Conformational Analysis of Stabilized Phosphonium Ylides by ^{1}H Nuclear Magnetic Resonance Spectroscopy

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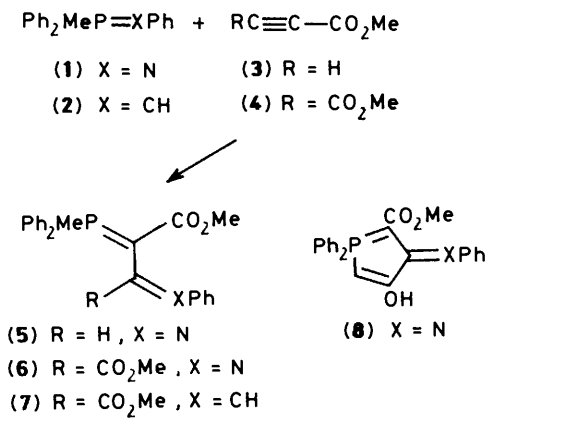
Rotational barriers ($\Delta G^{\ddagger}$) for methoxycarbonyl groups in methyl 4-hydroxy-1,1-diphenyl-3-[(*E*)-phenylimino]-3*H*-λ^5-phosphole-2-carboxylate (**8**) ($\Delta G^{\ddagger}$ = 62 ± 4 kJ mol^{-1}, T_c = 283 ± 5 K) and its synthetic precursor, dimethyl 2-(methyldiphenylphosphoranylidene)-3-phenyliminosuccinate (**6**) ($\Delta G^{\ddagger}$ = 45 ± 2 kJ mol^{-1}, T_c = 208 ± 5 K), as well as the related compounds, dimethyl 3-benzylidene-2-(methyldiphenylphosphoranylidene)succinate (**7**) ($\Delta G^{\ddagger}$ = 62 ± 3 kJ mol^{-1}, T_c = 278 ± 5 K) and methyl 2-(methyldiphenylphosphoranylidene)-3-phenyliminopropionate (**5**) ($\Delta G^{\ddagger}$ = 52 ± 2 kJ mol^{-1}, T_c = 243 ± 5 K), were determined by low-temperature ^{1}H n.m.r. Individual rotamers were identified and their n.m.r. signals assigned by means of low-temperature nuclear Overhauser effect (n.O.e.) studies on the ester (**5**). Protonation of the phenylimino derivatives (**5**) and (**6**) was found to occur at the nitrogen atom rather than at the phosphorane α-carbon atom.

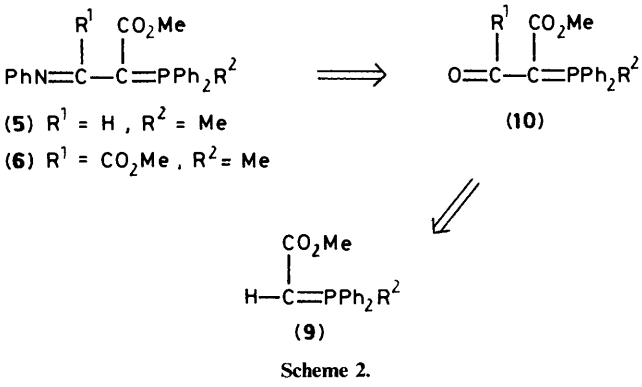
The reaction of phosphine imines (**1**) or phosphoranes (**2**) with dimethyl acetylenedicarboxylate (**4**) has been shown to yield 1:1 adducts (**6**) and (**7**) which upon treatment with potassium hydride can be converted into 3*H*-λ^5-phospholes such as (**8**) (Scheme 1). Similarly, reaction of the phosphine imine (**1**) with methyl propiolate (**3**) yielded the 1:1 adduct (**5**). The ylidic nature of the phosphole (**8**) was evidenced by low-temperature ^{1}H n.m.r. experiments, in which restricted rotation around the C(2)–CO_2Me bond was established.[1] This restricted rotation, due to partial double-bond character, has long been recognised in simple methoxycarbonylmethylenetriphenylphosphonium ylides (**9**), for which rotation barriers ($\Delta G^{\ddagger}$) in the range 71—77 kJ mol^{-1} have been found by variable-temperature ^{1}H n.m.r. studies.[2] On the other hand, up to four rotamers have been detected by ^{31}P n.m.r. at low temperatures in the case of tetramethyl 1,1,2-trimethoxy-2*H*-1λ^5-phosphole-2,3,4,5-tetracarboxylate, due to restricted rotation of both the C(3) and the C(5) ester groups,[3] which delocalize the ylide negative charge.

