Intramolecular Reactions of o-Alkoxy- and o-Alkylthio-benzyl Radicals

J. I. G. Cadogan *
B. P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN
James B. Husband and Hamish McNab *
*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ*

We report new gas-phase reactions of o-substituted benzyl radicals produced by flash vacuum pyrolysis of 2,3-dihydro-1,3,2-benzoxazaphosph(v)oles (4)—(6), dibenzyl sulphone (8), and dibenzyl oxalates (9)—(11). Both o-ethoxy- and o-methoxy-benzyl radicals rearrange to o-tolualdehyde via intramolecular hydrogen transfer, as shown by experiments using 2-[²H₃]methoxybenzyl radicals. o-Methylthiobenzyl radicals do not give the corresponding thioaldehyde, but produce a mixture of benzocyclobutene and isomeric dihydrobenzothiophens by novel rearrangement reactions. o-Ethylthio- and o-propylthio-benzyl radicals give o-methylstyrene and o-propenyltoluenes respectively as major products.

Although the intramolecular gas-phase chemistry of aryl-nitrenes and arylcarbenes is now well understood,[1,2] little attention has so far been paid to the corresponding free-radical reactions. In one isolated example, de Mayo obtained o-hydroxybenzaldehyde (1; Y = O) from the o-methoxy-phenoxyl radical (2; Y = O) and proposed the hydrogen-transfer rearrangement sequence of Scheme 1 (Y = O) to account for this transformation.[3] The feasibility of the re-arrangement of the anisyl radical to an aldehyde function [e.g. (3) ⟶ (1)] had earlier been demonstrated by Mulcahy,[4] by co-pyrolysis of anisole and di-t-butyl peroxide in a static system. However, studies of benzyl radicals have been restricted to intermolecular reactions which include useful syntheses of bibenzyls [5,6] and cyclophanes [7] via the expected dimerisation. It was of interest therefore to see whether the incorporation of suitable o-substituents would lead to intra-molecular reactions rather than the usual dimerisations. We have therefore begun a general investigation of the inter-actions of benzyl radicals with o-substituents, and we report here the results obtained with o-alkoxy- and o-alkylthio-groups.

Production of o-Substituted Benzyl Radicals.—The phos-phoranes (4)—(6), benzyl ether (7), sulphone (8), and oxalates (9)—(11) were employed as radical precursors (Scheme 2), under flash vacuum pyrolysis conditions. Ethers, sulphones, and oxalates are known radical generators,[8] and we have pre-viously shown that radicals are formed from 3-aryl- or 3-alkyl-1,3,2-benzoxazaphospholes.[9] The choice of precursor was dependent on a number of factors. The sulphones and phos-phoranes decompose under relatively mild conditions (650 °C), but their syntheses require two steps from the starting benzyl alcohol (13) which, in the case of the phosphoranes, results in a particularly low yield of the precursor. The ether and oxal-ates require more vigorous pyrolysis conditions (750—850 °C): nevertheless the latter derivatives are obtained in a single step from the benzyl alcohol (13) and are the precursors of choice for the alkylthio-radicals (12; X = S) for which the sulphone method is inappropriate for synthetic reasons. The benzyl alcohols (13) were obtained from the corresponding phenol or thiophenol by alkylation using an alkyl halide and an-hydrous potassium carbonate in dimethylformamide.[10]

