The Chemistry of Heteroarylphosphorus Compounds. Part VI.[1] Alkaline Hydrolysis of 1-Methylpyrrol-2-yl- and 1-Methylpyrrol-2-ylmethyl-phosphonium Salts. A Comparison with 2-Furyl, 2-Thienyl, Phenyl, and Related Heteroarylmethyl and Benzyl Derivatives. Relative Stabilities of Forming Carbanions

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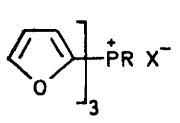
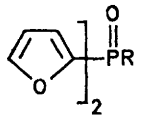
Studies of the products of alkaline hydrolysis of phenyl- and benzyl-phosphonium salts bearing 1-methylpyrrol-2-yl substituents show that while the forming 1-methylpyrrol-2-yl carbanion is more stable than the forming phenyl carbanion, in contrast to the 2-furyl and 2-thienyl analogues it is less stable than the forming benzyl carbanion. The order of cleavage of heteroaryl substituents from phosphorus is established as 2-thienyl > 2-furyl > benzyl > 1-methylpyrrol-2-yl > phenyl. Kinetic studies show that methyltris-1-methylpyrrol-2-ylphosphonium iodide (VII) undergoes hydrolysis considerably more slowly than the 2-furyl- and 2-thienyl analogues, but slightly faster than methyltriphenylphosphonium iodide. The ability of the 1-methylpyrrol-2-yl substituent to stabilise a forming negative charge on an adjacent carbon has been investigated by studies of the kinetics of hydrolysis of (1-methylpyrrol-2-ylmethyl)triphenylphosphonium iodide (XI). Comparison of the rate data with those for the 2-furylmethyl-, 2-thenyl-, and benzyl analogues indicates that the relative order of stability of the forming 2-heteroarylmethyl carbanions is 2-furylmethyl > 2-thenyl > benzyl > 1-methylpyrrol-2-ylmethyl.

RECENTLY we have shown that the 2-furylphosphonium salts (I; R = Me or $PhCH_2$, X = I or Br) undergo alkaline hydrolysis with loss of furan to form the oxides (II; R = Me or $PhCH_2$) *ca.* 10^{11} times faster than the analogous hydrolysis of methyltriphenylphosphonium iodide. Furthermore, the 2-furylphosphonium salts undergo hydrolysis *ca.* 10^2—10^3 times faster than the corresponding 2-thienylphosphonium salts (III; R = Me or $PhCH_2$, X = I or Br) which similarly yield thiophen and the oxides (IV; R = Me or $PhCH_2$).[2,3]



(I)



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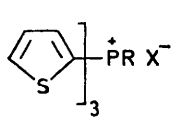

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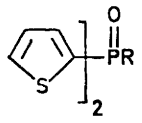

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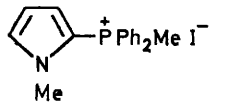
We have attributed the greater rate of hydrolysis of the heteroarylphosphonium salts to the greater electron-withdrawing character of the heteroaryl substituents, which cause increases in the equilibrium constants K_1 and K_2 of the pre-equilibria involved in the hydrolysis



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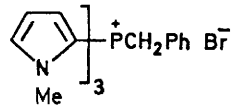


(VI)

reactions; in addition, the heteroaryl carbanions eliminated in the rate-determining step are more stable than phenyl and benzyl carbanions. Furthermore we have shown that although the forming 2-thienyl carbanion is more stable than the forming 2-furyl analogue, the 2-furylphosphonium salts undergo hydrolysis at a faster rate due to the effect of the more strongly electron-withdrawing 2-furyl substituent on the position of the pre-equilibria.[1] We now report an extension of our studies to an investigation of the hydrolysis of phosphonium salts (V) and (VI) bearing 1-methylpyrrol-2-yl substituents.

