The Chemistry of Heteroarylphosphorus Compounds, Part XIII [1]  
Some Reactions of 5-(2-Thienyl)dibenzophosphole and its Quaternary Salts

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Phosphonium Salt Hydrolysis, Ring Expansion, Dibenzo[b,d]phosphorins  
The preparation of 5-(2-thienyl)dibenzophosphole (1) is reported. It readily forms quaternary salts with iodomethane, diiodomethane and benzyl bromide, and also forms a complex with nickel(II) bromide. The methyl- and benzyl-quaternary salts (2, R = Me or PhCH₂; X = I or Br) undergo hydrolysis with preferential cleavage of the 2-thienyl group, forming the cyclic oxides (3, R = Me or PhCH₂). The iodomethyl salt (2, R = CH₃I, X = I) undergoes hydrolysis to give a mixture of products, which include the ring-expanded structure (8, R = 2-thienyl). The dibenzophosphole also reacts with ethylpropiolate and water in THF solution with ring-expansion to give the dibenzob[b,d]phorpin (9).

In recent years, the chemistry of the dibenzophosphole system has received considerable attention. Interest has centered around both the reactivity of the parent dibenzophospholes and that of the related quaternary phosphonium salts. In the case of the former, there has been much discussion of the extent to which the lone pair at phosphorus is delocalised over the essentially planar dibenzophosphole system [2-5], whereas for the latter the effects of bond angle strain at phosphorus on the rate and course of alkaline hydrolysis and the decomposition of related phosphonium betaines have been investigated [2, 5, 6-11]. Following our observations that certain heteroaryl groups e.g. 2-thienyl, act as markedly electron-withdrawing substituents when attached to phosphorus, having a significant effect on the rate and course of reactions [12], we thought it of some interest to investigate the effects of a 2-thienyl substituent on the reactivity of the phosphorus atom in the dibenzophosphole system, and now report some reactions of 5-(2-thienyl)dibenzophosphole (1) and the related salts (2, R = Me, PhCH₂ and CH₃I; X = I or Br).

![Structural formulas](image)

The dibenzophosphole (1) was prepared by the reaction of 2-thienylphosphonous dichloride with 2,2'-dilithiobiphenyl in ether, and isolated by distillation as a pale yellow viscous liquid. Treatment with hydrogen peroxide in ethanol readily formed the corresponding phosphole oxide (3, R = 2-thienyl). With iodomethane, quaternization occurred readily to give the methiodide (2, R = Me, X = I), and on heating with benzyl bromide in toluene, the salt (2, R = PhCH₂, X = Br) was formed. Treatment of the phosphole (1) with diiodomethane in hot toluene resulted in a black tarry mixture, aqueous extraction of which eventually yielded the impure methiodide (2, R = Me, X = I), and not the desired iodomethylphosphonium salt (2, R = CH₃I, X = I). The isolation of the methiodide (2, R = Me, X = I) from this reaction probably indicates that the initially formed iodomethyl salt (2, R = CH₃I, X = I) is undergoing subsequent attack by a second phosphate molecule (or alternatively by iodide ion) at the iodine of the iodomethyl group to form an ylide of the type R₂P-CH₃, which would then abstract a proton from the diiodomethane present in the reaction mixture to form the methylphosphonium salt. The desired iodomethyl salt (2, R = CH₃I, X = I) was, however, formed in good yield simply by allowing the phosphine to stand in an excess of diiodomethane in the cold over a period of several days. The salt crystallised from the reaction mixture. 31P NMR spectroscopy of the product showed the characteristic doublet due to the P-CH₃I unit (3J_PCH = 8 Hz), (consistent with values of 3J_PCH observed for related salts) [13], together with diiodomethane of crystallisation. The latter was lost on heating under vacuum at 65 °C for several hours.

The readily available nature of the lone pair at...
Table. Diffuse reflectance data* for phosphine-
nickel(II) bromide complexes.

