# Gas Phase Generation and Reactions of *o*-Dialkylaminobenzyl and *o*-Dialkylaminophenoxyl Radicals

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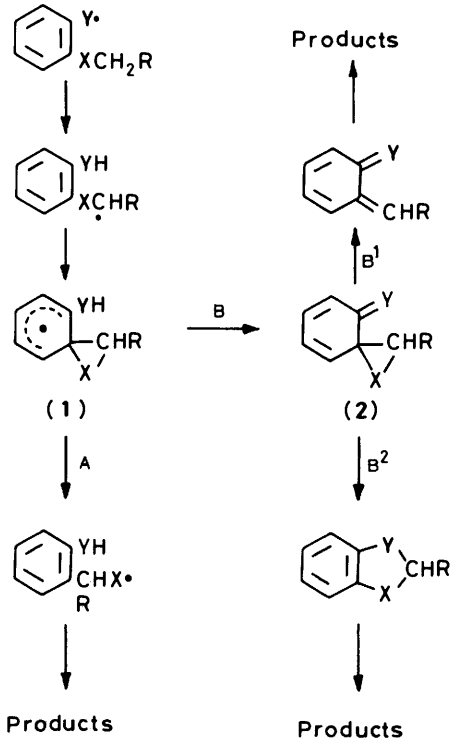
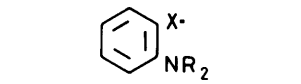
Generation of the title radicals was effected by flash vacuum pyrolysis of benzyl phenyl ethers, and *O*-allyl ethers, respectively. The major products are formed by a multi-step sequence involving (i) intramolecular hydrogen transfer from the alkylamino group to the initial radical centre, (ii) rearrangement of the resulting aminoalkyl radical, and (iii) expulsion of the nitrogen residue to give a benzyl radical which leads to products.

In recent papers, we have discussed the interaction of benzyl[1] and related[2] radicals (generated by flash vacuum pyrolysis) with *o*-alkoxy and with *o*-alkylthio substituents. The reactions can be rationalised by a mechanism which involves hydrogen abstraction from the *o*-substituent followed by *ipso*-attack of the resulting radical to give the key intermediates (**1**) and (**2**) (Scheme 1). The formation of products takes place by rearrangement (X = O), heteroatom extrusion (X = S) and/or cyclisation (X = O, S).[1,2] We now conclude these present studies with a description of the generation and unexpected properties of the related *o*-dialkylamino benzyl and phenoxyl radicals (**3**)—(**6**).

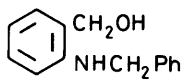



**Scheme 1.**

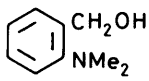
In both series, the design and synthesis of the radical precursor proved troublesome. Benzyl radicals have been generated by pyrolysis of oxalate esters,[3] sulphones,[4] phenyl ethers,[2] and phosphoranes,[5] with the former[3,4] being the methods of choice[1] for most purposes. Unfortunately, reaction



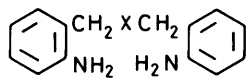

(**3**) X = $CH_2$, R = $CH_3$
(**4**) X = $CH_2$, R = $C[^2H_3]$
(**5**) X = O, R = $CH_3$
(**6**) X = O, R = $C_2H_5$




(**7**)

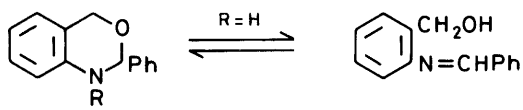



(**8**)




(**9**) X = S
(**10**) X = $SO_2$

of the readily available benzyl alcohols (**7**)[6] and (**8**)[7] with oxalyl chloride under standard conditions[8] gave intractable gummy materials which could not be characterised. Approaches to the corresponding sulphone were discarded when the dianil derivative of the well known sulphide (**9**)[9] could not be satisfactorily reduced to the *N*,*N*′-dibenzyl compound and the diamino sulphone (**10**) could not be cleanly obtained from the dinitro sulphone.[9] In an attempt to circumvent the problems of insolubility associated with these compounds, the nitrogen substituent was introduced prior to sulphide formation: however the anil (**13**) exists predominantly as its cyclic tautomer (**11**)[10] and is *N*-tosylated in this form, as shown by the AB pattern of the methylene protons in its $^1H$ n.m.r. spectrum.