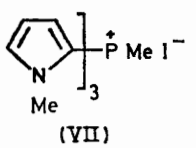
The relative stability of the forming 1-methylpyrrol-2-yl carbanion compared to phenyl and benzyl has been investigated by a study of the products of hydrolysis of the salts (V) and (VI). Alkaline hydrolysis of the salt

[1] Part V, D. W. Allen, S. J. Grayson, I. Harness, B. G. Hutley, and I. W. Mowat, *J.C.S. Perkin II*, 1973, 1912.
[2] D. W. Allen, *J. Chem. Soc.* (*B*), 1970, 1491.
[3] D. W. Allen, B. G. Hutley, and M. T. J. Mellor, *J.C.S. Perkin II*, 1972, 63.

(V) occurs with exclusive loss of 1-methylpyrrole to form methyldiphenylphosphine oxide, indicating that the forming 1-methylpyrrol-2-yl carbanion is more stable than the forming phenyl carbanion.

However, in the hydrolysis of the salt (VI), both toluene and 1-methylpyrrole are formed, in a 3 : 2 molar ratio. Allowing for statistical effects, it would appear that the relative stabilities of the forming benzyl and 1-methylpyrrol-2-yl carbanions are of the order of 4 : 1. The course of hydrolysis of the salt (VI) contrasts with those of the corresponding 2-furyl- and 2-thienyl-phosphonium salts (I and III; R = $PhCH_2$, X = Br), both of which proceed with exclusive loss of the heterocyclic substituents. Thus it would appear that the forming 1-methylpyrrol-2-yl carbanion is more stable than the forming phenyl carbanion, but less stable than the forming benzyl carbanion. The established order of cleavage of heteroaryl substituents with reference to phenyl and benzyl is therefore 2-thienyl > 2-furyl > benzyl > 1-methylpyrro-2-yl > phenyl.

In comparing the ability of the heterocyclic systems to stabilise the forming negative charge in the 2-position, it is necessary to consider both the σ- and π-electron systems of each ring. For each heterocyclic carbanion, the adjacent electronegative atom will stabilise the forming negative charge by a σ-inductive effect, and the marked difference in stability of the forming 1-methylpyrrol-2-yl carbanion compared to the 2-furyl- and 2-thienyl analogues must have its origin in the π-systems of the heterocycles. It has been shown recently that in furan and thiophen, the σ-electronic inductive effect of the heteroatom outweighs the π-electron moment (which increases electron density on the ring carbon atoms) and that the direction of the overall dipole moment is from the ring to the heteroatom. In contrast, in pyrrole systems, the π-moment predominates and the direction of the dipole moment is from the heteroatom to the ring.[4,5] Indeed, it would appear that in the forming 2-furyl and 2-thienyl carbanions, the σ-inductive effect predominates to stabilise the forming negative charge to a greater extent than in the resonance stabilisation of the forming benzyl carbanion. In the case of the forming 1-methylpyrrol-2-yl carbanion, the π-moment of the heterocycle directs electron density to the 2-position, thereby destabilising the forming negative charge at that position. That the latter is more stable than the phenyl carbanion, however, can only be due to the σ-inductive effect of the nitrogen atom.



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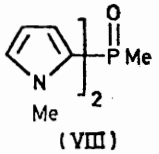


(VIII)

We have also studied the kinetics of alkaline hydrolysis of the salt (VII) in solution in aqueous ethanol; the salt (VII) [like the 2-thienyl analogue (III; R = Me, X = I)] underwent hydrolysis according to a third-order rate law, in accordance with the generally accepted mechanism for the alkaline hydrolysis of phosphonium salts,[6] with loss of the heterocycle, to form the oxide (VIII). The rate data for this reaction, together with that for the hydrolysis of the analogous 2-furyl-, 2-thienyl-, and phenyl-phosphonium salts, are given in Table 1.

