Reaction of Dibenzophospholes with Benzoyl Chloride; Ring Expansion to Dibenzo[*b,d*]phosphorins

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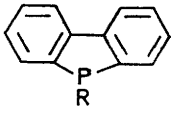
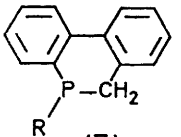
5-Substituted dibenzophospholes (I; R = Ph, Me, Et, or Pr^i), on treatment with benzoyl chloride in the presence of triethylamine, followed by hydrolysis, undergo ring expansion to form 5,6-dihydrodibenzo[*b,d*]phosphorin 5-oxides (XI; R = Ph, Me, Et, or Pr^i) in high yield. 5-t-Butyldibenzophosphole (I; R = Bu^t) did not form an acylphosphonium salt on treatment with benzoyl chloride.

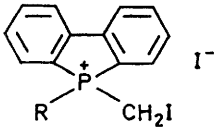
Two convenient procedures have been reported for the ring expansion of dibenzophospholes (I) to dihydrodibenzophosphorins (II). Alkaline hydrolysis of the iodomethyldibenzophospholium salts (III; R = Me or Ph)



(I)



(II)



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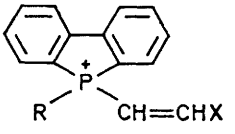
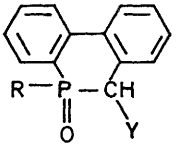


(IV)

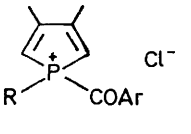


(V)

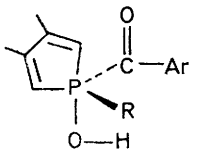
and of the vinyldibenzophospholium salts (IV; R = Me or Ph, X = CO_2Me or Ph) affords the dihydrodibenzophosphorin oxides (V; R = Me or Ph, Y = H, $CH_2{\cdot}CO_2Me$, or CH_2Ph).[1,2] We have now investigated the hydrolysis reactions of the acyldibenzophospholium salts obtained by the reaction of dibenzophospholes with benzoyl chloride as a third route to dihydrodibenzophosphorins.

Tertiary phosphines react with benzoyl chloride in the presence of triethylamine to form benzoylphosphonium salts, which undergo hydrolysis on treatment with water in a number of ways. Nucleophilic attack by water may occur at either the carbonyl group or at phosphorus. In the former case, the tertiary phosphine is displaced, with the formation of benzoic acid. This route is followed when the substituents at phosphorus are acyclic.[3] Nucleophilic attack at phosphorus is favoured when the phosphorus forms part of a small, strained ring system, leading to an intermediate phosphorane in which the ring system spans an apical-equatorial position with consequent reduction in ring strain. The mode of eventual collapse of the phosphorane depends on the degree of strain remaining in the phosphorane intermediate. In the hydrolysis of the acylphospholium salts (VI), some strain is still present in the intermediate (VII), which collapses by ring expansion to form (VIII).[4] In contrast, the acyl-Δ^2-phospholenium salts (IX) undergo hydrolysis to form the Δ^2-phospholen oxide (X) with displacement of the acyl carbanion to form the aldehyde on protonation.[5] The smaller degree of ring strain in the Δ^2-phospholen system enables the phosphorane intermediate to undergo pseudorotation, placing the ring diequatorial and the acyl group in an apical position from which it leaves.

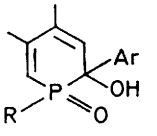
The 5-substituted dibenzophospholes (I, R = Ph, Me, Et, or Pr^i), on treatment with benzoyl chloride in the presence of triethylamine, followed by hydrolysis, afford the corresponding dihydrodibenzophosphorin oxides (XI; R = Ph, Me, Et, or Pr^i) in 60—95% yield. As in the case of the acylphospholium salts (VI), nucleophilic attack occurs at phosphorus to form the trigonal bipyramidal phosphorane (XII), which collapses with migration of the apical aryl group from phosphorus to the equatorially disposed carbonyl carbon, resulting in ring expansion. The driving force for the reaction is again relief of ring strain in both the acyldibenzophospholium salts and the phosphorane. That there is appreciable ring strain in dibenzophospholium salts is



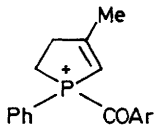
(VI)



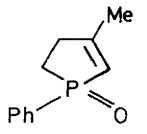
(VII)



(VIII)



(IX)



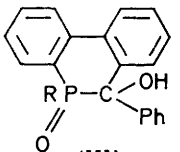
(X)

reflected in the reduced rate of quaternisation of 5-phenyldibenzophosphole relative to that of triphenylphosphine [6] and in the increased rate of retrocyano-