Results

Generation of the benzyl radical (2; Y = CH₂) from the phosphorane (4) at 650 °C, from the ether (7) at 800 °C, or from the sulphone (8) at 650 °C, gave no trace of coupling products, but rather o-tolualdehyde (1; Y = CH₂) was
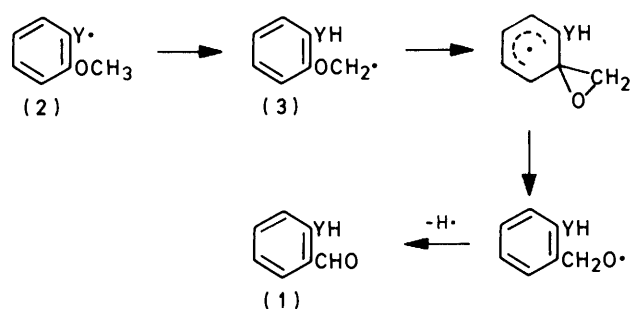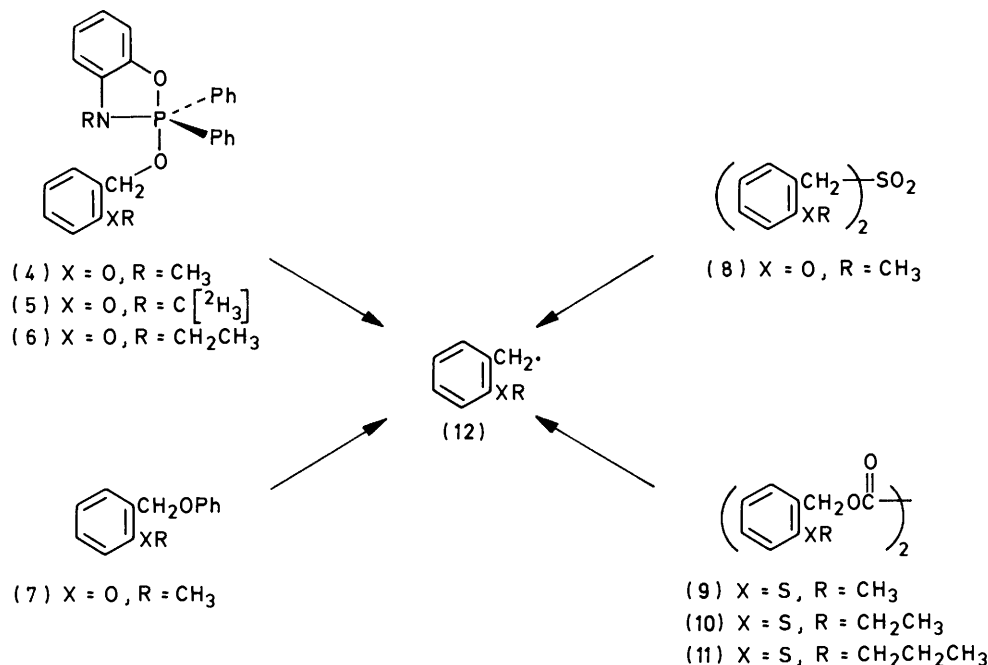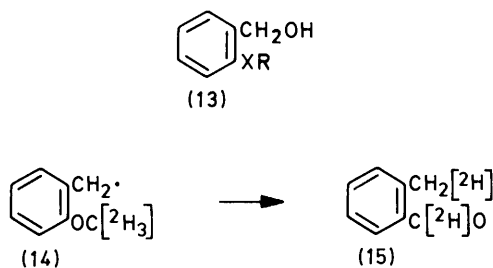

Scheme 1.

obtained in 36, 45, and 52% yield respectively. This trans-formation is analogous to that of the o-methoxyphenoxyl radical to o-hydroxybenzaldehyde obtained by de Mayo [3] (Scheme 1). We have obtained additional evidence for the mechanism outlined in Scheme 1 as follows. First, the hydrogen transfer step is supported by the results obtained from the 2-[²H₃]methoxybenzyl radical (4) (Scheme 3). Examination of the crude pyrolysate by ²H n.m.r. showed signals due to the aldehyde (15) at δ 2.66 and 10.29 in a ratio of ca. 1 : 1, as expected on the basis of Scheme 1. Secondly, evidence for the migration step is provided by the formation of o-tolualdehyde (1; Y = CH₂) (36%) rather than the aceto-phenone (16), when the o-ethoxybenzyl radical (17) is gener-ated from the phosphorane (6) (Scheme 4). Preferential loss of a methyl group rather than a hydrogen atom from a re-arranged α-methylbenzyloxyl radical was also observed by Mulcahy.[4] These results are of general significance, and are explained by the high heat of formation of the hydrogen atom in the gas phase,[4] and the relatively low strength of a carbon–carbon bond.