TABLE 1

Third-order rate constants and activation parameters for the alkaline hydrolysis of phosphonium salts in aqueous ethanol (50% v/v)

$R_3PCH_3\ I^-$	Temp. (°C)	k_{obs}/ $l^2\ mol^{-2}\ min^{-1}$	E_A/ kJ mol^{-1}
R = 1-Methylpyrrol-2-yl	70	3·21	86·3
	60	1·29	
R = Ph	60	0·27 *	131·2
R = 2-Thienyl	60	$8·3 \times 10^7$ *	60·8
R = 2-Furyl	60	*ca.* 10^{10} †	

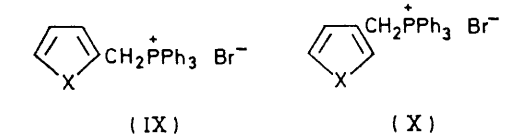
* Calculated from data in ref. 2. † Calculated from data in ref. 3.

The rate data reveal several features of interest. At 60°, methyltris-(1-methylpyrrol-2-yl)phosphonium iodide (VII) undergoes hydrolysis approximately five times more rapidly than methyltriphenylphosphonium iodide, the increase in rate being accompanied by a decrease in the energy of activation for the reaction. A comparison with the rate data for the corresponding 2-furyl- and 2-thienyl-phosphonium salts shows that the overall rates of hydrolysis for the above series of phosphonium salts decrease in the order 2-furyl > 2-thienyl > 1-methylpyrrol-2-yl > phenyl, the relative rates being of the order of $10^{11} : 10^8 : 5 : 1$. The above rate data clearly illustrate the major difference in electronic character between the 1-methylpyrrol-2-yl substituent and the other 2-heteroaryl substituents, which influences both the position of the pre-equilibria in the hydrolysis reaction, and the rate of the step in which the heterocycle is cleaved from phosphorus to form a carbanion. As indicated above, although the forming 1-methylpyrrol-2-yl carbanion is less stable than the other 2-heteroaryl carbanions, it is nevertheless more stable than the forming phenyl carbanion, and this will lead to an increase in the rate of the cleavage step of the reaction, relative to the phenyl derivative. However, it is more difficult to assess the effect of the 1-methylpyrrol-2-yl substituent on the position of the pre-equilibria on the reaction. It would seem reasonable to assume that the 1-methylpyrrol-2-yl group will behave as an overall electron-donating substituent, compared to 2-furyl, 2-thienyl, and phenyl. Thus pyrrolecarboxylic acids are weaker acids than benzoic acid, whereas furan- and thiophen-carboxylic acids are stronger.[4,7] Furthermore, we have shown that whereas

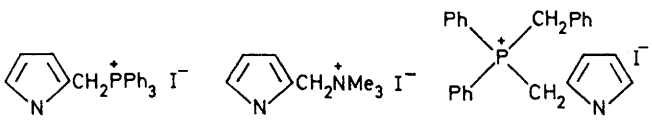
[4] G. Marino, *J. Heterocyclic Chem.*, 1972, **9**, 817.
[5] T. J. Barton, R. W. Roth, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1972, **94**, 8854.
[6] W. E. McEwen, G. Axelrad, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1965, **87**, 3948.
[7] G. Marino, *Adv. Heterocyclic Chem.*, 1971, **13**, 242 and references therein.

the diethyl ester of 2-furylphosphonic acid undergoes alkaline hydrolysis faster than diethyl phenylphosphonate, the corresponding ester of 1-methylpyrrol-2-ylphosphonic acid undergoes hydrolysis more slowly than diethyl phenylphosphonate.[8] It would seem likely, therefore, that the position of the pre-equilibria involved in the alkaline hydrolysis of the above phosphonium salts will lie further to the right for the phenyl compound than for the 1-methylpyrrol-2-yl analogue. Thus, since the forming 1-methylpyrrol-2-yl carbanion is more stable than the phenyl carbanion, this factor alone must be dominant in determining the relative rates of hydrolysis of the phenyl- and 1-methylpyrrol-2-yl-phosphonium salts.

We have also recently reported a study of the kinetics of alkaline hydrolysis of a series of heteroarylmethyltriphenylphosphonium halides (IX and X; X = O or S, which on hydrolysis give triphenylphosphine oxide and the respective methyl-substituted heterocycle.[9] The rate data were discussed in terms of the electron-withdrawing nature of the heteroaryl substituent and the relative stability of the forming 2-heteroarylmethyl carbanions.



