View Article Online / Journal Homepage / Table of Contents for this issue

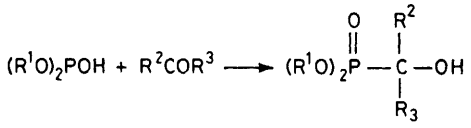
Some Rearrangements of Unsaturated Phosphonate Esters

By **Dianne Cooper** and **Stuart Trippett,*** Department of Chemistry, The University, Leicester LE1 7RH

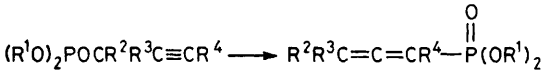
α-Hydroxyalk-2-enylphosphonates undergo Claisen orthoester rearrangement on heating with orthoesters, and their arylsulphenates undergo [2,3]-sigmatropic rearrangement to give 3-arylsulphinylalk-1-enylphosphonates. The addition of allyloxide anion to the central carbon of the allene $Me_2C{=}C{=}CHP(O)(OEt)_2$ is followed by rapid Claisen rearrangement of the resulting allylic carbanion to give the two possible β-ketoalkylphosphonates. Allenic phosphonates of the general formula $R^1R^2C{=}CH[CH_2]_nCR^3{=}C{=}CHP(O)(OEt)_2$ have been prepared: when $R^1 = R^2 = H$, $R^3 = Me$, and $n = 2$, Cope rearrangement occurs to give isomeric dienes; when $R^1,R^2,R^3 = Me$ and $n = 0$, [1,5] hydride shift gives a triene which then cyclises to a cyclohexadiene; when $R^1 = Me$, $R^2 = H$, $R^3 = H$ or Me, and $n = 0$, the diene component can be used in Diels–Alder reactions.

Published on 01 January 1981. Downloaded by Cornell University Library on 21/09/2016 16:33:51.

Among the more readily prepared phosphonates [1] are α-hydroxyalkylphosphonates (1), obtained by the acid- or base-catalysed addition of dialkyl phosphonates to carbonyl compounds, and allenic phosphonates (3) resulting from the ready rearrangement of propargylic phosphites (2).[2] We have sought to prepare new types of phosphonates using α-hydroxyphosphonates (1) derived from αβ-unsaturated carbonyl compounds and



(1)



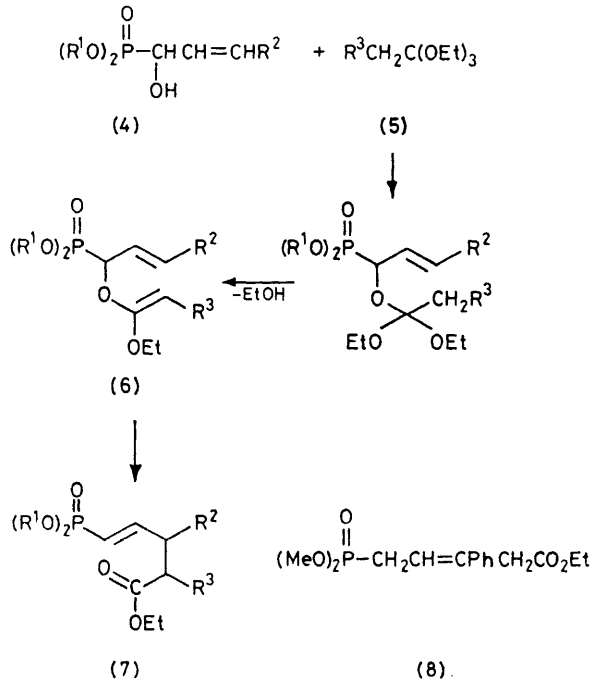
(2) (3)

allenic phosphonates (3) as components in intramolecular rearrangement reactions.

RESULTS AND DISCUSSION

α-Hydroxyalk-2-enylphosphonates.—Attempts to use the phosphonates (4) as the allylic alcohols in normal Claisen rearrangements were not successful, *e.g.* no reaction occurred on refluxing (4; $R^1 = Et$, $R^2 = H$) in an excess of ethyl vinyl ether in the presence of either mercury(II) acetate [3] or 2,4-dinitrophenol.[4] This unreactivity in transetherification is probably due to the strong hydrogen bonding in (4).[5] However, on heating the unsaturated phosphonates (4; $R^2 = H$ or Ph) with triethyl orthoesters (5; $R^3 = H$ or Me) at 130—175 °C in the presence of a catalytic amount of propionic acid [6] condensation and rearrangement occurred as shown to give the ester phosphonates (7) in *ca.* 50% isolated yields. The ester (7; $R^1 = Me$, $R^2 = Ph$, $R^3 = H$) rearranged on prolonged heating or on chromatography on alumina to give the βγ-unsaturated phosphonate (8).

Monitoring the reaction of (4) with (5) by means of ^1H and ^{31}P n.m.r. spectroscopy showed a build-up of the allyl vinyl ethers (6), the slow step being the subsequent Claisen rearrangement. This required considerably higher temperatures than with other allyl vinyl ethers analogous to (6), and the dialkoxyphosphinyl substituent



(4) (5)

(6)

(7) (8)

