Reactions of Phosphines with Acetylenes. Part XVI.[1] Formation of β-Alkoxyphosphonium Ylides and Vinyl Ethers via Methanolysis of Vinylphosphonium Salts

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Triphenylphosphine in alcohol reacts (a) with dimethyl acetylenedicarboxylate to give a stabilised β-alkoxy-ylide, (b) with methyl phenylpropiolate to give (Z)-methyl 2-methoxycinnamate, and (c) with methyl propiolate to give a mixture of three isomeric methyl methoxyacrylates. The reactions proceed via nucleophilic attack of the phosphine on the acetylene and then of methoxide on the intermediate vinylphosphonium salt by the pathway which involves least build up of negative charge. Methoxide attacks at the β-carbon atom when the vinyl α-carbon atom which bears the phosphonium group possesses an additional stabilising group, e.g. methoxycarbonyl as in (a), or phenyl as in (b). Methoxide attacks both α- and β-positions when there are balancing α- and β-stabilising groups as in (c). The reactions (b) and (c) involve two trans-addition steps followed by a trans-elimination step.

TRIPHENYLPHOSPHINE reacts with dimethyl acetylenedicarboxylate in aprotic solvents to give brightly coloured stable ylides.[1] When these reactants were combined in methanol or ethanol no colour developed but a ^{31}P n.m.r. spectrum (δ −24 p.p.m. only) showed that a reaction had occurred. Evaporation of the solvent and the addition of ether gave colourless crystals.

Elemental analysis and n.m.r. and mass spectra showed that in each case the product was derived from one molecule each of phosphine, acetylene, and alcohol. The i.r. spectra possessed two carbonyl bands, one characteristic of a normal carbonyl group and the other of a carbonyl group stabilising an ylidic carbanion. Hydrolysis gave triphenylphosphine oxide, dimethyl fumarate, and dimethyl maleate. The adducts from dimethyl acetylenedicarboxylate are formulated as the ylides (1; R = Me or Et) according to the alcohol used.

ing via the vinylphosphonium salt (3). The second stage of the reaction is analogous to the addition of dimethyl malonate to the α-acylvinylphosphonium salt (4) to give the stable ylide (5).[2]

Two sharp singlets at τ 6·42 and 6·86 in the n.m.r. spectrum of the adduct (1; R = Me) correspond to the β-methoxycarbonyl and β-methoxy-groups respectively; the higher field resonance was absent from the spectrum of the ethyl derivative (1; R = Et). An area of general absorption between these two peaks was simplified to give a third sharp singlet at τ 6·66 due to the α-methoxycarbonyl group upon raising the temperature or adding acid. The remainder of the spectrum was little changed. This is in accord with a change from a spectrum showing restricted rotation for the α-methoxycarbonyl group with an ambient coalescence temperature to a spectrum showing free rotation. The ylide could not be regenerated from acidified solutions by treatment with aqueous base. The isolation of the sulphonate betaine (6) after the
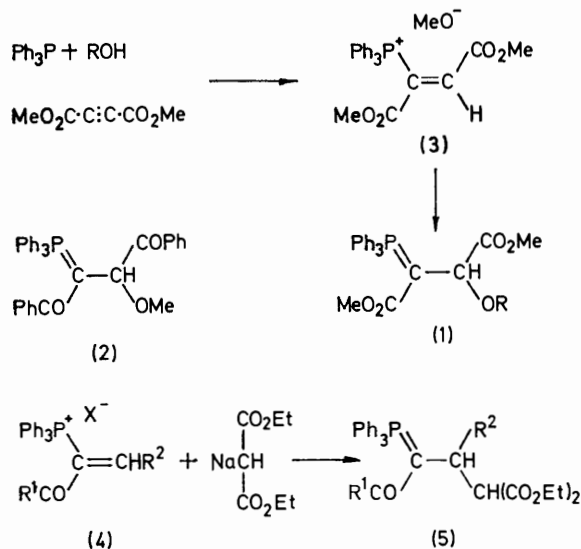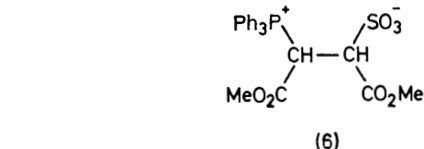

A similar adduct (2) was obtained from the reaction of triphenylphosphine and dibenzoylacetylene in methanol.

