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Phosphonium Salts and Phosphoranes. Part 5.[1] Thermal and Electron-Impact Induced Fragmentation of Heteroaroylmethylenetriphenylphosphoranes.

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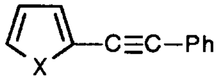
Abstract - A modification of Trippett's pyrolysis of aroylmethylenephosphoranes provides a general procedure for the synthesis of five-membered heteroarylethynes. The electron-impact induced fragmentation of the phosphoranes also produced ions corresponding in mass to the ethynes, but metastable ion data indicate that the extrusion of the ethyne follows the initial loss of H• from the molecular ion.

In the course of our photochemical studies of pyrrole derivatives and in connection with our quest for extended heteroaryl systems possessing electrical semi-conducting properties, we required a convenient and simple synthesis of heteroarylethynes and, in particular, of the (2-pyrrolyl)ethynes (**1** - **3**, X = NMe) and the 1,2-diheteroarylethynes (**4**, X = NMe, Y = S, O, NMe).



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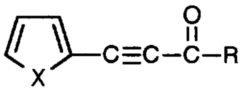

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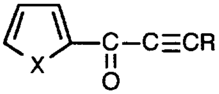

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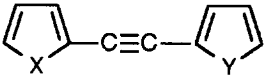

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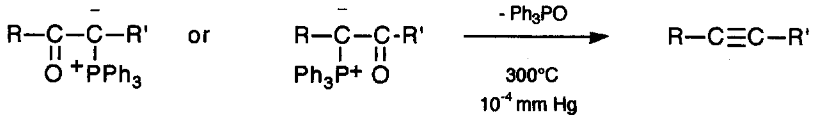
A wide number of methods is available for the synthesis of arylalkynes,[2] but many procedures are not generally applicable or convenient for the preparation of five-membered heteroarylethynes owing, either to the inaccessibility of the required precursor, or to the susceptibility of the rings to electrophilic attack.[3] Syntheses of several (3-pyrrolyl)ethynes in low yield have been recorded previously,[4,5] but the procedures referred specifically to the preparation of polysubstituted pyrroles and are not suitable for adaption to simple (2-pyrrolyl)ethynes. During the course of this work, the synthesis of (2-pyrrolyl)ethynes *via* the pyrolysis of a (2-pyrrolyl)isoxazolone precursor has been reported.[6] However, our experience with the preparation of mono-[7] and dipyrrolylethenes[8] suggested that the previously reported successful applications of a Wittig-type reaction for the synthesis of phenylethynes[9] could be extended to the heterocyclic analogues *via* the extrusion of triphenylphosphine oxide from the appropriate heteroaroylmethylenephosphorane **5**.[10]



a **b**

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Pyrolysis of the heteroaroylphosphoranes under the conditions described in the literature[9a] met with limited success, as the greater reactivity of the five-membered heterocycles, compared with the phenyl ring, promoted decomposition or polymerisation of the resultant ethynes. Thus, at 280°C, under a vacuum of 0.1 mm of Hg, only the propiolic esters (**2**, R = OEt) could be isolated in reasonable yields (> 75%) and, although the recovery of the triphenylphosphine oxide was almost quantitative, the 1-(2-heteroaryl)-2-phenylethynes **1** and 1,2-di(2-heteroaryl)ethynes **4** were isolated only in low yields (<20%). Variation of the pyrolysis temperature over a range from 240 to 300°C at 0.1 mm of Hg failed to improve the yields and, in the majority of experiments conducted at the two extremes of the temperature range, no acetylenic products were isolated. However, reduction of the pressure to less than 10^{-4} mm of Hg resulted in an almost quantitative distillation of the ethynes from the pyrolysis mixtures at 300°C. Examination of the ^{31}P n.m.r. spectral data of the phosphoranes **5a** and **5b**[10] indicated small, but significant, differences in the electron distribution in the isomeric pairs of the α-heteroaroyl-α-heteroarylmethylenephosphoranes **5a** and **5b** (R and R' = heteroaryl), but there was no apparant advantage in the pyrolysis of either isomer to form the required ethyne.