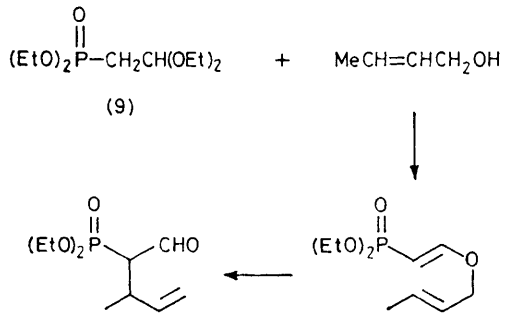
is clearly making the rearrangement more difficult. This deactivation was even more marked in other variations of the Claisen rearrangement. Thus heating a mixture of the acetal (9) with crotyl alcohol at 130 °C gave the allyl vinyl ether (10); slow rearrangement to give the aldehyde (11) at higher temperatures was accompanied by extensive decomposition. Similarly the acetoacetate (12; R = Me) was stable to distillation at 110 °C and prolonged heating at higher temperatures gave only polymeric material.[7] The ester was also unchanged on flash vacuum thermolysis at 700 °C. The preparation and stability of (12; R = Et) have been subsequently reported.[8]

Allylic sulphenates (13) derived from the phosphonates (4) underwent rapid [2,3] sigmatropic rearrangement [9] at or below room temperature to give the sulphoxides (14). These had low thermal stability but showed no

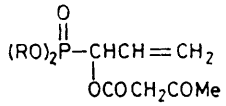
View Article Online

Published on 01 January 1981. Downloaded by Cornell University Library on 21/09/2016 16:33:51.

tendency to rearrange to the corresponding αβ-unsaturated sulphoxides in agreement with data on the base-catalysed equilibria found in alkenyl sulphoxides [10] and phosphonates.[11]

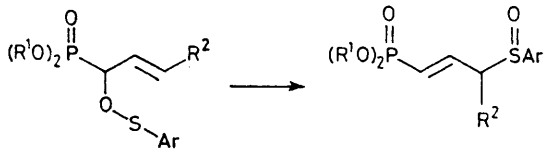


(9) (11) (10)

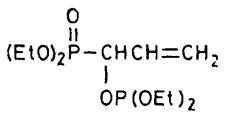


(12)

In contrast to the allylic sulphenates (13), the phosphite (15) showed no tendency to rearrange to bisphosphonate at temperatures up to 180 °C.



(13) (14)



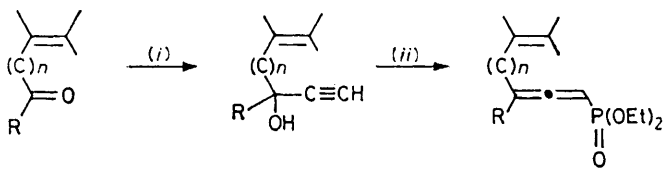
(15)

Addition of Allyloxides to an Allenic Phosphonate.—Cookson and Gopalan [12] showed that the addition of sodium allyloxide to the allenic sulphoxide (16) at room temperature gave one or other of the sulphoxides (17) or (19), depending on the solvent used, and that these rearranged on distillation from zinc carbonate to give the sulphoxide (18) or, after elimination of sulphenic acid, the dienone (20), respectively. A similar addition of sodium allyloxide in THF at room temperature to the allenic phosphonate (19) gave a crude product showing four major absorptions in the ^{31}P n.m.r. spectrum. *Distillation* was accompanied by little change in composition and the mixture was separated by preparative g.l.c. The major components were the ketones (22) (37%) and (24) (19%) formed formally by addition of allyl alcohol to the allene followed by rearrangement. The rapid Claisen rearrangements at room temperature are probably rearrangements of the intermediate allylic anion (20) to give the enolate anions (21) and (23), the acceleration being analogous to that observed in oxy-Cope rearrangements.[13] The minor components proved to be the allyl ethyl phosphonate (25) (7%), formed from (22) by ester exchange, and the product (26) (16.4%) from the addition of ethanol to the starting phosphonate. The last product was first prepared by Pudovik [14] who originally formulated it as (26) but subsequently [15] amended this to (27) on the basis of ozonolysis and oxidation experiments. Structure (26) is clearly indicated from the n.m.r. spectrum.

In contrast to the addition of sodium allyloxide to the phosphonate (19), the addition of secondary or tertiary allyloxides at room temperature gave complex reaction mixtures containing considerable amounts of starting material and none of the products expected from Claisen rearrangement. The spectra of the reaction mixture from the addition of the tertiary oxide (18) to (19) did, however, show features characteristic of the phosphonate (29). On distillation this rearranged and the keto-phosphonate (30) was isolated, albeit in low yield.

Allenic Phosphonates derived from Unsaturated Carbonyl Compounds.—A number of allenic phosphonates containing an additional double bond have been prepared according to the Scheme and their reactions investigated.

Allylacetone readily gave the phosphonate (31). At 140 °C this underwent Cope rearrangement to give (32)



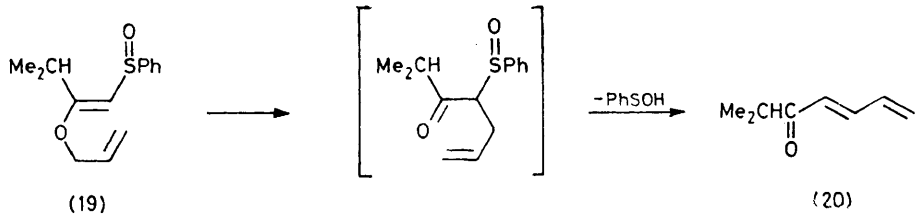
SCHEME (*i*) NaC≡CH; (*ii*) $(EtO)_2PCl$–NR_3

