

The Reactivity of Organophosphorus Compounds. Part 31.^{1,†} On the Formation of 1,4-Diphenylnaphthalene from *o*-Bromophenol and 1,2,5-Triphenylphosphole, and Related Reactions

By J. I. G. Cadogan,* Alan G. Rowley, Robert J. Scott, and Norman H. Wilson, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Attempted synthesis of the 1,2,5-triphenylphospholium betaine (2) *via* thermolysis at 250 °C of *o*-bromophenol in the presence of 1,2,5-triphenylphosphole failed, the reaction giving instead bromobenzene (8%), diphenyl phenylphosphonate [(PhO)₂P(O)Ph, 7.5%] copious amounts of hydrogen bromide, and 1,4-diphenylnaphthalene (34%). The last-named has been shown to arise *via* intramolecular rearrangement of 1,2,5-triphenylphosphole, catalysed by hydrogen bromide produced by the thermolysis of *o*-bromophenol. Diphenyl phenylphosphonate is also formed on thermolysis of 1-phenoxy-1,2,5-triphenylphospholium bromide (8), which may therefore be an intermediate in the reaction of *o*-bromophenol with 1,2,5-triphenylphosphole. 1-Phenylnaphthalene is also formed in the former reaction and in the hydrogen bromide-catalysed decomposition of 1,2,5-triphenylphosphole oxide. These reactions are interpreted in terms of ring expansion of strained phospholium species.

NINE years ago ² it was reported that the triphenylphosphonium betaine (1) underwent a Smiles rearrangement (Scheme 1) rather than surmount the alternative steric

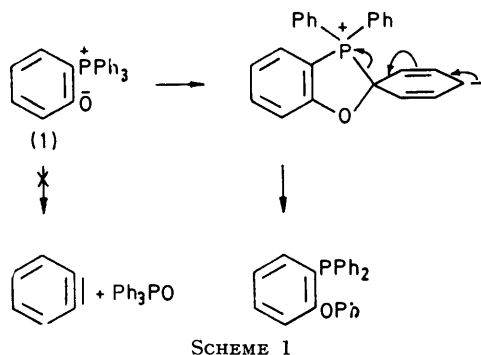
† Preliminary communication, J. I. G. Cadogan, R. J. Scott, and N. H. Wilson, *J.C.S. Chem. Comm.*, 1974, 902.

barrier to give benzyne and triphenylphosphine oxide. The rationale of the experiments we now describe lies in

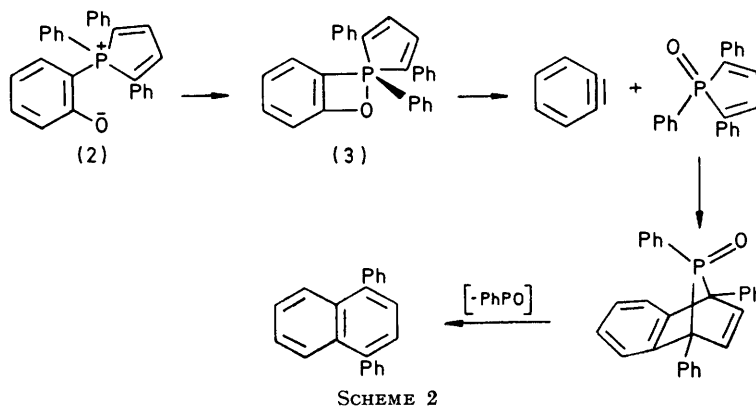
¹ Part 30, J. I. G. Cadogan, R. J. Scott, R. D. Gee, and I. Gosney, *J.C.S. Perkin I*, 1974, 1694.

² H. J. Bestmann and G. Hofmann, *Annalen*, 1968, 716, 98.

