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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

THE PREPARATION AND REACTIONS OF THE 1,2-DIPHOSPHORANES FORMED ON REACTION OF TRIALKYL PHOSPHITES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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To cite this Article Caesar, J. C. , Griffiths, D. V. , Griffiths, P. A. and Tebby, J. C.(1987) 'THE PREPARATION AND REACTIONS OF THE 1,2-DIPHOSPHORANES FORMED ON REACTION OF TRIALKYL PHOSPHITES WITH DIMETHYL ACETYLENEDICARBOXYLATE', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 34: 3, 155 – 162

To link to this Article: DOI: 10.1080/03086648708074320

URL: <http://dx.doi.org/10.1080/03086648708074320>

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THE PREPARATION AND REACTIONS OF THE 1,2-DIPHOSPHORANES FORMED ON REACTION OF TRIALKYL PHOSPHITES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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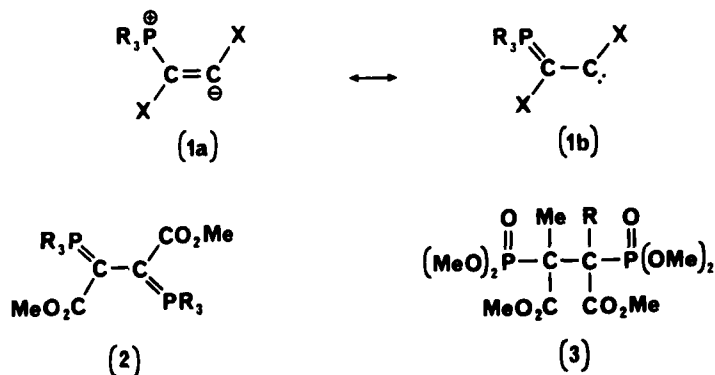
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(Received March 20, 1987; in final form April 30, 1987)

Contrary to previous reports, the reaction of excess trialkyl phosphites with dimethyl acetylenedicarboxylate gives 1,2-diphosphoranes (**2**; R = alkoxy) which are readily converted into the diphosphonates (**6**; R = Me, H). Heating the 1,2-diphosphorane (**2**; R = OMe) with methyl iodide led to the formation of the diphosphonates (**3**; R = Me, H) while its thermal rearrangement led to the novel diphosphonates (**8**) and (**9**; R = Me).

The reactions of triarylphosphines and trialkyl phosphites with dimethyl acetylenedicarboxylate have been studied in some detail^{1,2} and the products rationalised as proceeding via 1:1 intermediates (**1**; R = aryl or alkyl, X = CO₂Me) which can be envisaged as having both anionic (**1a**) and carbenoid (**1b**) forms contributing to their overall structure.



In the presence of excess triarylphosphine the reaction with dimethyl acetylenedicarboxylate leads to the formation of the 1,2-diphosphoranes (**2**; R = aryl). This can be viewed as a nucleophilic attack by the triarylphosphine on the 1:1 intermediate (Figure 1) but since ylides can be generated by the action of carbenes on phosphines³ an alternative mechanism is also possible involving the

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Fig. 1

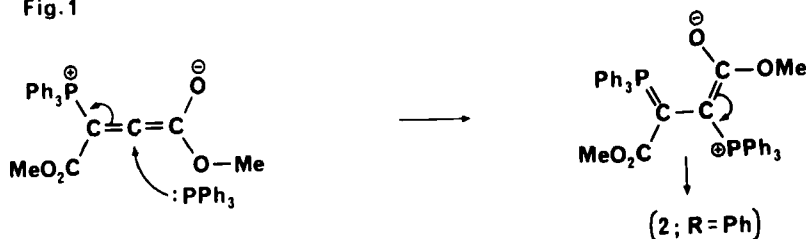
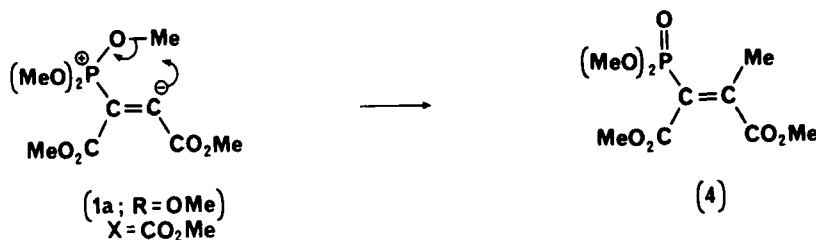


