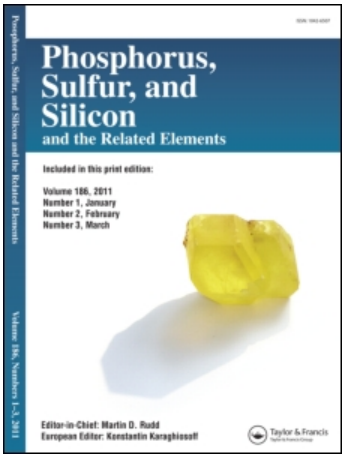

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DIRECT FORMATION OF λ5-PHOSPHOLES FROM DIALKYL PHOSPHONITES AND DIMETHYL ACETYLENEDICARBOXYLATE

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The reaction of dialkyl phosphonites with dimethyl acetylenedicarboxylate proceeds via an analogous route to that previously established for the reaction of trialkyl phosphites although the intermediates are less stable. The five-coordinate phosphole (**3**; R = Et, R′ = Ph) is sufficiently stable at −70°C to enable it to be converted to the oxo-phosphole (**5**; R′ = Ph) by treatment with anhydrous hydrogen bromide.

INTRODUCTION

During our investigations into the reaction of trimethyl phosphite with dimethyl acetylenedicarboxylate we were able to identify a number of intermediates including the five-coordinate (λ^5) phosphole intermediate (**3**; R = Me, R′ = OMe).[1,2] Furthermore, this intermediate was sufficiently stable at temperatures below about −10°C to enable its reactions to be investigated. In particular, we found that the addition of hydrogen bromide to the λ^5-phosphole (**3**; R = Me, R′ = OMe) caused dealkylation to give the novel four-coordinate oxo-phosphole (**5**; R′ = OMe) in good yield.

We have now investigated the scope of this reaction further and, in particular, the possibility of using dialkyl arylphosphonites and dialkyl alkylphosphonites for the production of the aryl- and alkyl-substituted oxo-phospholes (**5**; R = aryl or alkyl) which unlike (**5**; R = OMe) should be amenable to further reduction to give the phospholes (**6**; R′ = aryl and alkyl).

RESULTS AND DISCUSSION

We have now established that dialkyl arylphosphonites and dialkyl alkylphosphonites react with two molar equivalents of dimethyl acetylenedicarboxylate by an analogous pathway to that previously established for the trimethyl

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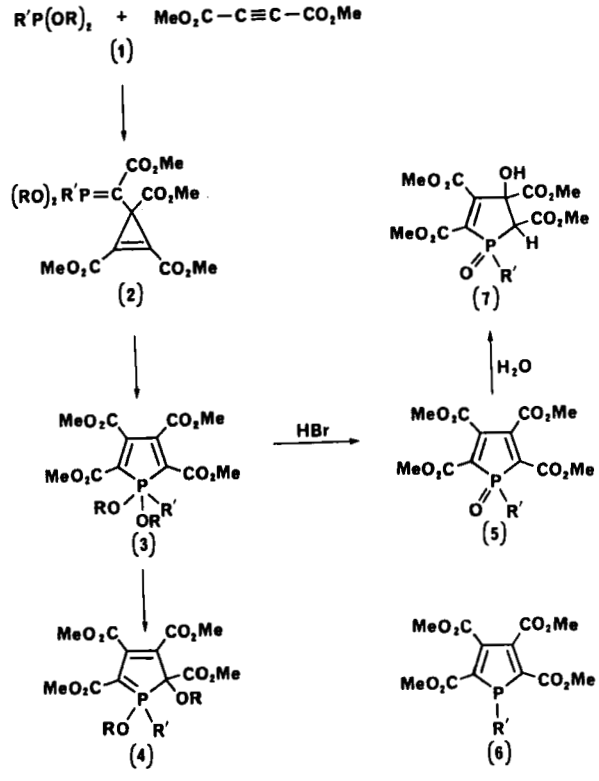

SCHEME 1

phosphite reaction.[1,2] However, the phosphonites were found to be more reactive towards the acetylenic ester and the intermediates less stable than the corresponding ones formed from trimethyl phosphite. Thus, while the reaction of diethyl phenylphosphonite (**1**; R = Et, R′ = Ph) with dimethyl acetylenedicarboxylate, at low temperature in toluene, led to the initial formation of the ylide (**2**; R = Et, R′ = Ph) in almost quantitative yield, the reaction time of approximately 30 min at −70°C was considerably shorter than the 1–2 h at −50°C observed in the phosphite reaction at similar concentrations.

