The Reactivity of Organophosphorus Compounds. Part 35.[1] Pyrolysis of 3-Aryl- and 3-Alkyl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles

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Pyrolysis of 2,2-diphenyl-2-methoxy derivatives of the title compounds in the gas phase gives phosphinates or phosphinamidates derived from the substrate by formal loss of methylene. Control experiments show that the reaction involves radical cleavage initiated by rupture of the oxazaphosph(v)ole ring. Pyrolysis of 3-aryl-2,2-dimethoxy-2-phenyl derivatives of the title compounds under similar conditions results in the formation of 3-aryl-2,3-dihydro-2-oxo-2-phenyl-1,3,2-benzoxazaphospholes. No significant products could be isolated from 2,2,2-trimethoxy derivatives, though vigorous conditions were required for their complete breakdown. The pyrolysis of the corresponding 2,2-diphenyl-2-ethoxy, 2,2-diethoxy-2-phenyl, and 2,2,2-triethoxy compounds gave higher yields of similar products, possibly *via* a six-centre concerted elimination.

Pyrolysis reactions of five-co-ordinate phosphorus compounds are dominated by the formation of phosphorus(IV) species, generally by the extrusion of a low molecular weight phosphorus oxide. Familiar examples include the formation of epoxides by phosphate extrusion from 1,3,2-dioxaphosph(v)-olans [2] and the generation of nitrile ylides from 2,3-dihydro-1,4,2-oxazaphosph(v)oles.[3] Less commonly, the phosphorus(IV) state may be attained by ligand reorganisation, as in the formation of the phosphoramidate (4) from a thiazaphosph(v)ole (1) [4,5] (Scheme 1). In contrast, the related oxazaphosph(v)-oles (2) are known to have high thermal stability,[6] though under photolysis conditions phosphorus(IV) extrusion leads to the formation of carbazoles (5) [7] (Scheme 1). We now report the thermolysis reactions of benzoxazaphosph(v)oles (2) and (3), which are observed in the gas phase under flash vacuum pyrolysis conditions.

The *N*-aryl compounds (2) were made, under anhydrous conditions, by the standard deoxygenation route.[6] *N*-Alkyl-benzoxazaphosph(v)oles (3) have not hitherto been prepared,[8] but were obtained in moderate yield by *N*-chlorodi-isopropyl-amine [9,10] oxidation of the appropriate *o*-(*N*-alkylamino)-phenol [11] in the presence of the appropriate phosphorus(III) reagent. Because this method consumes just 1 mol equiv. of phosphorus(III) reagent per mol equiv. of phosph(v)ole formed, it was more convenient for the preparation of phosphoranes with complex ligands [*e.g.* (3d—f)]. The phosph(v)-oles (3) can be isolated by column chromatography and handled in air without apparent decomposition. In their ^1H n.m.r. spectra, the *N*-alkyl group shows a three-bond coupling to phosphorus of *ca.* 10 Hz, while their ^{31}P n.m.r. spectra show shifts of *ca.* −38 p.p.m. The mass spectra of (3) show loss of the 2-alkoxy group from the molecular ion, and also a peak at *m/z* 201 corresponding to the $[Ph_2PO]^+$ moiety.

The major identified product from the pyrolysis of the 2-methoxy derivative (2a) at 650 °C was the phosphinate (6) (25%): the phosphinate (7) (3%) was detected in the pyrolysate from the *N*-methyl derivative (3a), but in this case the isomeric phosphinamidate (8) (35%) was dominant. This latter compound must be the primary product of the thermolysis, since it rearranges quantitatively to the phosphinate (7) at 700 °C (Scheme 2).

The products in Scheme 2 are formed by formal α-elimination of methylene from the phosph(v)oles (*e.g.* Scheme 3), for which a reasonable driving force is the strength of the P=O bond generated. Flash vacuum pyrolysis conditions are not well suited to the detection of reactive intermediates by
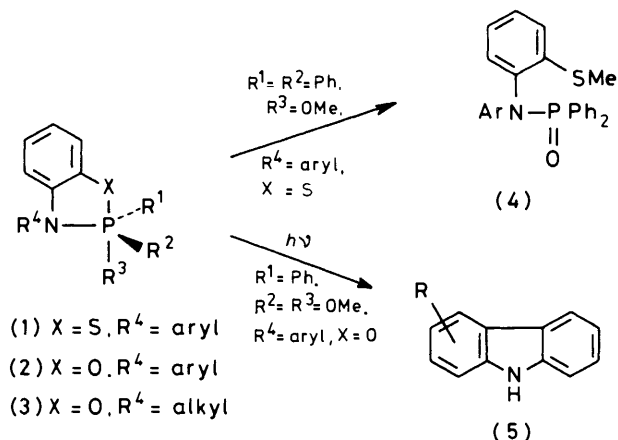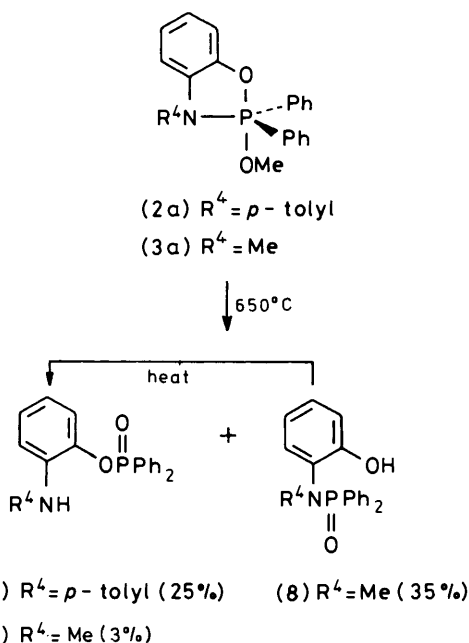
Scheme 1.

intermolecular reactions because of the dilute conditions involved and so no attempts were made to trap methylene. Instead, we investigated the potential of phosph(v)oles as possible gas-phase carbene generators by pyrolysis of the neopentoxy derivatives (3d) and (3e) and the benzyl derivatives (3f) and (3g). These compounds should give t-butylcarbene and arylcarbenes respectively which would be trapped by intramolecular processes. The behaviour of the latter intermediates in the gas phase is now well understood,[12] but t-butylcarbene has been studied predominantly in solution,[13,14] wherein a mixture of alkenes and 1,1-dimethylcyclopropane (9) was obtained. However, the cyclopropane (9) was the only isolated product from the pyrolysis of the tosylhydrazone salt (10) (Scheme 4) under gas-phase conditions: it was readily characterised by low frequency signals in its ^1H and ^{13}C n.m.r. spectra. It was therefore easy to show that the cyclopropane (9) was unambiguously *absent* from the pyrolysates derived from (3d) and (3e), even though the expected phosphinate (7) was detected. Hence these phosph(v)oles do *not* act as carbene generators under flash pyrolysis conditions.