Fig. 2



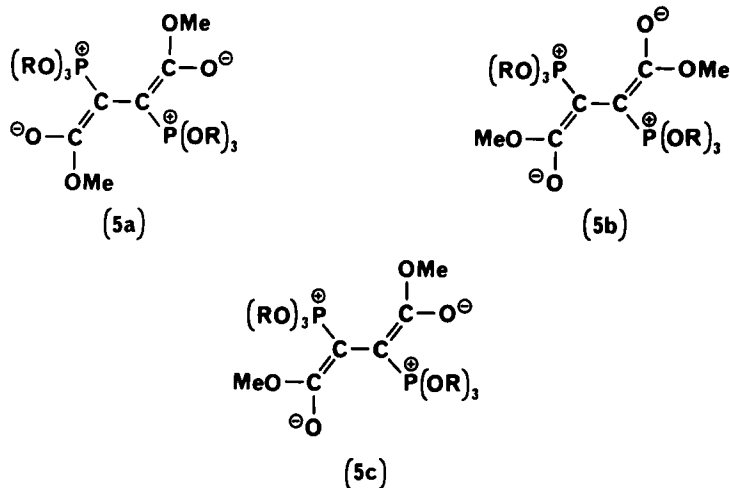
reaction of the triarylphosphine with the carbenoid form of the 1:1 intermediate (**1b**; R = aryl, X = CO₂Me).

In contrast it has been reported that the reaction of dimethyl acetylenedicarboxylate with trimethyl phosphite leads to the formation of the diphosphonate (**3**; R = Me).⁴ This has been rationalised as proceeding via the vinylphosphonate (**4**) which in turn can be envisaged as arising by an intramolecular dealkylation of the 1:1 intermediate (**1**; R = alkoxy, X = CO₂Me) (Figure 2).

We have now investigated the reaction of dimethyl acetylenedicarboxylate with excess trimethyl phosphite and can find no evidence for any significant production of either the diphosphonate (**3**; R = Me) or its proposed precursor, the vinylphosphonate (**4**). Thus, the slow addition of a dilute solution of dimethyl acetylenedicarboxylate to two molar equivalents of either trimethyl or triethyl phosphite, cooled in ice, led to the rapid formation of clean samples of the corresponding 1,2-diphosphoranes (**2**; R = OMe or OEt).

As with the 1,2-diphosphorane (**2**; R = Ph) previously studied, the n.m.r. spectra of the 1,2-diphosphoranes (**2**; R = alkoxy) were temperature dependent due to restricted rotation about the bond to the α -methoxycarbonyl groups. For (**2**; R = OMe) the ³¹P n.m.r. spectrum at room temperature thus showed the presence of three slowly interconverting conformers (**5a**, **5b**, and **5c**; R = Me). The symmetrical conformers (**5a** and **5b**; R = Me) were observed as singlets in the proton-decoupled ³¹P n.m.r. spectrum (δ_P 60.2 and 64.2) while the asymmetrical conformer (**5c**; R = Me) was observed as a 4 line AB type system at δ_P 61.3 and 62.6 ppm (J_{PP} 10 Hz). Warming the sample increased the rate of exchange between these conformers and led to line broadening and the eventual coalescence of some of the signals. Treatment of the diphosphorane (**2**; R = OMe) with anhydrous hydrogen bromide led to protonation and subsequent dealkylation to give the diphosphonate (**6**; R = Me), while treatment with concentrated hydrochloric acid led to the formation of the diphosphonic acid (**6**; R = H).

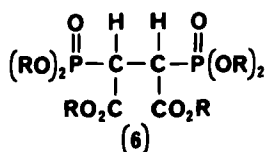
We have also investigated the reaction of trimethyl phosphite with dimethyl



acetylenedicarboxylate under the conditions previously reported⁴ to lead to the formation of the diphosphonate (3; R = Me) and have monitored the course of this reaction by ³¹P n.m.r. spectroscopy.