The formation of the adducts is envisaged as proceed-

addition of sodium disulphite to the acidified solutions suggests that the formation of the adduct is reversible, and that in the presence of other nucleophiles the reactions may take another course.

The mass spectra of compounds (1; R = Et or Me) and the analogue derived from [$^2H_4$]methanol showed molecular ions and abundant fragment ions due to loss of methoxy- and methoxycarbonyl groups; the probable origins and structures of the main fragments are shown in Scheme 1. The ion at m/e 287 has been noted previously[3] in the mass spectra of ylides possessing more than one alkoxycarbonyl group, but its structure and origin have not been discussed.

The analogous reaction of tertiary phosphines with

[1] Part XV, N. E. Waite, D. W. Allen, and J. C. Tebby, Phosphorus, 1971, 1, 139.
[2] E. Zbiral, M. Rasberger, and H. Hengstberger, Annalen, 1969, 725, 22.

[3] R. G. Cooks, R. S. Ward, D. H. Williams, M. A. Shaw, and J. C. Tebby, Tetrahedron, 1968, 24, 3289; R. T. Aplin, A. R. Hands, and A. J. H. Mercer, Org. Mass Spectrometry, 1969, 2, 1017.

electrophilic acetylenes which possess only one strong electron-withdrawing group, such as methyl propiolate and methyl phenylpropiolate, in the presence of alcohols, would be expected to follow a different course since no

(3%) (30%)

(100%) (30%)

*

Ph$_3$P–C⋮CH

m/e 287 (6%)

(25-45%)†
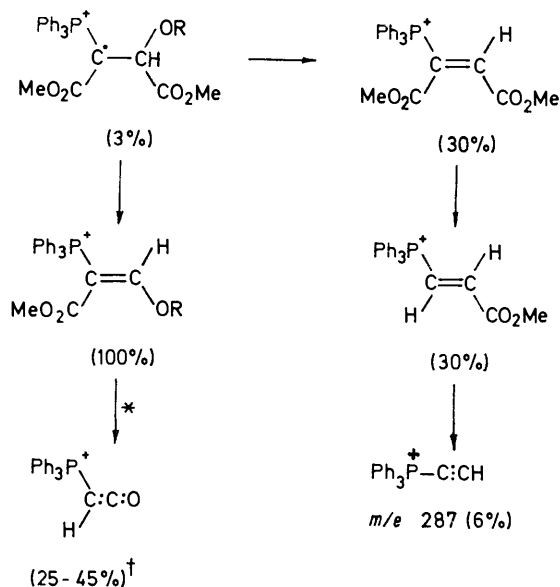
SCHEME 1

* Corresponding metastable ion observed. † 25% Abundance for (1; R = Me), 45% for (1; R = Et).

stable ylide can be formed. The reaction of triphenylphosphine and methyl phenylpropiolate in methanol gave a colourless solution which contained triphenylphosphine

Ph$_3$P + MeOH + PhC⋮C·CO$_2$Me

(7;X = MeO) (10)

(8Z) (10)
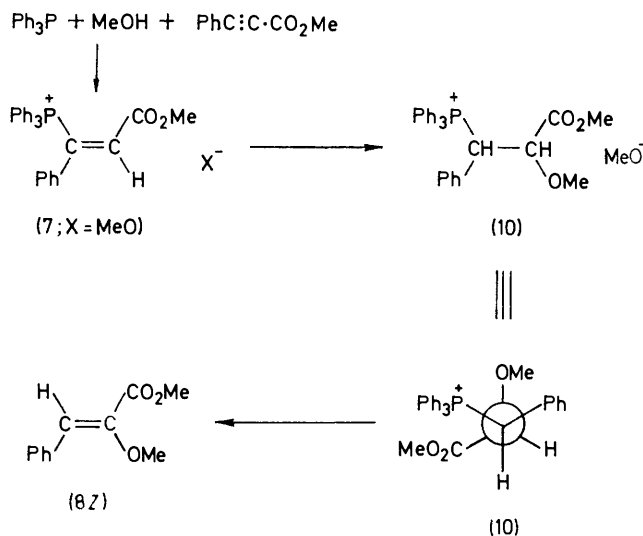
SCHEME 2

and a single volatile compound. The same compound was formed when the (Z)-vinylphosphonium bromide (7;

