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PHOSPHONIUM SALTS AND PHOSPHORANES—VI[1]

^{31}P NMR SPECTRA OF ACYLMETHYLENEPHOSPHORANES

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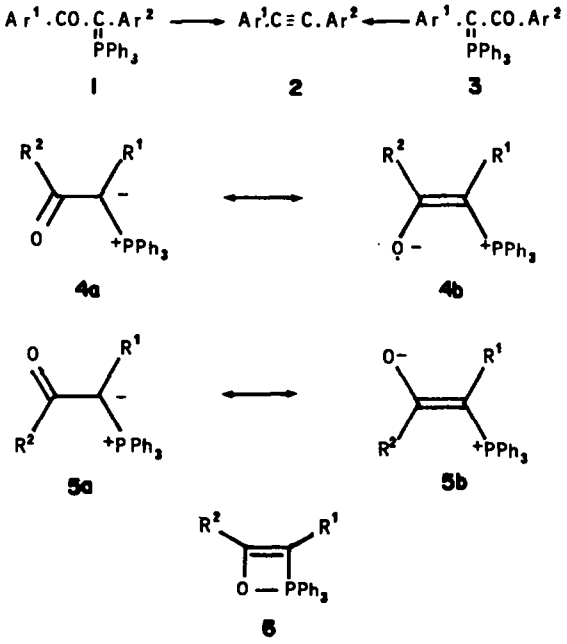
Abstract—The ^{31}P NMR spectra of 36 acylmethylenephosphoranes have been measured and the chemical shifts have been interpreted in terms of steric interactions and the resonance stabilization of the ylides. It is proposed that the observed solvent shift effects are best accounted for by a change in the resonance stabilization and not, as previously suggested, by a change in the conformational equilibrium position. The inductive electron-withdrawing interaction of α-aryl groups leads to a deshielding of the phosphorus nucleus, whilst the deshielding effect produced by α-acyl substituents can be rationalised in terms of a combination of the mesomeric and inductive interactions. Syntheses of 21 new phosphoranes are described.

In the course of our study of the thermal decomposition of the heteroaroylmethylenephosphoranes,[1] **1** and **3**, it was of interest to discover whether there was any difference in the electronic structures and in the preferred conformations of the isomeric phosphoranes, which would affect the efficiency of their conversion into the heteroarylalkynes, **2**.



In previous conformational studies of acylmethylenephosphoranes **4**⇌**5** extensive use has been made of variable temperature ^{1}H NMR spectroscopy[2-7] and it is evident that, when $R^2 \neq H$, the *cisoid* structure **4** predominates, although it has been noted that the bulk of the R^1 substituent affects the equilibrium position.[7] Both conformers of the formylmethylenephosphorane (**4** and **5**; $R^1 = R^2 = H$) exist in equilibrium in a *ca.* 1:1 ratio at room temperature,[4-7] but the presence of a strongly electron withdrawing substituent, R^1, produces an increase in the relative concentration of the *transoid* conformer.[5] The ^{1}H NMR data also indicated that there is negligible interaction between the quaternary P^+ atom and the anoinic O^- atom of the *cisoid* zwitterionic structure (**4**) and, although at low temperature, structures analogous to the 4-membered ring **6** have been confirmed as intermediates in the Wittig synthesis of alkenes,[8] such structures have little importance in the ground state structures of the acylmethylenephosphoranes.

The equilibrium position for the two conformers, **4** and **5**, and the rotational energy barrier between these conformers should be affected not only by the electronic character of R^1 but should also depend upon the degree of interaction of R^2 with the CO group. In particular, an electron-withdrawing R^2 substituent would be expected to destabilize the zwitterionic structures **4b** and **5b**. Similarly, steric interaction between the aryl substituents and the triphenylphosphoryl group should reduce the coplanarity of the phosphorane system with a consequent destabilization of the canonical forms **4b** and **5b**.

^{31}P Chemical shift data have been accumulated for a wide range of phosphorous compounds[9] and it is apparent that ^{31}P NMR spectroscopy could provide a diagnostic probe for the study of the interaction of the P atom of the phosphoranes with the acylmethylene group. However, no systematic survey of the ^{31}P NMR spectra of acylmethylene phosphoranes has been reported.