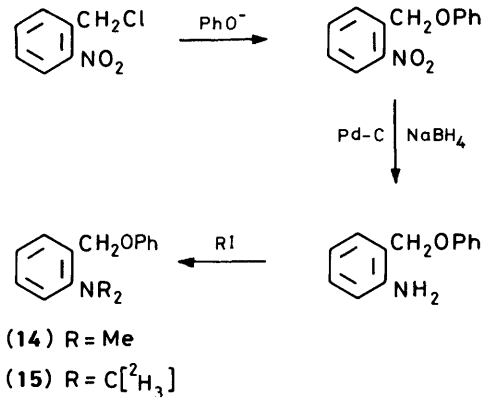



(**11**) R = H
(**12**) R = tosyl

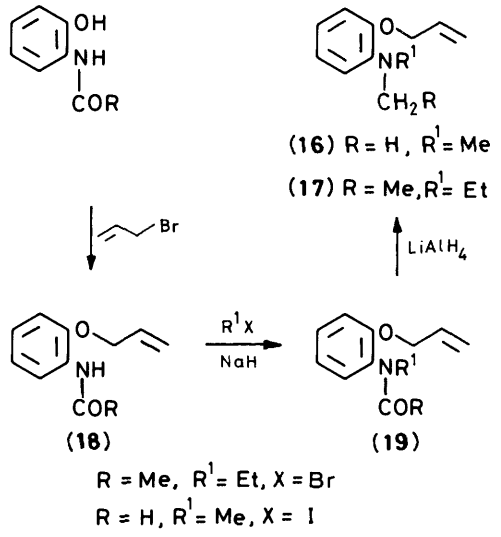
(**13**)

The simplest approach to an ether precursor involves *O*-alkylation of the benzyl alcohol (**8**) under basic conditions, but this does not lead to a compound with a satisfactory radical leaving group. For example, pyrolysis of the *O*-methyl derivative of (**8**) gave no major product and at least twelve minor components. The phenyl ethers (**14**) and (**15**), whose pyrolyses ultimately proved to be acceptable, were therefore prepared by an alternative sequence (Scheme 2).

The pyrolysis of *O*-allyl ethers is generally the most satisfactory method of obtaining phenoxyl radicals in the gas




Scheme 2.




Scheme 3.

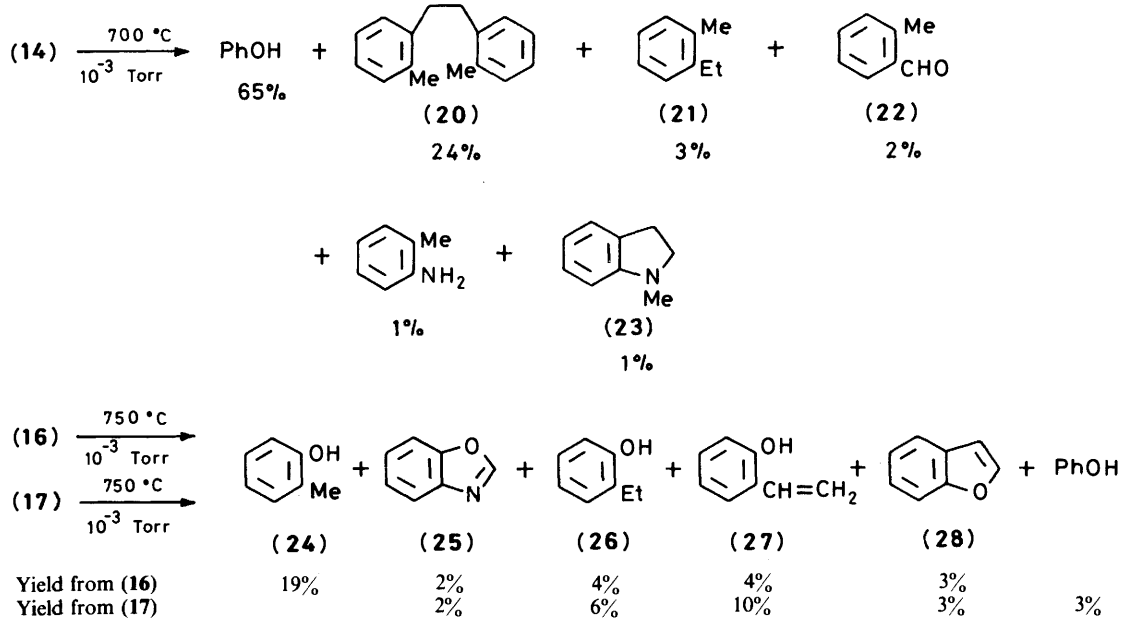
phase,[2,11] and so the major synthetic problem involved the specificity of *N*- and *O*-alkylations. For example, attempted ethylation of 2-allyloxyaniline[12] under basic conditions[13] gave an inseparable mixture of alkylated products. These problems were overcome by the use of an amide as a protecting group, which was specifically alkylated, and then reduced to form the second *N*-alkyl group in the final step of the sequence (Scheme 3). Unfortunately, the corresponding secondary amines could not be prepared by reduction of the amides (**18**; R = Me or R = H) under identical conditions, or by acid hydrolysis of the amide (**19**; R = Me, $R^1$ = Et) under conditions successfully employed for the preparation of 2-allyloxyaniline from (**18**; R = Me).[12] Similarly, attempted *O*-allylation of 2-hydroxy-*N*-ethylaniline[14] only gave a black tar: further routes to these compounds have not been pursued.