X = Br) was treated with 1 equiv. of sodium methoxide. Its n.m.r. spectrum corresponded to the (Z)-vinyl ether structure (8Z) (vinyl proton τ 3·02; calc.[4] 3·50). Similar calculations using Pascual constants[4] for the isomers (8E), (9Z), and (9E) gave τ 3·87, 4·79, and 5·04, respectively. The product had a shorter retention time on g.l.c. than the (Z)-vinyl ether (9Z) (vinyl proton τ 4·75; calc.[4] 4·79) which was obtained from the methoxide-catalysed addition of methanol to methyl phenylpropiolate. The large difference in chemical shifts between the two types of vinyl ether (8) and (9) leaves little doubt that the vinyl ether obtained from the

(8E) (9E) (9Z)
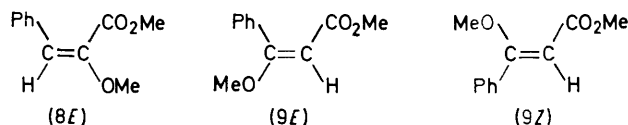
phosphine–acetylene reaction arises from β-addition. This is to be contrasted with the α-attack proposed[5] for the reactions of sodium ethoxide with the closely related salts (11; R = OEt or Me).

Ph$_3$Ṗ·CPh⋮CH·COR   Br$^-$

(11)
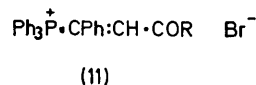
The vinyl ether (8Z) is the product which would be expected for a mechanism involving three consecutive *trans* processes as shown in Scheme 2: *trans*-addition of Ph$_3$P–H$^+$ to the acetylene, *trans*-addition of methanol to the intermediate (7), and *trans*-elimination of Ph$_3$P–H$^+$ from the saturated salt (10). The isolation of the vinyl ether (8Z) and not (9Z) from this reaction, together with the formation of the adduct (1) quantitatively from triphenylphosphine and dimethyl acetylenedicarboxylate, shows that triphenylphosphine is not sufficiently basic to catalyse the addition of alcohol to these electrophilic acetylenes. Also methoxide did not regenerate the acetylene from the vinyl salt under conditions in which the base-catalysed reaction was slow, but the elimination was induced by the use of potassium t-butoxide.

The reaction of triphenylphosphine and methyl propiolate in methanol gave three volatile compounds in the ratio 41 : 35 : 24. Their i.r., mass, and n.m.r. spectra showed them to be the vinyl ethers (12), (13E), and (13Z). The (E)- and (Z)-vinyl ethers (13E) and (13Z), which were distinguished by the method of Pascual[4] and from the magnitude of their coupling constants, were also obtained from the methoxide-catalysed addition of methanol to methyl propiolate. Although the addition of methanol to methyl propiolate occurs by a predominantly *trans* process[6] to give mainly the (Z)-(cis) vinyl ether, the methoxide ion catalyses the isomerisation of (13Z) to (13E) and a Z : E ratio of 40 : 60 was obtained.

Treatment of the vinylphosphonium bromide (14E; X = Br) (prepared from methyl *trans*-3-bromoacrylate)[7]

[4] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164.
[5] E. E. Schweizer and A. T. Wehman, *J. Chem. Soc.* (C), 1970, 1901.
[6] E. Winterfeldt and H. Preuss, *Chem. Ber.*, 1966, **99**, 450.
[7] G. Pattenden and B. J. Walker, *J. Chem. Soc.* (C), 1969, 531.

with 1 equiv. of sodium methoxide in methanol gave tri-phenylphosphine and the vinyl ethers (12) and (13E) (see Table). The stereospecific conversion of the (E)-vinyl-phosphonium salt into the (E)-vinyl ether is to be expected since *trans*-addition of methanol to the (E)-salt