Application of these reactions to the appropriate o-alkyl-thiobenzyl radical might have been expected to provide a source of the elusive thioaldehydes. These labile compounds frequently trimerise,[11] though they have been isolated pre-viously under f.v.p. conditions.[12] In practice, the reactions provided much more complex pyrolysates than the alkoxy-derivatives, and neither thioaldehydes, their trimers, nor radical coupling products were detected amongst the products. The major volatile products were hydrocarbons, together with small amounts of isomeric dihydrobenzothiophens.
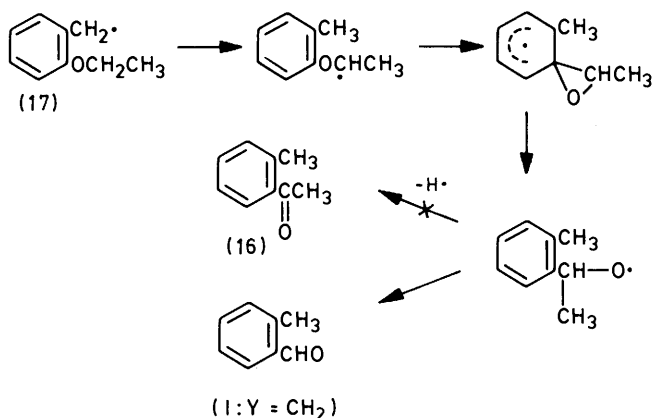
Thus, the 2-methylthiobenzyl radical gave benzocyclo-butene (18) as the principal product, and dihydrobenzo[b]- and dihydrobenzo[c]-thiophen (19) and (20) were detected in the pyrolysate by comparison (g.l.c., g.c.-m.s., and n.m.r.)

(4) X = O, R = CH_3
(5) X = O, R = $C[^2H_3]$
(6) X = O, R = CH_2CH_3

(8) X = O, R = CH_3

(7) X = O, R = CH_3

(12)

(9) X = S, R = CH_3
(10) X = S, R = CH_2CH_3
(11) X = S, R = $CH_2CH_2CH_3$

Scheme 2.

(13)

(14)   →   (15)

Scheme 3.

(17)

(16)

(1:Y = CH_2)

Scheme 4.

with authentic samples (Scheme 5). In contrast, the 2-ethyl-thiobenzyl radical gave o-methylstyrene (21) as the hydrocarbon product, while the dihydrothiophens (22) and (23) were detected by g.c.–m.s., and identified by analogy with the results for (9) (Scheme 5). Only isomeric propenyltoluenes (24) and (25) were present in significant concentration in the pyrolysate of the S-propyl compound (11) (Scheme 5).

We have little direct evidence bearing on the specific mechanisms of these diverse reactions, but it is reasonable to suppose that Scheme 6 may be followed. Thus the formation of the spirodienyl radical (26) follows the familiar sequence of Scheme 1, but instead of rearranging further, this species loses a hydrogen atom to generate the o-quinonedimethide monoepisulphide (27), which on rearrangement gives the dihydrothiophens directly. Alternatively, loss of sulphur from (27) generates the dimethide (28) which can ring-close to the benzocyclobutene, or rearrange to the styrene derivatives. It is known that alkylbenzocyclobutenes rearrange to styrenes under the conditions of our experiments.[13,14]
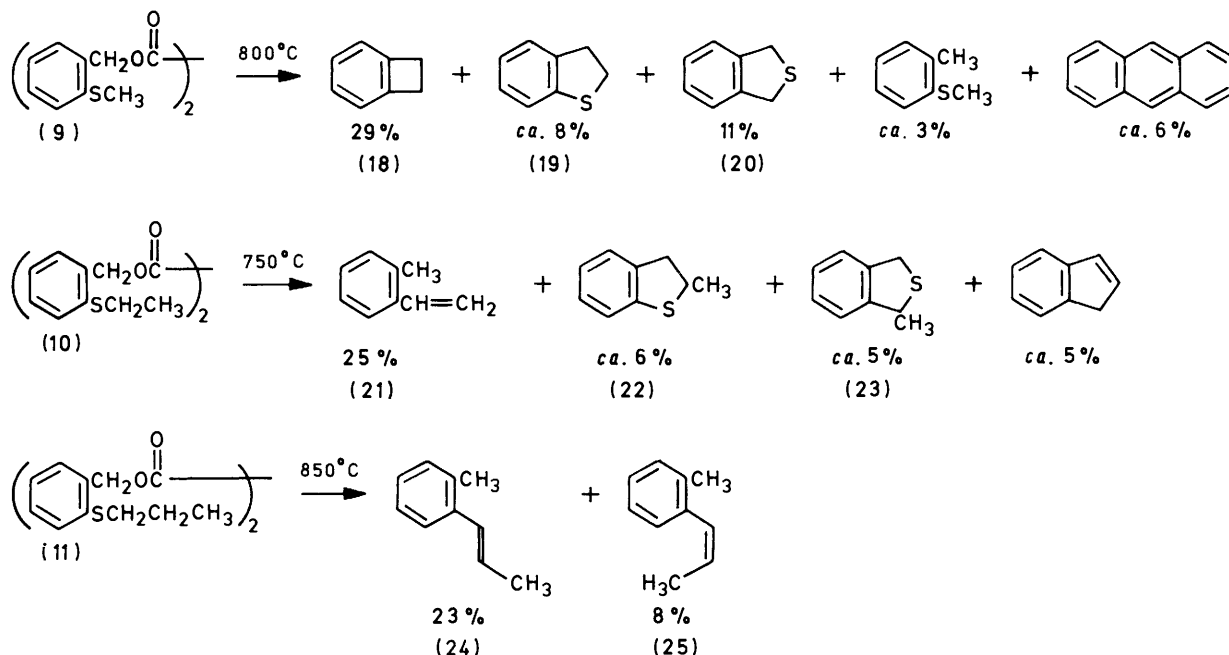
The observed product distribution from the ethylthiyl and propylthiyl radicals lends general support to the proposed mechanism, if preferential loss of alkyl groups rather than hydrogen atoms (as above) is assumed. Alternative pathways, such as direct formation of (27) from (29) are unlikely, since ejection of the group R would be expected. Similarly, sulphur extrusion from the radical (26) can be excluded since the propenyltoluenes are formed from (11): the radical (30; R = Et) would be expected either to dimerise,[15] or to give 2-methylstyrene by preferential loss of a methyl radical.