The most remarkable feature of the pyrolyses of the amines (**14**), (**16**), and (**17**) (Scheme 4), is the almost complete absence of products which contain nitrogen. In some respects, this is reminiscent of sulphur extrusion from *o*-alkylthiobenzyl radicals[1] (Scheme 1; X = S, Y = $CH_2$, R = H), though in this case, the cleavage must take place at a different stage of the reaction, since di-*o*-tolylethane (**20**) and not benzocyclobutene is formed from (**14**). Route B[1] extrusion of a nitrene, for which there is no precedent in aziridine chemistry* can therefore be excluded.

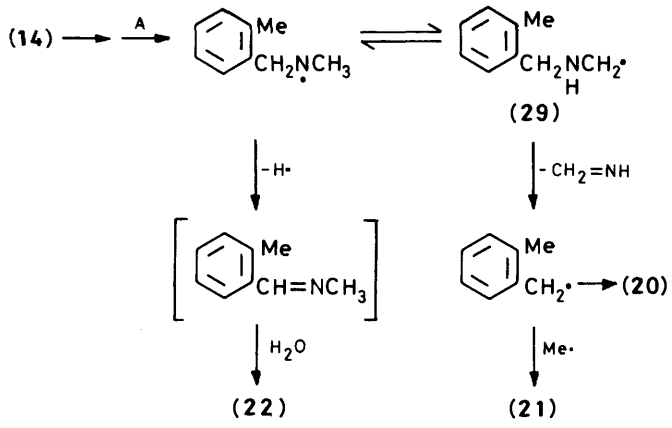
In order to investigate the source of the dimer (**20**) in more detail, the *N*,*N*-[$^2H_6$] compound (**15**) was pyrolysed, and the crude product was analysed directly by $^2H$ n.m.r. spectroscopy. The methyl and methylene signals were present in a ratio of *ca.* 2.3:1 (computer 'integral' value) which is consistent with complete scrambling of the deuterium between these sites (theoretical ratio 2.0:1). This behaviour is expected of a 2-methylbenzyl radical, which therefore leads to (**20**) by dimerisation.

A reasonable explanation for the degradation of the *o*-(*N*,*N*-dimethylamino)benzyl radical to the 2-methylbenzyl radical is given in Scheme 5. Route A (Scheme 1) ring opening of the spiroaziridine gives an aminyl radical which may tautomerise to the aminoalkyl radical (**29**): the driving force for this step may

* Thermal decomposition of aziridines is normally characterised by ring opening to an azomethine ylide.[15]



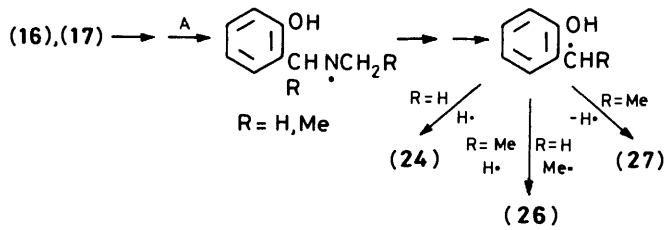

Scheme 4.