SCHEME 3
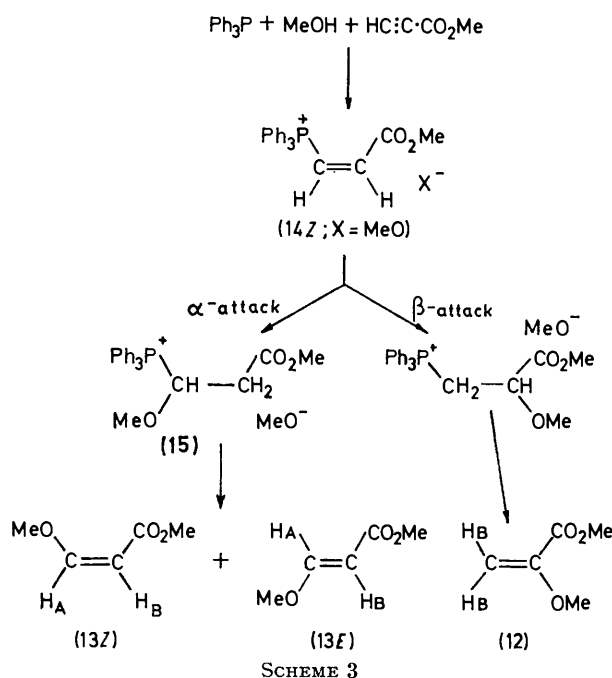
will give an intermediate with the conformation (15a) which will be readily converted into the conformer (15b) [the precursor of the (E)-vinyl ether *via trans*-elimination] but it will not be readily converted into (15c) [the
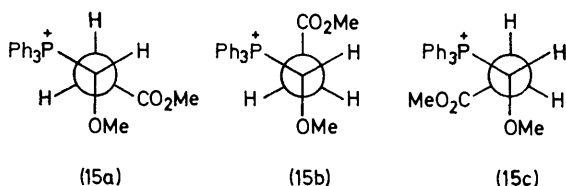
corresponding precursor of the (Z)-vinyl ether]. The absence of (13Z) shows once again that the regeneration

TABLE

Ratios of methyl methoxyacrylates formed from methyl propiolate and vinylphosphonium salts

Solvent	Reactants	Products		
		(12)	(13E)	(13Z)
MeOH	Ph₃P, HC≡C·CO₂Me, MeOH	41	35	24
Et₂O	Ph₃P, HC≡C·CO₂Me, MeOH	15	72	13
CH₂Cl₂	Ph₃P, HC≡C·CO₂Me, MeOH	29	64	7
MeOH	Buⁿ₃P, HC≡C·CO₂Me, MeOH	0	54	46
MeOH	(14E; X = Br), NaOMe	55	45	0
MeOH	(17), NaOMe	0	100	0

of acetylene from a vinylphosphonium salt is not a favourable process. If it was involved in the reaction,

recombination of the acetylene and the phosphine would be expected to proceed *via* the (Z)-vinylphosphonium methoxide (14Z; X = MeO) to give both (Z)- and (E)-vinyl ethers (see Scheme 3).

In the actual reaction of triphenylphosphine with methyl propiolate this salt [*i.e.* (14Z; X = MeO)] must be the precursor of the (Z)-vinyl ether (13Z), and is probably the main source of the (E)-vinyl ether, as well. Thus the *trans*-addition of methanol to this salt gives the less stable conformer (15c) which is set up for immediate *trans*-elimination of Ph₃P–H⁺ to give (13Z), but it is also prone to conversion into the more stable conformers (15a) and (15b), which are the precursors of (13E).