As expected the major product (> 80%) after mixing the reactants but prior to distillation was the 1,2-diphosphorane (2; R = OMe) although a number of minor products were also present. This would strongly suggest that the 38% yield of the diphosphonate (3; R = Me), reported by previous workers,⁴ had resulted from the thermal rearrangement of the 1,2-diphosphorane (2; R = OMe) during distillation rather than via the vinyl phosphonate (4). However, we have been unable to bring about the desired rearrangement of the 1,2-diphosphorane (2; R = OMe) to the diphosphonate (3; R = Me) to any significant extent under the distillation conditions previously reported (190°C at 0.5 mmHg).

Although the ³¹P n.m.r. spectrum of the product from the distillation showed that the major component was a phosphonate (δ_P 23.2) it was clear from the corresponding ¹³C n.m.r. spectrum that this major component did not contain any C-methyl groups. A second component was also produced in considerable quantities, a diphosphonate which appeared to contain a C-methyl group, but this system gave an AB type pattern in the ³¹P n.m.r. spectrum (δ_P 23.4, 26.0 J_{PP} 19 Hz) and was therefore clearly not the symmetrical 1,2-diphosphonate (3; R = Me) previously reported. Attempts to bring about the thermal rearrangement of the 1,2-diphosphorane (2; R = OMe) to give (3; R = Me) at lower temperatures were also unsuccessful. Thus, for example, there was no indication of the formation of the diphosphonate (3; R = Me) when a sample of (2; R = OMe) was heated at 150°C for 7 h.



Efforts were therefore made to convert (2; R = OMe) into the diphosphonate (3; R = Me) by heating a solution of the pure diphosphorane with methyl iodide in an autoclave. After a number of attempts this proved successful and a quantity of the desired diphosphonate (3; R = Me) was obtained as a mixture of two diastereoisomers (δ_P 25.7, 26.1; 27:73). However, the conditions required for the dialkylation, namely 70 h at 95°C in benzene, indicate the resistance of the diphosphorane (2; R = OMe) to undergo dialkylation. Furthermore, even after this reaction period the major product isolated was not the dialkylated system (3; R = Me) but the mono-alkylated system (3; R = H), formed from the corresponding mono-ylide (7). After shorter reaction periods the mono-ylide (7) could be observed in large quantities in the reaction mixture. At room temperature the ^{31}P n.m.r. spectrum of (7) gave a sharp doublet at δ_P 28.8 (J 6 Hz) and a broad signal at δ_P 57.2, the broadening due to restricted rotation about the bond to the α -methoxycarbonyl group. As expected heating the sample to 50°C caused the lower field ylide signal to sharpen and reveal the $^3J_{PP}$ coupling to the phosphonate resonance. Treatment of this mono ylide with dilute hydrochloric acid led to the immediate formation of the diphosphonate (3; R = H). The identification of the two diphosphonates (3; R = Me and H) was confirmed by combustion analysis, mass spectroscopy, and n.m.r. spectroscopy. The n.m.r. data for the diastereoisomers of (3; R = Me), (3; R = H) and (6; R = Me) are compared in Table I. Unfortunately the ^{13}C spectrum of these