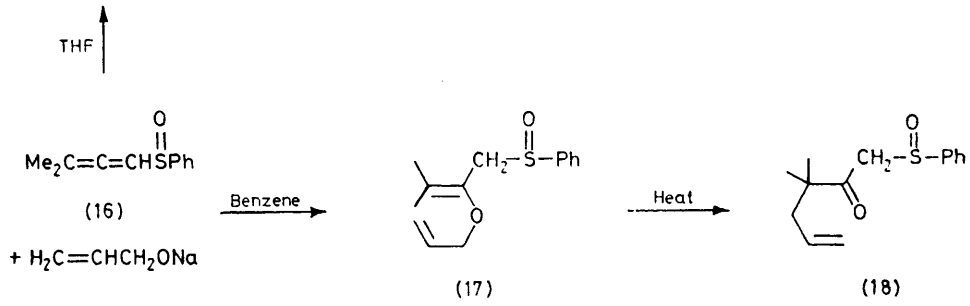
and (33) in the ratio 4 : 1. These phosphonates were reluctant to function as dienes in Diels–Alder reactions; no reaction occurred on heating with dimethyl acetylenedicarboxylate at 100 °C, whereas at 150 °C a slow reaction with maleic anhydride gave a complex reaction mixture. However, after 1 h at 96 °C with *N*-phenylmaleimide, the minor isomer (33) had reacted completely and after a further 6 h reaction was complete; the assignment of isomeric structures to (32) and (33) is based on this difference in reactivity Chromatography of the product led to isolation only of the major adduct, which probably has structure (34).

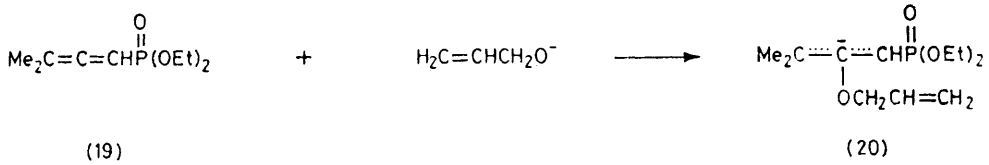
The major phosphorus-containing product from the reaction of the acetylene alcohol (35) with diethyl chlorophosphite in the presence of pyridine was diethyl phosphonate (58%), probably formed by elimination from the initial phosphite ester *via* the stable carbonium ion (36). Distillation and preparative g.l.c. led to isolation of the phosphonates (39)—(41). Monitoring

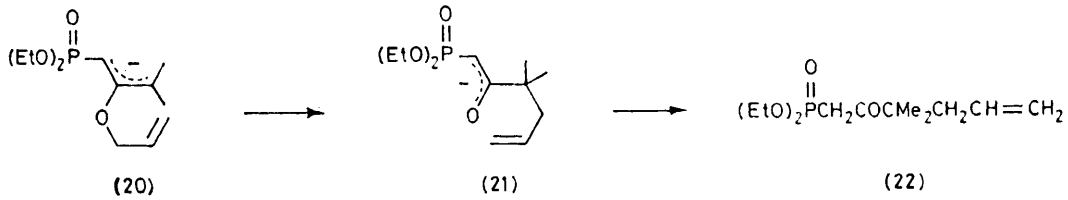
View Article Online

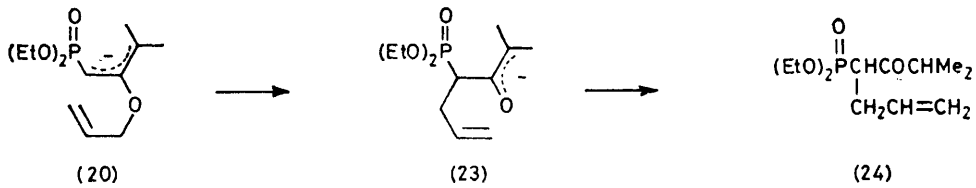
Published on 01 January 1981. Downloaded by Cornell University Library on 21/09/2016 16:33:51.

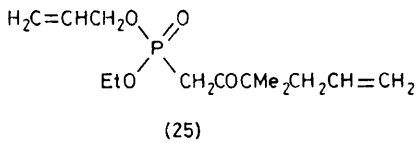


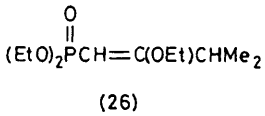


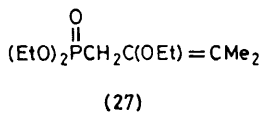








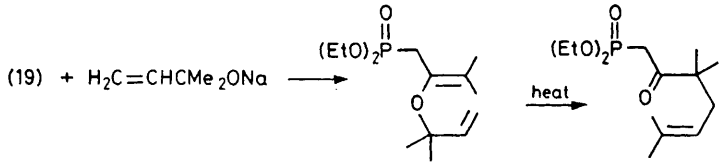




View Article Online

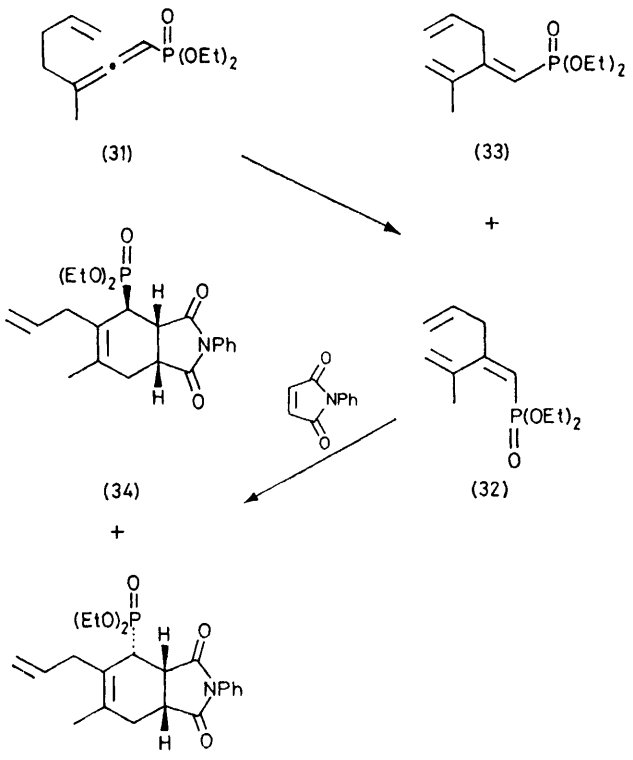
Published on 01 January 1981. Downloaded by Cornell University Library on 21/09/2016 16:33:51.

of the reaction by i.r. and n.m.r. spectroscopy showed that the allenic phosphonate (37) was the initial species.