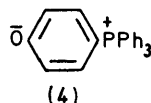
the possible application of the organophosphorus small ring effect³ to overcome this barrier. This concept arose from kinetic experiments performed by Westheimer, Aksnes, Hudson, and others and has been reviewed.³



One of its manifestations is that five- (and four-) membered cyclic phosphonium salts are hydrolysed much faster than analogous acyclic systems. This is attributed, at least in part, to the release of strain during the former reaction, though entropic factors also are likely to be important.³



Thus, to return to the present case, it might be expected that thermolysis of the strained 1,2,5-triphenylphospholium betaine (2) would give the relatively unstrained phosphorane (3) and thence benzyne and triphenylphosphole oxide (Scheme 2). The driving force for reaction *via* (3) would be derived in part from the ease with which the phosphorane (3) could accommodate the five-membered ring in an apical-equatorial sense, in contrast to the acyclic case (Scheme 1) where there is no such advantage from release of strain. In this event it would be



predictable⁴ that cycloaddition of benzyne to 1,2,5-triphenylphosphole oxide followed by extrusion to give 1,4-diphenylnaphthalene would occur (Scheme 2).

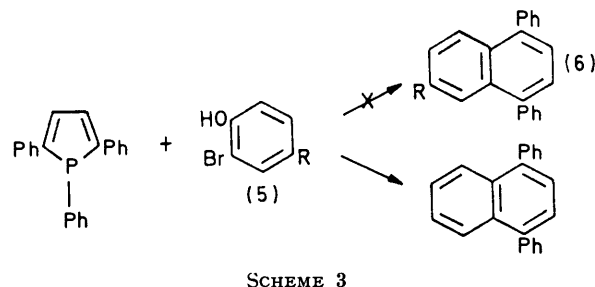
First it was necessary to synthesise the phospholium

³ R. F. Hudson and C. Brown, *Accounts Chem. Res.*, 1972, **5**, 204.

betaine (2). Having failed to obtain identifiable products by thermolysis or photolysis of benzenediazonium-2-oxide in the presence of 1,2,5-triphenylphosphole, we followed McDonald and Campbell's claim⁵ to have produced the related betaine (4), from *p*-bromophenol and triphenylphosphine, by attempting the synthesis of the phospholium betaine (2) by a sealed-tube reaction of 1,2,5-triphenylphosphole with *o*-bromophenol at 250 °C under nitrogen. No betaine was isolated but the reaction gave instead bromobenzene (8%), diphenyl phenylphosphonate [(PhO)₂P(O)Ph] (7.5%), a trace of phenol, copious amounts of hydrogen bromide and 1,4-diphenylnaphthalene (34%). The formation of the last product at first sight pointed to the realisation of the expectation outlined in Scheme 2 *via in situ* formation of the betaine (2). The experiments now described, however, show that this is an oversimplification, that benzyne is not an intermediate, and that there is no evidence for the betaine (2). Rather they reveal the occurrence of a series of ring opening, cycloaddition, and extrusion reactions of complexity belied by the simplicity of the products.

That benzyne was not an intermediate followed from its non-interception by cycloaddition with anthracene, 1,4-diphenylnaphthalene again being formed. Further

it was shown that the latter was not derived from the aromatic moiety in *o*-bromophenol as required by Scheme



2 when the use of 2-bromo-4-methylphenol (5; R = Me) or 3-bromo-4-hydroxybiphenyl (5; R = Ph) instead of *o*-bromophenol gave only 1,4-diphenylnaphthalene (16

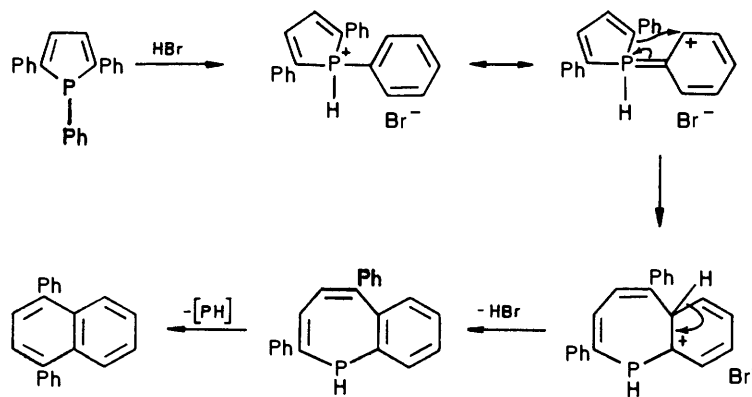
⁴ U. Schmidt, I. Boie, C. Osterroht, R. Schröder, and H.-F. Gruntzmacher, *Chem. Ber.*, 1968, **101**, 1381.