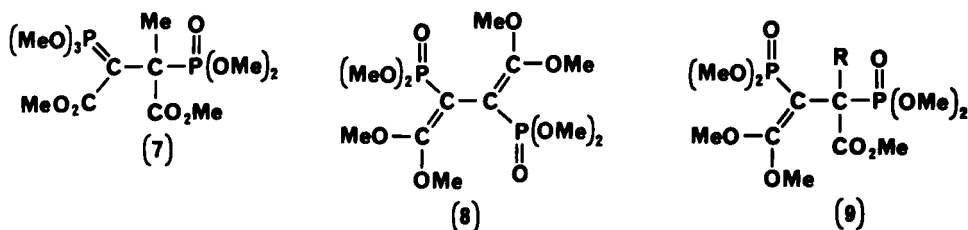
TABLE I
N.m.r. data

$ \begin{array}{c} \text{O} \quad \text{R}' \quad \text{R}'' \quad \text{O} \\ \parallel \quad \quad \quad \parallel \\ (\text{MeO})_2\text{P}-\text{C}_\alpha-\text{C}_\beta-\text{P}(\text{OMe})_2 \\ \quad \\ \text{CO}_2\text{Me} \quad \text{CO}_2\text{Me} \end{array} $						
$\delta_C(\text{CDCl}_3)^a$	R' = R'' = H (6; R = Me)		R' = H; R'' = Me (3; R = H)		R' = R'' = Me (3; R = Me)	
	Major	Minor	Major	Minor	Major	Minor
αC	43.9 (m, 193, 126)	43.4 (m, 145, 131)	47.6 (dd, 125, 6)	48.4 (d, 132)	53.4 (m, 207, 134)	53.8 (m, 164, 137)
βC	43.9 (m, 193, 126)	43.4 (m, 145, 131)	49.7 (dd, 126, 6)	49.9 (d, 132) ^b	53.4 (m, 207, 134)	53.8 (m, 164, 137)
$\alpha\text{C}=\text{O}$	167.0 (t, <1)	167.4 (t, 3)	166.9 (t, 4)	167.8 (dd, 5, 18)	168.9 (s)	169.4 (t, 4)
$\beta\text{C}=\text{O}$	167.0 (t, <1)	167.4 (t, 3)	169.7 (dd, 2, 5)	170.5 (dd, 6, 17)	168.9 (s)	169.4 (t, 4)
MeOP	53.6 (t, 3)	53.6 (t, 3)	54.4 (d, 7) 54.7 (d, 7) 53.3 (d, 7) 53.1 (d, 7)	55.2 (d, 7) _b _b _b	53.9 (t, 3) 53.3 (t, 3)	 _b
MeOC	52.9 (s)	52.8 (s)	52.6 (s) 53.1 (s)	52.6 (s) _b	52.7 (s)	 _b
R'/R''	—	—	15.0 (t, 4)	16.5 (dd, 5, 3)	18.4 (br s)	18.0 (br s)
$\delta_P(\text{CDCl}_3)^c$	21.8	21.5	25.1 (d, 78) 21.6 (d, 78)	25.1 (d, 10) 21.1 (d, 10)	26.0	25.7

^a Shifts in p.p.m. from Me_4Si ; values in parentheses are observed splittings and not necessarily true coupling constants. Multiplicities indicate signal appearance rather than accurate spectral analysis. Signals denoted m are five line multiplets (X of AA'X) for which the band width and the value of ($J_{AX} + J_{A'X}$) are both given.

^b Signals are either partially or completely obscured by overlapping resonances.

^c Shifts in p.p.m. from 85% phosphoric acid; positive shifts to low field of reference; J_{PP} in parentheses.



diphosphonates are complex because of the strong coupling between the two phosphorus atoms in these compounds. Furthermore, since in (3; R = Me) and (6; R = Me) the value of this coupling is unknown, it has not been possible to fully analyse these spectra from the available data. Nevertheless in these latter cases the observed multiplicities of the ^{13}C n.m.r. signals have been shown to be entirely consistent with that expected for the X portion of an AA'X type system.

The availability of the 1,2-diphosphonate (3; R = Me) enabled us to confirm that a small quantity of this material was produced during the thermal rearrangement of the 1,2-diphosphorane (2; R = OMe) but in all the rearrangements we carried out we only found this component to account for 5–10% of the rearrangement product. In view of this efforts were made to identify the major components which had been formed.

Although chromatography led to the isolation of a pure sample of the major rearrangement product (δ_{P} 23.2) it was interesting to note that substantial quantities of the diphosphonate (6; R = Me) were also isolated suggesting that the major component was being converted into the diphosphonate (6; R = Me) on the column. The component at δ_{P} 23.2 has therefore been assigned the structure (8). This structure is consistent with spectroscopic data available (see Table II) and such a compound would be expected to undergo hydrolysis to give the diphosphonate (6; R = Me) as observed. The formation of (8) during the distillation of the 1,2-diphosphorane (2; R = OMe) can also be readily rationalised as an intramolecular dealkylation of a zwitterionic structure such as (5a). A pure sample of the partially hydrolysed system (9; R = H) was also isolated from the chromatography column and its n.m.r. data is given in Table II.