Compounds (**5**) and (**6**) can be regarded as masked tri-*P*-substituted 2-phosphoranylidene-3-oxoalkanoic esters (**10**), from which (**5**) and (**6**) would be formally derived by imine formation. α-Triphenylphosphoranylidene-β-oxocarboxylates (**10**) are routinely prepared[4] by acylation of phosphoranylideneacetates (**9**) (Scheme 2), and have recently found synthetic applications.[5] Structural studies on the highly functionalized phosphoranes (**10**), which are known to undergo protonation on the ketone carbonyl oxygen,[6,7] have led to the conclusion that neither the phosphorane (P=C) nor the zwitterion (P^+–C=C–O^-) canonical form could adequately explain the observed ^{13}C chemical shifts and ^{13}C–^{31}P coupling constants.[8] However, rotational isomerism in the ylides (**10**) has not been investigated previously, in spite of the number of conceivable restricted rotation processes, *viz.* ester or ketone delocalization of the ylide negative charge.

We report here a structural study of compounds (**5**)—(**8**), using low-temperature ^{1}H n.m.r., with the following targets: (i) distinguishing the type of restricted rotation process (ester or phenylimino or both: see Scheme 3); (ii) unambiguous identification of rotamers; and (iii) determination of the site of protonation.



Scheme 1.



Scheme 2.

Results and Discussion

The 80 MHz ^{1}H n.m.r. spectra of compounds (**5**)—(**8**) in $CDCl_3$ at 32 °C (Table 1) showed sharp singlets for the ester methoxy group of the P=C–CO_2Me moiety, indicating fast rotation of the ester group. This is in contrast to the behaviour of phosphoranes of type (**9**), which in our hands showed broad methoxy signals (sometimes two broad signals) at this

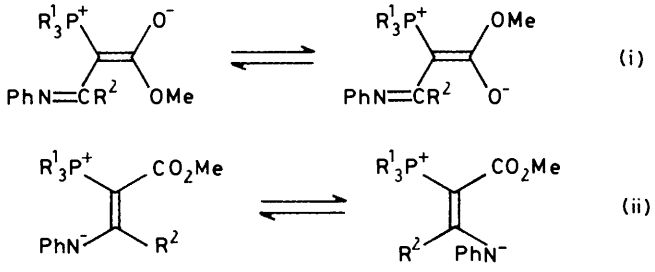
Table 1. Variable-temperature ^1H n.m.r. spectra (δ values) of compounds (**5**)—(**8**): coalescing signals of individual rotamers

		Fast rotation				Slow rotation								
						E-Rotamer					*Z*-Rotamer			
Cpd.	Solv.	*T*/K	$PCCO_2Me$	PMe	X=CH	*T*/K	%	$PCCO_2Me$	PMe	X=CH	%	$PCCO_2Me$	PMe	X=CH
(**5**)	$(CD_3)_2CO$	273	3.48	2.49	8.68	208	67.5 ± 2	3.53	2.49	8.60	32.5 ± 2	3.28	2.49	8.68
(**6**)	$CDCl_3$–Me_4Si	305	3.64	2.45		193	67 ± 5	3.67	2.34		33 ± 5	3.67	2.44	
(**7**)	$CDCl_3$	340	3.48	2.31	6.04	228	70 ± 2	3.61	2.40	5.95	30 ± 2	3.43	2.30	5.84
(**8**)	$CDCl_3$	305	3.19		4.29	263	2.5 ± 0.5	3.67		4.29	97.5 ± 0.5	3.19		4.29

Table 2. Determination of rotational barriers ($\Delta G^‡$) for compounds (**5**)—(**8**) at coalescence[a]

