The Chemistry of Some Quaternary Derivatives of the 10,11-Dihydrodibenzo[*b,f*]phosphepin System. The Kinetics of Alkaline Hydrolysis, and Products of Betaine Collapse, and a Comparison with Other Phosphonium Salts

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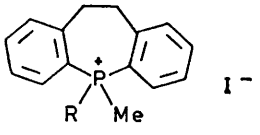
Alkaline hydrolysis of 10,11-dihydro-5-methyl-5-phenyldibenzo[*b,f*]phosphepinium iodide (1; R = Ph) proceeds with cleavage of the exocyclic phenyl group at a rate fifty times faster than that observed for the ring-opening hydrolysis of the 5,5-dimethyl analogue (1; R = Me). Comparison of the rate data and activation energies for hydrolysis of these seven-membered ring salts with those for the acyclic salts $[PMePh_3][I]$ and $[PMe_2Ph_2][I]$ indicates the existence of a ' seven-membered-ring effect ', which may be due to the preferential occupation by the ring of diequatorial positions in intermediate trigonal-bipyramidal phosphoranes. Hydrolysis of these seven-membered-ring salts proceeds much more slowly than those of related five-membered-ring salts, indicating that relief of ring strain on phosphorane formation is of little importance for the seven-membered-ring compounds. The betaine (9) derived from 10,11-dihydro-5-phenyldibenzo[*b,f*]phosphepin and styrene oxide collapses in refluxing ethanol to form styrene and the related cyclic phosphine oxide (5; R = Ph); no rearrangement products are formed, in contrast to the reactions of the corresponding betaine derived from triphenylphosphine.

COMPARED with four-, five-, and six-membered ring phosphorus heterocycles, little has been reported on the chemistry of compounds in which the phosphorus forms



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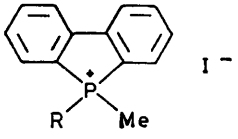

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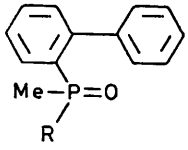

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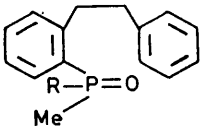
part of a seven-membered ring system. In this paper, we describe some reactions of quaternary derivatives (1) of the 10,11-dihydrodibenzo[*b,f*]phosphepin system, together with a comparison with those of related acyclic and five-membered ring systems.

RESULTS AND DISCUSSION

We have previously shown that on alkaline hydrolysis, the salts (2; R = Me or Ph) undergo exclusive ring-opening to form the oxides (3; R = Me or Ph).[1,2] These results are accommodated in terms of the involvement of an intermediate trigonal-bipyramidal hydroxyphosphorane, in which the five-membered ring spans an apical–equatorial position. Cleavage of the apical bond leads to ring-opened products. For the salt (2; R = Ph), no cleavage of the exocyclic phenyl group is observed, presumably due to its equatorial siting in the intermediate hydroxyphosphorane.

We now find (as expected from carbanion stability considerations), that the salt (1; R = Me), also undergoes alkaline hydrolysis with ring-opening to form the oxide (4; R = Me). In contrast, the salt (1; R = Ph) undergoes hydrolysis with predominant cleavage of the exocyclic phenyl substituent to form the cyclic phosphine oxide (5; R = Me). Only a very small amount of the ring-opened product (4; R = Ph) is formed.

The formation of products in which the ring remains intact can be accommodated in terms of the decomposition of a trigonal-bipyramidal hydroxy-phosphorane in which the seven-membered ring spans a diequatorial position, cleavage of the phenyl group occurring from an apical position. The ring-opened products (4; R = Me or Ph) probably arise as a result of attack of hydroxide ion opposite the P–aryl bond, the ring system spanning an apical–equatorial position, which may be less favourable than the diequatorial mode for the seven-membered cyclic system (see below). These results are in accord with Marsi's work on the hydrolysis of the *cis* and *trans* isomers of the cycloalkyl phosphonium salt (6), which undergoes exclusive cleavage of the exocyclic benzyl



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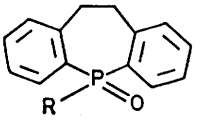

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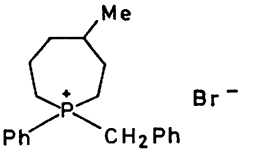

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group with complete *inversion* of configuration at phosphorus, indicating a diequatorial position for the seven-membered ring in the intermediate phosphorane.[3] Granoth *et al.*[4] have also reported loss of the exocyclic

phenyl group on sodium hydroxide fusion of the cyclic oxide (5; R = Ph).