TABLE II
N.m.r. data

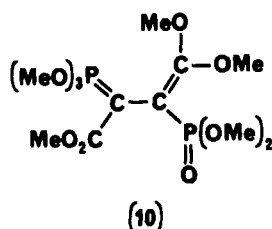
$\delta_{\text{C}}(\text{CDCl}_3)^{\text{a}}$	(8)	(9; R = H)	(9; R = Me)
MeOP	52.4 (t, 3) 52.3 (t, 3)	52.4 (t, 4)	52.3 (br d, 6 ^b)
C—P	80.6 (dd, 206, 4)	80.2 (dd, 203, 9)	87.2 (d, 192)
C=CP	166.7 (t, 12.5)	167.4 (dd, 14, 7)	166.6 (dd, 13, 7)
MeOC	57.7 (s)	58.4 (br s)	58.3 (dd, 2, 2)
	57.0 (s)	56.4 (d, 2)	56.0 (d, 2)
MeOPCR	—	53.5 (d, 7) 53.1 (d, 7)	53.7 (d, 7) 53.6 (d, 7)
C—R	—	43.2 (dd, 151, 6)	50.2 (dd, 145, 10)
C=O	—	167.9 (dd, 6, 1)	172.1 (d, 8)
MeO ₂ C	—	52.5 (s)	52.3 (br s)
R	—	—	21.6 (dd, 4, 4)
$\delta_{\text{P}}(\text{CDCl}_3)^{\text{c}}$	23.2	23.9 (16) 23.0 (16)	26.0 (19) 23.4 (19)

^{a-c} See footnotes to Table I.

Exposure of both (8) and (9; R = H) to the atmosphere over a period of weeks led to slow hydrolysis and the formation of the diphosphonate (6; R = Me). Interestingly in these circumstances only the more stable diastereoisomer of the diphosphonate (6; R = Me) was formed. More rapid hydrolysis of these two diphosphonates, for example, by use of dilute aqueous acid, led to the formation of both diastereoisomers of the diphosphonate (6; R = Me).

The other major product formed during the distillation of the 1,2-diphosphorane (2; R = OMe) was identified as the diphosphonate (9; R = Me). This material could not be isolated in a completely pure state but its ^{13}C n.m.r. spectrum (Table II) was entirely consistent with the proposed structure. Furthermore, the slow hydrolysis of this component led to the formation of the diphosphonate (3; R = H). The quantity of the diphosphonate (9; R = Me) formed during the distillation of the 1,2-diphosphorane (2; R = OMe) varied to some extent but in our experience it was never formed in quantities greater than that of the diphosphonate (8).

Two other minor products were also observed in the ^{31}P n.m.r. spectra of the product from the distillation of (2; R = OMe), both apparently containing an ylide group. Since one could be identified as the monoylide (7), the likely precursor of the diphosphonate (9; R = Me), the second component is probably (10), the precursor of the major rearrangement product (8).



We have also subjected a pure sample of (2; R = OMe) to distillation at (0.5 mmHg) and have subsequently allowed the product mixture to slowly hydrolyse in the air to give three diphosphonates (6; R = Me), (3; R = H) and (3; R = Me). As expected their product ratio (47:45:8) supports our earlier conclusion that while the methylation of one ylidic carbon can occur to a significant extent, the extent of dimethylation to give (3; R = Me) is usually relatively small.

If earlier workers were able to isolate significant quantities of the diphosphonate (3; R = Me) from the distillation of the 1,2-diphosphorane (2; R = OMe) we can only conclude that their product mixture prior to distillation contained impurities which inhibited the rearrangement of the zwitterionic structures such as (5a) in favour of that leading to the formation of (3; R = Me). At no time during our studies did we see any evidence to suggest the formation of the vinyl phosphonate (4).

EXPERIMENTAL

^1H , ^{13}C and ^{31}P n.m.r. spectra were obtained on a JEOL FX 100 spectrometer.

1,2-Bis(methoxycarbonyl)ethane-1,2-bis(trimethoxyphosphorane) (2; R = OMe). A solution of dimethyl acetylenedicarboxylate (4.9 g) in dry diethyl ether (50 cm³) was added slowly over a period of 2.5 h to a stirred solution of trimethyl phosphite (8.5 g) in dry ether (50 cm³), cooled in an ice–water bath, under nitrogen. After the addition the reaction mixture was allowed to stir overnight. During this period a fine yellow precipitate settled from the solution. This was removed by filtration, washed with cold ether, and then dried under vacuum (0.01 mmHg). This product (7.8 g, 58%) was shown by n.m.r. spectroscopy (see discussion) to be the 1,2-diphosphorane (2; R = OMe). A further quantity of the 1,2-diphosphorane (5.3 g, 39%) was obtained by removing the solvent and other volatile components from the filtrate. Although the resulting oil resisted crystallisation ³¹P n.m.r. spectroscopy showed that there were no other products present in significant quantities. Found: C, 37.2; H, 6.15. C₁₂H₂₄O₁₀P₂ requires C, 36.9; H, 6.2%; m.p. 87–90°C.