Pyrolysis of the α-acetyl-α-heteroaroylmethylenephosphoranes **5a** (R = Me, R' = heteroaroyl) and the α-benzoyl-α-heteroaroylmethylenephosphoranes **5a** (R = Ph, R' = heteroaroyl) respectively produced the isomeric pairs of the acylethynes **2** and **3** (R = Me or Ph). The higher yield of the 1-(1-methyl-2-pyrrolyl)prop-2-yn-1-one **3** (X = NMe, R = Ph), compared with isomer **2** (X = NMe, R = Ph), reflects the destabilising effect of the electron-donating ring upon the canonical structure **6b**, as indicated by the ^{31}P n.m.r. data.[10] The effect is less noticeable in the formation of the isomeric butynones **2** and **3** (R = Me), which were formed in a *ca.* 2:3 ratio and are readily distinguished by their νC=O frequencies and by the ^{1}H n.m.r. chemical shift for the methyl group (Table 1).

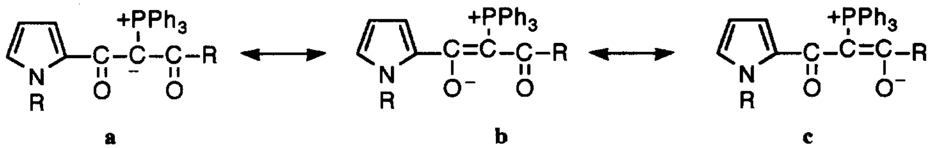

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Table 1. Spectral Data[a] for the Isomeric Heteroarylbutynones[b] **2** and **3**

R'	**2** (R = Me)			**3** (R = Me)		
	$\nu C\equiv C$	$\nu C=O$	δMe	$\nu C\equiv C$	$\nu C=O$	δMe
2-furyl	2185	1670	2.38	2220	1645	2.10
2-thienyl	2185	1668	2.40	2235	1625	2.08
1-methyl-2-pyrrolyl	2175	1668	2.23	2255	1618	1.90

[a] IR spectra measured as 0.2M solutions in $CHCl_3$ in a 0.1mm cell using a Perkin-Elmer 125 spectrometer. ^1H n.m.r.spectra (ppm from Me_4Si) were obtained at 60MHz for *ca.* 20% solutions in $CDCl_3$ using a Perkin-Elmer R12 spectrometer. [b] 1-phenylbut-1-yn-3-one 2205 and 1675 cm^{-1}, 2.38 ppm; 1-phenylbut-2-yn-1-one 2245 and 1645 cm^{-1}, 2.12 ppm (*cf.* refs. 9a, 11).

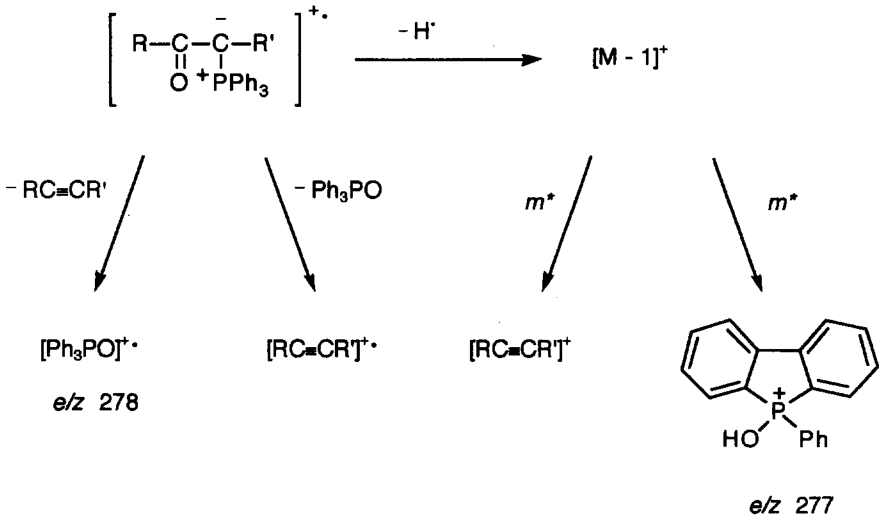
The electron-impact induced cleavage of the acylmethylenephosphoranes **5a** and **5b** produces fragment ions corresponding in mass to the expected ethynes. Their formation, however, appears to occur in two discrete routes: (a) by direct extrusion of triphenylphosphine oxide, analogous to the thermal degradation and (b) by a two-step pathway, which involves the initial loss of H˙ and the subsequent formation of the ethyne from the $[M - 1]^+$ ion.[12] The two processes (Scheme 1) are respectively characterised by (a) a peak corresponding in mass to the triphenylphosphine oxide ion (*e/z* 278), arising from the direct cleavage pathway, and by (b) the presence of an *e/z* 277 ion, either as the base peak, or a peak of high abundance (>80%), together with metastable ion peaks corresponding to the $[M - 1]^+ \rightarrow$ e/z 277 fragmentation and the alternative $[M - 1]^+ \rightarrow [\text{ethyne}]^+$ cleavage (Tables 2 and 3). Although the intensities for the metastable ion peaks corresponding to theformation of the $[\text{ethyne}]^+$ ion were strong for the (α-aroyl-α-arylmethylene) phosphoranes, they were weak or absent in the mass spectra of the α-acetylmethylene and α-ethoxy- carbonylmethylene derivatives and, in general, evidence for either of the two fragmentation routes, based on these metastable ions, was not conclusive (Table 2). In contrast, metastable ions corresponding to the formation of the ethyne via the $[M - 1]^+ \rightarrow$ m/e 277 fragmentation (Table 3) were unambiguous and of high abundance for all of the phosphoranes.