<table>
<thead>
<tr>
<th>Complex L\textsubscript{2}NiBr\textsubscript{2}</th>
<th>Absorption bands [( \tilde{\nu}, \text{cm}^{-1} ) ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L = triphenylphosphine</td>
<td>22,700; 16,650; 10,850</td>
</tr>
</tbody>
</table>
| L = 5-phenyldibenzo-
phosphole       | 22,700; 18,100; 11,450         |
| L = diphenyl(2-thienyl)-
phosphine   | 15,723; 10,989                 |
| L = 5-(2-thienyl)-
dibenzo-phosphole | 22,400; 16,900; 11,350         |

* Recorded using an SP 700 spectrophotometer, using MgO as diluent and reference.

phosphorus in the dibenzophosphole (1) was also shown by the formation of deep brown crystals of a complex of composition (phos)\textsubscript{2}NiBr\textsubscript{2} with nickel(II) bromide, on addition of the ligand in acetic acid solution to a hot solution of nickel(II) bromide in ethanol and acetic acid. The similarity of the diffuse reflectance spectrum of the complex to that of the distorted tetrahedral complex [14] (Ph\textsubscript{3}P)\textsubscript{2}NiBr\textsubscript{2} indicates that the dibenzophosphole complex has a similar tetrahedral geometry. A comparison of the diffuse reflectance spectrum of the complex with that of the related acyclic phosphine diphenyl-
(2-thienyl)phosphine [15] shows that the position of the bands in the spectrum of the former are at higher energies than those in the spectrum of the latter (Table), indicating that the dibenzophosphole complex has a better donor towards the metal ion than the acyclic phosphine. A similar difference has been noted in the spectra of the nickel(II) bromide complexes of 5-phenyldibenzo-phosphole and triphenylphosphine, the dibenzophosphole again appearing to be the better donor [4]. It is likely that the above differences in donor power are due to the difference in steric bulk of the ligands, the dibenzophosphate phosphorus being able to approach closer to the metal than that of the acyclic phosphines, due to the linking together of two of the benzene rings.

![Image of molecular structures](image)

We have also studied the course of alkaline hydrolysis of the above phosphonium salts. In contrast to the methiodide (4, R = Me, X = I) of 5-phenyldibenzo-phosphole, which undergoes hydrolysis with cleavage of a ring P-C bond to form the acyclic phosphine oxide (5) [6] the salt (2, R = Me, X = I) undergoes hydrolysis with cleavage of the 2-thienyl group to give the cyclic phosphine oxide (3, R = Me). Ring-opened products were not detected. Ring-opening of the former salt has been attributed to the involvement of a trigonal bipyramidal hydroxyphosphorane in which the five-membered ring spans apical-equatorial positions, cleavage of the apical bond giving rise to the ring-opened product [6]. The preferential loss of the 2-thienyl group with ring retention in the hydrolysis of (2, R = Me, X = I) is of some interest. We have shown that in the hydrolysis of acyclic phosphonium salts, the 2-thienyl group is preferentially cleaved compared to phenyl (and benzyl) groups as a result of the greater stabilisation of the forming 2-thienyl carbanion due to the presence of the sulphur atom adjacent to the carbanionic carbon [12]. Clearly, in the above case, cleavage of the 2-thienyl group is favoured relative to ring-opening. Making the common assumptions that in nucleophilic displacement reactions at tetrahedral phosphorus, both entering and leaving groups occupy apical positions in trigonal bipyramidal intermediates, and that a five-membered ring will preferentially span apical-equatorial positions, then the course of the above reaction may be viewed in terms of the initial formation of a hydroxyphosphorane (6), in with the 2-thienyl group is equatorial. Pseudorotation of 6 to give e.g. 7 would then allow departure of the 2-thienyl group from an apical position.