Similarly, pyrolysis of the benzyl derivatives (3f) and (3g), gave none of the expected products of arylcarbene automerisation. Instead, bibenzyl (38%) and di-*p*-tolylethane (30%), respectively, were obtained, which strongly suggests that the thermolyses proceed *via* free radical intermediates. Co-
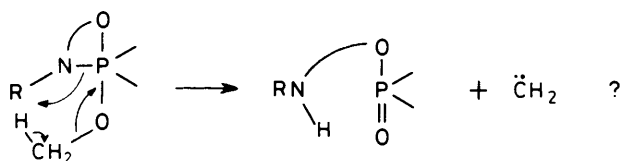
(2)

(3)
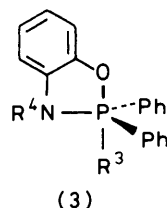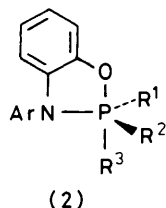
a; $R^1 = R^2 = Ph$, $R^3 = OMe$, Ar = p-tolyl
b; $R^1 = R^2 = Ph$, $R^3 = OEt$, Ar = p-tolyl
c; $R^1 = R^2 = Ph$, $R^3 = OEt$, Ar = 2,4,6-$Me_3C_6H_2$
d; $R^1 = Ph$, $R^2 = R^3 = OMe$, Ar = p-tolyl
e; $R^1 = Ar = Ph$, $R^2 = R^3 = OMe$
f; $R^1 = Ph$, $R^2 = R^3 = OEt$, Ar = p-tolyl
g; $R^1 = R^2 = R^3 = OMe$, Ar = p-tolyl
h; $R^1 = R^2 = R^3 = OEt$, Ar = p-tolyl

a; $R^3 = OMe$, $R^4 = Me$
b; $R^3 = OEt$, $R^4 = Me$
c; $R^3 = OEt$, $R^4 = Et$
d; $R^3 = OCH_2Bu^t$, $R^4 = Me$
e; $R^3 = OCH_2Bu^t$, $R^4 = Et$
f; $R^3 = OCH_2Ph$, $R^4 = Me$
g; $R^3 = OCH_2(p$-tolyl), $R^4 = Me$

(2a) $R^4 = p$- tolyl

(3a) $R^4 = Me$

650 °C

(6) $R^4 = p$- tolyl (25 %)   (8) $R^4 = Me$ (35 %)

(7) $R^4 = Me$ (3 %)

Scheme 2.
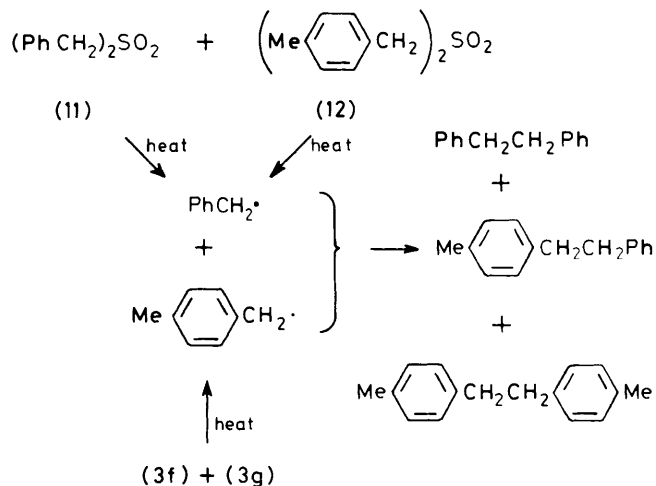

Scheme 3.

Scheme 4.

Scheme 5.

pyrolysis of (3f) and (3g) gave the mixture of bibenzyl derivatives (Scheme 5) expected from random coupling reactions of the radicals. A similar mixture was obtained by co-pyrolysis of the sulphones (11) and (12) which have long been suspected to be generators of benzyl radicals.[15] We have recently reported other examples of the similarity between phosph(v)ole and sulphone pyrolysis.[8]

The products obtained by variation of the ligands around the phosphorus atom in (2) provide evidence for the mechanism of breakdown of the phosph(v)ole ring. The dimethoxy compounds (2d) and (2e) give the 2-oxo compound [e.g. (13) (65%)] as major product, and in one case the phosphonate (14)
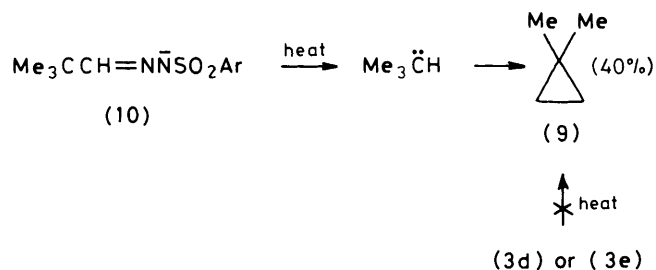
(15%) was isolated (Scheme 6). Although no products could be isolated from the pyrolysis of the trimethoxy compound (2g), it is significant that complete decomposition requires much more vigorous pyrolysis conditions (800 °C). This suggests that the phosph(v)ole ring cleaves to give a phosphoranyl radical,[16,17] since these are stabilised by aryl substituents [18,19] and could be formed under milder conditions when $R^1(R^2) = Ph$. Two mechanisms are possible (Scheme 7): P-O bond cleavage leads to phosphoramidates after β-scission [16] (to give the alkyl radical) and hydrogen abstraction (Route a), while a similar sequence initiated by P-N bond cleavage gives phosphinates, (or phosphonates) (Route b). There is good evidence that Route a is followed by the N-alkyl derivatives (3a) and (3d—g), since the phosphoramidate (8) is the primary product from