(28) (29) (30)

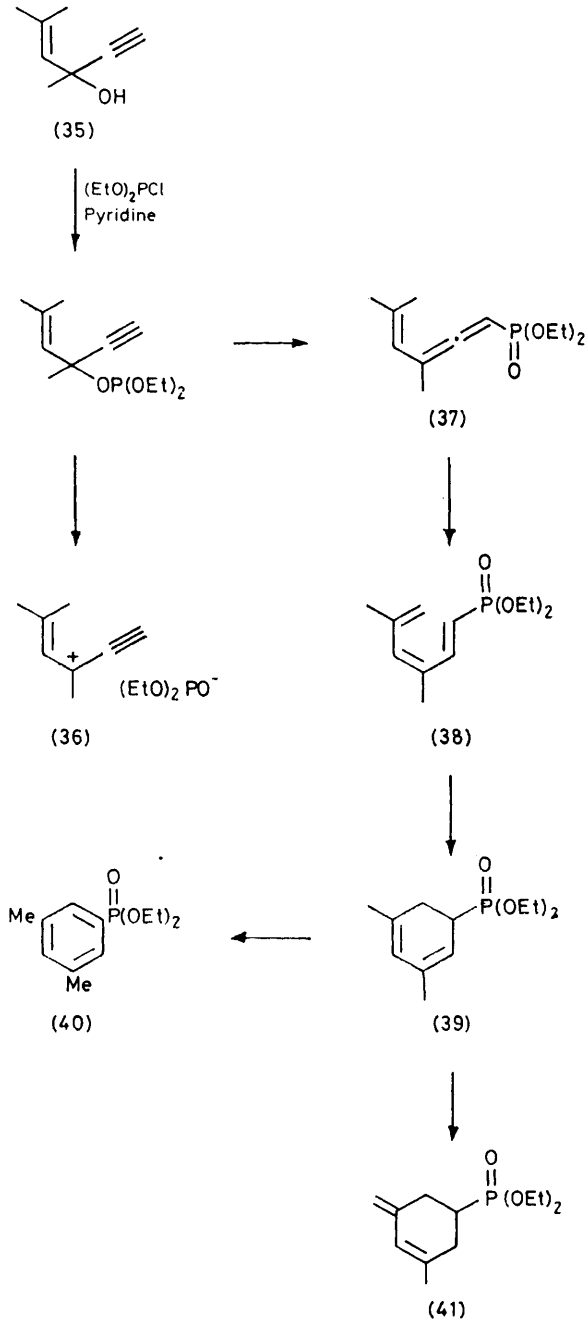
At 75 °C a [1,5] hydride shift gave the triene phosphonate (38), which cyclised slowly at this temperature, and more rapidly at 110 °C, to give the cyclohexadiene (39). Small amounts of the isomeric phosphonate (41) were also formed at this time; although formally the result of a [1,5] hydride shift in (39), this is clearly geometrically *improbable*. Prolonged heating at high temperatures led to formation of the aromatic phosphonate (40). Refluxing the original high-boiling distillate in nitrobenzene in the presence of Pd–C converted 80% of this material into (40).



(31) (33) (34) (32)

The allenic phosphonate (43; R = H) was readily formed from the acetylene alcohol (42; R = H), but above 80 °C rapidly formed a *ca.* 1 : 9 equilibrium mixture with the enyne (44). The undistilled phosphonate (43; R = H) added to *N*-phenylmaleimide at room temperature to give not the expected diene (45; R = H), but its isomer (46; R = H). Chromatography of this over alumina led to isolation of the aromatic phosphonate (47).

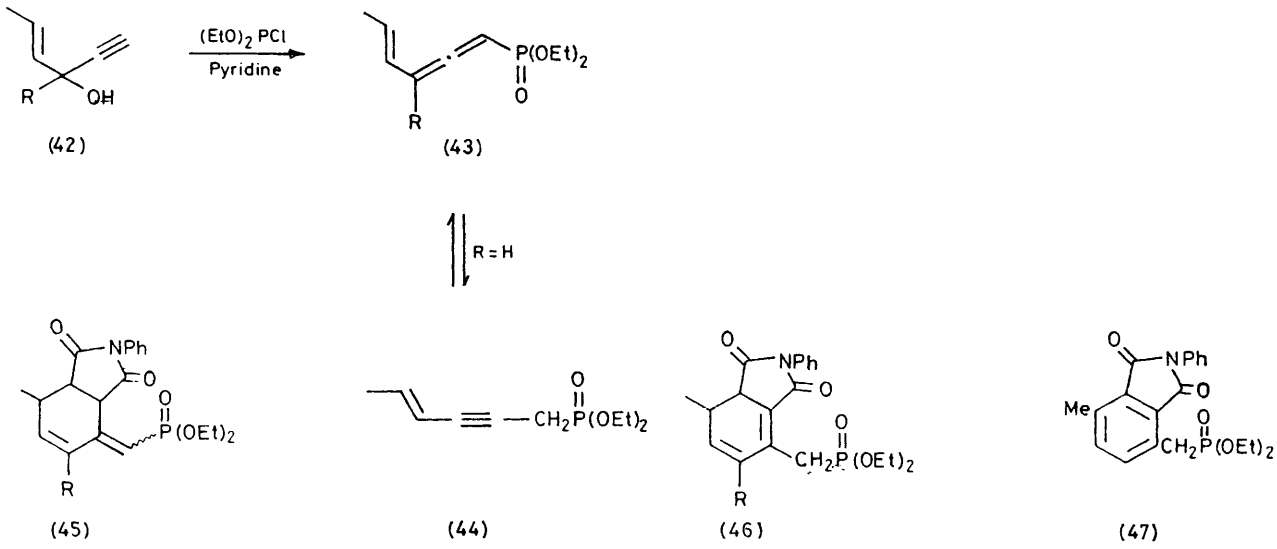
In order to avoid isomerisation of the allenic phosphonate (43) the phosphonate (43; R = Me) was prepared, albeit in the expected low yield [*cf.* (37) above]. It added to *N*-phenylmaleimide in refluxing THF to give (46; R = Me) which was chromatographed on silica without aromatisation.