The predominance of α-addition of methanol is not in accord with (a) the generally accepted greater electron-withdrawing power of the triphenylphosphonium group as compared with the methoxycarbonyl group nor with (b) the greater size of the former group. On the other hand, coulombic forces will attract the methoxide ion to the phosphonium centre, thereby bringing it near to the α-carbon atom. This effect should be enhanced in a less polar medium; indeed the proportion of α-addition increases when ether or dichloromethane is used as solvent (see Table). α-Addition to the bromides (11) was rationalised [5] in terms of formation of the oxyphos-phorane (16) followed by α-attack on the vinyl group by
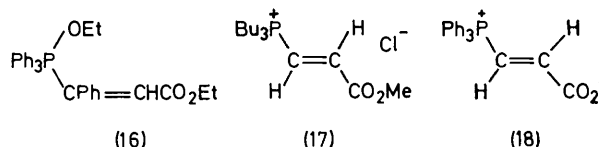
a second methoxide ion. If this explanation is correct, phosphorane formation, and hence α-attack, should be reduced by replacing the triphenylphosphonium group by a trialkylphosphonium group; however this change accentuated α-attack. Thus tributylphosphine and methyl propiolate in methanol gave a mixture of isomers (13Z) and (13E), and the action of sodium methoxide on the (E)-vinyltributylphosphonium chloride (17) gave (13E) only. The decrease in β-addition is in accord with the weaker electron-withdrawing properties of the tri-butylphosphonium group.

The reaction of triphenylphosphine and propiolic acid in methanol gave 3-triphenylphosphonioacrylate (18) in high yield and purity. It was assigned the Z-configuration shown. The preparation of pure samples of this betaine from the corresponding acid [8] was much more difficult.

EXPERIMENTAL

Dimethyl 2-Methoxy-3-triphenylphosphoranylidenesuccinate (1; R = Me).—Dimethyl acetylenedicarboxylate (1·42 g, 10 mmol) in dry ether (10 cm³) was added slowly to a solution of triphenylphosphine (2·88 g, 11 mmol) in ether (25 cm³) containing dry methanol (5 cm³) cooled in ice–salt. Scratch-ing produced white crystals of the *phosphorane* in quantita-

[8] E. Hoffmann and H. J. Diehr, *Chem. Ber.*, 1965, **98**, 363.

tive yield. The ylide could not be purified by crystallisation since hydrolysis occurred. After being washed with dry ether it had m.p. 153—154°, $\nu_{max.}$ (KBr) 695, 720, 760, 765, 1015, 1065, 1100, 1135, 1180, 1200, 1305, 1320, 1435, 1630, and 1730 cm^{-1}, τ (CDCl$_3$) 2·1—2·65 (15H, m, ArH), 5·5—6·2 (1H, s, CH), 6·42 (3H, s, OMe), 6·5—6·8 (3H, hump, α-CO$_2$Me), and 6·86 (3H, s, OMe) (the methine proton appeared as a doublet, J_{PH} 19 Hz at τ 5·67 for a 10 : 1 benzene–chloroform solution; raising the temperature or addition of a small quantity of trifluoroacetic acid converted the hump to a sharp singlet at τ 6·66), m/e 436 (3%), 405 (30), 377 (100), 347 (30), 303 (45), and 262 (37) (Found: C, 69·2; H, 6·0. C$_{25}$H$_{25}$O$_5$P requires C, 68·8, H, 5·7%).

The corresponding [^{2}H$_4$]ylide, prepared similarly on a small scale by use of [^{2}H$_4$]methanol, had m.p. 149°, τ (CDCl$_3$) 2·1—2·7 (15H, m, ArH), 6·4 (3H, s, β-CO$_2$Me), and 6·5—6·8 (3H, hump, α-CO$_2$Me), m/e 440 (0·5%), 409 (7), 406 (23), 381 (100), 350 (10), and 304 (20).

Dimethyl 2-Ethoxy-3-triphenylphosphoramylidenesuccinate (1; R = Et).—Prepared by the method used for (1; R = Me) but with ethanol in place of methanol, the *phosphorane* had m.p. 138—139°, ν_{CO} 1605 and 1735 cm^{-1}, τ (CDCl$_3$) 2·04—2·75 (15H, m, ArH), 6·40 (3H, s, OMe), 6·53 (2H, q, O·CH$_2$), 6·6—7·0 (3H, hump, α-CO$_2$Me), and 8·90 (3H, t, Me) (the addition of a small quantity of trifluoroacetic acid converted the hump into a sharp singlet at τ 6·63), m/e 450 (1%), 419 (4), 450 (30), 391 (100), 347 (30), 303 (25), 287 (7), and 262 (50) (Found: C, 69·3; H, 6·1. C$_{26}$H$_{27}$O$_5$P requires C, 69·3; H, 6·0%).