As the direct fragmentation pathway could also arise *via* the initial thermal degradation of the acylmethylenephosphoranes at the high source temperatures, the ion abundances of a representative selection of compounds were examined over a range of probe temperatures from 180 to 300°C. Below 180°C, the majority of the phosphoranes were insufficiently volatile to give a mass spectrum but, above 180°C, it was noted that the peak intensities of both the molecular ions and a majority of the fragment ions increased uniformly with the increase in the probe temperature. The relative abundance of the $[M - 1]^+$ ion was always found to be greater than that of the molecular ion and the ratio $[M]^{+\cdot}/[M - 1]^{+}$ was almost constant for all compounds examined over the full temperature range. The intensities of the ethyne ion peaks increased relative to both the $[M]^{+\cdot}$ and the $[M - 1]^{+}$ peaks, while the abundance of the ions of mass 277 and 278 remained relatively constant. These observations suggest that pyrolysis of the phosphoranes under the "direct insertion" conditions of measurement was negligible and that the appearance of *e/z* 278 peak results from electron-impact fragmentation of the molecular ion (*cf.* ref. 12b). The observation of a metastable peak near *e/z* 276 for several of the phosphoranes indicates that an alternative source of the *e/z* 277 ion involves loss of $H^\cdot$ from the triphenylphosphine oxide. Ions characteristic of the fragmentation of triphenylphosphine oxide[13] were also observed.

Table 2. Representative Metastable Ion Data for Electron-impact Induced Formation of Ethyne Fragment Ions from the phosphoranes **5a** and **5b**.

	phosphorane		observed m*	calc. for.	calc. for
	R	R'		$M^{+\cdot} \rightarrow [\text{ethyne}]^+$	$[M - 1]^+ \rightarrow [\text{ethyne}]^+$
5a	phenyl	1-methyl-2-pyrrolyl	71.4 ± 0.2	71.37	71.53
5b	1-methyl-2-pyrrolyl	phenyl	71.5 ± 0.2	71.37	71.53
5a	2-furyl	1-methyl-2-pyrrolyl	65.2 ± 0.2	65.12	65.27
5b	1-methyl-2-pyrrolyl	2-furyl	65.1 ± 0.2	65.12	65.27
5a	phenyl	2-thienyl	73.4 ± 0.2	73.28	73.44
5a	1-methyl-2-pyrrolyl	CO_2Et	absent	68.86	69.01
5a	1-methyl-2-pyrrolyl	COMe	absent	50.85	50.97
5a	2-thienyl	CO_2Et	absent	70.74	70.89

In contrast with the mass spectra of the α-substituted-α-acylmethylenephosphoranes, no peaks corresponding in mass to extruded monosubstituted ethynes were observed in the electron-impact induced fragmentation of the simple acylmethylene compounds (**5a**, R' = H), *cf.* thermal degradation. Instead, the mass spectra were dominated by the $[M]^{+\cdot}$ and $[M - 1]^{+}$ ions and by the *e/z* 277 ion, which provided the base peak for a majority of the compounds examined (*cf.* ref. 12). The absence of the ethyne ion may be rationalised in terms of the energetically more favourable cleavage of the R group to produce the acylium ion, $[Ph_3P{=}CH.C{\equiv}O]^+$, of mass 303.[12a] This ion is also prominant in the fragmentation of (α-ethoxycarbonylmethylene)triphenylphosphorane (45%) and in the mass spectrum of (α-acetyl-α-ethoxycarbonylmethylene)triphenylphosphorane (95%).