Scheme 5.

be the pronounced thermodynamic stability of α-aminoalkyl radicals.[16–18] Cleavage of an imine fragment leads directly to the 2-methylbenzyl radical. It is of interest that toluene and benzene are major products from pyrolysis of *N,N*-dimethylaniline under drastic conditions (425 °C; 90 min); a similar mechanism involving imine extrusion is proposed.[19]

Application of similar principles to the phenoxyl radicals (**5**) and (**6**) leads to *o*-cresol (**24**) and to 2-hydroxystyrene (**27**), which are indeed the major identified products from the dimethylamino and diethylamino derivatives (**16**) and (**17**) respectively (Scheme 6). In addition, the styrene may give rise to benzofuran (**28**).[2]



Scheme 6.

The structures of certain minor products from the benzyl radical (**3**) and the phenoxyl radicals (**5**) and (**6**) show common features. In both series, capture by a methyl radical after imine extrusion gives *o*-ethyl derivatives (**21**) and (**26**), from (**3**) and (**5**) respectively. The source of the methyl radicals is not clear at this stage, but alkyl capture is also required to explain the formation of the styrene (**27**) and of certain trace components, from the *N,N*-dimethyl compound (**16**). In both series, heterocyclisation (Scheme 1, route B[2]) leads to small quantities of the nitrogen-containing compounds (**23**), and, after aromatisation[2] (**25**). Finally, the trace of 2-methylbenzaldehyde (**22**) detected in the pyrolysate from the ether (**14**) may be evidence for standard[1] route A aldehyde imine formation (Scheme 5), followed by hydrolysis during work-up.

## Experimental

Unless otherwise stated, $^1H$ and $^{13}C$ n.m.r. spectra were obtained at 100 MHz and 20 MHz respectively for solutions in deuteriochloroform. Ether refers to diethyl ether.

*Reaction of 2-Alkylaminobenzyl Alcohols with Oxalyl Chloride.*[8]—A solution of oxalyl chloride (5 mmol) in dry ether (4 ml) was added dropwise to a solution of the benzyl alcohol (9 mmol) and triethylamine (14 mmol) in dry ether (50 ml). A white precipitate formed immediately, and was filtered off after 5 min. After the solid had been washed with water to remove triethylammonium chloride, a gummy material remained, which showed only broad unresolved peaks in its $^1H$ n.m.r. spectrum. Both 2-(*N,N*-dimethylamino)[7]- and 2-(*N*-benzylamino)[6]-benzyl alcohols showed this behaviour.

*1,2-Dihydro-2-phenyl-1-p-tolylsulphonyl-3,1-benzoxazine.*—A solution of the 2-phenylbenzoxazine[20] (1.40 g, 6.6 mmol) in pyridine (10 ml) was added dropwise to a stirred solution of toluene-*p*-sulphonyl chloride (2.11 g, 11 mmol) in pyridine (20 ml). The solution was stirred overnight at room temperature, and then water, followed by sulphuric acid (50%, 20 ml) was added. The mixture was extracted with methylene chloride (2 × 25 ml), and the combined organic layers were dried ($MgSO_4$) and concentrated, to give a purple residue which slowly crystallised. Recrystallisation from isopropyl alcohol gave colourless crystals of the *sulphonamide* (0.23 g, 9.3%), m.p. 150—153 °C (Found: C, 68.9; H, 5.15; N, 4.0. $C_{21}H_{19}NO_3S$ requires C, 69.0; H, 5.25; N, 3.85%); $\delta_H$ 7.90 (1 H, dd), 6.8—7.6 (12 H, m), 6.58 (1 H, dd), 4.48 (1 H, dd), 4.12 (1 H, dd), and 2.32 (2 H, s); $\delta_C$ 143.64 (q), 135.82 (q), 135.45 (q), 132.96 (q), 129.06, 128.38, 128.08, 127.73, 127.09, 126.81, 126.30, 125.83, 124.23, 83.66, 60.76, and 21.39 (one quaternary signal not apparent); *m/z* 365 ($M^+$, 82%), 259 (100), 194 (71), 180 (53), 91 (71), and 77 (65).

*Bis[2-(benzylideneamino)benzyl] Sulphide.*—A solution of bis(2-aminobenzyl) sulphide[9] (0.81 g, 3.3 mmol) and benzaldehyde (0.70 g, 6.6 mmol) in ethanol (30 ml) was heated under reflux for 30 min. The solvent was removed under reduced pressure to give the *dianil* (0.83 g, 62%), m.p. 81—82 °C (from ethanol) (Found: C, 80.2; H, 5.75; N, 6.6. $C_{28}H_{24}N_2S$ requires C, 79.95; H, 5.75; N, 6.65%); $\delta_H$ 8.22 (2 H, s), 6.4—8.0 (18 H, m), and 3.85 (4 H, s); $\delta_C$ 159.59, 150.31 (q), 136.14 (q), 132.33 (q), 131.00, 129.66, 128.63, 128.44, 127.68, 125.60, 117.64, and 31.74. (These data show that only one isomer is present); *m/z* 420 ($M^+$, 1%), 226 (100), 195 (94), 193 (54), and 91 (67).