⁵ R. N. McDonald and T. W. Campbell, *J. Amer. Chem. Soc.*, 1960, **82**, 4669.

and 9% respectively) rather than the 6-methyl- or 6-phenyl-substituted analogue (6) (Scheme 3). This suggested that the benzene moieties of 1,4-diphenylnaphthalene were derived exclusively from 1,2,5-triphenylphosphole. In accord with this, 1,2,5-tri-*p*-tolylphosphole and *o*-bromophenol gave the expected trimethylated 1,4-diphenylnaphthalene (14%).

Since *o*-bromophenol evolves hydrogen bromide on being heated [Scheme 5(i)], and control experiments

unchanged *o*-bromophenol to give phenol and bromine [step (ii)]. Evidence for step (i) comes from our observation that thermolysis of *o*-bromophenol at 250 °C for 48 h gave phenol (14%) and hydrogen bromide; support for step (ii) is provided by O'Bara and his co-workers,⁷ who showed that bromination of phenols is reversible at room temperature. Removal of bromine, and hence movement of the equilibrium (ii) in the required direction to the right, to give triphenylphosphole dibromide (7)

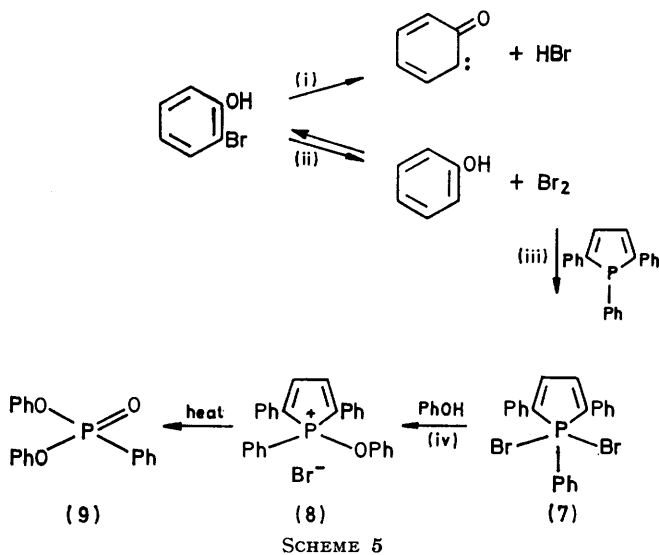


having shown that 1,4-diphenylnaphthalene did not arise when 1,2,5-triphenylphosphole or its oxide was heated alone, we investigated the reactions of these compounds with catalytic quantities of hydrogen bromide: 1,2,5-triphenylphosphole was rapidly and totally consumed to give 1,4-diphenylnaphthalene (14%) and much tar. Again, the anthracene test ruled out the intermediacy of benzyne.

It is suggested, therefore, that the formation of 1,4-diphenylnaphthalene in the reaction of *o*-bromophenol with 1,2,5-triphenylphosphole is best represented by Scheme 4, in which HBr performs a catalytic function, and wherein the strained protonated phosphole undergoes ring expansion with subsequent loss of the [HP] moiety which is lost as a tar. Whether the latter is extruded as such or bimolecularly is not known.

The genesis of diphenyl phenylphosphonate in the reaction is less easily understood. From the foregoing it is likely to involve a separate reaction, unconnected with the formation of 1,4-diphenylnaphthalene. In this connection it is noteworthy that Hoffmann and Horner⁶ postulated phenoxytriphenylphosphonium bromide ($\text{PhOPPh}_3^+\text{Br}^-$) as an intermediate in the reaction of *o*-bromophenol with triphenylphosphine which gives bromobenzene and triphenylphosphine oxide. We therefore investigated the possibility that 1-phenoxy-1,2,5-triphenylphospholium bromide (8) was an intermediate in our reaction. This could arise, as outlined in Scheme 5, *via* thermolysis of *o*-bromophenol to give hydrogen bromide [step (i)], which in turn reacts with