Minor products of Scheme 5 probably arise by secondary reactions from Scheme 6. Thus hydrogen abstraction by (29; R = H) will give the o-methylthioanisole, while the indene probably arises by dehydrogenation of the styrene (21). The formation of anthracene from (9) is more unusual, and may occur via dimerisation of the diradical (31) obtained by aryl-sulphur cleavage from (29; R = H).
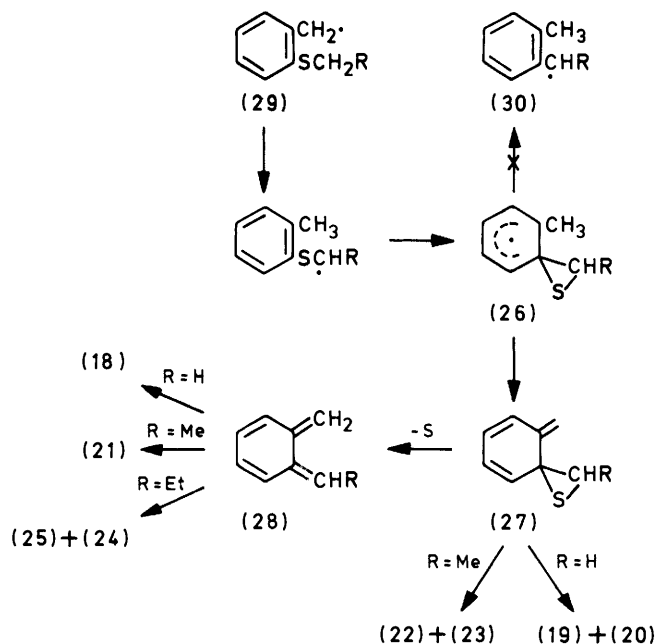
Experimental

Unless otherwise stated, ^1H n.m.r. spectra were recorded at 100 MHz and ^{31}P n.m.r. spectra were recorded at 24 MHz for solutions in [^2H]chloroform. Positive shifts are to high frequency of the reference standard.

Alkyl Diphenylphosphinites.—Prepared by the action of the appropriate benzyl alcohol on chlorodiphenylphosphine in the presence of triethylamine,[16] these compounds were used without purification for the preparation of the phosphoranes:

Scheme 5.

Scheme 6.

2-methoxybenzyl diphenylphosphinite (*ca.* 83%), δ_P 114.3 p.p.m. (Found: M^+, 322.1098. $C_{20}H_{19}O_2P$ requires M^+, 322.1123); 2-[$^2H_3$]methoxybenzyl diphenylphosphinite (*ca.* 90%), *m/e* 325 (the alcohol was made by methylation of 2-hydroxybenzyl alcohol using [$^2H_3$]iodomethane in dimethylformamide in the presence of potassium carbonate [10]); and *2-ethoxybenzyl di-*

phenylphosphinite (*ca.* 75%), δ_P 113.4 p.p.m. (Found: M^+, 336.1272. $C_{21}H_{21}O_2P$ requires M^+, 336.1279).