(35) (37) (36) (38) (40) (39) (41)

View Article Online

Published on 01 January 1981. Downloaded by Cornell University Library on 21/09/2016 16:33:51.



(42) (43) (45) (44) (46) (47)

EXPERIMENTAL

^{31}P N.m.r. spectra were recorded in $CDCl_3$ unless otherwise stated; positive chemical shifts are to low field of the standard, 85% H_3PO_4. Short-path distillation was carried out using a Leybond-Heraeus laboratory still KDLI.

Diethyl 4-Ethoxycarbonylbut-1-enylphosphonate.—A mixture of diethyl 1-hydroxyallylphosphonate [16] (19.4 g), triethyl orthoacetate (22.7 g), and propionic acid (0.44 g) was heated for 3 h at 175 °C (oil bath) with removal of ethanol using a short fractionating column. Short-path distillation then gave *diethyl 4-ethoxycarbonylbut-1-enylphosphonate* (55%), b.p. 81 °C at 0.01 mmHg; δ_H 1.3 (9 H, m), 2.5 (4 H, br s), 4.05 (6 H, quintet, *J* 7 Hz), 5.6 (1 H, t, *J* 17 Hz), and 6.8 (1 H, m); δ_P +17.9; δ_C 14.28, 16.43 (d, *J* 5.8 Hz), 29.15 (d, *J* 21.5 Hz), 32.33, 60.51, 61.61 (d, *J* 5.8 Hz), 118.31 (d, *J* 187.5 Hz), 150.6 (d, *J* 5.8 Hz), and 171.9; *m/e* 264, 191, 163, 135, 117, and 99; $\nu_{max.}$ 1 735 cm^{-1}.

A similar reaction with triethyl orthopropionate gave *diethyl 4-ethoxycarbonylpent-1-enylphosphonate* (48%), b.p. 130—135 °C at 0.3 mmHg; δ_H 1.3 (12 H, m), 2.5 (3 H, m), 4.05 (6 H, q, *J* 7 Hz), 5.6 (1 H, t, *J* 17 Hz), and 6.8 (1 H, m); δ_P +17.7; *m/e* 278, 205, 177, and 149; $\nu_{max.}$ 1 735 cm^{-1}.

A similar reaction gave *diethyl 4-ethoxycarbonyl-3-phenylbut-1-enylphosphonate* (68%), b.p. 95 °C at 0.01 mmHg; δ_H 1.3 (9 H, m), 2.8 (2 H, d, *J* 8 Hz), 4.05 (7 H, m), 5.6 (1 H, t, *J* 17 Hz), 6.8 (1 H, m), and 7.25 (5 H, br s); δ_P +18.1; *m/e* 340, 295, 267, 176, 161, 132, and 131; $\nu_{max.}$ 1 735 cm^{-1} (Found: C, 59.85; H, 7.45; P, 9.25. $C_{17}H_{25}O_5P$ requires C, 60.0; H, 7.4; P, 9.1%) and the corresponding *dimethyl ester* (57%), b.p. 92 °C at 0.09 mmHg, δ_P +21.0. Chromatography of the latter over alumina gave *dimethyl 4-ethoxycarbonyl-3-phenylbut-2-enylphosphonate*, δ_P +29.2; δ_H 1.2 (3 H, t, *J* 7 Hz), 2.8 (2 H, dd, *J* 8 and 22 Hz), 3.6 (2 H, s), 3.75 (6 H, d, *J* 11 Hz), 4.1 (2 H, q, *J* 7 Hz), 5.9 (1 H, q, *J* 8 Hz), and 7.3 (5 H, br s); $\nu_{max.}$ 1 735 cm^{-1}.

p-*Chlorophenyl 3-Di-isopropoxyphosphinylprop-2-enyl Sulphoxide.*—*p*-Chlorophenylsulphenyl chloride (6.26 g) in ether (30 ml) was added to di-isopropyl 1-hydroxyallylphosphonate (7.8 g) and triethylamine (3.89 g) in ether (400 ml) at 0 °C with stirring. After 2 h at room temperature, filtration and evaporation gave an orange oil which, after repeated crystallisation from light petroleum, gave the sulphoxide (16%), m.p. 75—77 °C; δ_H 1.3 (12 H, dd, *J* 1 and 4 Hz), 3.65 (2 H, d, *J* 8 Hz), 4.7 (2 H, sextet, *J* 6 Hz), 5.8 (1 H, t, *J* 17 Hz), 6.2—7.05 (1 H, m), and 7.6 (4 H, s); δ_P +12.5; *m/e* (^{35}Cl) 364, 316, 306, 280, 222, 205, 181, 163, 159, 121, and 103 (Found: C, 49.4; H, 6.1; P, 7.9; S, 8.55. $C_{15}H_{22}ClO_4PS$ requires C, 49.38; H, 6.08; P, 8.49; S, 8.78%). The corresponding dimethoxyphosphinyl (δ_P +17.7) and diethoxyphosphinyl (δ_P +14.9) sulphoxides and 3-dimethoxyphosphinyl-1-phenylprop-2-enyl sulphoxide (δ_P +20.37) could not be crystallised and decomposed on attempted chromatography or distillation.