(2d) $R^4 = p$-tolyl
(2e) $R^4 = $Ph

650°C

(13) $R^4 = p$-tolyl (65%)
(15) $R^4 = $Ph
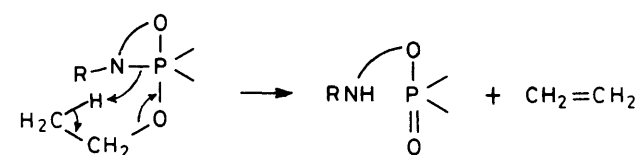
(14) $R^4 = p$-tolyl (15%)
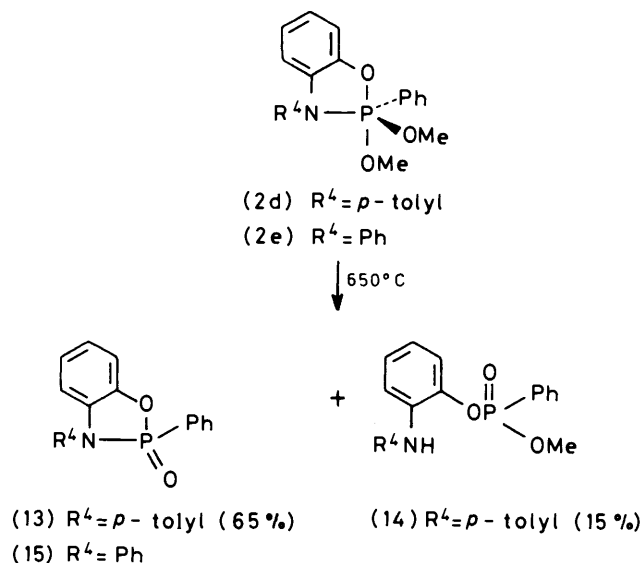
Scheme 6.

(2a), and since the feasibility of axial P−O bond cleavage is demonstrated by the formation of neopentyl alcohol (33%) and benzyl alcohol (14%) from (3d) and (3f) respectively. The high levels of phosphinates from the N-aryl compounds [e.g. (2a)] are best explained * by Route b, in which the added driving force is provided by delocalisation of the aminyl into *two* aromatic rings. A similar mechanism is probably involved in the formation of a phosphorus(IV)oxide from a 1,2,5-oxazaphosph(V)olan, by formal elimination of benzyne, which was reported by Huisgen.[20,21]

It is significant that none of the routes in Scheme 7 involves cleavage of the aryl−oxygen bond which would be required if phosphorus(IV) extrusion to give carbazoles were to take place. It is known that such bonds are particularly strong, and can resist cleavage under pyrolytic conditions.[22,23]
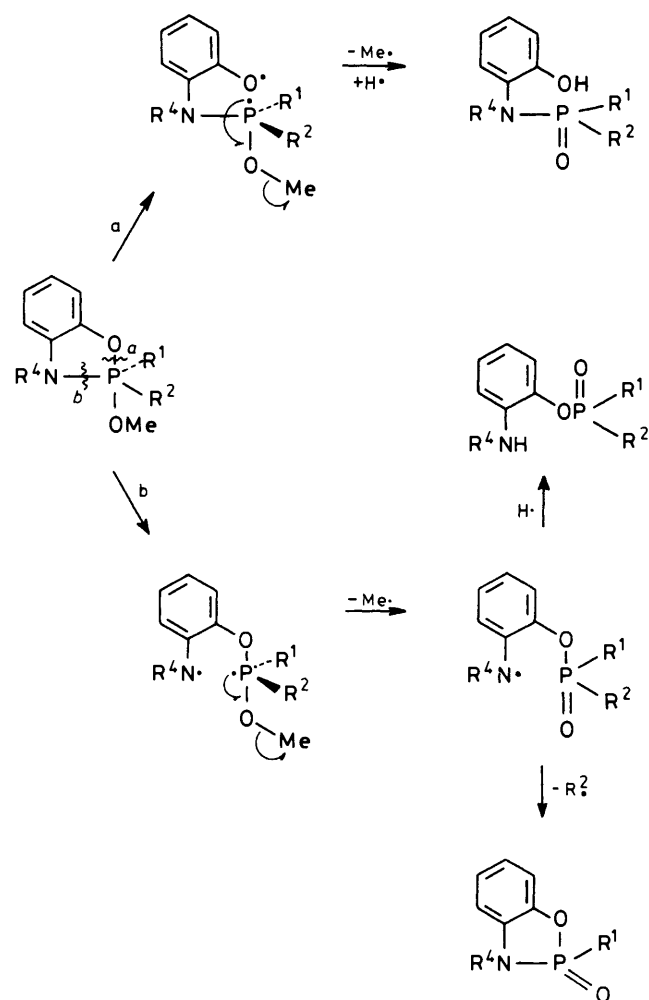
An alternative fragmentation mechanism is available for the 2-ethoxyphosph(V)oles (2b, c, f, h) and (3b, c), which have a hydrogen atom on the β-carbon of the alkoxy group, since formation of an alkene can take place *via* a cyclic transition state (Scheme 8). This may explain why the decomposition temperatures of these compounds are lower, and the yields and accountance of products are higher than those of the corresponding methoxy compound, though the free radical pathway (*cf.* Scheme 7) cannot be unambiguously ruled out.

The isolation of ethanol from the pyrolysis of (2f) is evidence that the 2-oxo compounds (13) [or (15)] are formed by a stepwise cleavage of the ligands, rather than by concerted loss of diethyl ether (Scheme 7).

It is clear that the mechanisms of benzoxazaphosph(V)ole pyrolyses are complex, and it has only been possible in this study to rationalise the principal fragmentation modes. However, some non-phosphorus-containing products were isolated from pyrolyses of the 3-aryl derivatives (2) which suggest that the expected extrusion reactions may be obtained with appropriate choice of substrate. Thus the 2-phenyl derivative (2d) gave a low yield of 3-methylcarbazole (16) (14%) by extrusion of dimethyl phenylphosphonate, which was also detected in the pyrolysate. Surprisingly, the 2,2-diphenyl derivatives (2a, b) gave in low yield a compound with m/z 197,

* However, Route a cannot be excluded because of the known [1] thermal isomerisation of phosphoramidates [*cf.* (8)].

Scheme 7.

Scheme 8.

which was tentatively identified as 3-methylphenoxazine (17). This formally derives from the phosph(V)oles by cheleotropic elimination of a phosphorus(III) species, a reaction which has some precedent in phosphorane chemistry.[24] Although no phosphinites could be detected amongst the products in the present cases, methyl diphenylphosphinite was shown to decompose to a variety of products under the thermolysis conditions.