Interestingly, in the phosphonite reaction the formation of the ylide (**2**; R = Et, R′ = Ph) occurs via its less stable rotamer, that giving a signal at δ_P 69.8 ppm, since this is the only signal seen during the early period of the reaction. However, as the reaction proceeded this rotamer was converted to that giving a signal at δ_P 70.9 ppm so that after a period of about 2 h at −70°C about 70% of the dialkoxyphosphonium ylide (**2**; R = Et, R′ = Ph) was adopting this more stable conformation. Similar observations were made when the reaction of dimethyl acetylenedicarboxylate with dimethyl phenylphosphonite (**1**; R = Me, R′ = Ph) was investigated. However, in this latter case the rate of formation of the ylide (**2**; R = Me, R′ = Ph) was slower, by a factor of about four, than that observed for the formation of the ylide (**2**; R = Et, R′ = Ph). The two phosphonites (**1**; R = Me, R′ = Ph) and (**1**; R = Et, R′ = Ph) were also observed to differ in their reactivities towards methyl iodide although here the difference was less marked. It would thus appear that the significantly lower reactivity of the dimethyl phenylphosphonite

towards dimethyl acetylenedicarboxylate cannot be explained entirely in terms of the reduced nucleophilicity of this phosphonite.

The reduced stability of the dialkoxyphosphonium ylide (**2**; R = Et, R′ = Ph) from the phosphonite reaction in comparison with the trialkoxyphosphonium ylide (**2**; R = Me, R′ = OMe) from the phosphite reaction was clearly demonstrated by the observation that rearrangement of the dialkoxyphosphonium ylide (**2**; R = Et, R′ = Ph) to the λ^5-phosphole (**3**; R = Et, R′ = Ph) occurred at a significant rate even at −70°C. Thus, after 1.5 h at −70°C about 30% of the ylide (**2**; R = Et, R′ = Ph) had undergone rearrangement. Furthermore, on warming to −50°C, the temperature at which the ylide from the phosphite reaction (**2**; R = Me, R′ = OMe) had been stable for many hours, the rearrangement of the remaining ylide (**2**; R = Et, R′ = Ph) was complete after only about 15 min. It should be noted that although the major product at this time was still the λ^5-phosphole (**3**; R = Et, R′ = Ph) an almost equivalent quantity of the cyclic ylide (**4**; R = Et, R′ = Ph), resulting from rearrangement of the λ^5-phosphole (**3**, R = Et, R′ = Ph), was also present. After a further period of 45 min at −50°C the rearrangement of the λ^5-phosphole (**3**; R = Et, R′ = Ph) to the cyclic ylide (**4**; R = Et, R′ = Ph) was more than 90% complete.

To study the dealkylation of the λ^5-phosphole (**3**; R = Et, R′ = Ph) it was therefore necessary to use temperatures considerably lower than those used previously for the study of the λ^5-phosphole (**3**; R = Me, R′ = OMe). However, by using a temperature of −70°C during the addition of the hydrogen bromide, the dealkylation of the λ^5-phosphole (**3**; R = Et, R′ = Ph) to the oxo-phosphole (**5**; R′ = Ph) could be carried out reasonably efficiently. ^{31}P nmr spectroscopy showed the reaction product to contain about 40% of the oxo-phosphole (**5**; R′ = Ph) (δ_P 38.7 ppm, t, J_{PH} 14 Hz).

A modest quantity of this phosphole was isolated in a pure state, but attempts to purify the bulk of the phosphole proved to be difficult. Although the crude phosphole gradually crystallised to give a pure compound, the compound isolated was not the expected oxo-phosphole (**5**; R′ = Ph) but the phospholene (**7**; R′ = Ph). The same compound was also obtained when attempts were made to purify the crude phosphole (**5**; R′ = Ph) by chromatography despite the use of dry solvents. This clearly demonstrates the susceptibility of this system to nucleophilic attack. Attempts to dehydrate the phospholene (**7**; R′ = Ph) to regenerate the phosphole (**5**; R′ = Ph) have so far been unsuccessful.