We have also compared the rates of hydrolysis of the above seven-membered ring salts with those of related five-membered ring salts and with acyclic analogues. All the salts studied undergo hydrolysis according to a third-order rate law as is usually found. The rate data are presented in the Table. In both series of salts

Rates of alkaline hydrolysis of phosphonium salts in 50% aqueous ethanol

Salt	Temperature (°C)	k/ l^2 mol^{-2} min^{-1}	E_a/ kcal mol^{-1}	Relative rate at 54.5 °C
(1; R = Me)	54.5	5.05×10^{-3}	33.0	1.0
	64.5	2.25×10^{-2}		
[PMe_2Ph_2][I]	54.5	1.43×10^{-2}	33.5	2.8
	64.5	4.17×10^{-2}		
(2; R = Me) [a]	54.5	49.2	18.9	9.7×10^3
(1; R = Ph)	54.5	2.57×10^{-1}	23.15	50.9
	64.5	7.38×10^{-1}		
[$PMePh_3$][I]	54.5	1.18×10^{-1}	30.3 [b]	23.4
(2; R = Ph)	54.5	8.33×10^2	19.6	1.65×10^5
	64.5	2.03×10^3		

[a] Calculated from data in D. W. Allen and I. T. Millar, *J. Chem. Soc.* (*B*), 1969, 263. [b] Calculated from data in D. W. Allen, *J. Chem. Soc.* (*B*), 1970, 1490.

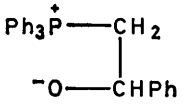
studied, the rate of hydrolysis of the seven-membered ring salt is comparable with that of the related acyclic analogue, but is much slower than the hydrolysis of the corresponding five-membered ring system. The much faster rate of hydrolysis of the latter is presumably due to relief of ring strain attending the formation of the intermediate phosphoranes, where the ring system spans apical–equatorial positions.[5,6] Such relief of ring strain present in the phosphonium salt will lead to an increase in the magnitude of the equilibrium constant for phosphorane formation, and this is reflected in the overall rate constant for the reaction. Due to the larger endocyclic angle at phosphorus in the seven-membered ring salts, ring strain will be much reduced, with consequent reduction in rate of hydrolysis.

Comparing related salts in each series, it is seen that replacement of methyl by phenyl leads to a significant increase in the rate of hydrolysis. For the acyclic salts, and for the dibenzophospholium salts (2), this increase can be largely accounted for in terms of the greater electron-withdrawing effect of the phenyl group which will favour phosphorane formation.[7] However, in the case of the seven-membered ring phosphonium salts, other factors are also involved.

Hydrolysis of the salt (1; R = Ph) with loss of the exocyclic phenyl group occurs 2.2 times as fast as that of [$PMePh_3$][I]. Taking statistical effects into consideration, a true relative rate ratio of *ca.* 7 : 1 would seem valid. Significantly, the energy of activation for the hydrolysis of the seven-membered cylic salt is some 7 kcal lower than for the hydrolysis of [$PMePh_3$][I]. The rate and activation data may reflect a preference of the seven-membered ring to span diequatorial positions in the intermediate phosphorane, *i.e.* a ' seven-membered-ring effect '. The phenyl group would occupy the presumably preferred apical position for subsequent loss. Inspection of molecular models lends support to this suggestion. It is noticeable that the apical–equatorial ring conformation involves some degree of bond-angle strain at phosphorus, which is much reduced in the diequatorial conformation.