Diethyl 1-Diethoxyphosphinylallyl Phosphite.—Triethylamine (3.13 g) in ether (50 ml) was added to diethyl 1-hydroxyallyphosphonate (6 g) and diethyl chlorophosphite (4.8 g) in ether (200 ml) at 0 °C with stirring. After 1 h at room temperature, filtration and evaporation gave the phosphite (9.5 g); δ_P +140.4 (d, *J* 17 Hz) and +18.7 (d, *J* 17 Hz). Distillation gave the phosphite, b.p. 130—136 °C at 0.1 mmHg, and the corresponding phosphate, b.p. 136—150 °C at 0.1 mmHg; δ_P +16.5 (d, *J* 29 Hz) and −1.2 (d, *J* 29 Hz).

Addition of Sodium Allyloxide to Diethyl 3-Methylbuta-1,2-dienylphosphonate.—Diethyl 3-methylbuta-1,2-dienylphosphonate (12.24 g) in THF (10 ml) was added at 0 °C to a stirred solution of sodium allyloxide [from sodium hydride (1.44 g) and allyl alcohol (3.48 g)] in THF (40 ml) and the solution set aside at room temperature for 2 h. Dilute hydrochloric acid (1M; 60 ml) was then added. Ether extraction and removal of solvent gave an orange oil (11.8 g) showing four major ^{31}P n.m.r. absorptions. This was subjected to preparative g.l.c. (10% OV17 at 186 °C) to give, in order of increasing retention time, diethyl 2-ethoxy-3-methylbut-1-enylphosphonate (26) (16%); δ_H 1.1 (6 H, d, *J* 6.5 Hz), 1.3 (6 H, t, *J* 7 Hz), 3.35 (1 H, sept, *J* 6.5 Hz), 3.75 (2 H, q, *J* 7 Hz), 4.1 (4 H, quintet, *J* 7 Hz), and 4.3 (1 H, d, *J* 8 Hz); δ_P +23.2; *m/e* 250, 235, 220, 178, 164, 150, 123, and 105; $\nu_{max.}$ 1 610 cm^{-1}: *diethyl 1-allyl-3-methyl-2-oxobutylphosphonate* (24) (19%); δ_H 1.05 (3 H, d, *J* 3 Hz), 1.15 (3 H, d, *J* 3 Hz), 1.3 (6 H, t, *J* 7 Hz), 2.25—3.2 (4 H, m), 4.1 (4 H, septet, *J* 7 Hz), 4.95 (1 H, m), 5.1 (1 H, m), and 5.65 (1 H, m); δ_P +22.0; $\nu_{max.}$ 1 705 and 1 640 cm^{-1}; *m/e* 262, 219, 191, 179, 163, 109, and 81: *diethyl*

View Article Online

Published on 01 January 1981. Downloaded by Cornell University Library on 21/09/2016 16:33:51.

3,3-dimethyl-2-oxohex-5-enylphosphonate (22) (37%); δ_H 1.15 (6 H, s), 1.3 (6 H, t, *J* 7 Hz), 2.2 (2 H, d, *J* 7 Hz), 3.1 (2 H, d, *J* 21 Hz), 4.1 (4 H, quintet, *J* 7 Hz), 4.95 (1 H, m), 5.1 (1 H, s), and 5.65 (1 H, m); δ_P +21.4; $\nu_{max.}$ 1 710 and 1 640 cm^{-1}; *m/e* 262, 179, 151, 137, 125, 109, 97, and 81: *allyl ethyl 3,3-dimethyl-2-oxohex-5-enylphosphonate* (25) (7%); δ_H 1.15 (6 H, s), 1.3 (3 H, t, *J* 7 Hz), 2.2 (2 H, d, *J* 7 Hz), 3.1 (2 H, d, *J* 21 Hz), 4.1 (2 H, quintet, *J* 7 Hz), 4.95 (2 H, m), 5.1 (2 H, s), and 5.65 (2 H, m); δ_P +21.8; $\nu_{max.}$ 1 710 and 1 640 cm^{-1}; *m/e* 274, 233, 191, 163, and 149.

A similar reaction with sodium 2-methylbut-3-en-2-olate (from sodium hydride and the alcohol in refluxing THF) gave a crude product having spectral properties characteristic of the phosphonate (29); δ_H 2.8 (d, *J* 21 Hz); δ_P +27.2; $\nu_{max.}$ 1 610 cm^{-1}. Distillation, followed by preparative g.l.c., gave *diethyl 3,3,6-trimethyl-2-oxohept-5-enylphosphonate* (30) (8%); δ_H 1.1 (6 H, s), 1.3 (6 H, t, *J* 7 Hz), 1.65 (6 H, d, *J* 7 Hz), 2.2 (2 H, d, *J* 7 Hz), 3.1 (2 H, d, *J* 21 Hz), 4.1 (4 H, quintet, *J* 7 Hz), and 5.0 (1 H, m); δ_P +21.2; $\nu_{max.}$ 1 710 cm^{-1}; *m/e* 290, 275, 248, 222, 179, 151, and 137.