The course of this reaction will doubtless also be influenced by the apicophilicity of the 2-thienyl group. Although as yet little information is available on the relative apicophilicities of phenyl and heteroaryl groups, preliminary work [16] has shown that the 2-furyl group is considerably more apicophilic than phenyl. A similar conclusion would seem likely for 2-thienyl.
Similarly, the salt (2, R = PhCH₂, X = Br) also undergoes alkaline hydrolysis with predominant cleavage of the 2-thienyl group to form the cyclic oxide (3, R = PhCH₂); a small amount of the benzyl-cleavage product (3, R = 2-thienyl) is also formed.

Alkaline hydrolysis of the iodomethylphosphonium salt (2, R = CH₂I, X = I) gave a mixture of products, which we were unable to separate fully. GC analysis of the reaction mixture showed the presence of thiophen and iodomethane, arising from cleavage of the thienyl and iodomethyl groups respectively. Preparative tlc gave the oxide (3, R = 2-thienyl) and a second band which appeared to consist largely of the ring-expanded phosphine oxide (8, R = 2-thienyl), together with a trace of the oxide (3, R = CH₂I). The NMR spectrum of the mixture showed a complex signal centred at δ 6.2, consistent with the expected appearance as an ABX multiplet of the diastereotopic protons of the CH₂ group in the ring-expanded oxide, as found for the related compounds from 5-methyl- and 5-phenyl-dibenzophosphole [6]. The UV spectrum of this band also supported the above assignment, the spectrum showing distinct resemblance to those of related ring-expanded systems, and major differences from the very characteristic spectra of dibenzophosphole oxides.

It is of interest to recall that alkaline hydrolysis of the related iodomethyl salt of 5-phenyl dibenzophosphole gave predominantly the ring-expanded phosphine oxide (8, R = Ph); only a trace of 5-phenyl dibenzophosphole oxide was obtained [6]. The complexity of the above reaction is no doubt attributable to the greater leaving group ability of the 2-thienyl group compared to phenyl.

Ring expansion to give 9 was, however, achieved in good yield in the reaction of the phosphole (1) with ethyl propiolate and water in THF solution, a reaction which also gives high yields of ring-expanded systems derived from 5-methyl, 5-phenyl- and 5-benzyl dibenzophospholes [8]. Such reactions are believed to proceed via the initial formation of vinylyphosphonium salts (10), which then undergo hydrolysis in situ, with migration of the apical phenyl group of the dibenzophosphole system to adjacent carbon, the originally exocyclic substituent at phosphorus remaining in an equatorial position in the phosphorane (11).

It is of interest that in the hydrolysis of the salt (10, R = 2-thienyl) the 2-thienyl group is not lost from phosphorus. Ring-expansion is obviously preferred to a pathway involving a pseudorotation to place the 2-thienyl group in an apical position from which it could leave or migrate to adjacent carbon, as has been observed in the related reaction of diphenyl(2-thienyl)phosphine with ethyl propiolate and water [17]. The UV spectrum of the product from 5-(2-thienyl)dibenzophosphole shows the very characteristic absorptions of the ring-expanded system (9), thus ruling out the alternative structure (12), which would have been expected to have the characteristic spectrum of a dibenzophosphole oxide.

Experimental

Operations involving tertiary phosphines or organolithium reagents were conducted under nitrogen. ¹H NMR spectra were recorded at 60 MHz using a Jeol spectrometer. Mass spectra were recorded at 70 eV using an AEI MS 30 instrument. Preparative tlc separations were carried out using 20 × 20 cm plates coated with a 1 mm thickness of Kieselgel HF 254. After several developments with hexane-ethyl acetate (1:1 v/v), individual bands were extracted with ethanol.