Scheme 1

Table 3. Representative Metastable Ion Data for Electron-impact Induced Formation of Fragment Ions *e/z* 277 and *e/z* 278 from the Heteroaroylmethylephosphoranes **5a** and **5b**

	phosphorane R	R'	observed m*	calc. for $[M - 1]^+ \rightarrow e/z$ 277	calc. for $M^{+\cdot} \rightarrow e/z$ 278
5a	phenyl	1-methyl-2-pyrrolyl	167.5 ± 0.2	167.53	168.37
5b	1-methyl-2-pyrrolyl	phenyl	167.0 ± 0.2	167.53	168.37
5a	2-furyl	1-methyl-2-pyrrolyl	171.5 ± 0.2	171.27	172.12
5b	1-methyl-2-pyrrolyl	2-furyl	171.0 ± 0.2	171.27	172.12
5a	phenyl	2-thienyl	166.0 ± 0.2	166.4	167.28
5a	1-methyl-2-pyrrolyl	CO2Et	169.0 ± 0.2	169.01	169.86
5a	1-methyl-2-pyrrolyl	COMe	181.0 ± 0.2	180.96	181.85
5a	2-thienyl	CO2Et	169.0 ± 0.2	167.90	168.74

The mass spectra of the α-aroyl-α-ethoxycarbonylmethylene- and α-acetyl-α-aroylmethylenephosphoranes are characterised by the fragmentation of the substituted methylene group. The molecular ions for the esters (**5a**, R = OEt, R' = heteroaroyl) readily lose C_2H_4 and CO_2 to produce the α-acylmethylenephosphorane ion $[Ph_3P{=}CH.COAr]^{+\cdot}$, but subsequent loss of the aryl group to give the *e/z* 303 ion is insignificant (10 ± 5%). The α-acetyl derivatives (**5a**, R = Me, R' = heteroaroyl) fragment to give the $[Ph_3P{=}C.COAr]^+$ ion through the loss of a methyl radical and carbon monoxide.

Extrusion of the acylalkyne from the $[M - 1]^+$ ion, produced from the α,α-diacylmethylenephosphoranes (**5a**, R = heteroaryl, R' = COMe or COPh) is substantiated by the appearance of the appropriate metastable ions (Table 3) and, as with the thermal degradation, the isomeric ethynes **2** and **3** appear to be formed, although evidence for their relative abundances is somewhat equivocal. Thus, low intensity peaks (<40%) of mass 43 were observed for the cleavage of the 1-heteroarylbut-1-yn-3-ones, whereas the percentage abundances of the heteroaroyl ion from the 1-heteroarylbut-2-yn-1-ones were high (>50%). While these observations could be taken as an indication of the isomer ratio, they clearly also reflect the relative stabilities of the acylium ions.

EXPERIMENTAL

General Procedure for Thermal Fragmentation of the Acylmethylenephosphoranes: An intimate mixture of the appropriate acylmethylenephosphorane[10] and double its volume of silica were heated to 300°C for 30 - 60 min at *ca.* 10^{-4} mm Hg. The alkyne, which sublimed or distilled from the mixture, was dissolved in ether and the dried solution was evaporated to give an almost pure product, which was purified further for analysis by distillation or recrystallisation.

1,2-Diarylethynes: Pyrolysis of (α-benzoyl-α-phenylmethylene)triphenylphosphorane gave 1,2-diphenylethyne (99%), m.p. 63°C (lit.,[14 - 16] m.p. 60 - 61°C; 59.5- 61°C).

1-Heteroaryl-2-phenylethynes **1** and 1,2-di(heteroaryl)ethynes **4** were obtained from the appropriate aroylmethylenephosphorane[10] (Tables 4 and 5).