RESULTS AND DISCUSSION

The ^{31}P NMR chemical shifts of the simple acylmethylene phosphoranes ($Ph_3P{=}CH{\cdot}COR$), presented in Table 1, were in accord with previously reported ^{1}H NMR data for analogous acylmethylenephosphoranes[2-7] and indicated that, with the exception of the formyl compound, only one conformation exists in deuterochloroform and in deuterobenzene. Comparison of the magnitudes of the observed ^{31}P chemical shifts with previously reported values for acylphosphoranes of known conformation[7,12] confirms that the compounds under investigation have the *cisoid* structure **4**. The shielding effect on the P atom of the ylides, as observed in the upfield shift of the resonance signal compared with the chemical shifts of the corresponding phosphonium salts, is compatible with either the $d\pi - p\pi$ interaction between the P atom and the carbanionic methylene group of **4a** or the conjugation of the phosphonium group with the enolate anion π-system

Table 1. ^{31}P NMR chemical shifts for acylmethylene phosphoranes ($Ph_3P{=}CH{\cdot}COR$) and the corresponding phosphonium salts ($Ph_3\overset{+}{P}CH_2COR$)

R	Phosphorane in $CDCl_3$	Phosphorane in C_6D_6	Phosphonium Salt in $CDCl_3$
Hydrogen	-15.0 -19.1 [a]	-	-
Methyl	-14.8 [b]	-15.8	-13.6 -20.1 [c]
1-Methyl-2-pyrrolyl	-16.6	-17.2	-22.9
2-Thienyl	-16.9	-17.5	-22.1
2-Furyl	-17.2	-17.8	-22.3
Phenyl	-17.2 [d]	-17.9	-22.3 [e]

[a] cisoid form[7] -15.0 p.p.m.; transoid form[7] -19.1 p.p.m. [b] lit.,[12] -14.7 p.p.m.
[c] high field signal due to enol form.[12] [d] lit.,[13,14] -16.7 p.p.m.
[e] lit.,[13] -20.7 p.p.m.

of **4b**. The upfield shifts of the resonance signals for the phosphoranes in deuterochloroform, relative to the chemical shifts of the corresponding compounds measured in deuterobenzene, are consistent with a greater contribution of the extended conjugated system (**4b**) to resonance hybrid in the more polar solvent. Such an effect would be enhanced by the ability of the deuterochloroform to specifically solvate the ylide through H- bonding with the enolate O atom. This interpretation of the solvent shift differs from that proposed for the solvent effect upon the ^1H chemical shifts of the conformationally mobile ethoxycarbonylmethylene-phosphoranes[10] and for the formylmethylene-phosphoranes,[7] in which it was suggested that the more polar solvent stabilized the *transoid* conformation. There is no evidence from the ^{31}P NMR spectra for the presence of the four-membered cyclic structure (**6**)[11] in either solvent.

The variation in the deshielding effect of the aryl substituent upon the phosphorous nucleus of the aroylmethylenephosphoranes is small and follows the order:

phenyl > 2-furyl > 2-thienyl > 1-methyl-2-pyrrolyl.

This order approximates to the expected inductive electron-withdrawing properties of the aryl rings and is the inverse of their mesomeric electron-donating ability. This implies that the non-coplanarity of the aryl ring with the P–C–CO plane, as indicated by X-ray measurements in the solid state for analogous compounds,[15] persists in solution. Both the inductive effect and the cross-conjugation of the CO group with the aryl ring and the carbanionic centre have a destabilizing effect upon the canonical structure **4b**, which would result in an upfield shift in the ^{31}P resonance. The effect was also reflected, to the lesser extent, in the variation of the ^1H chemical shifts of the methylene proton with the change of the aroyl substituent. However, the small range of the chemical shifts (δ 4.05–4.38 ppm) indicated that the overriding conjugative interaction for the simple acylmethylenephosphoranes is best represented by **4b**. This conclusion differs from that previously reached from a consideration of ^{13}C NMR data for alkoxycarbonylmethylene ylides,[16] but may be rationalized in terms of the greater conjugating ability of an acyl group, compared with that of an ester. The low C=O stretching frequencies observed for the α-acyl compounds[17] are also in agreement with the delocalized enolate anion structure.[18]