Tetramethyl 1,2-bis(methoxycarbonyl)ethane-1,2-diphosphonate (6; R = Me). A solution of 1,2-bis(methoxycarbonyl)ethane-1,2-bis(trimethoxyphosphorane) (2 g) in a mixture of dry diethyl ether (15 cm³) and chloroform (5 cm³) was treated with anhydrous hydrogen bromide until the orange colour of the solution had been discharged. Removal of the solvent on a rotary evaporator gave a viscous oil which solidified on standing. The waxy solid was broken up under dry diethyl ether and the resulting white solid separated. After washing with more dry diethyl ether the solid was dried under reduced pressure (0.01 mmHg) at room temperature. The desired diphosphonate (1.75 g, 94%) was obtained as a white hygroscopic solid δ_P (CDCl₃) 21.5, 21.8 (76:24) (diastereoisomers), for ¹³C n.m.r. data see Table I, (Found: C, 32.85; H, 5.6. C₁₀H₂₀O₁₀P₂ requires C, 33.15; H, 5.55%), M⁺ 362.

1,2-Bis(carbohydroxy)ethane-1,2-diphosphonic acid (6; R = H). To the 1,2-diphosphorane (2; R = OMe) (5.95 g) was slowly added cold concentrated hydrochloric acid (40 cm³). This mixture was allowed to stand at room temperature for 2 days and the hydrochloric acid was removed on a rotary evaporator (40°C at 16 mmHg). The resulting oil was dissolved in a little water and the solution treated with decolourising charcoal. The solution was filtered and the water removed under reduced pressure. Final traces of water were removed under higher vacuum (0.01 mmHg) to give a viscous oil which solidified on standing. The solid was broken up under dry diethyl ether, separated and dried to give the diphosphonic acid (2.54 g, 60%) as a white hygroscopic solid (δ_P (DMSO) 21.4, J_{PH} 12 Hz; δ_C (DMSO) 46.0, d, 114 Hz; 169.5 p.p.m.) (Found: C, 17.1; H, 3.35. C₄H₈O₁₀P₂ requires C, 17.25; H, 2.9%).

1,2-Bis(methoxycarbonyl)ethane-1,2-bis(triethoxyphosphorane) (2; R = OEt). A solution of dimethyl acetylenedicarboxylate (6 g) in dry diethyl ether (25 cm³) was added dropwise over 2.5 h to a stirred solution of triethyl phosphite (2.57 g) in dry diethyl ether (25 cm³) cooled in an ice bath. The solvent was removed on a rotary evaporator (50°C at 16 mmHg) and the resulting oil was then heated under vacuum (50°C at 0.1 mmHg) until the volatile phosphorus components had been removed. ³¹P n.m.r. spectroscopy showed the resulting oil to be the 1,2-diphosphorane (3; R = OEt) (7.57 g, 89%) (δ_P 59.1, 58.0 (d), 56.3 (d), 55.4 p.p.m., J_{PP} 10 Hz) in a good state of purity. Attempts to purify this diphosphorane further were unsuccessful and tended to produce some decomposition. (Found: C, 44.6; H, 7.6. C₁₈H₃₆O₁₀P₂ requires C, 45.55; H, 7.65%) Hydrolysis of a sample of the 1,2-diphosphorane (3; R = OEt) by heating under reflux with concentrated hydrochloric acid led to the formation of 1,2-bis(carbohydroxy)ethane-1,2-diphosphonic acid (6; R = H), identified by comparison with the sample prepared by the hydrolysis of the diphosphorane (2; R = OMe).

Tetramethyl 1,2-bis(methoxycarbonyl)propane-1,2-diphosphonate (3; R = H). A solution of 1,2-bis(methoxycarbonyl)ethane-1,2-bis(trimethoxyphosphorane) (7 g) in dry benzene (60 cm³) containing methyl iodide (10 g) was heated at 90°C for 12 h in a PTFE-lined autoclave (150 ml; Berghof). At the end of this period ³¹P n.m.r. spectroscopy indicated that the major product at this stage was the monoylide (7).