(IX) (X)



(XI) (XII) (XIII)

While the rate data indicated that the transition state leading to the 3-thenyl carbanion is more stable than that for the formation of the 3-furylmethyl analogue, and that both the above 3-heteroarylmethyl carbanions are less stable than the forming benzyl carbanion, it did not allow an unambiguous assignment of the relative stabilities of the 2-furylmethyl, 2-thenyl, and benzyl carbanions. This problem was resolved by an investigation of the products of hydrolysis of a series of salts in which competitive loss of the benzyl and/or 2-heteroarylmethyl groups could occur.[1] The relative amounts of the respective hydrocarbons formed on hydrolysis indicated that the forming 2-furylmethyl carbanion is marginally more stable than the 2-thenyl analogue, and that both 2-heteroarylmethyl carbanions are more stable than the benzyl carbanion. In order to investigate the effect of the 1-methylpyrrol-2-ylmethyl substituent on the stability of a forming negative charge on an adjacent carbon atom, we have studied the kinetics of alkaline hydrolysis of the salt (XI).

The salt (XI) was prepared by the reaction of the methiodide (XII) with triphenylphosphine in refluxing absolute ethanol. On alkaline hydrolysis, the salt (XI) gave triphenylphosphine oxide and 1,2-dimethylpyrrole. A kinetic study of the hydrolysis reaction showed that the usual third-order rate law was followed, and the rate data indicated that the hydrolysis of (XI) proceeded at a slightly slower rate than that of benzyltriphenylphosphonium bromide, the relative rates being 1 : 1·2 respectively. The rate data and activation parameters for the hydrolysis of (XI), together with the data for other heteroarylmethyltriphenylphosphonium salts and benzyltriphenylphosphonium bromide are given in Table 2.

TABLE 2

Third-order rate constants and activation parameters for the alkaline hydrolysis of heteroarylmethyltriphenylphosphonium salts in aqueous ethanol (50% v/v; 0·1M in KCl)

Compound $Ph_3P^+RX^-$	Temp. (°C)	k_{obs}/ l² mol⁻² min⁻¹	E_A/ kJ mol⁻¹
R = 1-Methylpyrrol-2-ylmethyl; X = I⁻	50	16·6	80·6
	40	6·0	
R = Benzyl; X = Br⁻	40	7·2	76·2 *
R = 2-Thenyl; X = Br⁻	40	183·3	70·3 *
R = 2-Furylmethyl; X = Br⁻	40	356·5	64·3 *
R = 3-Thenyl; X = Br⁻	40	3·64	86·9 *
R = 3-Furylmethyl; X = Br⁻	40	2·95	101·8 *

* Data taken from ref. 9.

From the data in Table 2 it can be seen that the rates of hydrolysis of the heteroarylmethyltriphenylphosphonium halides relative to the benzyl analogue decrease in the order: 2-furylmethyl > 2-thenyl > benzyl > 1-methylpyrrol-2-ylmethyl > 3-thenyl > 3-furylmethyl. The decrease in rate is accompanied by a steady increase in the energies of activation for the reactions.

As shown in the above discussion of the relative stabilities of the forming benzyl, 2-furylmethyl, and 2-thenyl carbanions, the rate data do not allow us to decide unambiguously on the relative stabilities of the forming 1-methylpyrrol-2-ylmethyl and benzyl carbanions, since the contribution of the pre-equilibrium constants to the overall rate constants is difficult to assess. In order to resolve this point, we have investigated the products of hydrolysis of the salt (XIII). This was prepared in a similar manner to (XI) by the reaction of benzyldiphenylphosphine and the methiodide (XII), in refluxing ethanol. Alkaline hydrolysis of (XIII) gives toluene and 1,2-dimethylpyrrole in a 2·4 : 1 molar ratio, indicating that the forming benzyl carbanion is more stable than the 1-methylpyrrol-2-ylmethyl carbanion. Thus the relative order of stability of carbanions of this type is: 2-furylmethyl > 2-thenyl > benzyl > 1-methylpyrrol-2-ylmethyl. This order again illustrates the very considerable differences in electronic character of these simple heterocyclic systems. Clearly the effect of the electronegative heteroatoms in the 2-furylmethyl and 2-thenyl carbanions completely outweighs the greater possibilities of mesomeric delocalisation in the benzyl case, whereas the overriding effect of the 1-methylpyrrol-2-yl substituent

