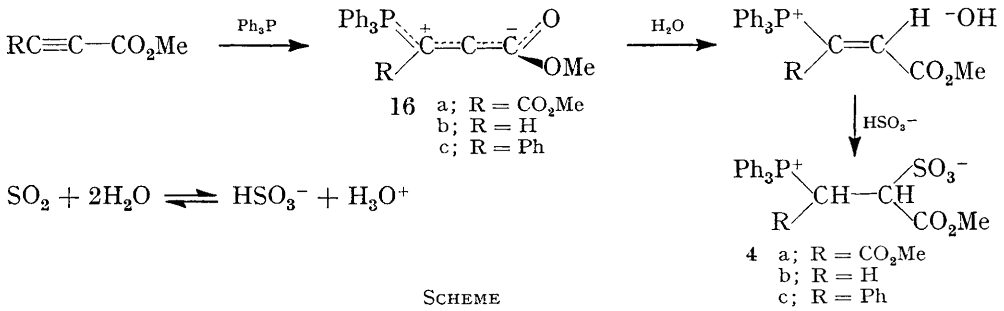
a; R = CO_2Me

b; R = Ph



(15)

Smith and Smith [14] treated triphenylphosphine with liquid sulphur dioxide and postulated (15) as the intermediate which decomposes to triphenylphosphine oxide, sulphur dioxide, and sulphur. It was possible therefore that the adducts were formed by the reaction of (15) with dimethyl acetylenedicarboxylate and water with subsequent rearrangement. However, the structures of the adducts (4b) and (4c) and the synthesis of (4a) and (4c) from the vinylphosphonium salts provides strong evidence that the reaction pathway involves a 1 : 1 phosphine–acetylene intermediate as shown in the Scheme. Triphenylphosphine is known to attack the β-carbon atom of methyl propiolate and methyl phenylpropiolate and therefore the corresponding 1 : 1 dipolar intermediate will have the structures (16b) and (16c). The interaction of sulphur dioxide and water to give the bisulphite ion, prior to reaction with the vinylphosphonium salt, was established beyond doubt by the use of $^2H_2{}^{18}O$. The adduct (4a) was prepared using $^2H_2{}^{18}O$ and examined by mass spectrometry. No molecular ion was observed due to the thermal instability of the adducts and the ions due to triphenylphosphine oxide showed the small enrichment in $Ph_3P^{18}O$ that would be expected from complete exchange of ^{18}O between water and sulphur dioxide.



SCHEME

EXPERIMENTAL

The n.m.r. spectra were obtained using a Varian HA 100 instrument. Tetramethylsilane was used as an internal reference for the spectra in trifluoroacetic acid solution, and as an external reference (capilliary) for the spectra in $[^2H_6]$dimethyl sulphoxide solution. The i.r. spectra were determined using a Unicam SP 200 spectrophotometer.

Preparation of 1,2-Dimethoxycarbonyl-2-triphenylphosphoniaethanesulphonate (4a).—Triphenylphosphine (5·0 g.) dissolved in moist ether (30 ml.) was cooled to 0°, stirred, and saturated with sulphur dioxide. Dimethyl acetylenedicarboxylate (4·0 g.) in ether (10 ml.) was added dropwise. The solution developed an orange-red colour and was stirred for a further 20 min. During this time an orange-yellow solid was precipitated. The excess of sulphur dioxide was removed with a current of nitrogen and the solid (5·2 g.) was separated. The crude product was heated under reflux in acetone (30 ml.) for 30 min. and was then separated and crystallised from methanol to give white *needles* (4·0 g.), m.p. 182—183° (decomp.) (Found: C, 58·0; H, 4·6. $C_{24}H_{23}O_7PS,\frac{1}{2}H_2O$ requires C, 58·2; H, 4·6%); $\nu_{max.}$ (KBr disc) 665, 687, 702, 722, 758, 812, 841, 885, 998, 1038, 1100, 1150, 1188, 1225, 1250, 1295, 1352, 1440, 1485, 1582, 1722, 2970, 3090, and 3500 cm.$^{-1}$.