5-(2-Thienyl)dibenzophosphole and its derivatives

To a stirred solution of 2,2'-dilithiobiphenyl (prepared from 2,2'-diodobiphenyl (10.15 g) and lithium (1.5 g, excess)) in ether (150 cm³) was added a solution of 2-thienyl phosphonium dichloride (4.55 g)
in benzene (50 cm$^3$), the reaction mixture being cooled in ice during the addition. The reaction mixture was then heated under reflux for 30 min, before being cooled and hydrolysed with aqueous ammonium chloride solution (10% w/v, 100 cm$^3$). The organic layer was separated, dried over anhydrous sodium sulphate, and evaporated. The residue was fractionated under reduced pressure to give the phosphole as a viscous yellow oil (4.15 g, (63%) b.p. 180 °C at 0.33 mm Hg), which was characterised by conversion to the following derivatives:

(a) Treatment with an excess of iodomethane gave 5-methyl-5-(2-thienyl)dibenzophospholium iodide (2, R = Me, X = I), m.p. 195–197 °C (from ethanol-ethyl acetate-ether).

C$_{17}$H$_{14}$PS  
Found C 49.9 H 3.4;  
Calcd C 49.7 H 3.4.

$\delta$(CDCl$_3$) ppm: 1.0–2.7 (m, 11H); 6.65 (d, 3H, $\delta_{J_{PCH}} = 15$ Hz).

(b) Treatment with benzyl bromide in toluene at reflux gave 5-benzyl-5-(2-thienyl)dibenzophospholium bromide (2, R = PhCH$_2$, X = Br), m.p. >300 °C decom. (from ethanol-ethyl acetate-ether).

C$_{26}$H$_{18}$BrPS  
Found C 63.1 H 4.1;  
Calcd C 63.1 H 4.1.

$\delta$(CF$_3$COOH) ppm: 1.4–3.2 (m, 16H), 5.4 (d, 2H, $\delta_{J_{PCH}} = 15$ Hz).

(c) Treatment with an excess of diiodomethane at room temperature for 7 days gave 5-iodomethyl-5-(2-thienyl)dibenzophospholium iodide (2, R = CH$_2$I, X = I), m.p. > 150 °C decom. The salt was found to be insoluble in the usual range of recrystallising solvents. Before analysis, the salt was dried at 65 °C in vacuo for several hours.

C$_{17}$H$_{14}$I$_2$PS  
Found C 37.7 H 2.4;  
Calcd C 38.2 H 2.5.

$\delta$(CF$_3$CO$_2$H) ppm: 1.5–2.7 (m, 11H), 5.1 (d, 2H, $\delta_{J_{PCH}} = 8$ Hz).

(d) Treatment of the phosphole (100 mg) in ethanol (3 cm$^3$) with hydrogen peroxide (100 vol., 1 cm$^3$) for 30 min, followed by pouring into water and extraction of the product into chloroform gave 5-(2-thienyl)dibenzophosphole-5-oxide, m.p. 170 °C (from ethyl acetate-hexane).

C$_{16}$H$_{12}$OP  
Found C 67.8 H 4.0;  
Calcd C 68.0 H 3.9.

(e) To a solution of nickel(II) bromide (28 mg) in ethanol (0.5 cm$^3$) was added a hot solution of the phosphole (60 mg, > 2 mol) in glacial acetic acid (2 cm$^3$), to give a deep brown solution from which separated dark brown crystals of the complex, di-

bromobis[5-(2-thienyl)dibenzophosphole]-nickel(II).

C$_{28}$H$_{22}$Br$_2$NiP$_3$S$_2$  
Found C 51.6 H 2.9;  
Calcd C 51.2 H 2.9.

Hydrolysis of phosphonium salts

(a) 5-Methyl-5-(2-thienyl)dibenzophospholium iodide (2, R = Me, X = I). The salt (35 mg) was dissolved in ethanol (1 cm$^3$) and treated with sodium hydroxide solution (2 mol·dm$^{-3}$; 1 cm$^3$) and the solution allowed to stand at room temperature for 24 h. Glc analysis of the resulting solution indicated the presence of thiophen. The solution was then poured into an excess of dilute hydrochloric acid and the product extracted into chloroform solution. After drying over anhydrous sodium sulphate, the chloroform was evaporated to give 5-methyl dibenzophosphole oxide (3, R = Me) as the sole phosphorus-containing product, identical with an authentic sample [6].