It has been reported previously that the rotamer ratio of alkoxycarbonylmethylenephosphoranes is sensitive to the steric bulk of alkyl groups, R^1, on the carbanionic centre,[7] although aryl substituents tend to stabilize the *cisoid* rotamer.[19,20] Consistent with these observations, each α-aryl-α-aroylmethylene-phosphorane exhibited only one ^{31}P resonance signal, which, by analogy with the simple aroylmethylene compounds, we have assigned to the *cisoid* isomer (Table 2). However, the introduction of the (hetero)aryl substituent at the α-position of the α-heteroaroylmethylenephosphoranes produced a distinct deshielding effect upon the phosphorus nucleus, when the spectra were measured in $CDCl_3$. The greatest effect was observed upon the introduction of the 2-furyl group (1.8–1.9 ppm), whilst the phosphorus nucleus of the corresponding 2-thienyl and 1-methyl-2-pyrrolyl derivatives was deshielded to a smaller extent (0.7–0.9 ppm). The smallest effect was observed for the α-phenyl compounds (0.2–0.3 ppm). In contrast to these observations, the introduction of a phenyl, 2-thienyl or 1-methyl-2-pyrrolyl group at the α-position of the benzoylmethylenephosphorane produced an *upfield* shift, whereas the 2-furyl derivative resonated at lower field.

Molecular models show that, for the *cisoid* rotomer, neither heterocyclic ring can lie in the same plane as the $\overset{+}{P}$–C=C–$\bar{O}$ system and the deshielding effects can be rationalized in terms of a reduction in the $d\pi - p\pi$ "back bonding" of the phosphorus atom with the delocalized π-system, as a result of the inductive electron-withdrawal by the α-heteroaryl substituents.[21,22] The "α-substituent effect" was less regular, when the spectra were measured in deuterobenzene but, in general, a deshielding effect was observed for all α-aryl derivatives, with the exception of the α-(2-furyl) compounds. It

Table 2. ^{31}P chemical shifts for (α-aroyl-α-arylmethylene)triphenylphosphoranes

Ar^1-C(=Ph_3P)-C(=O)-Ar^2		^{31}P Chemical Shift	
Ar^1	Ar^2	in $CDCl_3$	in C_6D_6
Phenyl	Phenyl	-16.0	-15.0
"	1-Methyl-2-pyrrolyl	-16.8	-16.2
"	2-Thienyl	-17.1	-16.5
"	2-Furyl	-17.5	-16.8
1-Methyl-2-pyrrolyl	Phenyl	-16.7	-
"	1-Methyl-2-pyrrolyl	-17.4	-16.9
"	2-Thienyl	-17.7	-17.8
"	2-Furyl	-18.1	-
2-Thienyl	Phenyl	-16.9	-
"	1-Methyl-2-pyrrolyl	-17.3	-16.2$_5$
"	2-Thienyl	-17.7	-17.3
"	2-Furyl	-18.7	-
2-Furyl	Phenyl	-17.6	-17.2
"	1-Methyl-2-pyrrolyl	-18.4	-17.8
"	2-Thienyl	-18.8	-18.7
"	2-Furyl	-19.1	-18.8

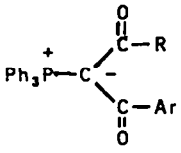
Table 3. ^{31}P chemical shifts of α-acetyl- and α-benzoylmethylenephosphoranes ($Ph_3P{=}CR^2{\cdot}COR^1$)

R^1	R^2	$\delta^{31}P$ in $CDCl_3$	Δ [a]
Me	H	-14.8	0
Me	acetyl	-16.8	-2.0
Me	1-methyl-2-pyrroloyl	-17.0	-2.2
Me	2-thenoyl	-17.9	-3.1
Me	2-furoyl	-17.8	-3.0
Me	benzoyl	-18.8	-4.0
Ph	H	-17.2	0
Ph	acetyl	-18.8	-1.6
Ph	1-methyl-2-pyrroloyl	-17.7	-0.5
Ph	2-thenoyl	-19.0	-1.8
Ph	2-furoyl	-19.1	-1.9
Ph	benzoyl	-19.0	-1.8

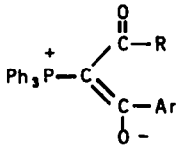
[a] $\Delta = \delta\ (R^2{=}\text{acyl}) - \delta\ (R^2{=}H)$

is probable that, with the destabilizing effect of the deuterobenzene upon canonical structure **4b**, the ylide structure **4a** becomes more important and partial rotation about the C–C bond of the $\overset{+}{P}$–$\bar{C}$–C=O system would allow a greater degree of mesomeric interaction with the heteroaryl rings.