The reaction of dimethyl methylphosphonite (**1**; R = R′ = Me) with dimethyl acetylenedicarboxylate has also been studied. Here the intermediates were even less stable than those from the corresponding phenylphosphonite. Thus, for example, attempts to prepare a pure sample of the dialkoxyphosphonium ylide (**2**; R = R′ = Me) (δ_P 85.1, 86.8 ppm) were always accompanied by the formation of not only the λ^5-phosphole (**3**; R = R′ = Me) (δ_P −34.3 ppm) but also a small quantity of the cyclic ylide (**4**; R = R′ = Me) (major rotamers at δ_P 96.2 and 96.9 ppm). In all cases some rearrangement of the initially formed ylide (**2**; R = R′ = Me) had occurred during the mixing of the starting materials despite considerable efforts to avoid this. Nevertheless, once formed the mixture of intermediates was reasonably stable at −70°C and the only significant change observed in the ^{31}P nmr spectrum, over a period of 2 h, was the change in the ratio of the rotamers of the ylide (**2**; R = R′ = Me). Attempts to maximise the quantity of the λ^5-phosphole (**3**; R = R′

TABLE I (nmr data)

$\delta(^{13}C)$[a]	(2)	(3)	(4)	(5)	(7)
R = Et, R′ = Ph					
αC	40.78(229)[b]	147.60(98)[b]	63.01(140)[c]	132.58(88)[c]	59.83(59)[c]
βC	35.93(14)	134.18(26)	160.91(29)	145.76(20)	79.05(15)
γC	116.5[d]		101.94(19)		156.50(16)
δC			85.40(85)		133.02(84)
C = O	158.88	163.81(22)	163.43(13)	160.29(12)	161.45(9)
	159.02	167.58(10)	164.09(11)	162.07(18)	162.68(19)
	168.78(27)		166.31(19)		164.99
	173.41(4)		167.26		169.41
OMe	49.22	51.72	50.53	53.08	52.55
	52.21	52.09	51.16	53.35	53.20
	52.21		52.38		53.20
	52.21		52.79		53.64
R′	e	e	120.35(125)	123.33(107)	126.49(110)
	e	e	128.42(14)	129.14(13)	127.97(13)
	e	e	133.29(11)	130.30(12)	131.84(11)
	e	e	134.06(3)	133.73(3)	133.19(3)
R	16.0[d]	16.28(8)	14.59		
			16.11(7)		
	61.9[d]	62.06(10)	61.52(5)		
			66.75(7)		
$\delta(^{31}P)$[f]					
R = Et, R′ = Ph					
	69.8[b]	−34.0[b]	83.9[c]	38.7[c]	43.4[c]
	70.9				
R = Me, R′ = Ph					
	73.3[b]	−31.9[b]	86.1[c]	38.7[c]	43.4[c]
	74.5				
R = R′ = Me					
	85.1[b]	−34.3[b]	96.2[b,g]	46.1[c]	
	86.8		96.9		

[a] Shifts in ppm from Me_4Si; J_{PC} in parentheses.
[b] [$^2H_8$] Toluene, −70°C.
[c] [^2H] Chloroform, room temperature.
[d] Broad signals.
[e] Signals obscured by solvent resonances.
[f] Shifts in ppm from 85% phosphoric acid, positive shifts to low field.
[g] Major rotamers.

= Me) present in the sample, in preparation for the trapping reaction, were disappointing. The conditions necessary to facilitate the rearrangement of the ylide (**2**; R = R′ = Me) also led to the rearrangement of the product, the λ^5-phosphole (**3**; R = R′ = Me), to the cyclic ylide (**4**; R = R′ = Me). It was therefore difficult to obtain a signal for the λ^5-phosphole greater than about 20% of the total ^{31}P nmr signal. Although this was not sufficiently high to enable the oxo-phosphole (**5**; R′ = Me) to be produced on a preparative basis, ^{31}P nmr studies confirmed that the λ^5-phosphole (**3**; R = R′ = Me) was converted to the phosphole (**5**; R′ = Me) (δ_P 46.1 ppm, q, J_{PH} 15 Hz) on treatment with anhydrous hydrogen bromide.

Attempts to reduce the phosphole (**5**; R′ = Ph) to give the phosphole (**6**; R′ = Ph) have, as yet, been unsuccessful. This may be due to the susceptibility of the oxo-phosphole (**5**; R′ = Ph) to nucleophilic attack.