Diethyl 3-Methylhepta-1,2,6-trienylphosphonate.—Pyridine (14.2 g) in ether (50 ml) was added at 0 °C with stirring to 3-methylhept-6-en-1-yn-3-ol (22.3 g) and diethyl chlorophosphite (28.1 g) in ether (250 ml) and the mixture set aside at room temperature for 2 h. Filtration and distillation then gave the *phosphonate* (31) (72%), b.p. 110—112 °C at 0.6 mmHg; δ_H 1.3 (6 H, t, *J* 7 Hz), 1.8 (3 H, dd, *J* 7 and 3 Hz), 2.2 (4 H, m), 5.15 (2 H, m), and 5.9 (1 H, m); δ_P +15.7; $\nu_{max.}$ 1 960 cm^{-1}; *m/e* 244, 215, 214, 188, 187, 151, 146, 125, 107, 106, and 91.

The above phosphonate was kept at 150 °C until the allene absorption at 1 960 cm^{-1} had disappeared (*ca.* 2 h). Distillation then gave *diethyl 2-isopropenylpenta-1,4-dienylphosphonate* (89%) as a 4 : 1 mixture of the isomers (32) and (33), b.p. 110—112 °C at 0.6 mmHg; δ_H 1.3 ((6 H, t, *J* 7 Hz) 1.9 (3 H, s), 2.9 (2 H, d, *J* 6 Hz), 4.1 (4 H, quintet, *J* 7 Hz), and 4.9—6.1 (6 H, m); δ_P +16.9 (major) and +18.1 (minor); *m/e* 244, 215, 214, 188, 187, 173, 107, 106, 105, and 91. This phosphonate (8 g) and *N*-phenylmaleimide (5.67 g) were heated together at 96 °C for 7 h. The signals in the ^{31}P n.m.r. spectrum due to the dienes had then been replaced by signals at δ_H +26.8 and +25.2 in the same ratio. Chromatography on silica and distillation gave the *adduct* (34) (66%), b.p. 250 °C (oven) at 0.005 mmHg; δ_H 1.3 (6 H, two t, *J* 3 and 7 Hz), 1.75 (3 H, d, *J* 5 Hz), 2.2—3.6 (7 H, m), 4.1 (4 H, two quintets, *J* 3 and 7 Hz), 4.9 (2 H, two d, *J* 11 and 15 Hz), 5.4 (1 H, m), and 7.25 (5 H, m); δ_P (CH_2Cl_2) +26.8; $\nu_{max.}$ 1 715 cm^{-1} (br); *m/e* 417, 376, 280, 279, 252, 251, 213, 186, and 132 (Found: H, 6.6; N, 3.15; P, 7.05. $C_{22}H_{28}NO_5P$ requires H, 6.76; N, 3.36; P, 7.42%. A satisfactory analysis for carbon could not be obtained).

Preparation and Rearrangement of Diethyl 3,5-Dimethylhexa-1,2,4-trienylphosphonate.—Pyridine (7.9 g) in THF (50 ml) was added at 0 °C with stirring to 3,5-dimethylhex-4-en-1-yn-3-ol (12.4 g) and diethyl chlorophosphite (15.6 g) in THF (200 ml) and the mixture set aside at room temperature for 2 h, and at 66 °C for a further 0.5 h. After cooling, filtration and evaporation of solvent gave an oil (23.9 g); δ_P +7.2, +16.1, and +19.9. Distillation gave diethyl phosphonate (58%), b.p. 50 °C at 0.5 mmHg, and a fraction (2.05 g), b.p. 120—124 °C at 0.5 mmHg; δ_P +16.1, +19.9, +30.4, and +31.4. Preparative g.l.c. (10% OV17 at 200 °C) gave, in order of increasing retention time, *diethyl 3,5-dimethylcyclohexa-2,4-dienylphosphonate* (39), (10%); δ_H 1.3 (6 H, t, *J* 7 Hz), 1.75 (6 H, m), 2.1—3.1 (3 H, m), 4.1 (4 H, quintet, *J* 7 Hz), 5.3 (1 H, d, *J* 9 Hz), and 5.55 (1 H, s); δ_P +30.4: *diethyl 3-methyl-5-methylenecyclohex-3-enylphosphonate* (41) (1.4%); δ_H 1.3 (6 H, t, *J* 7 Hz), 1.75 (3 H, s), 1.85—2.8 (5 H, m), 4.1 (4 H, quintet, *J* 7 Hz), 4.8 (2 H, s), and 5.95 (1 H, s); δ_P +31.4: and diethyl 3,5-dimethylphenylphosphonate (40) (6%); δ_H 1.3 (6 H, t, *J* 7 Hz), 2.35 (6 H, s), 4.1 (4 H, quintet, *J* 7 Hz), 7.1 (1 H, s), and 7.4 (2 H, d, *J* 14 Hz); δ_P +19.3. The mass spectra of (39), (40), and (41) were similar; *m/e* 242, 214, 186, 171, and 105.