The benzene and excess methyl iodide were removed from the reaction mixture under reduced pressure and the residue dissolved in ethyl acetate (10 cm³). This solution was chromatographed on a 22 × 2.5 cm medium pressure column packed with Kieselgel 60 (Merck) with ethyl acetate as the eluant. Analysis of the fractions by ³¹P n.m.r. indicated that the ylide had protonated and dealkylated on the column to give tetramethyl 1,2-bis(methoxycarbonyl)propane-1,2-diphosphonate. Fractions containing the pure diphosphonate were combined and the solvent removed under reduced pressure. The resulting oil was subjected to short path distillation (0.05 mmHg) to give an analytically pure sample of *tetramethyl 1,2-bis(methoxycarbonyl)propane-1,2-diphosphonate* as a waxy solid. (Found: C, 35.1; H, 6.2. C₁₁H₂₂O₁₀P₂ requires C, 35.1; H 5.9%). For n.m.r. data see Table I.

Tetramethyl 2,3-bis(methoxycarbonyl)butane-2,3-diphosphonate (3; R = Me). A solution of 1,2-bis-

(methoxycarbonyl)ethane-1,2-bis(trimethoxyphosphorane) (7 g) in dry benzene (60 cm³) containing methyl iodide (10 g) was heated at 90°C for 70 h in a PTFE-lined autoclave (150 ml; Berghof). A fine white solid (1.4 g) was formed, which was separated, and recrystallised from benzene, to give the pure diphosphonate (3; R = Me) as a mixture of diastereoisomers [δ_P (CDCl₃) 26.0, 25.7 (85:15)]. (Found: C, 36.83; H, 6.22. C₁₂H₂₄O₁₀P₂ requires C, 36.93; H, 6.19%) m.p. 166–168°C (lit.,⁴ m.p. 164.5–165.5°C). Removal of the solvent from the reaction solution left a viscous oil which was largely the diphosphonate (3; R = H) although some diphosphonate (3; R = Me) was also present.

The thermal decomposition of (2; R = OMe). The reaction of trimethyl phosphite with dimethyl acetylenedicarboxylate was also investigated under conditions previously reported⁴ to lead to the formation of tetramethyl 2,3-bis(methoxycarbonyl)butane-2,3-diphosphonate.

Thus, dimethyl acetylenedicarboxylate (7.1 g) was added dropwise to a stirred solution of trimethyl phosphite (12.65 g) in dry ether (100 cm³) under nitrogen, while keeping the temperature of the reaction between 5–10°C. The reaction mixture was stirred at room temperature for 1 h and then heated under reflux for 1 h. The ether was removed under reduced pressure to give a viscous oil which was shown by ³¹P n.m.r. spectroscopy to contain 1,2-bis(methoxycarbonyl)ethane-1,2-bis(trimethoxyphosphorane) (2; R = OMe) as the major product (>80%) together with a number of minor components.

The crude 1,2-diphosphorane (2; R = OMe) was distilled under reduced pressure (0.5 mmHg) and the distillate subsequently analysed by n.m.r. spectroscopy. An initial small fraction was shown to be a mixture of dimethyl methylphosphonate, dimethyl phosphite and trimethyl phosphate, presumably arising from the slight excess of trimethyl phosphite used in the reaction. However, subsequent fractions (b.p. 193°C) were shown to contain two major components (8) and (9; R = Me) together with a number of minor signals.

Chromatography on Kieselgel 60 (Merck) using ethyl acetate followed by 10% methanol in ethyl acetate as the eluant enabled a pure sample of the major component (δ_P 23.2) to be isolated and identified as the diphosphonate (8) M⁺ 390 (for n.m.r., data see Table II), although considerable decomposition of this material occurred on the column to give the diphosphonates (6; R = Me) and (9; R = H) (for n.m.r. data see Tables I and II respectively).

The second major component (δ_P 26.0, 23.4 J_{PP} 19) could not be obtained in a completely pure form but could be readily identified as the diphosphonate (9; R = Me) (for n.m.r. data see Table II). On exposure to the air this component slowly hydrolysed to give (3; R = H), this being identified by comparison with the sample prepared by the action of methyl iodide on the 1,2-diphosphorane (2; R = OMe).

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