The reduced rate of hydrolysis of the salt (1; R = Me) compared with that of [PMe_2Ph_2][I] may also, in part, be a consequence of the conformational preference of the seven-membered ring in the intermediate phosphoranes. As noted above, in the hydrolysis of (1; R = Me), the ring system is probably required to span an apical–equatorial position prior to ring-opening, and this would seem to be less favourable than the diequatorial mode. However, in addition in the case of the seven-membered-ring compound, the leaving group is effectively an *o*-tolyl carbanion, which might be expected to be less stable than the phenyl carbanion cleaved in the hydrolysis of [PMe_2Ph_2][I]. The fifty-fold difference in rate for the hydrolysis of (1; R = Ph) and that of (1; R = Me) is therefore probably due to a combination of (*i*) the greater electron-withdrawing effect of the exocyclic phenyl group relative to methyl; (*ii*) the diequatorial preference of the seven-membered ring; and (*iii*) the loss of a phenyl as opposed to an effectively *o*-tolyl carbanion.

As an extension of our work on factors affecting the mode of decomposition of phosphonium betaines in protic solvents,[8] we have now investigated the effect of enclosing the phosphonium centre in a seven-membered ring system. Whereas the betaine (7), derived from



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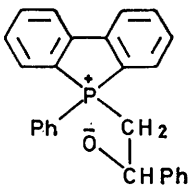

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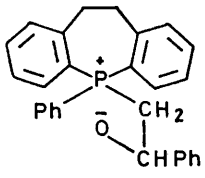

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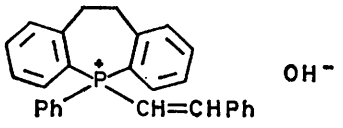
triphenylphosphine and styrene oxide, decomposes in ethanol to form mainly 1,2-diphenylethyldiphenylphosphine oxide *via* the hydrolysis of the intermediate triphenyl-β-styrylphosphonium cation,[9] the related betaine (8) derived from 5-phenyldibenzophosphole decomposes to form styrene and the phosphole oxide, presumably as a result of the increased rate of betaine collapse in the latter case due to the ring-strained dibenzophospholium centre.[10] We now find that the betaine (9) also gives rise to styrene and the cyclic phosphine oxide (5; R = Ph) in high yield. No rearranged products were detected.

In view of the course of hydrolysis of the salt (1; R = Ph) and the similarity in the rates of hydrolysis of the

seven-membered ring salts and the acyclic analogues, it would seem unlikely that the products from (9) arise from direct collapse of the betaine *via* a spirophosphorane, since the related acyclic betaine does not decompose in this way. It is probable that the betaine (9) undergoes protonation, followed by dehydration to form the substituted vinylphosphonium salt (10), which undergoes subsequent hydrolysis with loss of the β-styryl group from an apical position of a trigonal-bipyramidal phosphorane in which, as suggested for hydrolysis of (1; R = Ph), the ring spans a diequatorial position.



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EXPERIMENTAL

Operations involving organolithium reagents or tertiary phosphines were carried out under nitrogen. Hydrogen-1 n.m.r. spectra were recorded at 60 MHz on a JEOL spectrometer and are relative to tetramethylsilane (δ = 0 p.p.m.). Mass spectra were recorded on an AEI MS30 instrument. T.l.c. separations were carried out using commercial 20 × 20-cm preparative plates (Kieselgel, 2-mm thickness), which were developed with hexane–ethyl acetate (1 : 1 v/v).

Preparation of Phosphines and Phosphonium Salts.—10,11-Dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*]phosphepin was prepared from 2,2′-dibromobibenzyl as described in the original method by Mann *et al.*[11] However, compared to the published procedure, we found the following procedure advantageous in isolating the pure phosphepin. After hydrolysis of the initial reaction mixture, the organic layer was dried (Na_2SO_4) and the solvents removed *in vacuo*. The crude residue was then oxidised with hydrogen peroxide (100-vol)–ethanol and set aside overnight. After addition of water, the products were extracted into chloroform. Evaporation of the chloroform gave the crude phosphepin oxide, which was purified by vacuum sublimation (115 °C, 0.001 mmHg), and then reduced to the phosphepin using trichlorosilane in benzene.[12] The phosphepin had m.p. 94—95 °C (lit.,[11] 94—95 °C), M^+ 288 (Found: C, 83.6; H, 5.85. Calc. for $C_{20}H_{17}P$: C, 83.3; H, 5.95%). Treatment of the phosphepin with iodomethane gave the salt (1; R = Ph), m.p. 251—252 °C (from EtOH) (lit.,[11] m.p. 251—252 °C) (Found: C, 58.25; H, 4.95. Calc. for $C_{21}H_{20}IP$: C, 58.60; H, 4.7%).