2-Methylaminophenol.—This compound was prepared by methylation of benzoxazolone and subsequent hydrolysis.[17] It was purified by sublimation at 150° and 0.1 Torr and was obtained in 38% yield as cream crystals, m.p. 90—92 °C (lit., 92—95 °C).

2-Alkoxy-2,3-dihydro-2,2-diphenyl-3-methyl-1,3,2-benz-oxazaphosph(v)oles.—The following 2,3-dihydro-2,2-diphenyl-3-methyl-1,3,2-benzoxazaphos(v)oles were prepared on a 5 mmol scale by oxidation of 2-methylaminophenol and the alkyl diphenylphosphinite using N-chlorodi-isopropylamine,[18] and purified by chromatography on an active alumina column (320 × 15 mm) using dry ether as eluent: 2-(2-*methoxy-benzyloxy*)- (4) (7%), m.p. 124—126 °C (from ether), δ_H 7.6—8.0 (4 H, complex), 6.5—7.5 (14 H, complex), 4.15 (2 H, d, $^3J_{PH}$ 5 Hz), 3.63 (3 H, s), and 3.39 (3 H, d, $^3J_{PH}$ 10 Hz); δ_P −38.1 p.p.m., *m/e* 443 (M^+, 21%), 428 (68), 322 (97), 306 (35), 201 (70), 121 (100), and 91 (84) (Found: C, 73.3; H, 6.0; N, 3.1. $C_{27}H_{26}NO_3P$ requires C, 73.15; H, 5.9; N, 3.15%); 2-[$^2H_3$]methoxybenzyloxy- (5) (10%), m.p. 126—128 °C, *m/e* 446 (M^+, 30%) (isotopic purity 95%); 2-*ethoxybenzyloxy*- (6) (6%), m.p. 143—145 °C (from ether), δ_H 7.6—8.0 (4 H, complex), 6.5—7.5 (14 H, complex), 4.12 (2 H, d, $^3J_{PH}$ 6 Hz), 3.87 (2 H, q), 3.39 (3 H, d, $^3J_{PH}$ 10 Hz), and 1.24 (3 H, t), δ_P −38.1 p.p.m., *m/e* 457 (M^+, 10%), 442 (39), 322 (70), 306 (27), 201 (37), 91 (43), and 77 (40) (Found: C, 73.75; H, 6.15; N, 2.85. $C_{28}H_{28}NO_3P$ requires C, 73.5; H, 6.15; N, 3.05%).

Bis-(2-methoxybenzyl) Sulphone (8).[19]—A solution of sodium sulphide nonahydrate (1.27 g, 5.3 mmol) in water (5 ml) was added to a refluxing solution of 2-methoxybenzyl chloride (1.64 g, 10.5 mmol) in ethanol (25 ml). The mixture was heated under reflux for a further 15 h, poured onto crushed ice, and extracted with ether (50 ml). The organic layer was dried (MgSO$_4$), concentrated, and distilled (Kugelrohr) to give *bis-(2-methoxybenzyl) sulphide* (0.84 g, 58%), as an oil, b.p. 140—147 °C at 0.1 Torr, δ_H 6.7—7.4 (8 H, complex),

3.80 (6 H, s), and 3.71 (4 H, s), m/e 274 (M^+, 39%), 153 (29), 121 (100), and 91 (57) (Found: C, 70.0; H, 6.8. $C_{16}H_{18}O_2S$ requires C, 70.75; H, 6.6%). A solution of the sulphide (0.82 g, 3 mmol) in hot acetic acid (5 ml) was heated under reflux with hydrogen peroxide (30%, 1.02 g, 9 mmol) for 15 min, and then poured onto crushed ice. The resulting orange solid was filtered, and was purified by chromatography on an alumina column (150 × 15 mm). Elution with ether (135 ml), and then with 10% ethanol in ether (45 ml) gave the *sulphone* (8) as a solid (0.23 g, 25%), m.p. 120—121 °C (from ethanol), δ_H 6.8—7.5 (8 H, complex), 4.32 (4 H, s), and 3.81 (6 H, s), m/e 306 (M^+, 5%), 242 (31), 121 (100), and 91 (53) (Found: C, 62.7; H, 6.05. $C_{16}H_{18}O_4S$ requires C, 62.75; H, 5.9%).