(16)

(17)

Experimental

^{1}H, ^{13}C, and ^{31}P N.m.r. spectra were recorded at 100, 20, and 24 MHz respectively, for solutions in deuteriochloroform.

Tervalent Phosphorus Reagents.—The following reagents were prepared by the action of the appropriate alcohol on chlorodiphenylphosphine in the presence of triethylamine in dry ether [25]—neopentyl diphenylphosphinite (64%), b.p. 135—136 °C (0.5 Torr), ^{1}H n.m.r. δ 7.1—8.0 (10 H, complex), 3.50 (2 H, d,), and 0.92 (9 H, s); ^{31}P n.m.r. δ 112.3 p.p.m. [characterised as *neopentyl diphenylphosphinothionate* (*cf.* ref. 26), m.p. 62—65 °C [From light petroleum (b.p. 60—80 °C)], ^{1}H n.m.r. δ 7.7—8.1 (4 H, complex), 7.2—7.6 (6 H, complex), 3.63 (2 H, d) and 0.97 (9 H, s), ^{31}P n.m.r. δ 80.4 p.p.m., *m/z* 304 (*M*$^+$, 93%), 235 (48), 234 (44), and 201 (100) (Found: C, 67.15; H, 6.95. $C_{17}H_{21}OPS$ requires C, 67.1; H, 6.95%)]: benzyl diphenylphosphinite (crude yield 93%, used without purification), ^{31}P n.m.r. δ 114.2 p.p.m. [characterised as *benzyl diphenylphosphinothionate* (*cf.* ref 26), m.p. 57—58 °C (from methanol), ^{1}H n.m.r. δ 7.7—8.1 (4 H, complex), 7.1—7.6 (11 H, complex), and 5.03 (2 H, d), ^{31}P n.m.r. δ 82.4 p.p.m., *m/z* 324 (*M*$^+$, 28%), 218 (100), and 91 (53) (Found, C, 70.15; H, 5.35. $C_{19}H_{17}OPS$ requires C, 70.35; H, 5.3%)]: 4-methylbenzyl diphenylphosphinite (crude yield 77%, used without purification), ^{31}P n.m.r. δ 113.6 p.p.m. [characterised as *4-methyl benzyl diphenylphosphinate* (obtained by lead tetraacetate oxidation [27], m.p. 88—89 °C [from light petroleum (b.p. 60—80 °C)], ^{1}H n.m.r. δ 7.6—8.0 (4 H, complex), 6.9—7.6 (10 H, complex), 5.01 (2 H, d), and 2.31 (3 H, s), ^{31}P n.m.r. δ 32.2 p.p.m., *m/z* 322 (*M*$^+$, 34%), 202 (100), 105 (34), and 77 (29) (Found: C, 74.6; H, 5.65. $C_{20}H_{19}O_2P$ requires C, 74.5; H, 5.95%)].

3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)*oles.*—The following phosphoranes were made by deoxygenation of the appropriate *o*-nitrophenyl aryl ether by the appropriate tervalent phosphorus reagent in super-dry cumene.[6] (The usual precautions for handling phosphorus(v) species were observed). 2-*Ethoxy-2,2-diphenyl-3-p-tolyl*(75%), m.p. 133—135 °C [from light petroleum (b.p. 60—80 °C)], ^{1}H n.m.r. δ 6.4—8.0 (17 H, complex), 6.05 (1 H, m), 2.70 (2 H, apparent quintet), 2.37 (3 H, d) and 0.30 (3 H, t), ^{31}P n.m.r. δ —41.7 p.p.m., *m/z* 427 (*M*$^+$, 100%), 399 (37), 382 (26), 201 (68), and 77 (25) (Found: C, 75.85; H, 6.2; N, 3.15. $C_{27}H_{26}NO_2P$ requires C, 75.9; H, 6.1; N, 3.3%): 2-*ethoxy-2,2-diphenyl-3-(2,4,6-trimethylphenyl)* (76%), m.p. 143—145 °C [from light petroleum (b.p. 60—80 °C)], ^{1}H n.m.r. δ 6.4—8.0 (15 H, complex), 5.90 (1 H, d,) 2.75 (2 H, apparent quintet), 2.27 (3 H, s), 2.01 (6 H, s), and 0.48 (3 H, t), ^{31}P n.m.r. δ —43.9 p.p.m., *m/z* 455 (*M*$^+$, 100%), 410 (16), 208 (85), 201 (36), and 77 (20) (Found: C, 76.45; H, 6.7; N, 3.0. $C_{29}H_{30}NO_2P$ requires C, 76.5; H, 6.6; N, 3.1%): 2,2-*diethoxy-2-phenyl-3-p-tolyl* (71%), m.p. 107—111 °C [from light petroleum (b.p. 60—80 °C)], ^{1}H n.m.r. δ 6.4—7.8 (12 H, complex), 6.14 (1 H, m), 3.71 (4 H, m), 2.34 (3 H, s), and 0.93 (6 H, t), ^{31}P n.m.r. δ —46.0 p.p.m., *m/z* 395 (*M*$^+$, 88%), 367 (32), 199 (100), 183 (24), 141 (36) and 77 (32) (Found: C, 69.8; H, 6.6; N, 3.5. $C_{23}H_{26}NO_3P$ requires C, 69.85; H, 6.65; N, 3.55%): 2,2,2-*triethoxy-3-p-tolyl* (87%), b.p. 180—185 °C (0.05 Torr) (solidified to a yellow waxy material after several days at —20 °C), ^{1}H n.m.r. δ 6.4—7.4 (7 H, complex), 6.07 (1 H, m), 3.86 (6 H, d of q), 2.36 (3 H, s), and 1.00 (9 H, d of t), ^{31}P n.m.r. δ —57.9 p.p.m., *m/z* 363 (*M*$^+$, 100%), 335 (59), and 261 (38) (Found: C, 63.0; H, 7.1; N, 4.15. $C_{19}H_{26}NO_4P$ requires C, 62.8; H, 7.2; N, 3.85%).