[step (iii)] followed by reaction of (7) with phenol could then give 1-phenoxy-1,2,5-triphenylphospholium bromide (8) [step (iv)]. In the event, thermolysis of the



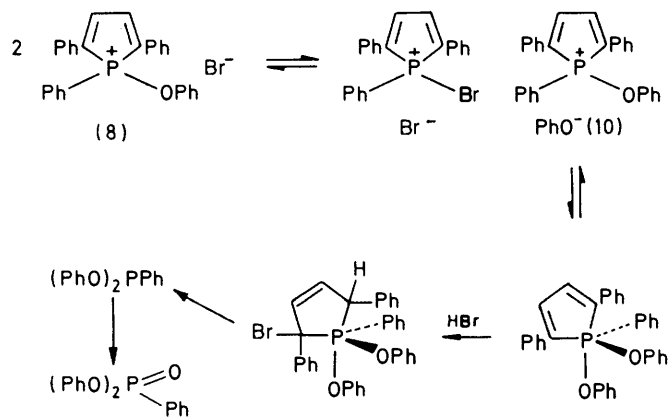
salt (8), easily prepared from the phosphole dibromide (7) and phenol, gave hydrogen bromide, much tar, and diphenyl phenylphosphonate (9) [0.35 mole per mole of (8)], detection of which could be taken as circumstantial evidence, at least, for the intermediacy of the phospholium salt (8) in the reaction of *o*-bromophenol and 1,2,5-triphenylphosphole. Against this, however, is the concomitant formation, in the thermolysis of (8), of a small amount (4%) of 1-phenylnaphthalene. If (8) was,

⁶ H. Hoffmann and L. Horner, 'Newer Methods of Organic Chemistry,' vol. II, ed. W. Foerst, Academic Press, New York, 1963; H. Hoffmann, L. Horner, G. Wippel, and D. Michael, *Chem. Ber.*, 1962, **95**, 523.

⁷ E. J. O'Bara, R. B. Balsley, and I. Storer, *J. Org. Chem.*, 1970, **35**, 16.

indeed, an intermediate in the formation of diphenyl phenylphosphonate, as in Scheme 5, then 1-phenylnaphthalene should be formed to the extent of 1% in the reaction of *o*-bromophenol with triphenylphosphole (which gave diphenyl phenylphosphonate in 7.5% yield). This quantity was below the certainty level of our analysis.

Regardless of whether or not (8) is an intermediate in this reaction, however, the fact of the remarkable conversion of (8) into diphenyl phenylphosphonate requires explanation. Reaction as in Scheme 6 is suggested *via*



SCHEME 6

ligand exchange of the phospholium bromide (8) to give the diphenoxy-derivative (10). Addition of HBr to

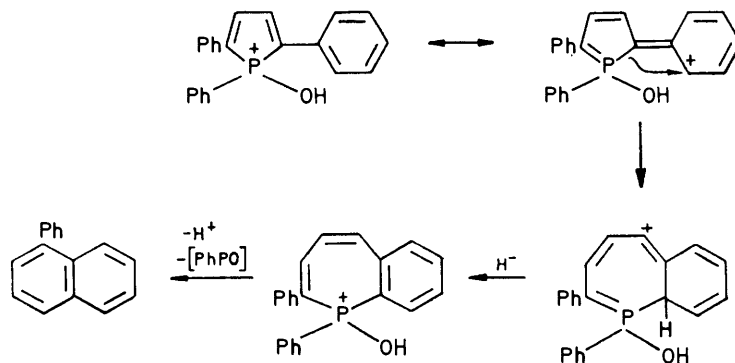
ring expansion reaction involving a *C*-phenyl group of the phospholium nucleus rather than *via* the *P*-phenyl group as observed in the case of the reaction of hydrogen bromide and 1,2,5-triphenylphosphole to give 1,4-diphenylnaphthalene (Scheme 4). The reaction of 1,2,5-triphenylphosphole oxide with hydrogen bromide also gives 1-phenylnaphthalene (17%) but no 1,4-diphenylnaphthalene. The mechanism outlined in Scheme 7 suggests itself but an explanation of the different modes of ring expansion observed on varying the phosphole derivative must await the results of further experiments.