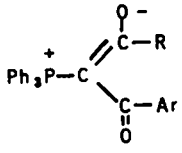
The introduction of a second α-acyl substituent to give the α,α-diacylmethylenephosphoranes had a significant deshielding effect upon the phosphorus nucleus (Table 3). The "α-acyl effect" had a greater influence upon the ^{31}P chemical shift of the α-acetylmethylenephosphoranes (2.0–4.0 ppm), compared with the α-benzoylmethylenephosphoranes (0.5–1.9 ppm). By analogy with the preferred conformation of the "free" anion of β-diketones,[23] the α,α-diacylmethylenephosphoranes would be expected to adopt the conformation (**7**). An inspection of molecular models, however, indicated that only one acyl group could conjugate effectively with the carbonionic centre.



7a



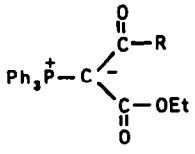
7b



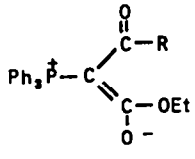
7c

The almost constant and small "α-acyl effect" observed for the benzoylmethylenephosphoranes and the relatively constant value for the ^{31}P chemical shifts of these derivatives is compatible with (**7c**, R = Ph) being the more important canonical structure. The "α-acyl deshielding effect" for these compounds consequently arises from the inductive electron-withdrawing effect of the twisted non-conjugating heteroaroyl group. This postulate is in accord with the observed preferential thermal fragmentation of the α-benzoyl-α-heteroaroylmethylenephosphoranes to give the 1-heteroaroyl-2-phenylethynes (Ar·CO·C≡C·Ph).[1] The larger and more variable "α-acyl effect" resulting from the introduction of heteroaroyl groups at the α-position of the acetylmethylenephosphorane indicated a greater degree of conjugation of the heteroaroyl group with the carbanionic centre and that both (**7b**, R=Me) and (**7c**, R=Me) are important canonical structures. This resonance stabilization is reflected in the almost equivalent yields of the 1-heteroarylbut-1-yn-3-ones (Ar·C≡C·CO·Me) and 1-heteroarylbut-3-yn-1-ones (Ar·CO·C≡C·Me), obtained upon thermal fragmentation of the α-acetyl-α-heteroaroylmethylenephosphoranes.[1]

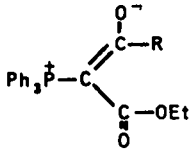
Similarly, the downfield shift of the ^{31}P resonance signals, observed upon the formation of the α-acyl derivatives of ethoxcarbonylmethylenephorane, can be attributed to a greater delocalization of the carbanionic charge. Hence, although steric hindrance prevents coplanarity of both the R group and the ester substituent with the $\overset{+}{P}$–C=C–$\bar{O}$ system, canonical structure (**8c**) would be expected to provide a major contribution to the resonance hybrid. By analogy with chemical shifts observed with the simple aroylmethylene compounds (Table 1), it is apparent that the aryl groups have essentially only an inductive electron-withdrawing influence on the system and the variation of the ^{31}P chemical shift with the change in the aryl group is negligible (Table 4).



8a



8b



8c

Table 4. ^{31}P chemical shifts for α-ethoxycarbonylmethylenetriphenylphosphoranes (Ph_3P=CR·CO_2Et)

R	$\delta^{31}P$ in $CDCl_3$	Δ [a]	Δ [b]
H	-17.0[c]	0	+3.3
acetyl	-18.1	-1.1	-3.3
benzoyl	-19.4	-2.4	-2.2
2-furoyl	-19.4	-2.4	-2.2
2-thenoyl	-19.4	-2.4	-2.5
1-methyl-2-pyrroloyl	-19.4	-2.4	-2.8

[a] Δ = δ (R=acyl)-δ (R=H)

[b] Δ = δ (Ph_3P=CR.CO_2Et)-δ (Ph_3P=CHR)

[c] lit.,[24] -16.8 p.p.m.