2-(Alkylthio)benzyl Alcohols.—The following sulphides were prepared by alkylation of 2-mercaptobenzyl alcohol using an appropriate alkyl halide in dimethylformamide in the presence of potassium carbonate:[10] 2-methylthiobenzyl alcohol (75%), b.p. 105—110 °C at 0.05 Torr (lit.,[20] 88 °C at 10^{-3} Torr); 2-ethylthiobenzyl alcohol (65%), b.p. 80—85 °C at 0.05 Torr (lit.,[21] 96—98 °C at 0.2 Torr); *2-n-propylthio-benzyl alcohol* (74%), b.p. 100—105 °C at 0.1 Torr, δ_H 7.0—7.5 (4 H, complex), 4.74 (2 H, s), 2.88 (2 H, t), 2.40br (1 H, s), 1.5—1.9 (2 H, m), and 1.00 (3 H, t), m/e 182 (M^+, 69%), 139 (100), 135 (19), 111 (16), and 77 (29) (Found: C, 66.15; H, 7.9. $C_{10}H_{14}OS$ requires C, 65.9; H, 7.75%).

Dibenzyl Oxalates.—The following oxalates were made from oxalyl chloride and the appropriate benzyl alcohol, by the method of Trahanovsky:[6,22] *bis-[2-(methylthio)benzyl]* (9) (61%), m.p. 104—105 °C (from ethanol), δ_H 7.0—7.5 (8 H, complex), 5.39 (4 H, s), and 2.42 (6 H, s), m/e 362 (M^+, 38%), 153 (23), 137 (100), 91 (15), and 45 (33), $\nu_{max.}$ (Nujol) 1 772 and 1 750 cm^{-1} (Found: C, 59.75; H, 5.0. $C_{18}N_{18}O_4S_2$ requires C, 59.65; H, 5.0%); *bis-[2-(ethylthio)benzyl]* (10) (59%), m.p. 71—73 °C (from ethanol), δ_H 7.0—7.5 (8 H, complex), 5.42 (4 H, s), 2.88 (4 H, q), and 1.22 (6 H, t), m/e 390 (M^+, 42%), 167 (25), 151 (100), 149 (33), and 123 (25), $\nu_{max.}$ (Nujol) 1 770 and 1 748 cm^{-1} (Found: C, 61.75; H, 5.8. $C_{20}H_{22}O_4S_2$ requires C, 61.5; H, 5.7%); *bis-[2-(n-propylthio)benzyl]* (11) (57%), m.p. 66—68 °C (from ethanol), δ_H 7.0—7.5 (8 H, complex), 5.43 (4 H, s), 2.85 (4 H, t), 1.4—1.8 (4 H, m), and 0.97 (6 H, t), m/e 418 (M^+, 52%), 181 (41), 165 (100), 163 (55), 135 (30), and 123 (67), $\nu_{max.}$ (Nujol) 1 770 and 1 743 cm^{-1} (Found: C, 62.9; H, 6.55. $C_{22}H_{26}O_4S_2$ requires C, 63.15; H, 6.25%).

Pyrolysis Experiments.—Small-scale (0.1—0.5 mmol) pyrolyses were carried out as previously described[23] and the results are quoted as follows: compound, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, and pyrolysis time. Products were generally identified by g.l.c., g.c.–m.s., and n.m.r. Where necessary, relative peak intensities in ^{31}P n.m.r. are given as percentages of the largest peak.

2,3-Dihydro-2-(2-methoxybenzyloxy)-3-methyl-2,2-diphenyl-1,3,2-benzoxazaphosph(v)*ole* (4). 0.043 g (0.10 mmol), 200 °C, 650 °C, 10^{-3} Torr, 1 h. The ^{31}P n.m.r. spectrum of the crude pyrolysate showed six peaks in the P=O region, at δ 33.9 (22%), 32.4 (100), 27.0 (40), 17.8 (44), 16.1 (44), and 6.6 p.p.m. (24). The major peak was assigned to 2-methylaminophenyl diphenylphosphinate (26%) by comparison (^{31}P and ^{1}H n.m.r.) with an authentic sample.[9] Singlets at δ 2.67 and 10.31 in the ^{1}H n.m.r. spectrum were due to *o*-tolualdehyde (36%); this assignment was confirmed by g.l.c. comparison (2% Carbo-wax; 130 °C) with authentic *o*-, *m*-, and *p*-tolualdehyde. Under these conditions, the *p*-isomer was resolved from the mixture, but the *m*-isomer was discounted on the basis of its ^{1}H n.m.r. spectrum.