		P=C–CO_2Me signal					P–Me signal					X=C–H signal				
					$\Delta G^‡$/kJ mol^{-1}					$\Delta G^‡$/kJ mol^{-1}					$\Delta G^‡$/kJ mol^{-1}	
Cpd.	Solv.	T_c/K	Δp	Δf/Hz	$E \longrightarrow Z$	$Z \longrightarrow E$	T_c/K	Δp	Δf/Hz	$E \longrightarrow Z$	$Z \longrightarrow E$	T_c/K	Δp	Δf/Hz	$E \longrightarrow Z$	$Z \longrightarrow E$
(**5**)	$(CD_3)_2CO$	243 ± 3	0.35	19.4	53.1	51.8						233 ± 3	0.35	6.5	53.1	51.4
(**6**)	$CDCl_3$–Me_4Si						208 ± 5	0.34	7.7	46.8	45.6					
(**7**)	$CDCl_3$	278 ± 5	0.40	14.1	61.9	60.2	278 ± 5	0.40	7.6	63.5	61.4	268 ± 5	0.40	8.7	61.0	58.9
(**8**)	$CDCl_3$	283 ± 5	−0.95	38.3	65.6	58.5										

[a] Values of $\Delta G^‡$ determined according to the method of ref. 9; T_c, coalescence temperature for each signal; Δp, fractional population difference, as measured by integration at slow rotation; Δf, frequency separation at slow rotation of the two coalescing lines. Within the approximations stated in the introduction to the Experimental section, the $\Delta G^‡$ values thus calculated are valid at the coalescence temperature.



Scheme 3.

temperature. Only compound (**7**), lacking nitrogen in its structure, displayed a slightly broadened methoxy singlet at 32 °C.

A variable-temperature study of the spectra of compounds (**5**)—(**8**) revealed the data collected in Table 1. Thus, signal broadening, coalescence, and resolved signals corresponding to individual rotamers were successively observed for P=C–CO_2-Me and other groups. From the low-temperature spectra (slow rotation), integration of individual rotamer peaks yielded rotamer population differences (Δp). These data, together with the frequency separation (Δf) at slow rotation of the two merging peaks, as well as the coalescence temperature (T_c) allowed the calculation[9] of rotational barriers ($\Delta G^‡$) shown in Table 2.

As expected from the low coalescence temperatures, all $\Delta G^‡$ values found for compounds (**5**)—(**8**) were lower than those known for the ylides (**9**), but the barriers of the acyclic nitrogen-containing compounds (**5**) and (**6**) were significantly much lower (Table 2). In order to ascertain which of the two processes [(i) and (ii) in Scheme 3] was responsible for the hindered rotation observed in (**5**) and (**6**), a low-temperature n.O.e. difference experiment was performed on (**5**) by presaturating separately the methoxy singlet of each rotamer. Thus, in $(CD_3)_2CO$ solution, at −65 °C, selective irradiation at the frequency of the methoxy signal corresponding to the major rotamer at δ 3.53 resulted in a 2% n.O.e. enhancement (Figure) of the doublet at δ 8.60 (due to the azomethine proton of the major rotamer). This result showed that the configuration of the partial double bond between the carboxylate and the phosphorus-bearing carbon atoms was *E* (Scheme 4). On the other hand, a similar n.O.e. experiment performed by irradiation at the frequency of the minor methoxy singlet at δ 3.28 gave no enhancement at the minor azomethine doublet centred at δ 8.68. Therefore, the minor conformer should have the *Z*-configuration for the partial double bond.

The alternative possibility, *i.e.* fast rotation of the CO_2Me group and hindered rotation of the P=C–C=N moiety [Scheme 3, equation (ii)], was discarded because the coupling constants between the azomethine proton and the phosphorus atom were essentially equal for the two rotamers (26.9 Hz for the major, 26.4 Hz for the minor), contrary to what would have been expected for this alternative possibility. Indeed, it is well known that $^3J_{PH}$ follows a Karplus-type dependence on the torsion angle,[10] and in unsaturated systems, such as vinylphosphonium salts, the *cis*-coupling (17 ± 3 Hz) is considerably smaller than the *trans*-coupling (35 ± 5 Hz).[10] The value of this coupling constant in (**5**), almost the arithmetic average of the *cis*- and *trans*-couplings just mentioned, suggests a fast, unhindered rotation of the P=C–C=N moiety.