2-Alkoxy-3-alkyl-2,3-dihydro-2,2-diphenyl-1,3,2-benzoxazaphosph(v)*oles.*—These phosph(v)oles were made by *N*-chlorodi-isopropylamine oxidation [9,10] of the appropriate 2-alkylaminophenol [11] in the presence of the appropriate tervalent phosphorus reagent in super-dry ether at —20 °C, and were purified by chromatography on an active alumina column (320 × 15 mm, for 5 mmol scale) using ether as eluant (*ca.* 70 ml required for 5 mmol scale). The following phosphoranes were prepared: 2-*methoxy-3-methyl* (21%), m.p. 102—104 °C [from ether–light petroleum (b.p. 40—60 °C)], ^{1}H n.m.r. δ 7.5—7.9 (4 H, complex), 7.2—7.5 (6 H, complex), 6.4—6.9 (4 H, complex), 3.37 (3 H, d) and 2.92 (3 H, d), ^{31}P n.m.r. δ —36.0 p.p.m., *m/z* 337 (*M*$^+$, 100%), 306 (37), and 201 (37) (Found: C, 71.4; H, 6.05; N, 4.1. $C_{20}H_{20}NO_2P$ requires C, 71.2; H, 6.0; N, 4.15%): 2-*ethoxy-3-methyl* (33%), m.p. 112—116 °C [from ether–light petroleum (b.p. 40—60 °C)], ^{1}H n.m.r. δ 7.5—7.9 (4 H, complex), 7.2—7.5 (6 H, complex), 6.4—6.9 (4 H, complex), 3.39 (3 H, d), 3.05 (2 H, apparent quintet), and 0.99 (3 H, t), ^{31}P n.m.r. δ —38.1 p.p.m., *m/z* 351 (*M*$^+$, 100%), 306 (42), and 201 (71) (Found: C, 71.6; H, 6.4; N, 4.05. $C_{21}H_{22}NO_2P$ requires C, 71.8; H, 6.3; N, 4.0%): 2-*ethoxy-3-ethyl* (32%), m.p. 145—147 °C (from ether), ^{1}H n.m.r. δ 7.5—7.9 (4 H, complex), 7.0—7.5 (6 H, complex), 6.3—6.8 (4 H, complex), 3.99 (2 H, apparent sextet), 2.98 (2 H, apparent quintet), 1.42 (3 H, t), and 0.96 (3 H, t), ^{31}P n.m.r. δ —38.9 p.p.m., *m/z* 365 (*M*$^+$, 76%), 350 (64), 320 (40), and 201 (100) (Found: C, 72.35; H, 6.7; N, 3.8. $C_{22}H_{24}NO_2P$ requires C, 72.3; H, 6.6; N, 3.85%): 3-*methyl-2-neopentoxy* (31%), m.p. 114—118 °C [from ether–light petroleum (b.p. 40—60 °C)], ^{1}H n.m.r. δ 7.5—7.9 (4 H, complex), 7.2—7.5 (6 H, complex), 6.3—6.8 (4 H, complex), 3.50 (3 H, d), 2.63 (2 H, d), and 0.76 (9 H, s), ^{31}P n.m.r. δ —39.1 p.p.m., *m/z* 393 (*M*$^+$, 79%), 323 (100), 306 (63), 219 (47), and 201 (63) (Found: C, 73.5; H, 7.4; N, 3.5. $C_{24}H_{28}NO_2P$ requires C, 73.25; H, 7.15; N, 3.55%): 3-*ethyl-2-neopentoxy* (38%), m.p. 123—127 °C (from ether), ^{1}H n.m.r. δ 7.6—7.9 (4 H, complex), 7.2—7.5 (6 H, complex), 6.3—6.8 (4 H, complex), 4.14 (2 H, apparent sextet), 2.59 (2 H, d), 1.49 (3 H, t), and 0.74 (9 H, s), ^{31}P n.m.r. δ —38.9 p.p.m., *m/z* 407 (*M*$^+$, 94%), 337 (75), 322 (94), and 320 (100) (Found: C, 73.9; H, 7.6; N, 3.35. $C_{25}H_{30}NO_2P$ requires C, 73.7; H, 7.4; N, 3.45%): 2-*benzyloxy-3-methyl* (32%), m.p. 86—89 °C [from ether–light petroleum (b.p. 40—60 °C)], ^{1}H n.m.r. δ 7.6—8.0 (4 H, complex), 7.0—7.5 (11 H, complex), 6.4—6.8 (4 H, complex), 4.10 (2 H, d), and 3.43 (3 H, d), ^{31}P n.m.r. δ —38.5 p.p.m., *m/z* 413 (*M*$^+$, 43%), 398 (39), 322 (52), 306 (57), and 201 (100) (Found: C, 75.7; H, 5.9; N, 3.35. $C_{26}H_{24}NO_2P$ requires C, 75.55; H, 5.85; N, 3.4%): 3-*methyl-2-(4-methylbenzyloxy)* (28%), m.p. 112—114 °C (from ether), ^{1}H n.m.r. δ 7.6—8.0 (4 H, complex), 7.2—7.5 (6 H, complex), 7.02 (4 H, s), 6.4—6.8 (4 H, complex), 4.04 (2 H, d), 3.39 (3 H, d), and 2.28 (3 H, s), ^{31}P n.m.r. δ —38.5 p.p.m., *m/z* 427 (*M*$^+$, 27%), 412 (73), 322 (76), 306 (32), 201 (100), and 105 (89) (Found: C, 76.1; H, 6.15; N, 3.1. $C_{27}H_{26}NO_2P$ requires C, 75.85; H, 6.15; N, 3.3%).

Pyrolysis Experiments.—Small-scale pyrolyses (50—100 mg) were carried out as previously described,[28] and the results are reported as follows: quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time. Preliminary analysis was usually carried out by ^{1}H and ^{31}P n.m.r., and peak intensities are quoted as percentages of the major peak. Products were identified by spectroscopic comparison with authentic samples, and/or by their isolation, usually by the use of medium pressure chromatography (m.p.l.c.) on silica using mixtures of light petroleum (b.p. 40—60 °C) and ether as eluant.

2,3-*Dihydro-2,2-diphenyl-2-methoxy-3-p-tolyl-1,3,2-benzoxazaphosph*(v)*ole*[6]: 56 mg (0.13 mmol), 140 °C, 600 °C,

5 × 10⁻³ Torr, 30 min, ^{31}P n.m.r. δ 33.9 (100%) 33.7 (52), 30.7 (37), and −39.7 p.p.m. (41). The major products were recovered phosphorane (28%) and 2-(p-toluidino)phenyl diphenylphosphinate (21%). On a larger scale, the phosph(v)ole (0.54 g, 1.3 mmol) was pyrolysed at 650 °C and 1—2 × 10⁻²-Torr over 2 h. M.p.l.c. of the pyrolysate gave a compound tentatively identified as 3-methylphenoxazine (8.5%) from its mass spectrum (Found: M^+, 197.0847. $C_{13}H_{11}NO$ requires M, 197.0841) and from the singlet at δ 2.53 in its n.m.r. spectrum. The second major component which was isolated was the above phosphinate (8.6%), m.p. and mixed m.p. 112—114 °C (lit.,[1] 117—118 °C), whose ^{1}H and ^{13}P n.m.r. spectra were identical with those of an authentic sample. The low yields obtained in this, and the following preparative experiments are probably due to decomposition on the chromatography column.