[8] D. W. Allen, B. G. Hutley, and M. T. J. Mellor, to be published.

[9] D. W. Allen and B. G. Hutley, *J.C.S. Perkin II*, 1972, 67.

is a destabilisation of the forming negative charge on the adjacent carbon by the π-mesomeric effect of the ring system, which predominates over the electron-withdrawing inductive effect of the nitrogen.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded at 60 MHz on a JEOL spectrometer. G.l.c. analyses were carried out with a Pye series 104 chromatograph equipped with a 5 ft PEGA column and a flame ionisation detector. Operations involving phosphines or organolithium reagents were conducted under nitrogen. Mass spectra were recorded using an AEI MS 30 spectrometer.

Preparation of Phosphines and Phosphonium Salts.—*1-Methylpyrrol-2-yldiphenylphosphine.* n-Butyl-lithium (0·2 mol) in hexane (200 ml) was added dropwise with stirring under nitrogen to 1-methylpyrrole (27·0 g, >0·2 mol) in ether (200 ml) during 20 min. The resulting solution was heated under reflux for 2 h, before cooling in ice. Diphenylphosphinous chloride (22·0 g, 0·1 mol) in benzene (50 ml) was then added slowly. The mixture was heated under reflux for 1 h, cooled in ice, and hydrolysed by the addition of ammonium chloride solution (10% w/v; 100 ml). The organic layer was separated, dried (Na_2SO_4), evaporated, and the residue distilled to give *1-methylpyrrol-2-yldiphenylphosphine* (10·5 g, 40%), b.p. 149° at 0·15 mmHg. The phosphine, on treatment with methyl iodide, gave *methyl-1-methylpyrrol-2-yldiphenylphosphonium iodide* (V), m.p. 181—182° (from MeOAc–EtOH) (Found: C, 53·15; H, 4·65. $C_{18}H_{19}INP$ requires C, 53·05; H, 4·65%), τ (CF_3CO_2H) 2·0—2·6 (10H, m), 2·62—2·82 (1H, m), 3·2—3·4 (1H, m), 3·48—3·70 (1H, m), 4·42 (3H, s), and 7·23 (3H, d, $^2J_{PCH}$ 13·5 Hz).

Tris-1-methylpyrrol-2-ylphosphine. n-Butyl-lithium (0·6 mol) in light petroleum (b.p. 40—60°) was added dropwise with stirring under nitrogen to 1-methylpyrrole (52 g, >0·6 mol) in ether (200 ml). The resulting solution was heated under reflux for 14 h before being cooled in ice. Phosphorus trichloride (13·8 g, 0·1 mol) in ether (100 ml) was added slowly. The mixture was then heated under reflux for an additional 3 h before being cooled in ice and hydrolysed by the addition of ammonium chloride solution (10% w/v; 100 ml). The organic layer was separated, the aqueous layer extracted with ether, and the combined organic layers dried (Na_2SO_4). Evaporation of the solvent gave a brown oil which was distilled to give the *phosphine* (10·9 g, 40%), b.p. 132—140° at 0·04 mmHg, m.p. 121—122° (from EtOH) (Found: C, 66·25; H, 6·65; N, 15·55. $C_{15}H_{18}N_3P$ requires C, 66·40; H, 6·65; N, 15·5%), τ ($CDCl_3$), 3·2 (3H, m), 3·8—4·1 (6H, m), and 6·4 (9H, s). The phosphine, in benzene solution when treated with methyl iodide gave *methyltris-1-methylpyrrol-2-ylphosphonium iodide* (VII), m.p. 215° (from EtOAc–EtOH) (Found: C, 46·7; H, 5·2; N, 10·0. $C_{16}H_{21}IN_3P$ requires C, 46·5; H, 5·1; N, 10·15%), τ ($CDCl_3$) 2·65 (3H, m), 3·35 (3H, m), 3·6 (3H, m), 6·3 (9H, s), and 7·07 (2H, d, $^2J_{PCH}$ 13·5 Hz). The phosphine in solution in benzene with benzyl bromide gave *benzyltris-1-methylpyrrol-2-ylphosphonium bromide* (VI), m.p. 264° (from EtOAc–EtOH) (Found: C, 59·65; H, 5·55; N, 9·25. $C_{22}H_{25}BrN_3P$ requires C, 59·75; H, 5·7; N, 9·5%), τ ($CDCl_3$) 2·6—3·3 (11H, m), 3·65 (3H, m), 5·27 (2H, d, $^2J_{PCH}$ 14·25 Hz), and 6·67 (9H, s).