Similar low-temperature n.O.e. experiments could not be performed for compounds (**6**) and (**7**), in which the small frequency separation between the two signals of the ester methoxy groups prevented selective irradiations. Nonetheless, the partial double-bond character demonstrated for (**5**) was assumed to apply equally to (**6**) and (**7**). The similar chemical shifts and rotamer populations (Table 1) for the three compounds (**5**)—(**7**) support this view.

The case of the phosphole (**8**) is completely different. Thus, the minor rotamer population is only 2.5%, a value considerably smaller than the *ca.* 30% found for (**5**)—(**7**). A room-temperature n.O.e. experiment with irradiation at the ester methoxy signal of (**8**) at δ 3.19 gave a 0.25% n.O.e. enhancement of the signal due to the five *N*-phenyl protons at δ 7.0—7.35, and 0.3% n.O.e.

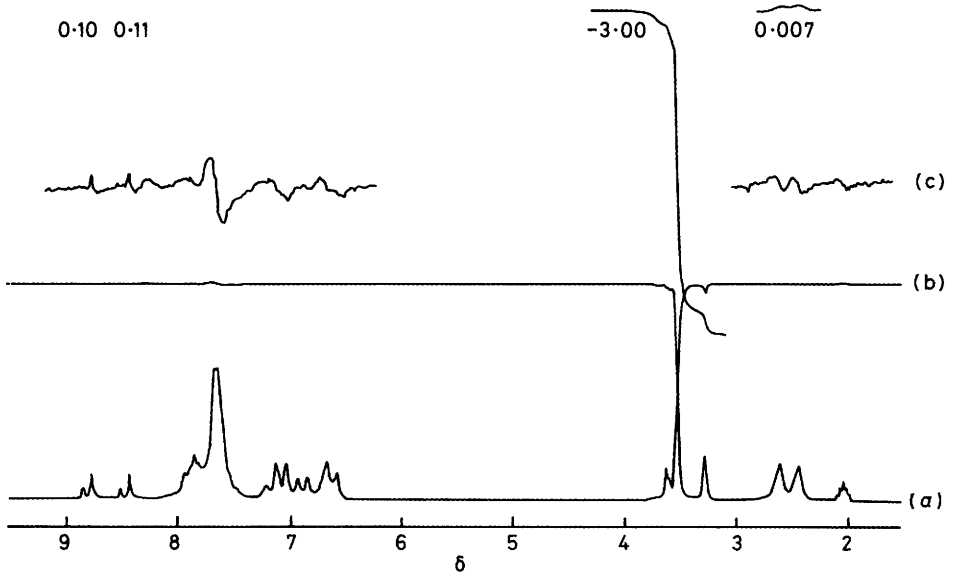
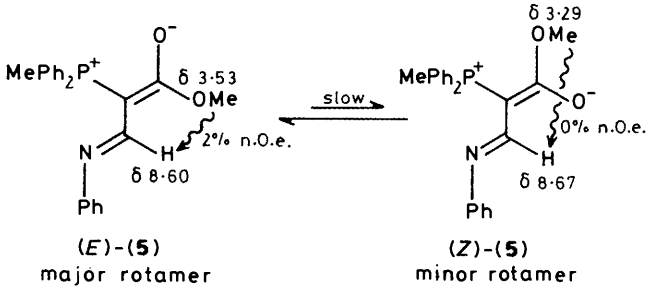
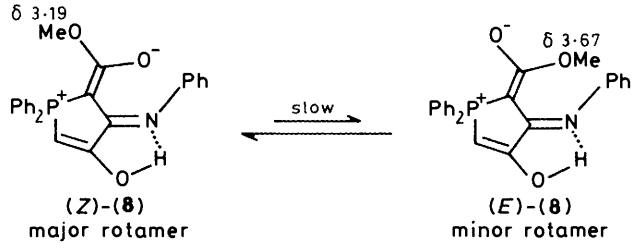


Figure. The 80 MHz ^{1}H n.m.r. and n.O.e. difference spectra of the phosphonium ylide (**5**) in $(CD_3)_2CO$ at −65 °C: (a) normal spectrum; (b) n.O.e. difference spectrum, irradiation at the major methoxy frequency; (c) same as (b), with 16-fold vertical expansion, to display the enhanced major azomethine proton doublet



Scheme 4.