EXPERIMENTAL

^{31}P NMR spectra were recorded using a Varian XL-100 spectrometer operating at 40.48072 MHz at 36°C. Samples were prepared as *ca.* 0.5M solutions in either $CDCl_3$ or C_6D_6. Chemical shifts were measured relative to a 85% H_3PO_4 external standard. Infrared and ^1H NMR spectra data were obtained for all compounds described in this communication and are available from the authors.

Preparation of phosphonium salts. With the exception of the syntheses of the two compounds described, all the phosphonium salts were prepared by the methods described in the literature.[25-32] The m.ps were in agreement with previously recorded values and IR and ^1H NMR spectral data were compatible with the structures. (1-Methyl-2-pyrrolyl)triphenylphosphonium bromide, which has been isolated previously as its monohydrate,[29] was obtained in an anhydrous form, m.p. 224–225° (Found: C, 65.7; H, 5.4; N, 3.1. $C_{24}H_{23}BrNP$ requires: C, 66.0; H, 5.3; N, 3.2%).

(2-Thenoylmethyl)triphenylphosphonium chloride. 2-Chloroacetylthiophen[33] (5.7 g, 0.035 mol) and triphenylphosphine (9.2 g, 0.035 mol) in benzene (40 ml) were refluxed for 24 hr. The ppt was collected, washed with benzene (20 ml), and recrystallised from chloroform-hexane to give *(2-thenoylmethyl)triphenylphosphonium chloride*, (12.8 g, 80%) m.p. 222–224° (Found: C, 68.1; H, 4.9. $C_{24}H_{20}ClOPS$ requires: C, 68.2; 4.8%).

(1-Methyl-2-pyrroloyl)triphenylphosphonium chloride. 1-Methylpyrrole (9.7 g, 0.12 mol) and 2,6-lutidine (12.8 g, 0:12 mol) in $CHCl_3$ (60 ml) were added over a period of *ca.* 1.5 hr to a refluxing soln of chloroacetyl chloride (13.6 g, 0.12 mol) in $CHCl_3$ (60 ml). The mixture was refluxed for 2 hr and the solvent removed. Addition of ether to the residual oil gave a solid, which was collected and washed with ether (50 ml). The combined ether extracts were washed successively with 3N HCl (2 × 30 ml) and water (5 × 100 ml), dried ($MgSO_4$), and evaporated to give a yellow oil, which on trituration with petroleum-ether (40–60°) solidified to give 2-chloroacetylpyrrole (12 g, 65%), m.p. 48° [lit.[34], m.p. 47–48°].

The 2-chloroacetylpyrrole (6.5 g, 0.04 mol) was converted into *(1-methyl-2-pyrroloyl)triphenylphosphonium chloride* (11 g, 64%), m.p. 238–239° (Found: C, 71.2; H, 5.5; N, 3.4. $C_{25}H_{23}ClNOP$ requires: C, 71.5; H, 5.5; N, 3.3%) by a procedure analogous to that described above for the synthesis of the thiophen analogue.

Preparation of phosphoranes. The known acylmethylenephosphoranes were obtained from the corresponding phosphonium salts by methods described in the literature.[26,30,35-37] Their m.ps were in agreement with previously reported values[38] and IR and ^1H NMR spectral data were compatible with the expected values.

The hitherto unreported compounds were prepared by the following general procedures.

(α-Aroyl-α-arylmethylene)triphenylphosphoranes

The appropriate arylmethyltriphenylphosphonium chloride (0.03 mol) was added with stirring to freshly prepared NaOEt (0.03 mol) in benzene (100 ml) under N_2.[39] The mixture was stirred for 45 min at 45° and the EtOH was removed by azeotropic distillation. The appropriate aroyl chloride (0.015 mol) in benzene (10 ml) was added dropwise to the phosphorane at room temp. over a period of *ca.* 20 min and the mixture was stirred for a further 24 hr. The precipitated arylmethylphosphonium salt was removed, washed with benzene (20 ml), and the combined benzene extracts were evaporated to give an oil which upon trituration with hexane, crystallised to give the (α-aroyl-α-arylmethylene)triphenylphosphorane.

(α - Benzoyl - α - (1 - methyl - 2 - pyrrolyl)methylene)triphenylphosphorane (75%) m.p. 197–198° (Found: C, 80.5; H, 6.0; N, 2.9. $C_{31}H_{26}NOP$ requires: C, 81.0; H, 5.7; N, 3.1%).