2,3-Dihydro-2-([2,2,2-^{2}H$_3$]methoxybenzyloxy)-3-methyl-2,2-

diphenyl-1,3,2-benzoxazaphosph(v)*ole* (5). 0.163 g (0.37 mmol), 200 °C, 650 °C, 10^{-3}—1.5 × 10^{-1} Torr, 2.5 h. Deuteriated *o*-tolualdehyde was identified from the ^{2}H n.m.r. spectrum of the crude pyrolysate, δ (CHCl$_3$) 10.29 (1 ^{2}H) and 2.66 (1 ^{2}H).

2-(2-Ethoxybenzyloxy)-2,3-dihydro-3-methyl-2,2-diphenyl-1,3,2-benzoxazaphosph(v)*ole* (6). 0.043 g (0.09 mmol), 180 °C, 650 °C, 10^{-3} Torr, 1 h, δ$_P$ 32.3 (100%), 26.7 (81), 17.5 (90), 15.6 (86), and 6.4 p.p.m. (42). Major products were identified, above, as 2-methylaminophenyl diphenylphosphinate (24%)as and *o*-tolualdehyde (36%), m/e 120 (by g.c.–m.s.).

2-Phenoxymethylanisole (7).[24] 0.097 g (0.45 mmol), 90 °C, 800 °C, 10^{-3} Torr, 40 min. *o*-Tolualdehyde (45%) was identified by comparison of the ^{1}H n.m.r. spectrum with that of an authentic sample, by g.l.c. (2% Carbowax; 130 °C) and by conversion to its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 191—192 °C (lit.,[25] 193—194 °C). G.c.–m.s. of the pyrolysate showed the molecular ion of the aldehyde at m/e 120.

Bis-(2-methoxybenzyl) sulphone (8). 0.041 g (0.13 mmol), 100—160 °C, 650 °C, 5 × 10^{-3} Torr, 1.5 h. *o*-Tolualdehyde (52%) was identified by ^{1}H n.m.r. and by g.l.c. as above.

Bis-[2-(methylthio)benzyl] oxalate (9). 0.033 g (0.09 mmol), 150 °C, 800 °C, 10^{-3} Torr, 100 min. Benzocyclobutene (29%), m/e 104, was identified by comparison [^{1}H and ^{13}C n.m.r.,[26] and g.l.c. (5% Carbowax; 80 °C)] with an authentic sample.[27] The presence of 1,3-dihydrobenzo[c]thiophen (11%; 21% of volatiles), m/e 136, was also confirmed by comparison with an authentic sample[28] [^{1}H n.m.r. and g.l.c. (5% Carbowax; 130 °C)]. Evidence for the presence of the following compounds was obtained by g.c.–m.s. and confirmed by g.l.c. comparison with authentic samples: 2,3-dihydrobenzo[b]thiophen (8% of volatiles), m/e 136, and 2-(methylthio)toluene (3% of volatiles), m/e 138.

In a preparative experiment, the oxalate (0.46 g, 1.3 mmol) was pyrolysed at 850 °C (pyrolysis time 5 h). The major volatile fraction was a mixture of benzocyclobutene and 1,3-dihydrobenzo[c]thiophen. The remainder of the pyrolysate was sublimed (Kugelrohr) at 150—180 °C and 0.7 Torr to give crystals of anthracene (0.026 g, 6%), identified by ^{1}H n.m.r. and by t.l.c. on silica.

Bis-[2-(ethylthio)benzyl] oxalate (10). 0.063 g (0.17 mmol), 120—200 °C, 750 °C, 10^{-3} Torr, 1 h. The major product was 2-methylstyrene (25%; 68% of volatiles), m/e 118, identical by g.l.c. (5% Carbowax; 100 °C) and ^{1}H n.m.r. with an authentic sample. The following compounds were identified by g.c.–m.s., and by analogy with the above results: indene (5% of volatiles), m/e 116, 1,3-dihydro-1-methylbenzo[c]thiophen (5% of volatiles), m/e 150, and 2,3-dihydro-2-methylbenzo[b]thiophen (6% of volatiles), m/e 150.