Scheme 5.

enhancement of that due to the ten *P*-phenyl protons at δ 7.4—8.0. This result demonstrated the *Z*-configuration for the exocyclic C=N double bond, and suggested that steric hindrance between the methoxy and *N*-phenyl groups was responsible for the high population difference of the two rotamers (95%). Also, the downfield position (δ 3.67) of the ester methoxy signal in the spectrum of the minor rotamer of (**8**) gives additional support to the *Z*-configuration of the exocyclic C=N bond. Thus, the major rotamer was assigned the *Z*-configuration at the P^+–C=C(O^-)–OMe moiety, contrary to (**5**)—(**7**). In addition, the rather deshielded OH proton [δ 9.5 in $CDCl_3$ and 9.7 in $(CD_3)_2SO$] indicated an intramolecular hydrogen bond with the suitably oriented lone pair of the nitrogen atom (Scheme 5).

Having identified the major and minor rotamers of (**5**)—(**8**), we could compare their $\Delta G^{\ddagger}$ values (Table 2) with those of simple phosphoranes (**9**). The $\Delta G^{\ddagger}$ values for (**7**) (62 ± 3 kJ mol^{-1}) and (**8**) (62 ± 4 kJ mol^{-1}) are not markedly different from those of (**9**) (71—77 kJ mol^{-1}), and therefore indicate a similar amount of double-bond character (or electron delocalization from phosphorus). However, the values of (**5**) (52 ± 2 kJ mol^{-1}) and (**6**) (45 ± 2 kJ mol^{-1}) are considerably lower, which indicates less electron delocalization from phosphorus to the ester carbonyl, possibly due to competing delocalization to nitrogen.

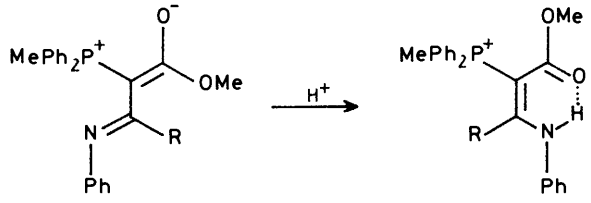
Addition of trifluoroacetic acid (TFA) confirmed this electron delocalization to nitrogen (Table 3). Thus, when TFA was added to (**7**) (which lacks nitrogen) in $CDCl_3$, the spectrum obtained was that of a typical phosphonium salt, with appearance of a new P^+–C–H doublet at δ 5.46 (*J* 17.6 Hz). A similar signal did not appear in the cases of (**5**) and (**6**), compounds which displayed major changes elsewhere in their spectra upon addition of TFA, particularly on the signals of the methine proton of (**5**), the β-ester methoxy group of (**6**) and the *ortho* *N*-phenyl protons of both (Table 3). If we recall that (**5**) and (**6**) are nitrogen analogues of α-phosphoranylidene-β-oxoesters (**10**) and that protonation of (**10**) is known to proceed at the ketone oxygen atom,[6,7] protonation of (**5**) and (**6**) on nitrogen could explain the observed shifts. Furthermore, this *N*-protonated form may be stabilized by an intramolecular hydrogen bond with the carbonyl oxygen atom (Scheme 6). Moreover, even on cooling well below the coalescence temperatures, after addition of TFA hindered rotation processes could no longer be detected for (**5**) and (**6**), as required by this *N*-protonation hypothesis.