Table 4. 1-(2-Heteroaryl)-2-phenylethynes **1**

Heteroaryl group	m.p./b.p. (°C)	% yield
2-furyl	90 (2mm Hg)[a]	90[b]
2-thienyl	48[c]	91,[b] 88[d]
1-methyl-2-pyrrolyl	36[e]	89[b]

[a] lit.,[17] b.p. 74°C at 0.1 mm Hg (Found: C, 86.0; H, 5.0 Calc. for $C_{12}H_8O$ C, 85.6; H, 4.8%); δ_H (CCl_4) 6.35(dd, 1H), 6.65 (dd, 1H), 7.20 - 7.60 (m, 6H); ν_{max} 2205 cm^{-1}. [b] from phosphorane **5a** (R = Ph).
[c] lit.,[16,18], m.p. 48 - 49°C; 48.5 - 49.5°C; δ_H (CCl_4) 6.90 (m, 1H), 7.10 - 7.40 (m, 7H); ν_{max} 2210 cm^{-1}.
[d] from phosphorane **5b** (R = Ph). [e] Found: C, 85.7; H, 5.7; N, 7.7 $C_{13}H_{11}N$ requires C, 86.15; H, 6.1; N, 7.7%; δ_H (CCl_4) 3.55 (s, 3H), 5.87 (dd, 1H), 6.45 (m, 2H), 7.10 - 7.40 (m, 5H); ν_{max} 2200 cm^{-1}

Table 5. 1,2-Di(heteroaryl)ethynes **2**

	precursor		ethyne		% yield	m.p./b.p.		analysis		
	R	R'	X	Y		(°C)		C	H	N
5a	2-furyl	2-furyl	O	O	25	oil[a]	Found:			
							Req'd:	76.0	3.8	
5a	2-furyl	2-thienyl	O	S	87	38.5[b]	Found:	68.7	3.8	
5b	2-thienyl	2-furyl	O	S	92		Req'd:	68.9	3.5	
5a	2-thienyl	2-thienyl	S	S	99	94[c]				
5a	2-furyl	1-methyl-2-pyrrolyl	O	NMe	70	200 (10^{-3} mm Hg)[d]	Found:	77.1	5.4	7.9
							Req'd:	77.2	5.3	8.2
5b	2-furyl	1-methyl-2-pyrrolyl	O	NMe	20					
5a	2-thienyl	1-methyl-2-pyrrolyl	S	NMe	70	oil[e]	Found:	70.7	5.1	7.1
							Req'd:	70.55	4.8	7.5
5a	1-methyl-2-pyrrolyl-	1-methyl-2-pyrrolyl	NMe	NMe	45	[f]				

[a] lit.,[19] m.p. 21°C; δ_H (CCl_4) 6.36 (dd, 1H), 6.60 (d, 1H), 7.30 (m, 1H). [b] δ_H (CCl_4) 6.35 (dd, 1H), 6.60 (dd, 1H), 6.91 (dd, 1H), 7.25 (m, 3H); ν_{max} 2205 cm^{-1}. [c] lit.,[17, 20, 21] m.p. 101 - 102°C; 95°C; 95 - 97°C; δ_H (CCl_4) 6.90 (m, 2H), 7.20 (m, 4H). [d] δ_H (CCl_4) 3.52 (s, 3H), 5.98 (m, 2H), 6.51 (m, 2H), 6.60 (m, 1H); ν_{max} 2200 cm^{-1}. [e] δ_H (CCl_4) 3.65 (s, 3H), 6.11 (t, 1H), 6.50 (dd, 1H), 6.68 (t, 1H), 6.90 (m, 1H), 7.30 (m, 2H); ν_{max} 2210 cm^{-1}. [f] highly unstable oil, no satisfactory elemental analysis was obtained; m/z = 184 a.m.u.; δ_H (CCl_4) 6.90 (m, 2H), 7.20 (m, 4H).