10,11-Dihydro-5-methyl-5H-dibenzo[b,f]*phosphepin.*—This was prepared from 2,2′-dibromobibenzyl and methylphosphonous dichloride using the procedure described by Mann *et al.*[11] for the 5-phenyl analogue. Distillation of the crude reaction mixture gave the *phosphepin*, b.p. 115—125 °C at 0.02 mmHg (20.5%) (Found: C, 80.05; H, 7.1. $C_{15}H_{15}P$ requires C, 79.96; H, 6.72%); *m/e* 226 (M^+). Treatment of the phosphine with iodomethane gave the *salt* (1; R = Me), m.p. 265—266 °C (from EtOH) (Found: C, 51.95. H, 4.9. $C_{16}H_{18}IP$ requires C, 52.17; H, 4.93%). Oxidation of the phosphine with hydrogen peroxide gave the *phosphepin oxide* (5; R = Me), m.p. 108 °C (from EtOH) (Found: C, 74.75; H, 6.25. $C_{15}H_{15}OP$ requires C, 74.66; H, 6.5%); *m/e* 242 (M^+); δ($CDCl_3$) 8.05—8.65 (m, 2 H, Ar-*H*), 7.80—7.10 (m, 6 H, Ar-*H*), 3.3 (s, 4 H, CH_2CH_2), and 1.95 [d, 3 H, $^2J_{PCH}$ 12 Hz, P(O)Me].

Hydrolysis of Phosphonium Salts.—(*a*) *Product analysis.* (*i*) The salt (1; R = Ph) was dissolved in ethanol and treated with an excess of aqueous hydroxide solution (2 mol dm^{-3}), and the solution heated under reflux for several hours. G.l.c. analysis of the reaction mixture indicated the presence of benzene. Following acidification, the products were extracted into chloroform and separated by preparative t.l.c. to give the *oxide* (5; R = Me) (74%), identical with the authentic material, and methyl(phenyl)-[2-(2-phenylethyl)phenyl]phosphine oxide (4; R = Ph) (3%), which we were unable to crystallise; δ($CDCl_3$) 8.0—6.9 (m, 14 H, Ar-H), 3.05 (broad s, 4 H, CH_2CH_2), and 2.05 [d, 3 H, $^2J_{PCH}$ 14 Hz, P(O)Me]; *m/e* 320 (M^+).

(*ii*) The salt (1; R = Me) was similarly treated to give, as the sole product, dimethyl[2-(2-phenylethyl)phenyl]-phosphine oxide (4; R = Me), as a hygroscopic liquid; δ($CDCl_3$) 8.0—6.9 (m, 9 H, Ar-H), 3.05 (s, 4 H, CH_2CH_2), and 2.05 [d, 6 H, $^2J_{PCH}$ 14 Hz, P(O)Me]; *m/e* 258 (M^+). A sample subjected to 'sublimation' (150—200 °C, 0.01 mmHg) analysed as the *hemihydrate* (Found: C, 71.75; H, 7.55. $C_{16}H_{19}OP{\cdot}0.5H_2O$ requires C, 71.95; H, 7.55%).

(*b*) *Kinetic studies.*—The hydrolysis reactions were carried out in 50% (v/v) aqueous ethanol, at initial concentrations of phosphonium salt and sodium hydroxide of 0.05 mol dm^{-3}, 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 °C. The reactions were followed to at least 50% of completion, and the data evaluated by using the method of integration. In all cases, a plot of $1/[OH]^2$ *vs.* time was linear, confirming a third-order rate law. The rate and activation data are tabulated in the text.

Reactions of Phosphonium Betaines.—10,11-Dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*]phosphepin (0.288 g, 10^{-3} mol) and styrene oxide (0.24 g, 2 mol) were heated together in dry ethanol (4 cm^3) under reflux for 24 h. G.l.c. analysis showed the presence of styrene (74%), and preparative t.l.c. of the reaction mixture gave the phosphepin oxide (5; R = Ph) identical with the authentic material. No other phosphine oxides were isolated.

Similarly, the Wittig reaction of the salt (1; R = Ph) with benzaldehyde in the presence of ethanolic ethoxide ion gave styrene (45%) and the phosphepin oxide (5; R = Ph).

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