Careful addition of a trace of TFA to the phosphole (**8**) in $CDCl_3$ at room temperature produced broadening of both the P=C–H doublet at δ 4.29 and the chelated OH signal at 9.5, indicating acceleration of the keto–enol tautomerism. The methoxy signal at δ 3.17 was also broadened in the presence of a trace of TFA. Further addition of an excess of TFA resulted in splitting of the methoxy absorption into two broad signals, at δ 3.2 (minor) and 3.8 (major), which upon heating at 80 °C merged into a broad singlet at δ 3.7, the same chemical shift as observed for (**5**)—(**7**) in the presence of TFA. No P^+–C–H signal at *ca.* 5.5 was observed, as opposed to the case of (**7**). All these facts indicate that protonation of (**8**) resulted in one or more of the following processes: (i) fast keto–enol tautomeriz-

Table 3. Addition of TFA to compounds (**5**)—(**8**) in $CDCl_3$ (figures in parentheses are coupling constants in Hz)

	Compound							
	(**5**)	(**5**)/TFA	(**6**)	(**6**)/TFA	(**7**)	(**7**)/TFA	(**8**)	(**8**)/TFA
P=C-CO_2Me	3.58	3.70	3.64	3.70	3.50	3.47	3.17	3.70[a]
X=C-CO_2Me			3.60	2.60	3.57	3.81		
P-C_6H_5	7.4—7.9	7.5—8.0	7.5—8.0	7.5—8.0	7.4—7.9	7.5—8.0	7.4—8.0	7.6—8.0
X-C_6H_5	6.7—7.2	6.8—7.2	6.3—7.1	7.0—7.5	6.8—7.2	6.8—7.3	7.0—7.35	7.1—7.6
P-CH_3	2.49	2.63	2.45	2.5	2.32	2.75		
(*J*)	(13.7)	(13.6)	(13.4)		(13.1)	(13.6)		
=C-H	8.68	11.20			5.97	7.05	4.29	
(*J*)	(26.6)	(13.6)			(2.9)	(4.3)	(26.6)	
P^+-C-H						5.46		
(*J*)						(17.6)		

[a] At 80 °C.



(**5**) R = H

(**6**) R = CO_2Me

Scheme 6.

ation, with exchange between the P^+-CH_2CO protons and the excess of TFA; (ii) inversion of the C=N-Ph system from the *Z*- to the *E*-configuration; and (iii) *N*-protonation with formation of an intramolecular hydrogen bond from the N-H to the ester carbonyl. The number of possible processes which could be brought about simultaneously by protonation of (**8**) does not allow their separate study.

Experimental

Room-temperature 80 MHz ^1H and 20 MHz ^{13}C n.m.r. spectra were taken at 32 °C, in the Fourier transform mode, using a Bruker WP 80 SY spectrometer, equipped with a 5 mm switchable $^1H/^{13}C$ dual probe, under Aspect 2000 computer control, and are referenced to internal Me_4Si. Variable-temperature spectra were obtained under BVT-1000 control. Temperatures were calibrated against methanol peak separation.[11] Solutions of sample (2—5 mg) in $CDCl_3$ or $(CD_3)_2CO$ (0.5 ml) were used for ^1H spectra. Nuclear Overhauser effect spectra, at room temperature or below, were obtained by interleaved acquisition of on-resonance-irradiated and off-resonance-irradiated free induction decays (240—800 total scans, recycled every 8 scans), using a decoupling excitation bandwidth γB_2 = 2 Hz, as described elsewhere,[12] with standard Bruker software. ^{31}P N.m.r. spectra were recorded with a Varian FT 80 instrument, at 32.38 MHz, and are referenced to 85% H_3PO_4. Mass spectra were recorded under electron impact (70 eV), using a Hewlett-Packard 5930A spectrometer. Elemental analyses were determined at Universidad de Oviedo, using a Perkin-Elmer 240 apparatus.

Calculation of rotational barriers ($\Delta G^{\ddagger}$) did not require the use of complete lineshape analysis methods,[13] because the case of exchange between two unequally populated sites can be adequately treated by simple methods,[9] developed as an extension to the case of exchange between two equally populated sites. Application of this simple method requires: (i) a single path for the exchange (interconversion); (ii) absence of coupling between the exchanging sites; (iii) equal linewidths for the exchanging lines in the slow exchange limit; and (iv) negligible linewidths as compared with frequency differences Δf. All these conditions were met in the cases of compounds (**5**)—(**8**). Chemical shift differences and rotamer populations should also be independent of temperature, which is not always the case. In this paper we have assumed this temperature independence.