Preparation of Methoxycarbonyl-2-triphenylphosphoniaethanesulphonate (4b).—The preparation was carried out in a similar manner to that described for (4a). From triphenylphosphine (3·0 g.) and methyl propiolate (2·0 g.), the pure *betaine* (3·4 g.) (4b) was obtained (from MeOH), m.p. 275—276° (decomp.) (Found: C, 61·75; H, 5·05; $C_{22}H_{21}O_5$ P S requires C, 61·5; H, 4·9%); $\nu_{max.}$ (KBr disc) 659, 690, 720, 745, 757, 768, 795, 820, 842, 982, 998, 1032, 1102, 1142, 1158, 1182, 1225, 1240, 1278, 1320, 1350, 1402, 1442, 1485, 1582, 1630, 1728, 2920, 2970, 3100, and 3500 cm.$^{-1}$.

Preparation of 1-Methoxycarbonyl-2-phenyl-2-triphenylphosphoniaethanesulphonate (4c).—The preparation was carried out in a similar manner to that described for (4a) except the solution was heated under reflux throughout the experiment. From triphenylphosphine (3·0 g.) and methyl phenylpropiolate (2·0 g.) the *betaine* (4c) (1·3 g.) (crystallised from methanol) was obtained m.p. 215—216° (decomp.) (Found: C, 66·3; H, 5·0; $C_{28}H_{25}O_5$ P S requires C, 66·8; H, 4·95%); $\nu_{max.}$ (KBr disc) 660, 690, 715, 722, 735, 758, 800, 808, 850, 870, 918, 932, 1000, 1038, 1100, 1147, 1220, 1243, 1263, 1322, 1442, 1458, 1630, 1738, 2980, 3100, and 3500 cm.$^{-1}$.

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[14] B. C. Smith and G. H. Smith, *J. Chem. Soc.*, 1965, **5516**.

Fragmentation of Compound (4a).—The betaine (4a) (300 mg.) was heated under reflux in dry toluene (10 ml.) for 18 hr. Sulphur dioxide was evolved. The residue was separated and the toluene solution was examined by v.p.c.; dimethyl fumarate was found to be present. The toluene was evaporated under reduced pressure and the residue was crystallised from aqueous methanol. Triphenylphosphine oxide (75 mg.), m.p. and mixed m.p. 153—156°, was obtained.

Fragmentation of Compounds (4b) *and* (4c).—The betaines were treated in a similar manner to that described for compound (4a). In each case sulphur dioxide was evolved. V.p.c. examination of toluene solutions of the compounds showed the presence of methyl acrylate for compound (4b) and methyl cinnamate for (4c). The formation of triphenylphosphine oxide was verified by t.l.c. on silica with ethyl acetate eluant.

Reaction of Compound (4a) *with Sodium Hydroxide.*—The betaine (4a) (500 mg.) was shaken with 2N-sodium hydroxide (25 ml.) and was then set aside for 3 hr. Colourless *sodium* 1,2-*dimethoxycarbonyl*-2-*triphenylphosphoranylidene-ethanesulphonate* (5) (400 mg.) was separated and was washed with a little cold water. A sample crystallised from ethanol had m.p. 203—205° (Found: Na, 3·85. $C_{24}H_{22}O_7$ Na P S requires Na, 5·6%); $\nu_{max.}$ (KBr disc) 650, 690, 717, 742, 752, 795, 902, 978, 999, 1040, 1078, 1100, 1130, 1195, 1240, 1318 1440, 1485, 1575, 1622, 1722, 2950, 3100, and 3500 cm.$^{-1}$. The sodium content was estimated by flame photometry and its low value may be due to interference by the phosphonium cation.

Reaction of Compound (5) *with Hydrogen Bromide.*—The phosphorane (5) (50 mg.) was added to 2N-hydrogen bromide in benzene (15 ml.); overnight solid separated. The i.r. spectrum of the product was identical with that of compound (4a).

Reaction of Compound (4b) *and* (4c) *with Sodium Hydroxide.*—The betaines (50 mg.) were treated with 2N-sodium hydroxide (3 ml.) and then shaken and finally set aside for 2 hr. The white residue was separated. The i.r. spectrum of this material was identical with that of authentic triphenylphosphine.