Ethyl alkynoic esters : Pyrolysis of (α-acetyl-α-ethoxycarbonylmethylene)triphenylphosphorane gave ethyl but-2-ynoate (100%), b.p. 163 - 165°C (lit.,[22] b.p. 165°C) $\nu_{max.}$ (liquid film) 2240 (C≡C), 1708cm^{-1} (C=O). Ethyl phenylpropynoate (97%) b.p. 152°C at 20mm Hg (lit.,[23] b.p. 150 - 153°C at 16mm Hg) $\nu_{max.}$ (liquid film) 2230 (C≡C), 1710 cm^{-1} (C=O) was obtained from (α-benzoyl-α-ethoxycarbonylmethylene)-triphenylphosphorane. The heteroarylpropiolic esters were obtained from the appropriate α-ethoxycarbonyl-α-heteroaryl methylenephosphoranes[10] (Table 6).

Acylalkynes : 1-Heteroarylbut-1-yn-3-ones **2** (R = Me) and the 1-heteroarylbut-2-yn-1ones **3** (R = Me) were obtained by the thermal fragmentation of the appropriate α-acetyl-α-heteroaroylmethylenephosphoranes **5**.[10] Pyrolysis of the α-benzoyl-α-(1-methyl-2-pyrroloyl)methylenephosphorane gave the isomeric (1-methyl-2-pyrrolyl)propynones **2** and **3** (R = Ph). Attempts to separate and purify the isomeric pairs by distillation or by chromatography failed to give analytically pure samples.

Table 6. Ethyl Heteroarylpropiolates **3** (R = OEt) from Heteroarylmethylenephosphoranes **5a** (R = heteroaryl, R' = CO_2Et)

X	m.p. (°C)	% yield	νC≡C (cm^{-1})[a]	νC=O (cm^{-1})
O	39 - 40[b]	91	2210	1715
S	28[c]	98	2210	1705
NMe	34 - 35[d]	86	2200	1700

[a] measured as mulls in Nujol. [b] lit.,[24] m.p. 39.5 - 39.8°C; δ_H (CCl_4) 1.30 (t, 3H), 4.25 (q, 2H), 6.45 (dd, 1H), 6.90 (dd, 1H), 7.48 (dd, 1H). [c] lit.,[25] b.p. 100 - 130°C at 0.1 mm Hg; Found: C, 59.8; H, 4.8; $C_9H_8O_2S$ requires C, 60.0; H, 4.5%; δ_H (CCl_4) 1.30 (t, 3H), 4.20 (q, 2H0, 7.05 (m, 1H), 7.45 (m, 2H). [d] Found: C, 67.4; H, 6.1; N, 7.8 $C_{10}H_{11}NO_2$ requires C, 67.7; H, 6.3; N, 7.9%; δ_H (CCl_4) 1.30 (t, 3H), 3.70 (s, 3H), 4.18 (q, 2H), 6.12 (dd, 1H), 6.62 (m, 2H).

Table 7. Acylalkynes **2** and **3**

	precursor		acylalkynes	overall %	ratio **2**:**3**
	R	R'	X	yield	
hetroarylbutynones					
5b	Me	2-furyl	O	92[a]	2:3
5b	Me	2-thienyl	S	80[b]	2:3
5b	Me	1-methyl-2-pyrrolyl	NMe	93[c]	1:1
heteroarylphenylpropynones					
5b	Ph	1-methyl-2-pyrrolyl	NMe	87[d]	1:3

[a] M^+ 134 a.m.u. Found: C, 71.4; H, 4.3%; $C_8H_6O_2$ requires C, 71.6; H, 4.5%; [b] M^+ 150 a.m.u. Found: C, 64.1; H, 4.2%; C_8H_6OS requires C, 64.0; H, 4.0%; [c] M^+ 147 a.m.u. Found: C, 73.2; H, 6.0; N, 9.5%; C_9H_8NO requires C,73.45; H, 6.2; N, 9.5%; [d] M^+ 209 a.m.u. Found: C, 80.0.; H, 5.2; N, 6.7%; $C_{14}H_{11}NO$ requires C, 80.4; H, 5.3; N, 6.7%.

Electron-Impact Induced Fragmentation: The mass spectra of the acylmethylenephosphoranes were measured at a probe temperature over the range 180 - 300°C using a Hitachi Perkin-Elmer RMU-6E mass spectrometer with an ionisation voltage of 70eV, Accurate mass measurements were obtained using an AEI MS902 mass spectrometer at a resolution of 10,000.

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