(b) 5-Benzyl-5-(2-thienyl)dibenzophospholium bromide (2, R = PhCH$_2$, X = Br). The salt (100 mg) was dissolved in ethanol (1 cm$^3$) and treated with aqueous alkali as above. Glc analysis of the resulting solution indicated the presence of thiophen and toluene, and tlc indicated the presence of two phosphine oxides which were subsequently separated on a preparative scale to give (i) 5-benzylidibenzophosphole oxide (3, R = PhCH$_2$), m.p. 142–143 °C (from hexane-ethyl acetate).

C$_{19}$H$_{15}$OP  
Found C 78.4 H 5.1;  
Calcd C 78.6 H 5.2.

$\delta$(CDCl$_3$): 2.0–3.0 (m, 13H); 6.55 (d, 2H, $\delta_{J_{PCH}} = 15$ Hz); m/e 290 (M$^+$) and 199 (C$_{16}$H$_{14}$PS).

(ii) 5-(2-thienyl)dibenzophosphole oxide (3, R = 2-thienyl) (5 mg), identical with an authentic sample. In a subsequent experiment, the mixture of phosphine oxides was analysed by $^1$H NMR, which indicated that the relative yields of 5-benzyl- and 5-(2-thienyl)dibenzophosphole oxides were in the ratio 85:15.

(c) 5-Iodomethyl-5-(2-thienyl)dibenzophospholium iodide (2, R = CH$_2$I, X = I). The salt (107 mg) was suspended in ethanol (5 cm$^3$) and treated with aqueous sodium hydroxide (0.1 mol·dm$^{-3}$, 2 cm$^3$). The resulting mixture was then heated under reflux for 5 h, during which time the salt dissolved slowly to give a clear solution. Glc analysis indicated the presence of both thiophen and iodomethane. The solution was then evaporated, and the residue dissolved in chloroform and subjected to preparative tlc from which two bands were separated. The first band on extraction gave 5-(2-thienyl)dibenzophosphole oxide, identical with an authentic sample. The second band gave a mixture of 5,6-dihydro-5-(2-thienyl)dibenzophosphine 5-oxide (8, R = 2-thienyl), m/e 296 (M$^+$), and 5-iodomethylidibenzophosphole oxide, m/e 340 (M$^+$). The $^1$H NMR spec-
trum of the mixture in CDCl₃, in addition to showing a multiplet at δ = 1.5–3.0 ppm due to hydrogen atoms attached to aromatic rings, also exhibited a complex signal between δ = 5.5–6.7 ppm which is attributed to the AB component of an ABX spectrum, similar to that observed for other 5,6-dihydro-5-(substituted)dibenzo[b,d]phosphorin-5-oxides. The UV spectrum of the mixture in ethanol also resembled the spectra of the latter compounds [6].

Reaction of 5-(2-thienyl)dibenzophosphole with ethyl propiolate in the presence of water: The phosphole (0.2 g) in THF (3 cm³) was treated with ethyl propiolate (0.2 g) and water (0.3 cm³), and the resulting solution heated under reflux for 2 h. The solvent was then evaporated, and the residue subjected to preparative tlc, to give one main band, which was extracted with ethanol to give 5,6-dihydro-6-ethoxycarbonylmethyl-5-(2-thienyl)dibenzo[b,d]phosphorin-5-oxide (9), m.p. 168–169 °C (from hexane-ethyl acetate).

C₂₁H₁₉O₃PS

Found C 66.1 H 5.0,
Calcd C 65.9 H 5.0.

m/e 382 (M⁺); δ(CDCl₃) ppm: 1.6–3.1 (m, 11H); 5.8 (q, 2H); 5.3–7.8 (m, 3H) and 8.7 (t, 3H); λmax (EtOH) nm (ε): 218 (23,684); 235 (18,718); 260 (10,696); 274 sh (8022) and 290 (4202).