EXPERIMENTAL

N.m.r. studies were carried out with Varian instruments (HA 100 for ^1H , CFT20 for ^{13}C , and XL 100 for ^{31}P ; ^{31}P shifts are positive to high frequency).

Materials.—1,2,5-Triphenylphosphole, prepared by the method of Campbell *et al.*,¹⁰ had m.p. 187–188 °C (lit.,¹⁰ 187–189 °C). 1,2,5-Tri-(*p*-tolyl)phosphole, prepared analogously from 4-tolylphosphonous dichloride¹¹ and 1,4-di-*p*-tolylbuta-1,3-diene,¹² had m.p. 182–183 °C (Found: C, 85.1; H, 6.7. $\text{C}_{25}\text{H}_{23}\text{P}$ requires C, 84.7; H, 6.5%), δ_{H} 6.8–7.25 (14 H, m), 2.16 (3 H, s), and 2.24 (6 H, s). 1,2,5-Triphenylphosphole oxide, obtained as described by Campbell,¹⁰ by oxidation of the phosphole with hydrogen peroxide, had m.p. 238–239 °C (lit.,¹⁰ 237–239 °C). 4-Hydroxy-3-bromobiphenyl¹³ had m.p. 91–93 °C (lit.,¹³ 93.5–94.5 °C). Diphenyl phenylphosphonite¹⁴ was oxidised quantitatively to the phosphonate by aqueous ethanolic hydrogen peroxide. The product, recrystallised from aqueous ethanol, had m.p. 71–72.5 °C (lit.,¹⁵ 73–74 °C).

1,4-Diphenylnaphthalene had m.p. 135–137 °C (lit.,¹⁶



SCHEME 7

diene moiety followed by extrusion of diphenyl diphenylphosphonite, which is then oxidised *via* bromination, followed by hydrolysis in work-up, leads to the phosphonate. Both ligand exchange in phosphonium-type salts *via* stable phosphoranes⁸ and extrusion from penta-co-ordinate species⁹ are precedented reactions.

The formation of 1-phenylnaphthalene indicates a

⁸ I. M. Downie, H. Heaney, and G. Kemp, *Tetrahedron Letters*, 1975, 3951.

⁹ C. D. Hall, J. D. Bramblett, and F. F. S. Lin, *J. Amer. Chem. Soc.*, 1972, **94**, 9264; D. E. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *ibid.*, p. 245.

¹⁰ I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J. Chem. Soc.*, 1965, 2184.

¹¹ B. Buckner and L. B. Lockhart, *J. Amer. Chem. Soc.*, 1951, **73**, 755.

135–137 °C). 1-Phenylnaphthalene, prepared by the method of Hartman and Rahrs,¹⁷ had b.p. 114–115 °C at 0.4 mmHg (lit.,¹⁷ 134–135 °C at 2 mmHg).

1-Phenoxy-1,2,5-triphenylphospholium Bromide.—This was prepared in 60% yield by the reaction of equimolar

¹² H. Burton and C. K. Ingold, *J. Chem. Soc.*, 1928, 904; R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, 1959, **24**, 1969.

¹³ S. E. Hazlet, *J. Amer. Chem. Soc.*, 1939, **61**, 1447.

¹⁴ A. E. Arbuzov, G. Kamai, and L. V. Nesterov, *Trudy Kagan Khim.-Tekhnol. Inst. im S.M. Khirouva*, 1951, 17 (*Chem. Abs.*, 1957, **51**, 5720).

¹⁵ G. M. Kosolapoff, 'Organophosphorus Compounds,' 1st edn., Wiley, New York, 1950, p. 163.

¹⁶ 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1965.