2-Ethoxy-2,3-dihydro-2,2-diphenyl-3-p-tolyl-1,3,2-benzoxazaphosph(v)ole: 66 mg (0.15 mmol), 160 °C, 600 °C, 7 × 10⁻³ Torr, 40 min, ^{31}P n.m.r. δ 33.8 (100%), 31.8 (15), 30.6 (16), and 21.9 p.p.m. (25). The first three components were identified as 2-(p-toluidino)phenyl diphenylphosphinate (60%), ethyl diphenylphosphinate and diphenyl-N-(2-hydroxyphenyl)-N-p-tolylphosphinamide respectively. Pyrolysis of the phosphorane (0.60 g, 1.4 mmol) at 600 °C during 1 h, and m.p.l.c. of the pyrolysate gave 3-methylphenoxazine (1.4%), m.p. 125—135 °C (lit.,[29] 123—125 °C), m/z 197 (tentative assignment as above), and the phosphinate (27%), m.p. and mixed m.p. 113—115 °C (lit.,[1] 117—118 °C).

2-Ethoxy-2,3-dihydro-2,2-diphenyl-3-(2,4,6-trimethylphenyl)-1,3,2-benzoxazaphosph(v)ole: 55 mg (0.12 mmol), 150 °C, 600 °C, 5 × 10⁻³ Torr, 20 min, ^{31}P n.m.r. δ 33.1 (37%), 32.7 (100), 21.8 (63), and −43.9 p.p.m. (27). The major component was 2-(2,4,6-trimethylphenyl)phenyl diphenylphosphinate (48%): starting material (ca. 10%) was also recovered.

2,3-Dihydro-2,2-dimethoxy-2-phenyl-3-p-tolyl-1,3,2-benzoxazaphosph(v)ole[6]*:* 34 mg (0.09 mmol), 120 °C, 650 °C, 1 × 10⁻³ Torr, 10 min, ^{31}P n.m.r. δ 29.5 (100%), 27.4 (26), and 21.7 p.p.m. (92). The major peak was due to 2,3-dihydro-2-oxo-2-phenyl-3-p-tolyl-1,3,2-benzoxazaphosphole (65%) (which also showed a peak at δ 2.24 in its ^{1}H n.m.r. spectrum), while the peak at δ 21.7 was due to dimethyl phenylphosphonate (25%) [^{1}H n.m.r. δ 3.42 (d)]. [Further evidence for the 2-oxobenzoxazaphosphole structure for the major component was obtained from a pyrolysis of the corresponding 3-phenyl derivative at 700 °C. Trituration of the pyrolysate with ether gave a white solid, m.p. 121—122 °C, m/z 307 (lit.,[6] m.p. of 2,3-dihydro-2,3-diphenyl-2-oxo-1,3,2-benzoxazaphosph(v)ole 127—128 °C)]. Pyrolysis of the title phosph(v)ole (0.34 g, 0.9 mmol) at 650 °C during 70 min, and m.p.l.c. of the pyrolysate gave four major fractions. The first had m/z 199, and was thought to be 2-(p-toluidino)phenol (10%), a known[1] hydrolysis product of the 2-oxo-compound. The second fraction was 3-methylcarbazole (0.025 g, 14%), m.p. 190—195 °C (lit.,[30] 199—202 °C), identical by ^{1}H n.m.r., mass spectroscopy, and t.l.c. (silica and alumina) with an authentic sample. The third fraction (0.028 g) was a mixture of the 2-oxo compound (ca. 5%), and methyl 2-(p-toluidino)phenyl phenylphosphonate,[31] which was the sole component of the final fraction (0.050 g, 15%), ^{1}H n.m.r. δ 7.7—8.0 (2 H, complex), 6.6—7.6 (12H, complex), 3.84 (3 H, d), and 2.28 (3 H, s), ^{31}P n.m.r. δ 18.6 p.p.m., m/z 353 (M^+, 100%), 183 (43), and 155 (79).

2,2-Diethoxy-2,3-dihydro-2-phenyl-3-p-tolyl-1,3,2-benzoxazaphosph(v)ole: 55 mg (0.14 mmol), 140 °C, 600 °C, 3—5 × 10⁻³ Torr, 10 min, ^{31}P n.m.r. δ 29.5 (50%) and 17.4 p.p.m. (100) p.p.m. These were identified as 2,3-dihydro-2-oxo-2-phenyl-3-p-tolyl-1,3,2-benzoxazaphosphole (71%) and diethyl phenylphosphonate (21%) by ^{1}H and ^{31}P n.m.r. spectroscopy. Pyrolysis of the phosphorane (0.44 g, 1.1 mmol) at 600 °C

during 80 min and m.p.l.c. of the pyrolysate gave only one identifiable fraction (0.14 g). This was itself a mixture of ethyl diphenylphosphonate (20%) and 2-(p-toluidino)phenol (39%), identified by g.c./m.s. on 1% SE30 at 220 °C (m/z 214 and 199 respectively). In a separate experiment, deuteriochloroform was added to the trap while it was still cold, to dissolve the volatile fraction of the pyrolysate. Ethanol (20%) was identified by ^{1}H n.m.r. spectroscopy, and by g.l.c. comparison with an authentic sample (10% PEGA, 55 °C).

2,3-Dihydro-2,2,2-trimethoxy-3-p-tolyl-1,3,2-benzoxazaphosph(v)ole[6]*:* 91 mg (0.28 mmol), 110—120 °C, 800 °C, 1—4 × 10⁻³ Torr, 10 min, ^{31}P n.m.r. δ 41.7 (16%), 13.3 (72), 10.7 (32), 8.2 (80), 6.9 (32), 2.3 (100), and −2.9 p.p.m. (17). (Unchanged phosphorane was present at temperatures up to 700 °C). Only trimethyl phosphate (δ 2.3) (19%) could be positively identified.