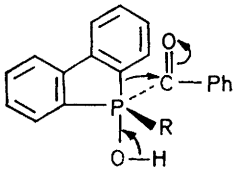
[1] D. W. Allen and I. T. Millar, *Chem. and Ind.*, 1967, 2178; *J. Chem. Soc.* (*C*), 1969, 252.
[2] E. M. Richards and J. C. Tebby, *J.C.S. Chem. Comm.*, 1967, 957; *J. Chem. Soc.* (*C*), 1971, 1064.
[3] K. Issleib and E. Priebe, *Chem. Ber.*, 1959, **92**, 3183.
[4] F. Mathey, *Tetrahedron*, 1973, **29**, 707.
[5] D. G. Smith and D. J. H. Smith, *J.C.S. Chem. Comm.*, 1975, 459.
[6] D. W. Allen, J. R. Charlton, and B. G. Hutley, *Phosphorus*, 1974, **5**, 9.

ethylation of cyanoethyldibenzophospholium salts.[7] Relief of ring strain in phosphorane intermediates derived from dibenzophospholium salts accounts for the course both of the above reactions of acyldibenzophospholium salts and of the hydrolysis of other dibenzophospholium salts in which either ring opening or ring expansion occurs,[1,2,8] indicating that the energy barrier to placing the ring system in a diequatorial position is prohibitively high.

In contrast to the reactions of the above 5-substituted dibenzophospholes, the attempted reaction of 5-t-butyldibenzophosphole with benzoyl chloride in the presence of triethylamine, followed by hydrolysis, led to the



(XI)



(XII)

recovery of the phosphole. No dibenzophosphorin oxide was formed. Subsequent investigation showed that 5-t-butyldibenzophosphole did not form the intermediate acylphosphonium salt, indicating the steric inhibition of quaternisation by the bulky t-butyl group.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded at 60 MHz with a JEOL spectrometer (Me_4Si as internal standard). Mass spectra were recorded with an A.E.I. MS30 instrument at 70 eV. U.v. spectra were recorded for solutions in 95% ethanol. The 5-substituted dibenzophospholes were prepared as previously described.[8-10]

Reaction of 5-Substituted Dibenzophospholes with Benzoyl Chloride; General Procedure.—To a stirred solution of the 5-substituted dibenzophosphole (I; R = Ph, Me, Et, or Pr^i) (2 mmol) and triethylamine (2 cm^3) in dry diethyl ether (30 cm^3) under dry nitrogen, was added benzoyl chloride (0.564 g, 4 mmol). The solution was stirred for 30 min and then hydrolysed with water (40 cm^3), and the resulting mixture was stirred for a further 2 h. The resulting white solid was separated, washed with water and ether, and dried before recrystallisation from dimethylformamide (DMF) or chloroform.

The following 5,6-dihydro-6-hydroxydibenzo[*b*,*d*]phosphorin 5-oxides were isolated and fully characterised (in each case, the u.v. spectrum was similar to the recorded [1,2] spectra of other dibenzophosphorin oxides): 5,6-diphenyl (XI; R = Ph) (65%), m.p. 276° (from DMF); *m/e* 370 (M^+) (Found: C, 77.9; H, 5.1. $C_{25}H_{19}PO_2$ requires C, 78.5; H, 5.0%); δ ($CDCl_3$) 6.9—8.0 (m, aromatic); $\lambda_{max.}$ 212 (ε 42 000), 266 (7 000), and 273 nm (6 800); *5-methyl-6-phenyl* (XI; R = Me) (98%), m.p. >177° (decomp.); *m/e* 320 (M^+) (Found: C, 74.85; H, 5.3. $C_{20}H_{17}PO_2$ requires C, 75.0; H, 5.3%); δ ($CDCl_3$) 6.8—8.0 (13 H, m), 5.3 (1 H, d, $^2J_{POH}$ 4.5 Hz), and 1.6 (3 H, d $^2J_{PCH}$ 13 Hz); $\lambda_{max.}$ 212 (ε 40 000), 265 (7 250), and 272 nm (7 800); *5-ethyl-6-phenyl* (XI; R = Et) (92%), m.p. 267°; *m/e* 334 (M^+) (Found: C, 75.0; H, 5.65. $C_{21}H_{19}PO_2$ requires C, 75.45; H, 5.7%); δ ($CDCl_3$) 6.8—7.9 (13 H, m), 4.4 (1 H, d, $^2J_{POH}$ 5.5 Hz), 1.4—2.5 (2 H, m), and 0.6—1.4 (3 H, m); $\lambda_{max.}$ 213 (ε 44 000), 235 (18 050), 265 (7 900), 272 (8 550), and 286 nm (6 500); *5-isopropyl-6-phenyl* (XI; R = Pr^i) (60%), m.p. 275°; *m/e* 348 (M^+) (Found: C, 75.85; H, 6.05. $C_{22}H_{21}PO_2$ requires C, 76.0; H, 6.0%); δ ($CDCl_3$) 6.5—8.0 (13 H, m), 3.87 (1 H, d, $^2J_{POH}$ 6.0 Hz), 1.5—2.2 (4 H, m), and 0.5—1.5 (3 H, m); $\lambda_{max.}$ 214 (ε 42 000), 237 (17 400), 265 (6 900), 273 (7 450), and 286 nm (5 700).

[6/262 *Received*, 9*th February*, 1976]

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[9] G. Wittig and A. Maercker, *Chem. Ber.*, 1964, **97**, 747.

[10] D. W. Allen, F. G. Mann, and I. T. Millar, *J. Chem. Soc.* (*C*), 1971, 3937.