¹⁷ W. W. Hartman and E. J. Rahrs, *Org. Synth.*, 1944, **24**, 81.

amounts of phenol and 1,2,5-triphenylphosphole 1,1-dibromide¹⁰ in dry benzene (250 ml benzene per 0.01 mol of starting material) at the b.p. until no more HBr was evolved (usually *ca.* 16 h). The resulting solid was filtered off, washed thoroughly with dry benzene, and dried under vacuum to give a red *solid*, m.p. 181–182° (decomp.), which decomposed on attempted recrystallisation to give the phosphole oxide (Found: C, 69.4; H, 4.6. C₂₈H₂₂BrOP requires C, 69.3; H, 4.6%); δ_{H} 7.0–8.1 (20 ArH, m) and 8.51 (2 H, d, $J_{\text{H,P}}$ 45 Hz) (decoupling confirmed the H,P-coupling); δ_{P} (¹H-decoupled spectrum) + 74.6 p.p.m. relative to external 85% H₃PO₄. The assigned structure has 14 types of carbon atom, but more ¹³C n.m.r. signals would be expected as a result of P,C-coupling. The observed spectrum showed 20 lines (Table) but 12 of these existed as pairs of equal

δ_{C}	Multiplicity	$J_{\text{C,P}}/\text{Hz}$	δ_{C}	Multiplicity	$J_{\text{C,P}}/\text{Hz}$
144.8	D	29.8	129.1	S	
137.1	D	3.1	128.4	S	
130.4	D	58.3	128.0	S	
131.1	S		126.6	D	7.0
130.1	S		124.8	S	
129.9	S		119.1	D	4.9
129.2	S		117.6	D	59.0

intensity which we interpret as being P,C-doublets. Thus the spectrum is consistent with the structure (14 magnetically different carbon atoms with six coupled to ³¹P). The two strongly coupled signals at δ 144.8 and 130.4 may be assigned to the two quaternary types of carbon attached to phosphorus; those in the phosphole ring and that of the 1-aryl group. The lower frequency signal with strong phosphorus coupling (δ 117.6) may be due to tertiary hetero-ring carbon atoms.

Reactions of 1,2,5-Triphenylphosphole.—1,2,5-Triphenylphosphole (0.005 mol) and an equimolar amount of *o*-bromophenol were heated in a sealed tube, under nitrogen,

at 250 °C for 48 h. When cool the products were dissolved in chloroform and examined by g.l.c. Qualitative analysis was performed by comparison of retention times with those of authentic samples and by mass spectrometry–g.l.c. (Micromass 12 system). Quantitative analysis was carried out by the internal standard technique.

1,4-Diphenylnaphthalene was also isolated by chromatography on alumina. It had m.p. 135–137 °C (lit.,¹⁶ 135–137 °C) and was identical with an authentic sample [mixed m.p. (135–137 °C) and comparison of i.r., ¹H n.m.r., and mass spectra].

Reactions in which the *o*-bromophenol was replaced by an equimolar amount of 3-bromo-4-hydroxybiphenyl or 2-bromo-4-methylphenol or where 1,2,5-tri-(*p*-tolyl)phosphole (0.005 mol) replaced the triphenyl derivative were carried out in a similar manner and the products were analysed by g.l.c. and g.l.c.–mass spectrometry.

Attempts to trap benzyne with anthracene (0.01 mol) were carried out on the same scale and in the same manner.

Thermolyses of 1,2,5-triphenylphosphole (0.005 mol) and its oxide (0.005 mol) in the presence of HBr were also carried out in a sealed tube, the method being as already described, except that the tubes were purged with HBr subsequent to the nitrogen purge and prior to sealing. Again analysis was performed by g.l.c. and g.l.c.–mass spectrometry.

1-Phenoxy-1,2,5-triphenylphospholium bromide (0.01 mol) was decomposed in a similar sealed-tube reaction. In addition to the normal analysis by g.l.c. and g.l.c.–mass spectrometry, 1-phenylnaphthalene was isolated by preparative g.l.c. and shown to be identical [mass, i.r., and n.m.r. (¹H and ¹³C) spectra] with an authentic sample.

o-Bromophenol heated alone in a sealed tube under nitrogen for 24 h at 250 °C gave phenol (18%), as shown by g.l.c. and g.l.c.–mass spectrometry.

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