Methyl 3-Phenylimino-2-(methyldiphenylphosphoranylidene)propionate (**5**).—To a solution of methyldiphenylphosphine *N*-phenylimide[14] (1.455 g, 5 mmol) in dichloromethane (25 ml) at 25 °C and under argon was added methyl propiolate (0.49 g, 5 mmol). Reaction was complete after 4 h. Solvent removal (by distillation) afforded an oil, which was purified by column chromatography (silica gel; ether). Recrystallization yielded the *ester* (**5**) (1.7 g, 88%), m.p. 146—147 °C (from hexane–dichloromethane) Found: C, 73.8; H, 5.6; N, 3.9. $C_{23}H_{22}NO_2P$ requires C, 73.6; H, 5.9; N, 3.7%); $\nu_{max.}$(KBr) 1 650, 1 300, and 1 100 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 8.68 (1 H, d, $^3J_{PH}$ 26.6 Hz, N=C-H), 7.9—7.4 (10 H, m, P-C_6H_5), 7.17—6.70 (5 H, m, N-C_6H_5), 3.58 (3 H, s, CO_2CH_3), and 2.49 (3 H, d, $^2J_{PH}$ 13.7 Hz, P-CH_3); δ_C (20 MHz; $CDCl_3$) 169.3 (d, $^2J_{PC}$ 16.8 Hz, C=O), 159.9 (d, $^2J_{PC}$ 6.0 Hz, C-N), 153.8—120.3 (18 C, arom.), 60.4 (d, $^1J_{PC}$ 115.7 Hz, P=*C*-CO_2Me), 49.8 (CO_2-CH_3), and 13.8 (d, $^1J_{PC}$ 62.5 Hz, P-CH_3); δ_P (32.38 MHz; $CDCl_3$) +13.4 p.p.m.; *m/z* 375 (M^+, 82%).

Dimethyl 3-Phenylimino-2-(methyldiphenylphosphoranylidene)succinate (**6**).—To a solution of methyldiphenylphosphine *N*-phenylimide (1.455 g, 5 mmol) in dichloromethane (25 ml) at 25 °C and under argon was added dimethyl acetylenedicarboxylate (0.71 g, 5 mmol). Reaction was complete after 4 h. Solvent removal (by distillation) afforded an oil, which was purified by column chromatography (silica gel; ether). Recrystallization yielded the *diester* (**6**) (1.7 g, 82%), m.p. 119—120 °C (from hexane–dichloromethane) (Found: C, 69.4; H, 5.6; N, 3.5. $C_{25}H_{24}NO_4P$ requires C, 69.3; H, 5.6; N, 3.2%); $\nu_{max.}$(KBr) 1 740, 1 660, 1 220, and 1 090 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 8.0—7.5 (10 H, m, P-C_6H_5), 7.10—6.70 (3 H, m, *meta*/*para* N-C_6H_5), 6.30 (2 H, d, *J* 8 Hz, *ortho* N-C_6H_5), 3.64 (3 H, s, P=C-CO_2CH_3), 3.60 (3 H, s, N=C-CO_2CH_3), and 2.45 (3 H, d, $^2J_{PH}$ 13.4 Hz, P-CH_3); δ_C (20 MHz; $CDCl_3$) 167.5 (d, $^2J_{PC}$ 16.8 Hz, P=C-*C*O_2Me), 165.5 (d, $^3J_{PC}$ 13.0 Hz, N=C-*C*O_2Me), 159.7 (d, $^2J_{PC}$ 7.0 Hz, C=N), 149.9—119.9 (18 C, arom.), 59.4 (d, $^1J_{PC}$ 118.4 Hz, P=*C*-CO_2Me), 50.4 (P=C-CO_2CH_3), 49.3 (N=C-CO_2CH_3), and 13.7 (d, $^1J_{PC}$ 63.4 Hz, P-CH_3); δ_P (32.38 MHz; $CDCl_3$) +24.2 p.p.m.; *m/z* 433 (M^+, 13%) and 374 (100%).