2-Methoxy-1,4-diphenyl-3-triphenylphosphoranylidene-butane-1,4-dione (2).—Prepared by the method used for (1; R = Me) but with dibenzoylacetylene in place of dimethyl acetylenedicarboxylate, the *phosphorane* had m.p. 164—166° $\nu_{max.}$ (KBr) 695, 710, 730, 735, 750, 760, 1085, 1100, 1380, 1440, 1480, 1520, and 1670 cm^{-1}, τ (CDCl$_3$) 1·90—2·84 (25H, m, ArH), 4·98 (1H, d, $^3J_{PH}$ 27 Hz, vinyl H), and 6·90 (3H, s, OMe) (Found: C, 79·6; H, 5·8. C$_{35}$H$_{29}$O$_3$P requires C, 79·5; H, 5·5%).

Hydrolysis of the Adduct (1; R = Me).—The ylide (1; R = Me) (450 mg, 1 mmol) was refluxed for 2 h in dilute aqueous sodium hydroxide (15 cm^3). The cooled solution was extracted with chloroform (3 × 15 cm^3) and the extracts were dried. Addition of petroleum and cooling gave triphenylphosphine oxide (230 mg, 81%), m.p. 154°, i.r. spectrum identical with that of an authentic sample. G.l.c. (PEGA 20M column at 140°) showed the presence in the solution of dimethyl fumarate and dimethyl maleate in a 6 : 1 ratio.

Treatment of the Adduct (1; R = Me) *with Acid.*—Dry hydrogen bromide was bubbled through a solution of the ylide (1; R = Me) (460 mg, 1·02 mmol) in dry methanol for 2 h. The solution was then evaporated and nitrogen blown over the sample to leave a gummy solid. Water (10 cm^3) was added followed by an excess of sodium disulphite. The mixture was stirred for 30 min and a white precipitate was formed in 82% yield (400 mg), m.p. 182° (from methanol), identical (i.r. spectrum) with authentic [9] 1,2-bismethoxycarbonyl-2-triphenylphosphonioethanesulphonate (6), m.p. 182—183°.

Methoxide-catalysed Addition of Methanol to Methyl Phenylpropiolate.—Sodium methoxide (0·25 mmol) was

added to the acetylene (0·8 g, 5 mmol) [10,11] in methanol (10 cm^3). After 4 h g.l.c. (PEGA 20M column at 175°) indicated the formation of only one vinyl ether (9Z), τ 2·4—2·8 (5H, m, ArH), 4·75 (1H, s, vinyl H), 6·56 (3H, s, CO$_2$Me), and 7·05 (3H, s, OMe).

Reaction of Triphenylphosphine with Methyl Phenylpropiolate in Methanol.—Triphenylphosphine (262 mg, 1 mmol) and the acetylene (640 mg, 4 mmol) reacted in methanol (5 cm^3) overnight. Excess of methyl iodide was added to quaternise the triphenylphosphine and the mixture was chromatographed on silica (50 g). The methyl 2-methoxycinnamate (8Z) was obtained upon elution with ether; ν_{CO} 1700 cm^{-1}, τ (CDCl$_3$) 2·5—2·7 (5H, m, Ar), 3·02 (1H, s, vinyl H), 6·16 (3H, s, OMe), and 6·23 (3H, s, OMe).

(Z)-2-Methoxycarbonyl-1-phenylvinyltriphenylphosphonium Bromide (7; X = Br).—Prepared by the method of the ethyl ester,[5] the *salt* was purified by dissolving in dichloromethane and adding ethyl acetate. The first fraction was a crude product of m.p. 110—125°, but a second fraction was pure, m.p. 159—161°, $\nu_{max.}$ (KBr) 1732, 1445, 1210, 1112, and 702 cm^{-1}, τ (CDCl$_3$) 2·0—3·1 (20H, m, ArH), 3·3 (0·5H, s, half of doublet due to vinyl H), 6·4 (3H, s, OMe), and 7·1 (2H, s, H$_2$O, removed by addition of D$_2$O) (Found: C, 66·4; H, 5·3. C$_{28}$H$_{24}$BrOP requires C, 66·6; H, 4·8%).