(1-Methylpyrrol-2-ylmethyl)triphenylphosphonium iodide (XI). To a solution of triphenylphosphine (1·05 g, 0·004 mol) in ethanol (10 ml) was added trimethyl-(1-methylpyrrol-2-ylmethyl)ammonium iodide [10] (0·9 g, 0·0032 mol). The resulting solution was heated under reflux for 12 h. After cooling, the precipitated *phosphonium salt* was filtered (1·1 g, 65%), m.p. 204° (from EtOAc–MeOH) (Found: C, 59·4; H, 4·75; N, 2·9. $C_{24}H_{23}INP$ requires C, 59·6; H, 4·8; N, 2·9%), τ ($CDCl_3$) 2·05—2·7 (15H, m), 3·4—3·55 (1H, m), 3·96—4·15 (1H, m), 4·25—4·45 (1H, m), 4·96 (2H, d, $^2J_{PCH}$ 12 Hz), and 6·93 (3H, s).

Benzyldiphenyl-(1-methylpyrrol-2-ylmethyl)phosphonium iodide (XIII). To a solution of trimethyl-(1-methylpyrrol-2-ylmethyl)ammonium iodide (1·0 g) in ethanol (10 ml) under nitrogen was added benzyldiphenylphosphine (1·0 g, 1 equiv.) and the resulting solution heated under reflux overnight. On cooling, a mass of needle-like *crystals* separated (1·65 g, 81%), m.p. 221° (decomp.) (from EtOH) (Found: C, 60·05; H, 5·2; N, 2·75. $C_{25}H_{25}INP$ requires C, 60·35; H, 5·05; N, 2·8%), τ ($CDCl_3$) 2·1—3·0 (15H, m), 3·55—3·8 (1H, m), 4·0—4·4 (2H, m), 4·89 (2H, d, $^2J_{PCH}$ 14·4 Hz), 5·12 (2H, d, $^2J_{PCH}$ 12·0 Hz), and 7·0 (3H, s).

Hydrolysis of Phosphonium Salts. Methyl-1-methylpyrrol-2-yldiphenylphosphonium iodide (V). To a solution of the salt in ethanol (1·5 ml) was added sodium hydroxide solution (2M; 2 ml) and the resulting solution heated under reflux for 12 h. The presence of 1-methylpyrrole in the mixture was confirmed by g.l.c. analysis; benzene was not detected. The mixture was evaporated, and the residue extracted with water (5 ml) and chloroform (2 × 10 ml). The chloroform extract was dried ($MgSO_4$) and evaporated to give methyldiphenylphosphine oxide, m.p. 112—113° (from hexane–benzene) (lit.,[11] 111—112°), τ ($CDCl_3$) 2·0—2·7 (10H, m) and 8·0 (3H, d, $^2J_{PCH}$ 13·5 Hz).