(α - 2 - Furyl - α - 2 - thenoylmethylene)triphenylphosphorane (94%) m.p. 189°, dec. (Found: C, 76.6; H, 4.9. $C_{28}H_{21}O_3P$ requires: C, 77.0; H, 4.9%).

(α - 2 - Furoyl - α - 2 - thienylmethylene)triphenylphosphorane (92%) m.p. 177–179° (Found: C, 74.2; H, 4.5. $C_{28}H_{21}O_2PS$ requires: C, 74.3; H, 4.7%).

(α - 2 - Furoyl - α - (1 - methyl - 2 - pyrrolyl)methylene-triphenylphosphorane (73%), m.p. 232–233° (Found: C, 77.2; H, 5.3; N, 3.5. $C_{29}H_{24}NO_2P$ requires: C, 77.5; H, 5.4; N, 3.1%).

(α - 2 - Furyl - α - 2 - thenoylmethylene)triphenylphosphorane (94%), m.p. 196–197°, dec. (Found: C, 74.0; H, 4.8. $C_{28}H_{21}O_2PS$ requires: C, 74.3; H, 4.7%).

(α - 2 - Furoyl - α - phenylmethylene)triphenylphosphorane (98%), m.p. 218° (Found: C, 80.9; H, 5.3. $C_{30}H_{23}O_2P$ requires: C, 80.7; H, 5.2%).

(α - Phenyl - α - thenoylmethylene)triphenylphosphorane (97%), m.p. 221° (Found: C, 77.8; H, 5.1. $C_{30}H_{23}OPS$ requires: C, 77.9; H, 5.0%).

(α - (1 - Methyl - 2 - pyrroloyl) - α - phenylmethylene)triphenylphosphorane (94%), m.p. 195–196° (Found: C, 80.8; H, 5.9; N, 3.2. $C_{31}H_{26}NOP$ requires: C, 81.0; H, 5.7; N, 3.1%).

(α - Benzoyl - α - 2 - furylmethylene)triphenylphosphorane (99%), m.p. 192–193° (Found: C, 80.8; H, 4.9. $C_{30}H_{23}O_2P$ requires: C, 80.7; H, 5.2%).

(α - Benzoyl - α - 2 - thienylmethylene)triphenylphosphorane (95%), m.p. 208° (Found: C, 77.7; H, 5.2. $C_{30}H_{23}OPS$ requires: C, 77.9; H, 5.0%).

(α - 2 - Thenoyl - α - 2 - thienylmethylene)triphenylphosphorane (96%), m.p. 188–190° (Found: C, 71.4; H, 4.6. $C_{28}H_{21}OPS$ requires: C, 71.8; H, 4.5%).

(α - (1 - Methyl - 2 - pyrrolyl) - α - 2 - thenoylmethylene)triphenylphosphorane (71%), m.p. 216–218° (Found C, 74.9; H, 5.6; N, 2.7. $C_{29}H_{24}NOPS$ requires: C, 74.7; H, 5.2; N, 3.0%).

(α - 2 - Furyl - α - (1 - methyl - 2 - pyrroloyl)methylene)triphenylphosphorane (90%), m.p. 188° dec. (Found: C, 77.1; H, 5.2; N, 3.3. $C_{29}H_{24}NO_2P$ requires: C, 77.5; H, 5.4; N, 3.1%).

(α - (1 - Methyl - 2 - pyrroloyl) - α - 2 - thienylmethylene)triphenylphosphorane (81%), m.p. 162° dec. (Found: C, 74.4; H, 5.3; N, 2.8% $C_{29}H_{24}$ NOPS requires: C, 74.7; H, 5.2; N, 3.0%).

(α - (1 - Methyl - 2 - pyrroloyl) - α - (1 - methyl - 2 - pyrrolyl)methylenetriphenylphosphorane (100%), m.p. 227–228° dec. (Found: C, 77.9; H, 5.9; N, 5.9% $C_{30}H_{27}N_2OP$ requires: C, 77.9; H, 5.9; N, 6.1%).

(α - Acetyl - α - heteroaroylmethylene)triphenylphosphoranes

Ac_2O (2.34 g, 0.02 mol) was added with stirring at room temp. to the heteroaroylmethylenephosphorane[37,39] (0.002 mol) in $CHCl_3$ (10 ml) and the mixture was refluxed for 10 hr and the solvent removed to give the corresponding (α - acetyl - α - heteroaroylmethylene)triphenylphosphorane.