EXPERIMENTAL

Nmr spectra were obtained on a JEOL FX100 spectrometer.

Diethoxyphenyl[methoxycarbonyl-(1,2,3,-trismethoxycarbonyl-cyclopropenyl)methylene]phosphorane (**2**; *R = Et, R′ = Ph*). Diethyl phenylphosphonite (0.2 g, 1 mmol) in dry [$^2H_8$] toluene (0.5 ml) was cooled to about −70°C and then added to a solution of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in dry [$^2H_8$] toluene (2 ml) also at −70°C in an nmr tube (1 cm diam.). The contents of the tube were shaken, then rapidly cooled in liquid nitrogen and the frozen sample placed in the nmr probe cooled to −70°C. ^{31}P nmr showed that after a period of 30 min at −70°C the ylide (**2**; R = Et, R′ = Ph) had been formed in essentially quantitative yield. The structure of this ylide was confirmed by ^{13}C nmr spectroscopy (see Table I) and by comparison with the trimethoxy system (**2**; R = Me, R′ = OMe) previously reported[2].

Tetramethyl 1,2-Diethoxy-1-phenyl-2H-1λ⁵-phosphole-2,3,4,5-tetracarboxylate. (**4**; *R = Et, R′ = Ph*). Diethyl phenylphosphonite (0.8 g) in dry toluene (8 ml) at −50°C was quickly added to a solution of dimethyl acetylenedicarboxylate (1.15 g) in dry toluene (8 ml) also at −50°C. The mixture was shaken and then allowed to stand at −50°C for 30 min before being allowed to warm up to room temperature. ^{31}P nmr spectroscopy indicated the presence of only the desired product (**4**; R = Et, R′ = Ph) (δ_P 83.9 ppm) in this reaction mixture. The solvent was removed under reduced pressure and the resulting material warmed at 50°C under high vacuum (0.1 Torr) to remove any other volatile impurities. This material was then taken up in a little dry ether and the desired product precipitated by careful addition of hexane. The product was filtered off and dried by warming at 56°C under vacuum (0.1 mm Hg). The desired product (**4**; R = Et, R′ = Ph) was obtained as a yellow-orange solid (1.8 g; 92%) M.p. 57–60°C (Found: C, 54.5; H, 5.7. $C_{22}H_{27}O_{10}P$ requires C, 54.76; H, 5.65%).

Tetramethyl 1-Oxo-1-phenyl-1H-1λ⁵-phosphole-2,3,4,5-tetracarboxylate (**5**; *R′ = Ph*). Diethyl phenylphosphonite (1 g) in dry toluene (10 ml) at −70°C was quickly added to a solution of dimethyl acetylenedicarboxylate (1.43 g) also in dry toluene (10 ml) at −70°C. The mixture was immediately shaken and allowed to stand for about 1 h at −70°C. Hydrogen bromide was bubbled into the toluene solution at −70°C until the orange-brown colour of the solution had been discharged. After allowing the resulting solution to warm to room temperature, the ^{31}P nmr spectrum indicated that the reaction mixture contained the desired component (**5**; R′ = Ph) δ_P 38.7 ppm as the major component (approximately 40% of the total ^{31}P nmr signal). Most of the toluene was removed under reduced pressure and dry ether was added. White hygroscopic crystals separated and were filtered off. The crystals were quickly washed with dry diethyl ether and then dried under vacuum to give (0.23 g, 11%) of the desired oxo-phosphole (**5**; R′ = Ph) (Found: C, 52.7; H, 4.65. $C_{18}H_{17}O_9P$ requires C, 52.95; H, 4.2%).

Attempts to isolate further quantities of the phosphole from the reaction product led to the isolation of a quantity of white solid (0.44 g, 21%) identified as the phospholene (**7**; R′ = Ph). Furthermore, the phosphole (**5**; R′ = Ph), previously isolated, was found to absorb moisture very readily to give the phospholene (**7**; R′ = Ph). The phospholene (**7**; R′ = Ph) was identified by its ^{13}C and ^{31}P nmr spectra (see Table I) (Found C, 50.7; H, 4.5. $C_{18}H_{19}O_{10}P$ requires C, 50.7.; H, 4.5%). M^+ 426.

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