Reaction of Triphenylphosphine with Ethane-1,2-*sulphite* (11a).—Triphenylphosphine (1·3 g.) and the sultone (0·54 g.) were heated under reflux in dry diglyme (15 ml.) for 24 hr. Sulphur dioxide was evolved immediately and the gases were bubbled through a solution of bromine in carbon tetrachloride. The diglyme solution was cooled and poured into water (200 ml.). The white solid (1·2 g.) which separated had an i.r. spectrum identical with that of authentic triphenylphosphine oxide. Nitrogen was bubbled through the carbon tetrachloride solution to remove excess bromine and the resulting solution was examined by v.p.c.; dibromoethane was detected.

Preparation of 1,2-*Dimethoxycarbonylethane*-1,2-*sulphite* (11b).—Pyridine (16 g.) was added to methyl tartrate (18 g.) dissolved in ethyl acetate (40 ml.) and the solution was stirred and cooled to 0°. Thionyl chloride (12 g.) in dry ether (10 ml.) was added dropwise. The pyridine hydrochloride was separated and washed with ethyl acetate and the washings were combined with the mother liquors. After evaporation of the ethyl acetate the residue was distilled and the fraction with b.p. 148—152°/15 mm. was collected. This was refractionated and the cyclic ester (11b), b.p. 106—108°/0·7 mm. was obtained (Found: C, 33·2; H, 3·7. $C_6H_8O_7$ S requires C, 32·7; H, 3·6%); $\nu_{max.}$ (liquid film) 738, 810, 880, 950, 1015, 1062, 1125, 1220, 1242, 1270, 1325, 1370, 1445, 1745, 2990, and 3500 cm.$^{-1}$.

Reaction of Compound (11b) *with Triphenylphosphine.*—Triphenylphosphine (1·3 g.) and 1,2-dimethoxycarbonylethanesulphite (11b) (1·1 g.) were dissolved in dry diglyme (15 ml.). The solution was heated under reflux and sulphur dioxide was evolved immediately. The solution became dark and after 6 hr. no more sulphur dioxide could be detected. The solution was poured into water (150 ml.) and the brown precipitate (1·2 g.) was crystallised from methanol. The product, triphenylphosphine, had m.p. and mixed m.p. 76—78°.

In a second experiment the reaction mixture was poured into water and extracted with ether. No dimethyl fumarate could be detected by v.p.c. examination of the extracts.

Similar results were obtained when the reaction was carried out in toluene solution.

Preparation of 2-*Triphenylphosphoniaethanesulphonate* (12).—A mixture of triphenylphosphine (2·0 g.) and sodium 2-bromoethanesulphonate (1·1 g.) was placed in a sealed tube and heated at 120° for 5 days. A green gum was obtained which was triturated with ether to give a white solid. The *betaine* (1·0 g.) was washed with water and ether and crystallised from ethanol, m.p. 285—286° (decomp.). The 100 Mc. n.m.r. spectrum in deuteriochloroform showed δ 7·70 (15H, m), 3·90 (2H, m), and δ 3·05 p.p.m. (2H, m). In trifluoroacetic acid the four methylene protons coincided and a 4H multiplet at δ 3·70 p.p.m. was observed (Found: C, 62·25; H, 5·45; $C_{20}H_{19}O_3PS,H_2O$ requires C, 62·0; H, 5·4%); $\nu_{max.}$ (KBr disc) 680, 717, 732, 740, 760, 810, 862, 913, 988, 1038, 1100, 1190, 1220, 1275, 1302, 1318, 1342, 1380, 1400, 1420, 1440, 1488, 1590, 1650, 2990, 3100, and 3500 cm.$^{-1}$.

Fragmentation of Compound (12).—2-Triphenylphosphoniaethanesulphonate (12) (2·0 g.) was heated in a tube to its m.p. when it began to decompose. The gases were bubbled through a solution of bromine in carbon tetrachloride. The residue in the tube was dissolved in chloroform and examined by t.l.c. Both triphenylphosphine oxide and triphenylphosphine were detected. Nitrogen was bubbled through the carbon tetrachloride to remove excess bromine and the solution was examined by v.p.c.; 1,2-dibromoethane was detected.

Reaction of Compounds (4a) *and* (12) *with Perchloric Acid.*—In each case the betaine (100 mg.) was dissolved in a mixture of glacial acetic acid (0·5 ml.) and 60% perchloric acid (0·5 ml.). After 30 min. ether (10 ml.) was added and the oil, which separated, was triturated with ether. The white solid (100 mg.) was slowly added to diazomethane (0·15 g.) in ether (15 ml.). The diazomethane was allowed to evaporate and the residue was separated. Crystallisation from methanol gave the starting material.