Reaction of the Salt (7; X = Br) *with Sodium Methoxide.*—Sodium methoxide (1·6 mmol) in methanol (1·6 cm^3) was added to the salt (7; X = Br) (810 mg, 1·6 mmol) in methanol (1 cm^3). G.l.c. (PEGA 20M column at 200°) indicated the presence of two major components, (8Z) and methyl cinnamate.

Reaction of the Salt (7; X = Br) *with Potassium Butoxide.*—To a solution of t-butyl alcohol (81 mg, 1·1 mmol) in dry tetrahydrofuran (10 cm^3) was added an excess of potassium metal. The mixture was stirred overnight under nitrogen. The unchanged potassium was removed and the salt (7; (X = Br) (350 mg, 0·7 mmol) was added. The solution immediately turned dark brown. G.l.c. (10% Apiezon–Diatomite column at 170°) showed that the major product was methyl phenylpropiolate (by comparison with an authentic sample).

Methoxide-catalysed Addition of Methanol to Methyl Propiolate.—Sodium methoxide (0·25 mmol) in methanol was added to a solution of methyl propiolate (0·82 g, 10 mmol) [11,12] in dry methanol (10 cm^3) under nitrogen. G.l.c. (PEGA 20M column at 140°) showed the presence of the methyl methoxyacrylates (13E) and (13Z) in the ratio 90 : 10. The n.m.r. spectrum of the mixture determined immediately after the addition of methoxide indicated the E : Z ratio to be 60 : 40. The vinyl ethers were distilled (b.p. at 241 torr, 110—130°) [13] and showed m/e 116 (32%), 101 (81), and 85 (100). The methyl methoxyacrylate (13E) had τ (CDCl$_3$) 2·37 (calc.[4] 2·39; 1H, d, J 13 Hz, vinyl H$_A$), 4·81 (calc. 4·94; 1H, d, vinyl H$_B$), 6·3 (3H, s, OMe), and 6·35 (3H, s, OMe). The isomer (13Z) had τ (CDCl$_3$) 3·54 (calc. 2·98; 1H, d, J 8 Hz, vinyl H$_A$), 5·16 (calc. 5·16; 1H, d, vinyl H$_B$), 6·13 (3H, s, OMe), and 6·3 (3H, s, OMe).

Reaction of Triphenylphosphine with Methyl Propiolate in Methanol.—Methyl propiolate (0·82 g, 10 mmol) in methanol (10 cm^3) was added dropwise to a solution of triphenylphosphine (262 mg, 1 mmol) in dry methanol (10 cm^3). G.l.c. as before showed the presence of the methyl methoxyacrylates (12), (13E), and (13Z) in the ratio 41 : 35 : 24.

[9] M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc. (C)*, 1968, 2795.
[10] M. Reimer, *J. Amer. Chem. Soc.*, 1942, **64**, 2510.
[11] C. H. Ingold, *J. Chem. Soc.*, 1925, 1203.

[12] V. Wolf, *Chem. Ber.*, 1953, **86**, 735.
[13] S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *J. Org. Chem.*, 1970, **35**, 3352.

A fraction containing 72% of (12) was obtained by preparative g.l.c. (wide-bore 9 in column containing PEGA 20M at 100°); $v_{max.}$ 925 cm^{-1} (C=CH$_2$), τ (CDCl$_3$) 4·65 (1H, d, J 3·5 Hz, H$_A$), 5·37 (1H, d, H$_B$), 6·20 (3H, s, CO$_2$Me), and 6·3 (3H, s, OMe). The methoxy-resonances of mixtures of the vinyl ethers overlapped in CDCl$_3$, but were better resolved in benzene solution.