Dimethyl 3-Benzylidene-2-(methyldiphenylphosphoranylidene)succinate (**7**).—To a solution of benzylidenemethyldiphenylphosphorane [generated *in situ* by addition of Bu^nLi (5 mmol) to benzylmethyldiphenylphosphonium bromide (1.855 g, 5 mmol) in THF (25 ml)] at 25 °C and under argon was added dimethyl acetylenedicarboxylate (0.71 g, 5 mmol). After 6 h vigorous stirring, the mixture was quenched with ice–water, extracted with dichloromethane, and dried (Na_2SO_4). Evaporation under reduced pressure afforded an oil, which after recrystallization from hexane–dichloromethane yielded the *diester* (**7**) (1.8 g, 86%), m.p. 135—136 °C (decomp.) (Found: C, 72.55; H, 5.7. $C_{26}H_{25}O_4P$ requires C, 72.2; H, 5.8%); $\nu_{max.}$(KBr) 1 730, 1 700, 1 240, and 1 110 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 7.9—7.4 (10 H, m, P–C_6H_5), 7.2—6.8 (5 H, m, C–C_6H_5), 5.97 (1 H, d, $^4J_{PH}$ 2.9 Hz, C=C–H), 3.57 (3 H, s, C=C–CO_2CH_3), 3.50 (3 H, s, P=C–CO_2CH_3), and 2.32 (3 H, d, $^2J_{PH}$ 13.1 Hz, P–CH_3); δ_C (20 MHz; $CDCl_3$) 171.1 (d, $^3J_{PC}$ 7.8 Hz, C=C–CO_2Me), 168.2 (d, $^2J_{PC}$ 17.1 Hz, P=C–CO_2Me), 136.3—124.9 (18 C, arom.), 50.2 (C=C–CO_2CH_3), 48.7 (P=C–CO_2CH_3), 48.1 (d, $^1J_{PC}$ 104.5 Hz, P=C–CO_2Me), and 12.7 (d, $^1J_{PC}$ 65.2 Hz, P–CH_3); δ_P (32.38 MHz; $CDCl_3$) +16.7 p.p.m.; *m/z* 432 (M^+, 22%) and 200 (100%).

4-Hydroxy-2-methoxy-1,1-diphenyl-3-[(E)-phenylimino]-3H-λ^5-phosphole (**8**).—A mixture of (**6**) (2.165 g, 5 mmol) and potassium hydride (5 mmol) was warmed at 50 °C in THF during 6 h. Then, methanolysis and aqueous work-up afforded a solid, which was recrystallized from hexane–dichloromethane, yielding the phosphole (**8**) (1.8 g, 91%), m.p. 199—200 °C (Found: C, 71.7; H, 5.0; N, 3.2. $C_{24}H_{20}NO_3P$ requires C, 71.8; H, 5.0; N, 3.5%); $\nu_{max.}$(KBr) 3 180, 1 660, 1 620, 1 340, and 1 110 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 9.5 (1 H, br s, OH), 8.0—7.4 (10 H, m, P–C_6H_5), 7.35—7.0 (5 H, m, N–C_6H_5), 4.29 (1 H, d, $^2J_{PH}$ 26.6 Hz, H-5), and 3.17 (3 H, s, CO_2CH_3); δ_C (20 MHz; $CDCl_3$) 172.5 (d, $^2J_{PC}$ 29.1 Hz, C-4), 162.9 (d, $^2J_{PC}$ 12.6 Hz, CO_2Me), 158.4 (d, $^2J_{PC}$ 29.1 Hz, C-3), 138.6—122.8 (18 C, arom.), 73.4 (d, $^1J_{PC}$ 110.2 Hz, C-2), 60.7 (d, $^1J_{PC}$ 114.1 Hz, C-5), and 50.2 (CO_2CH_3); δ_P (32.38 MHz; $CDCl_3$) +23.9 p.p.m.; *m/z* 401 (M^+, 100%).

Acknowledgements

One of us (F. S.-F.) thanks Fundación María Francisca de Roviralta for funding which allowed the purchase of the 80 MHz n.m.r. spectrometer, and Direcció General d'Ensenyament Universitari, Generalitat de Catalunya for the n.m.r. data system.

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Received 21*st July* 1987; *Paper* 7/1314