Reaction of 2-*Methoxycarbonyl*-1-*phenylvinylphosphonium Bromide* (14b) *with Sodium Bisulphite.*—The vinylphosphonium salt (0·5 g.) prepared by the method of Hoffmann and Diehr,[13] was dissolved in a solution of sodium metabisulphite (0·5 g.) in water (10 ml.). After 1 hr. the cream coloured solid (0·3 g.) was separated and crystallised from methanol. The i.r. spectrum was identical with that of (4c); m.p. and mixed m.p. 214—216°.

Preparation of 1,2-*Dimethoxycarbonylvinylphosphonium Bromide* (14a).—A solution of triphenylphosphine hydrobromide (1·7 g.) in chloroform (10 ml.) was cooled to 0° and dimethyl acetylenedicarboxylate (0·7 g.) in chloroform (1 ml.) was added dropwise. After 15 min. dry ether was added. The solid (2·2 g.) which separated began to deliquesce immediately. It had $\nu_{max.}$ 660, 685, 720, 747, 845, 870, 999, 1020, 1100, 1158, 1220, 1250, 1320, 1440, 1482, 1582, 1630, 1722, 2900, 2970, 3070, and 3450 cm.$^{-1}$.

Hydrolysis of Compound (14a).—The salt (14a) (500 mg.) was left in aqueous solution (20 ml.) for 6 hr. The mixture was extracted with chloroform and the extracts were examined by v.p.c. Dimethyl fumarate and dimethyl maleate were detected in a 3 : 1 ratio. The solution was evaporated and the residue was sublimed to give dimethyl fumarate, m.p. and mixed m.p. 102—103°. The residue was crystallised from aqueous methanol when triphenylphosphine oxide (350 mg.), m.p. and mixed m.p. 154—155°, was obtained.

Reaction of Compound (14a) *with Sodium Bisulphite*.—The vinylphosphonium salt (14a) (600 mg.) was added to a saturated solution of sodium metabisulphite in water (10 ml.). A yellow precipitate formed immediately. After 1 hr. the solid was separated and washed with acetone. The product (350 mg.) had an i.r. spectrum identical with that of (4a). A sample crystallised from methanol had m.p. and mixed m.p. 180—182°.

Formation of Compound (4a) *in the Presence of* $^2H_2{}^{18}O$.—The preparation was carried out as previously described but using triphenylphosphine which had been dried *in vacuo*, acetylenic ester which was freshly distilled, and dry ether. The $^2H_2{}^{18}O$ was added to the solution of triphenylphosphine and sulphur dioxide in ether, before addition of the dimethyl acetylenedicarboxylate. The crude product was examined by mass spectrometry.

Reaction of the Salt (*Ref.* 13), *M.p.* 143°, *with Aqueous Base*.—The salt (50 mg.) (prepared by the method of Hoffmann and Diehr [13]) was suspended in methanol (1 ml.) and 2N-sodium hydroxide solution (2 ml.) added. The orange precipitate (37 mg.) was separated and washed with methanol, m.p. and mixed m.p. 244—245° with the 1,4-diphosphorane (3).

Reduction of the Salt, m.p. 143°.—The salt (500 mg.) was dissolved in chloroform (10 ml.) and zinc dust (4 g.) was added. The solution was heated under reflux and acetic acid (20 ml.) was added dropwise during 1 hr. The reaction mixture was boiled for 6 hr. and then poured into excess water and extracted with chloroform. V.p.c. examination of the dried chloroform extracts showed the presence of tetramethyl butane-1,2,3,4-tetracarboxylate. No dimethyl succinate was detected.

Preparation of the Dihydrobromide of the 1,4-*Diphosphorane* (3).—A solution of the 1,4-diphosphorane (1 g.) in acetic acid (25 ml.) was stirred at room temperature and a 40% solution of hydrobromic acid in acetic acid (10 ml.) was added dropwise. The white precipitate (1 g.) was crystallised from ethyl acetate–acetonitrile. The dihydrobromide had m.p. and mixed m.p. 143° with the salt of Hoffmann and Diehr.

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