2-Methoxycarbonylvinyltriphenylphosphonium Bromide (14E; X=Br).—Bromoacrylic acid [14] (3 g, 20 mmol) was added to boron trifluoride–methanol reagent [15] (16 cm^3 of 14% solution; *ca.* 2 equiv). and dry methanol (10 cm^3). The mixture was refluxed for 4 h and left overnight. It was poured into saturated sodium hydrogen carbonate solution (100 cm^3) and then extracted with ether (2 × 50 cm^3). The dried extracts were evaporated and the residue was vacuum-distilled to give methyl 3-bromoacrylate, b.p. at 70 mmHg 78°.

Triphenylphosphine (2·7 g) was added to a solution of the ester (1·5 g) in dry benzene (15 cm^3). The mixture was warmed and set aside for 2 days. The crystalline bromide (14E; X = Br) (2·86 g, 74%) was removed; m.p. 169° (from dichloromethane–ethyl acetate) (lit.,[7] 158—160°; lit.,[16] 162—165°).

Reaction of the Salt (14E; X = Br) *with Sodium Methoxide.*—Sodium methoxide (1·1 mmol) in methanol was added to a solution of the salt (427 mg, 1 mmol) in dry methanol (2·5 cm^3). After 16 h the precipitated triphenylphosphine (0·22 g, 84%) was removed. The remaining solution was examined by g.l.c. (PEGA 20M column at 140°). Two vinyl ethers (12) and (13E) were present in the ratio 55 : 45. This was confirmed by n.m.r. spectroscopy.

Reaction of Tri-n-butylphosphine with Methyl Propiolate in Methanol.—The reaction was carried out as described for

triphenylphosphine. G.l.c. showed the presence of two methyl methoxyacrylates (13E) and (13Z) in the ratio 54 : 46.

(E)-Tri-n-butyl-2-methoxycarbonylvinylphosphonium Chloride (17).—Prepared by the method described for (14E; X = Br) from tri-n-butylphosphine and methyl 3-chloro-acrylate, the *chloride* (17) had m.p. 73—78°, $v_{max.}$ 1730, 1620, and 1000 cm^{-1}, τ (CDCl$_3$) *ca.* 2·4 (1H, dd, $^2J_{PH}$ 11, J_{HH} 17 Hz, H$_\alpha$), *ca.* 2·75 (1H, dd, $^3J_{PH}$ 25 Hz, H$_\beta$), 6·2 (3H, s, MeO), 7·3br (6H, s, P·CH$_2$), 8·4br (12H, s, CH$_2$), and 9·0 (9H, part-resolved t, Me). Pattenden and Walker,[7] who did not report the vinyl resonances, obtained an oil.

Reaction of the Chloride (17) *with Sodium Methoxide.*—Sodium methoxide (1 mmol) in methanol (1 cm^3) was added to compound (17) (322·5 mg) in methanol (1 cm^3). After 16 h g.l.c. showed the presence of the methyl 2-methoxy-acrylate (8E) only.

3-Triphenylphosphonioacrylate (18).—Triphenylphosphine (2·88 g, 1 mmol) was dissolved in ether (10 cm^3) and methanol (20 cm^3). Propiolic acid (0·7 g, 10 mmol) in methanol (15 cm^3) was added dropwise, slowly with stirring. The solvent was removed by distillation and ether was added to precipitate 3-triphenylphosphonioacrylate (2·74 g, 83%), m.p. 221° (from chloroform–ethyl acetate) (lit.,[16] 212—214°), $v_{max.}$ 1620, 1445, 1360, 1120, 1005, 855, 740, and 700 cm^{-1}, τ 1·9—2·5 (16H, m, ArH + vinyl H) and 2·9 (1H, dd, J_{PH} 22, J_{HH} 17·5 Hz). The chemical shift and coupling constant of the latter signal correspond to the β-proton of the Z-isomer (18) (Found: C, 75·9; H, 5·1. Calc. for C$_{21}$H$_{17}$OP: C, 75·5; H, 5·5%).

[14] K. Alder, F. Brochhagen, C. Kaiser, and W. Roth, *Annalen,* 1955, **593**, 1.

[15] G. Hallas, *J. Chem. Soc.,* 1965, 5770.
[16] E. M. Richards and J. C. Tebby, *J. Chem. Soc.* (*C*), 1971, 1059.