Bis-[2-(n-propylthio)benzyl] oxalate (11). 0.077 g (0.18 mmol), 160—190 °C, 850 °C, 10^{-3} Torr, 1 h. The major products were identified as propenyltoluenes by g.c.–m.s. (2% Carbowax; 50—190 °C), m/e 132. Assignment was confirmed by the aliphatic and olefinic signals in the ^{1}H n.m.r. of the pyrolysate, which showed (E)-2-(prop-1-enyl)toluene (23%),[29] δ_H 6.59 (1 H, dq, ^3J 15.4, ^4J 1.5 Hz), 6.07 (1 H, dq, ^3J 15.4, ^3J 6.5 Hz), 2.30 (3 H, s), and 1.89 (3 H, dd, ^3J 6.5, ^4J 1.5 Hz) and (Z)-2-(prop-1-enyl)toluene (7.6%),[29] δ_H 6.35 (1 H, dq, ^3J 11.7, ^4J 1.8 Hz), 5.80 (1 H, dq, ^3J 11.7, ^3J 6.9 Hz), 2.24 (3 H, s), and 1.73 (3 H, dd, ^3J 6.9, ^4J 1.8 Hz). Trace quantities of minor products were not identified.

References

1 C. Wentrup, *Adv. Heterocycl. Chem.*, 1981, **29**, 232.
2 C. Wentrup, *Top. Curr. Chem.*, 1976, **62**, 173.
3 R. A. Marty and P. de Mayo, *Chem. Commun.*, 1971, 127.
4 M. F. R. Mulcahy, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *Aust. J. Chem.*, 1967, **20**, 1155.
5 E. C. Leonard, jun., *J. Org. Chem.*, 1962, **27**, 1921.
6 W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, *J. Am. Chem. Soc.*, 1968, **90**, 2839.
7 F. Vögtle and L. Rossa, *Angew. Chem.*, 1979, **91**, 534; *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 515.
8 R. F. C. Brown, ' Pyrolytic Methods in Organic Chemistry,' Academic Press, New York, 1980, ch. 3.
9 J. B. Husband, Ph.D. Thesis, University of Edinburgh, 1982; J. I. G. Cadogan, J. B. Husband, and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, in the press.
10 For example, W. D. Crow and H. McNab, *Aust. J. Chem.*, 1979, **32**, 99.
11 E. Campaigne, N. F. Chamberlain, and B. E. Edwards, *J. Org. Chem.*, 1962, **27**, 135.
12 H. G. Giles, R. A. Marty, and P. de Mayo, *Can. J. Chem.*, 1976, **54**, 537.
13 T. Durst, M. Lancaster, and D. J. H. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1846.
14 T. Kametani, M. Tsubuki, Y. Shiratori, Y. Kato, H. Nemoto, M. Ihara, K. Fukomoto, F. Satoh, and H. Inoue, *J. Org. Chem.*, 1977, **42**, 2672.
15 *Cf.* D. H. R. Barton, G. C. Ramsay, and D. Wege, *J. Chem. Soc. C*, 1967, 1915.
16 *Cf.* L. D. Quin and H. G. Anderson, *J. Org. Chem.*, 1964, **29**, 1859.
17 G. de W. Anderson and F. Bell, *J. Chem. Soc.*, 1949, 2668.
18 S. Antczak, S. A. Bone, J. Brierley, and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, 1977, 278.
19 *Cf.* C. G. Overberger, S. P. Ligthelm, and E. A. Swire, *J. Am. Chem. Soc.*, 1950, **72**, 2856.
20 R. Grice and L. N. Owen, *J. Chem. Soc.*, 1963, 1947.
21 P. Stoss and G. Satzinger, *Chem. Ber.*, 1972, **105**, 2575.
22 W. S. Trahanovsky and C. C. Ong, *J. Am. Chem. Soc.*, 1970, **92**, 7174.
23 H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2200.
24 H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling, *J. Chem. Soc.*, 1961, 5239.
25 F. E. King, P. L'Ecuyer, and H. T. Openshaw, *J. Chem. Soc.*, 1936, 352.
26 W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, 1976, **41**, 751.
27 A. G. Loudon, A. Macoll, and S. K. Wong, *J. Am. Chem. Soc.*, 1969, **91**, 7577.
28 M. P. Dava and A. A. Deana, *J. Am. Chem. Soc.*, 1959, **81**, 4266.
29 V. W. Bilas, C. Duschek, and H. Schmidt, *J. prakt. Chem.*, 1973, **315**, 88.