Diethyl Hexa-1,2,4-trienylphosphonate.—Pyridine (7.9 g) in ether (20 ml) was added at 0 °C with stirring to a mixture of hex-4-en-1-yn-3-ol (9.6 g) and diethyl chlorophosphite (15.6 g) in ether (400 ml) and the mixture set aside at room temperature for 2 h. Filtration and evaporation then gave the crude phosphonate (43; R = H) (21.4 g); δ_H 1.3 (6 H, t, *J* 7 Hz), 1.8 (3 H, br s), 4.1 (4 H, quintet, *J* 7 Hz), and 5.0—6.4 (4 H, m); δ_P +13.7; $\nu_{max.}$ 1 945, 1 645, and 1 600 cm^{-1}. Distillation gave a mixture of this phosphonate and the isomeric hex-4-en-2-ynylphosphonate (44) (38%), b.p. 97—105 °C at 0.2 mmHg. The spectral characteristics of (44) are δ_H 1.35 (6 H, t, *J* 7 Hz), 1.75 (3 H, d, *J* 6 Hz), 2.8 (2 H, dd, *J* 2 and 22 Hz), 4.2 (4 H, quintet, *J* 7 Hz), 5.2 (1 H, br d, *J* 15 Hz), and 6.0 (1 H, m); δ_P +21.3; $\nu_{max.}$ 2 225 cm^{-1}. The mixture showed *m/e* 216, 188, 187, 160, 159, 151, 125, 121, and 109.

The crude phosphonate (43) (2.14 g) and *N*-phenylmaleimide (1.73 g) in THF (20 ml) were set aside at room temperature for two days when reaction was complete; δ_P (THF) +23.1 and +6.4. Chromatography on alumina then gave 6-(*diethoxyphosphinylmethyl*)-3-*methyl*-N-*phenylphthalimide* (47) (23%), m.p. 136—137 °C (from ethyl acetate–light petroleum); δ_H 1.3 (6 H, t, *J* 7 Hz), 2.75 (3 H, d, *J* 2 Hz), 3.8 (2 H, d, *J* 21 Hz), 4.1 (4 H, quintet, *J* 7 Hz), and 7.45 (7 H, m); δ_P +22.9; *m/e* 387, 359, 342, 331, 314, 313, 264, 250, 223, and 124 (Found: C, 61.1; H, 5.75; N, 3.45; P, 7.7. $C_{20}H_{22}NO_5P$ requires C, 62.0; H, 5.72; N, 3.6; P, 8.0%).

Diethyl 3-Methylhexa-1,2,4-trienylphosphonate.—This was prepared as for (43; R = H) above. Distillation gave diethyl phosphonate (60%) and (43; R = Me) (22%), b.p. 110 °C at 0.4 mmHg; δ_H 1.35 (6 H, t, *J* 7 Hz), 2.8 (6 H, m), 4.1 (4 H, quintet, *J* 7 Hz), and 5.2—6.2 (3 H, m); δ_P +14.1; $\nu_{max.}$ 1 945 cm^{-1}. This phosphonate (1 g) and *N*-phenylmaleimide (0.75 g) were heated to 66 °C for 1.5 h in THF (10 ml); chromatography on silica then gave the adduct (46; R = Me); δ_H 0.9 (3 H, d, *J* 6 Hz), 1.3 (6 H, t, *J* 7 Hz), 1.9 (3 H, s), 4.1 (4 H, quintet, *J* 7 Hz), 6.07 (1 H, d, *J* 7 Hz), and 7.4 (5 H, m) (the remaining signals could not be assigned with confidence); δ_P +23.1; *m/e* 403, 401, 278, 265, 264, and 213.

We thank S.R.C. and Ciba-Geigy for a CASE award.

[1/125 *Received*, 28*th January*, 1981]

REFERENCES

[1] K. H. Worms and M. Schmidt-Dunker in 'Organic Phosphorus Compounds,' vol. 7, eds. G. M. Kosolapoff and L. Maier, J. Wiley and Son, New York, 1976, p. 1.
[2] V. Mark, *Tetrahedron Lett.*, 1962, 281.
[3] W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, 1957, **79**, 2828.

View Article Online

[4] W. S. Johnson, T. J. Brocksom, P. Loew, D. H. Rich, L. Werthemann, R. A. Arnold, T.-T. Li, and D. J. Faulkner, *J. Am. Chem. Soc.*, 1970, **92**, 4463.
[5] E. J. Matrosov and M. I. Kabachnik, *Spectrochim. Acta, Part A*, 1972, **28**, 313; R. G. Islamov, I. S. Pominov, M. G. Zimin, A. A. Sobanov, and A. N. Pudovik, *J. Gen. Chem. USSR* (*Engl. Trans.*), 1974, **44**, 488.
[6] W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T.-T. Li, D. J. Faulkner, and M. R. Petersen, *J. Am. Chem. Soc.*, 1970, **92**, 741.
[7] M. F. Carroll, *J. Chem. Soc.*, 1940, 704, 1266; 1941, 507.
[8] A. N. Pudovik, M. G. Zimin, A. A. Sobanov, and N. G. Zabirov, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1976, **46**, 769.
[9] P. Bichart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4869; R. Tang and K. Mislow, *ibid.*, 1970, **92**, 2100; V. Rautenstrauch, *Chem. Commun.*, 1970, 526.
[10] D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, 1964, **86**, 3840.
[11] B. I. Ionin and A. A. Petrov, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1963, **33**, 426.
[12] R. C. Cookson and R. Gopalan, *J. Chem. Soc., Chem. Commun.*, 1978, 608.
[13] D. A. Evans and A. M. Golob, *J. Am. Chem. Soc.*, 1975, **97**, 4765.
[14] A. N. Pudovik, N. G. Khusainova, and I. M. Aladzheva, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1964, **34**, 2484.
[15] A. N. Pudovik and N. G. Khusainova, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1966, **36**, 1251.
[16] T. Kh. Gazigov, A. M. Kibardin, V. A. Kharlamov, A. A. Karelov, and A. N. Pudovik, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1977, **47**, 2253.

Published on 01 January 1981. Downloaded by Cornell University Library on 21/09/2016 16:33:51.