2,2,2-Triethoxy-2,3-dihydro-3-p-tolyl-1,3,2-benzoxazaphosph(v)ole: 54 mg (0.15 mmol), 110 °C, 650 °C, 1—2 × 10⁻² Torr, 10 min, ^{31}P n.m.r. δ 13.1 (100%), −3.8 (66), and −16.9 p.p.m. (55). Only triethyl phosphate (δ − 1.0) could be tentatively identified: a larger scale pyrolysis followed by m.p.l.c. of the pyrolysate gave no further information.

2,3-Dihydro-2-methoxy-3-methyl-2,2-diphenyl-1,3,2-benzoxazaphosph(v)ole: 66 mg (0.20 mmol), 130 °C, 650 °C, 1 × 10⁻³ Torr, 40 min, ^{31}P n.m.r. δ 32.6 (100%), 32.4 (31), 31.3 (28), and 26.7 (17). The major product was identified as diphenyl-N-(2-hydroxyphenyl)-N-methylphosphinamide (35%) by spectroscopic comparison with an authentic sample. 2-Methylaminophenyl diphenylphosphinate (ca. 3%) was similarly identified, and its presence was confirmed by t.l.c. (silica and alumina).

2-Ethoxy-2,3-dihydro-3-methyl-2,2-diphenyl-1,3,2-benzoxazaphosph(v)ole: 53 mg (0.15 mmol), 120 °C, 650 °C, 5 × 10⁻³, Torr, 40 min, ^{31}P n.m.r. δ 32.9 (23%) and 32.2 p.p.m. (100). Preparative t.l.c. (silica, trace ethanol in ether) gave diphenyl-N-(2-hydroxyphenyl)-N-methylphosphinamide (22%), m/z 323 identical (^{1}H n.m.r.) with an authentic sample (see below), and 2-methylaminophenyl diphenylphosphinate (49%), m/z 323. The latter compound was isolated by m.p.l.c. from a larger-scale pyrolysis of the phosphole (0.80 g, 2.3 mmol). The major fraction (0.17 g) crystallised overnight from light petroleum (b.p. 60—80 °C) at −20 °C to give 2-*methylaminophenyl diphenylphosphinate* (0.02 g, 2.8%), m.p. 80—82 °C, ^{1}H n.m.r. δ 7.7—8.0 (4 H, complex), 6.3—7.7 (11 H, complex), and 2.82 (3 H, s); ^{31}P n.m.r. δ 32.3 p.p.m., m/z 323 (M^+, 100%), 219 (26), 201 (70), and 122 (11) (Found: C, 70.4; H, 5.55; N, 4.2. $C_{19}H_{18}NO_2P$ requires C, 70.6; H, 5.6; N, 4.35%). In a separate experiment, ethylene (30%) was identified by its conversion into 1,2-dibromoethane, which was compared with an authentic sample by ^{1}H n.m.r. and by g.l.c. (1% SE30, 65 °C).

2-Ethoxy-3-ethyl-2,3-dihydro-2,2-diphenyl-1,3,2-benzoxazaphosph(v)ole: 55 mg (0.15 mmol), 140 °C, 650 °C, 1 × 10⁻³ Torr, 1 h, ^{31}P n.m.r. δ 34.6 (18%), 32.6 (25), and 32.2 p.p.m. (100). The major product was 2-*ethylaminophenyl diphenylphosphinate* (52%) and was isolated by m.p.l.c. in 17% yield from a pyrolysis of the phosph(v)ole (0.42 g, 1.2 mmol) at 650 °C during 2 h. The *phosphinate* had m.p. 85—87 °C [from light petroleum (b.p. 60—80 °C)], ^{1}H n.m.r. δ 7.7—8.1 (4 H, complex), 6.3—7.7 (10 H, complex), 4.40br (1 H, s), 3.13 (2 H, q), and 1.23 (3 H, t); ^{31}P n.m.r. δ 32.1 p.p.m.; m/z 337 (M^+, 100%), 322 (81), and 201 (62) (Found: C, 71.0; H, 5.9; N, 4.1. $C_{20}H_{20}NO_2P$ requires C, 71.2; H, 6.0; N, 4.15%).

2,3-Dihydro-3-methyl-2-neopentoxy-2,2-diphenyl-1,3,2-benzoxazaphosph(v)ole: 51 mg (0.13 mmol), 140 °C, 650 °C, 1 × 10⁻³ Torr, 30 min, ^{31}P n.m.r. δ 33.0 (69%), 32.3 (30), 31.7 (100), 27.1 (14) and 14.4 p.p.m. (16). The only phosphorus-containing product which was positively identified (by ^{1}H and

[31]P n.m.r. spectroscopy, and by t.l.c.) was 2-methylamino-phenyl diphenylphosphinate (12%). In addition neopentyl alcohol (33%) was identified by [1]H n.m.r. and [13]C n.m.r. spectroscopy (δ 73.3, 32.5, and 25.9 p.p.m.) and g.l.c. (2% Carbowax, 60 °C) comparison with an authentic sample. [13]C N.m.r. spectroscopy showed no evidence of 1,1-dimethyl-cyclopropane.

3-*Ethyl-2,3-dihydro-2-neopentoxy-2,2-diphenyl-1,3,2-benz-oxazaphosph*(v)*ole:* 62 mg (0.15 mmol), 140 °C, 650 °C, 1 × 10^{-3} Torr, 45 min, [31]P n.m.r. δ 112.1 (47%), 35.0 (46), 32.9 (57), 32.1 (100), 30.8 (43), and 26.4 p.p.m. (43). From the [13]C n.m.r. spectrum of the more volatile fraction of the pyrolysate, the presence of neopentyl alcohol (δ 73.1, 32.4, and 25.8 p.p.m.) was confirmed. Addition of an authentic sample of 1,1-di-methylcyclopropane to the mixture caused the appearance of three new peaks (δ 25.3, 13.5, and 11.2 p.p.m.) in its [13]C n.m.r. spectrum: clearly none of the cyclopropane was present in the original pyrolysis.

2-*Benzyloxy-2,3-dihydro-3-methyl-2,2-diphenyl-1,3,2-benz-oxazaphosph*(v)*ole:* 52 mg (0.13 mmol), 180 °C, 650 °C, 1 × 10^{-3} Torr, 45 min, [31]P n.m.r. δ 32.3 (100%), 26.1 (68), 17.0 (95), 15.3 (72), and 6.6 p.p.m. (64). The major component was identified as 2-methylaminophenyl diphenylphosphinate (19%), as described above. The presence of bibenzyl (38%) and benzyl alcohol (14%) was confirmed by [1]H n.m.r. spec-troscopy and g.l.c. (2% Carbowax, 160 °C).