(α - Acetyl - α - 2 - furoylmethylene)triphenylphosphorane (82%), m.p. 177–178° (Found: C, 76.0; H, 5.0. $C_{26}H_{21}O_3P$ requires: C, 75.7; H, 5.1%).

(α - Acetyl - α - 2 - thenoylmethylene)triphenylphosphorane (89%), m.p. 169–170° (Found: C, 72.5; H, 5.1. $C_{26}H_{21}O_2PS$ requires: C, 72.8; H, 4.9%).

(α - Acetyl - α - (1 - methyl - 2 - pyrroloyl)methylene)triphenylphosphorane (85%), m.p. 174–175° (Found: C, 76.1; H, 5.8; N, 3.1. $C_{27}H_{24}NO_2P$ requires: C, 76.2; H, 5.9; N, 3.3%).

(α - (1 - Methyl - 2 - pyrroloyl) - α - propionylmethylene)triphenylphosphorane. The *propionylmethylenephosphorane* (74%), m.p. 172–174° dec. (Found: C, 76.4; H, 5.8; N, 2.9. $C_{28}H_{26}NO_2P$ requires; C, 76.5; H, 5.9; N, 3.1%) was prepared by an analogous procedure to that used for the synthesis of the corresponding acetyl derivative.

(α - Aroyl - α - ethoxycarbonylmethylenetriphenylphosphoranes

The appropriate aroyl chloride (0.0375 mol) in benzene (20 ml) was added with stirring at room temp. to ethoxycarbonylmethylenetriphenylphosphorane (26.1 g, 0.075 mol) in benzene (250 ml) over a period of *ca.* 20 min. The mixture was stirred at room temp. for 18 hr and the precipitated ethoxycarbonylmethyltriphenylphosphonium salt was removed and washed with benzene (20 ml). The combined benzene extracts were evaporated to give an oil, which crystallised slowly to yield the (α-aroyl-α-'ethoxycarbonylmethylene)triphenylphosphorane.

(α - Ethoxycarbonyl - α - 2 - thenoylmethylene)triphenylphosphorane (100%), m.p. 122.5–123° (Found: C, 70.6; H, 5.0. $C_{27}H_{23}O_3PS$ requires: C, 70.7; H, 5.1%).

(α - Ethoxycarbonyl - α - (1 - methyl - 2 - pyrroloyl)methylene)triphenylphosphorane (97%), m.p. 119–120° (Found: C, 73.6; H, 5.6; N, 2.9. $C_{28}H_{26}NO_3P$ requires: C, 73.8; H, 5.75; N, 3.1%).

(*α - Benzoyl - α - (1 - methyl - 2 - pyrroloyl)methylene)triphenylphosphorane.* (1 - Methyl - 2 - pyrroloyl)methylenetriphenylphosphorane (1.14 g, 0.003 mol) and benzoic anhydride (1.1 g, 0.005 mol) in $CHCl_3$ (15 ml) were refluxed for 12 hr. The solvent was removed and the residual oil extracted with petroleum ether (b.p. 60–80°, 5 × 15 ml) to remove the excess benzoic anhydride. Trituration of the residue with diethyl ether : hexane (1 : 1) gave (*α - benzoyl - α - (1 - methyl - 2 - pyrroloyl)methylene)triphenylphosphorane* (1.36 g, 93%), m.p. 211–214° (Found: C, 80.1, H, 5.4; N, 2.7. $C_{32}H_{26}NO_2P$ requires: C, 79.8, H, 5.3; N, 2.9%).

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[38]*α* - Acetyl - *α* - ethoxycarbonylmethylenetriphenylphosphorane was found to have m.p. 179–180° [lit.,[35] m.p. 172–174°] (Found: C, 73.6; H, 6.0. Calc. for $C_{24}H_{23}O_3P$: C, 73.8; H, 5.9%).
[39](1 - Methyl - 2 - pyrroloyl)methylenetriphenylphosphorane, obtained from the corresponding phosphonium chloride, had m.p. 183–184° (Found: C, 77.9; H, 5.8; N, 3.9. $C_{25}H_{22}NOP$ requires: C, 78.2; H, 5.8; N, 3.7%).