Methyltris-1-methylpyrrol-2-ylphosphonium iodide (VII). The salt was decomposed as described above, and the products extracted into chloroform to give *methylbis-1-methylpyrrol-2-ylphosphine oxide* (VIII), m.p. 124° (from hexane–benzene) (Found: C, 58·8; H, 6·8; N, 11·95. $C_{11}H_{15}N_2OP$ requires C, 59·45; H, 6·75; N, 12·6%), τ ($CDCl_3$) 3·05—3·45 (2H, m), 3·5—3·7 (2H, m), 3·75—3·95 (2H, m), 6·21 (6H, s), and 8·03 (3H, d, $^2J_{PCH}$ 14·2 Hz). The presence of 1-methylpyrrole in the reaction mixture was confirmed by g.l.c. analysis.

Kinetic studies. The hydrolyses were carried out in aqueous ethanol (50% v/v) at initial concentrations of phosphonium salt and sodium hydroxide of 0·01M, and were followed by a conventional back-titration procedure in which the decrease in sodium hydroxide concentration was monitored. The solutions were thermostatted in a bath controlled to ±0·1°. The reactions were followed to 70% of completion and the data evaluated by the method of integration. In all cases, a plot of $1/[OH]^2$ *versus* time was linear, confirming a third-order law. Rate constants and activation parameters are given in Table 1.

Benzyltris-1-methylpyrrol-1-ylphosphonium bromide (VI). The salt (0·22 g), in ethanol (1 ml), was treated with sodium hydroxide solution (8% w/v; 2 ml) and the resulting solution left in a stoppered flask at room temperature for 1 week. The mixture was then centrifuged to separate the precipitated phosphine oxides. The supernatant liquid was then analysed by g.l.c. and shown to contain both toluene and 1-methylpyrrole in a 1·3 : 1 mole ratio. ^{1}H

[10] A. Treibs and A. Deitl, *Annalen*, 1958, **619**, 80.
[11] A. Michaelis and W. La Coste, *Ber.*, 1885, **18**, 2109.

N.m.r. analysis of the precipitated phosphine oxides confirmed that loss of the benzyl and 1-methylpyrrol-1-yl substituents had occurred in the above ratio.

(1-*Methylpyrrol-2-ylmethyl*)*triphenylphosphonium iodide* (XI). The salt (0·2 g) was dissolved in sodium hydroxide solution (8% w/v; 10 ml) and the solution was heated under reflux for 24 h. The mixture was then distilled to give an emulsion, which was extracted with ether (2 × 10 ml). The ether extract, after drying ($MgSO_4$), was evaporated to give 1,2-dimethylpyrrole, τ ($CDCl_3$) 2·4—2·6 (1H, m), 3·4—3·53 (1H, m), 3·9—4·22 (1H, m), 6·53 (3H, s), and 7·83 (3H, s). The residue in the distillation flask was extracted with chloroform (2 × 10 ml), and the chloroform extract dried ($MgSO_4$) before evaporation to yield triphenylphosphine oxide, m.p. 157—158°, identical with an authentic specimen.

Kinetic studies. The hydrolyses were carried out as described earlier for other heteroarylmethyltriphenylphosphonium salts.[9]

Benzyldiphenyl-(1-*methylpyrrol-2-ylmethyl*)*phosphonium iodide* (XIII). The salt (0·5 g) in ethanol (2·5 ml) was treated with sodium hydroxide solution (30% w/v; 2·5 ml) and the resulting solution was heated under reflux for 1 h. The mixture was poured into dilute hydrochloric acid and immediately extracted with chloroform (2 × 10 ml). The chloroform extract was dried ($MgSO_4$) and then evaporated. The residue was dried at 50° and 0·1 mmHg to remove volatile material, and then analysed by ^1H n.m.r. spectroscopy, showing it to consist of (1-methylpyrrol-2-ylmethyl)diphenylphosphine oxide (70%) and benzyldiphenyl phosphine oxide (30%), *i.e.* in a mole ratio of 2·4 : 1.

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