2,3-*Dihydro-3-methyl-2-(4-methylbenzyloxy)-2,2-diphenyl-1,3,2-benzoxaphosph*(v)*ole:* 83 mg (0.19 mmol), 120—200 °C, 650 °C, 1 × 10^{-3} Torr, 2 h [31]P n.m.r. δ 32.4 (100%), 17.2 (63), and 15.5 p.p.m. (65). The major component was identified, as above, as 2-methylaminophenyl diphenylphosphinate (3.5%). 1,2-Di-*p*-tolylethane (30%), m/z 210, was identified by [1]H n.m.r., g.l.c. (1% SE30, 155 °C) and g.c./m.s. comparison with an authentic sample.

Co-pyrolysis of 2-Benzyloxy- and 2-(4-Methylbenzyloxy)-2,3-dihydro-3-methyl-2,2-diphenyl-1,3,2-benzoxazaphosph(v)*oles.* —The two samples were contained in separate sample tubes to minimise solid-state co-decomposition. Benzyloxy derivative (73 mg, 0.18 mmol); 4-methylbenzyloxy derivative (76 mg, 0.18 mmol), 140 °C, 650 °C, 1 × 10^{-3} Torr, 3.5 h. G.c./m.s. showed that a mixture of bibenzyl (m/z 182), 1-phenyl-2-*p*-tolylethane (m/z 196) and di-*p*-tolylethane (m/z 210) were present in yields (calculated from the [1]H n.m.r. spectrum) of 15, 7.1, and 2.7% respectively.

' *Static* ' *Pyrolysis of Diphenyl-*N-*(2-hydroxyphenyl)-*N-p-*tolyl-phosphinamidate.*—A sample of the title compound [1] ([31]P n.m.r. δ 30.1 p.p.m.) was heated at 120 °C at a pressure of 5 × 10^{-3} Torr for 90 min. The material which was recovered had [31]P n.m.r. δ 33.8 p.p.m., and its [1]H n.m.r. spectrum was identical with that of 2-*p*-tolylaminophenyl diphenylphos-phinate.[1]

Pyrolysis of Methyl Diphenylphosphinite.—120 mg (0.56 mmol), 90 °C, 700 °C, 6—8 × 10^{-3} Torr, 10 min. The [31]P n.m.r. spectrum of the pyrolysate showed at least seven peaks, none of which was due to recovered starting material.

*Preparation and Pyrolysis of Diphenyl-*N-*(2-hydroxyphenyl)-*N-*methylphosphinamidate* (cf. *Ref.* 1).—An aqueous solution of toluene-*p*-sulphonic acid (40 μl of a 0.225м-solution) was added to a solution of 2,3-dihydro-2-methoxy-3-methyl-2,2-diphenyl-1,3,2-benzoxazaphosph(v)ole (0.33 g, 1 mmol) in super-dry ether, and the mixture was stirred overnight. The solid product was filtered off to give the *phosphinamidate* (0.27 g, 84%), m.p. 171—175 °C [from benzene–light petroleum (b.p. 60—80 °C)], [1]H n.m.r. δ 9.49 (1 H, s), 7.7—8.1 (4 H,

complex), 6.5—7.5 (10 H, complex), and 2.96 (3 H, d), [31]P n.m.r. δ 33.0 p.p.m., m/z 323 (M^+, 100%), 219 (26), 201 (79), 78 (37), and 77 (37) (Found: C, 70.5; H, 5.7; N, 4.15. $C_{19}H_{18}NO_2P$ requires C, 70.6; H, 5.6; N, 4.35%).

Pyrolysis of the phosphinamidate (46 mg, 0.14 mmol) at 700 °C and 1 × 10^{-3} Torr during 10 min (inlet temperature 190 °C) gave 2-methylaminophenyl diphenylphosphinate (84%), identical by [1]H n.m.r. spectroscopy and t.l.c. (alumina) with an authentic sample.

*Gas-phase Pyrolysis of the Sodium Salt of t-Butylmethylene-toluene-*p-*sulphonohydrazide.*[32]—0.34 g (1.2 mmol), 120 °C, 500 °C, 1—10 × 10^{-3} Torr, 20 min. The pyrolysate was dis-solved in deuteriochloroform while the trap was still cold. The ^{1}H and [13]C n.m.r. spectra [33,34] showed the presence of 1,1-dimethylcyclopropane (40%), [1]H n.m.r. δ 1.05 (6 H, s), and 0.24 (4 H, s), [13]C n.m.r. δ 25.3, 13.6, and 11.2 p.p.m. No alkenes were detected.

Dibenzyl Sulphone.[35]—123 mg (0.5 mmol), 160 °C, 650 C°, 1 × 10^{-3} Torr, 15 min. Bibenzyl (98%) was identified by [1]H n.m.r. spectroscopy and by its melting point [50—51 °C (from ethanol) (lit.,[36] 52.5 °C)].

Bis(4-methylbenzyl) Sulphone.[36]—129 mg (0.47 mmol), 200 °C, 650 °C, 1 × 10^{-3} Torr, 30 min. 1,2-Di-*p*-tolylethane (90%) was identified by its melting point [81—82 °C (from ethanol) (lit.,[36] 81—82 °C)] and [1]H n.m.r. spectrum, δ 7.10 (8 H, s), 2.86 (4 H, s), and 2.30 (6 H, s).

Co-pyrolysis of Dibenzyl Sulphone and Bis(4-methylbenzyl) Sulphone.—As before, the two samples were contained in separate tubes within the inlet system. Dibenzyl sulphone (62 mg, 0.25 mmol) bis(4-methylbenzyl) sulphone (67 mg, 0.25 mmol), 150 °C, 650 °C, 1 × 10^{-3} Torr, 50 min. Bibenzyl (72%) (m/z 182), 1-phenyl-2-*p*-tolylethane (47%) (m/z 196) and 1,2-di-*p*-tolylethane (48%) (m/z 210) were identified by g.c./ m.s., and in addition the symmetrical products were charac-terised by [1]H n.m.r. comparison with the authentic samples (see above). The singlet at δ 2.84 was assigned to the methylene protons of 1-phenyl-2-*p*-tolylethane. (Yields are based on 0.25 mmol.)

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