*Attempted Reduction of Bis[2-(benzylideneamino)benzyl] Sulphide.*—Treatment of the dianil (1 mmol) with an excess of sodium borohydride in methanol (15 ml) at 20—40 °C, under standard conditions[21] for imine reduction gave a mixture of products in low yield (< 20%) despite extended reaction times. Thus, the $^1H$ n.m.r. spectrum of the solid which was obtained showed two imine signals at $\delta_H$ 8.37 and 8.40, and two *N*-methylene signals at $\delta_H$ 4.27 and 4.31, which is consistent with the presence of a mixture of the dianil, the dibenzyl compound, and the monoanil monobenzyl derivative.

*Phenyl Ether of 2-(N,N-Dimethylamino)benzyl Alcohol.*—(*a*) *Phenyl 2-nitrobenzyl ether.* Alkylation of phenol (2.59 g, 27.5 mmol) with 2-nitrobenzyl chloride (4.72 g, 27.5 mmol) in dimethylformamide (50 ml) containing potassium carbonate (7.6 g, 55 mmol) at room temperature overnight[2] gave the required ether in 50% yield after work-up and recrystallisation from ethanol, m.p. 58—59 °C (lit.,[22] 63 °C), $\delta_H$ 6.8—8.3 (9 H, m) and 5.48 (2 H, s); *m/z* 229 ($M^+$, 11%), 136 (100), 123 (20), 94 (18), and 78 (41).

(*b*) *Phenyl 2-aminobenzyl ether.* Reduction of the above nitrocompound (4.58 g, 12 mmol) in methanol (300 ml) by sodium borohydride (1.52 g, 24 mmol) and palladium–charcoal (10%; 100 mg) in water (65 ml) was effected by the method of Wood.[23] The amine was obtained in 65% yield after standard work-up, and recrystallisation from ethanol, m.p. 70—71 °C (lit.,[22] 81—82 °C), $\delta_H$ 6.6—7.6 (9 H, m), 5.05 (2 H, s), and 3.87 (2 H, br s); *m/z* 199 ($M^+$, 97%), 136 (93), 107 (99), 106 (100), 104 (58), 94 (97), 79 (90), 78 (96), 77 (97), and 65 (92).

(*c*) *Phenyl* 2-(N,N-*dimethylamino*)*benzyl ether*. A solution of the above amine (0.40 g, 2 mmol) and iodomethane (0.85 g, 6 mmol) in dimethylformamide (10 ml) containing potassium carbonate (0.55 g, 4 mmol) was stirred for 48 h at room temperature. Water (10 ml) was then added, and the solution was extracted with ether (3 × 10 ml). The organic extracts were washed with water (4 × 20 ml) to remove any remaining dimethylformamide, and were then dried ($MgSO_4$) and the solvent was removed under reduced pressure. Distillation of the residue (Kugelrohr) gave the *dimethylamino compound* as a pale yellow oil (61%), b.p. 155—157 °C (0.2 Torr) (Found: C, 79.45; H, 7.35; N, 6.25. $C_{15}H_{17}NO$ requires C, 79.25; H, 7.55; N, 6.15%); $\delta_H$ 6.7—7.8 (9 H, m), 5.20 (2 H, s), and 2.75 (6 H, s); $\delta_C$ 158.88 (q), 152.43 (q), 131.03 (q), 129.44, 129.26, 128.48, 123.04, 120.54, 118.84, 114.73, 65.84, and 45.05; *m/z* 227 ($M^+$, 9%), 134 (100), 118 (21), and 91 (18).

The corresponding *N,N*-[$^2H_6$]dimethylamino compound was prepared in 57% yield as above, using [$^2H_3$]iodomethane, b.p. 115—125 °C (0.05 Torr); *m/z* 233 ($M^+$, 12%) and 140 (100).

Attempts to prepare the *N*-monomethylamino analogue, and the corresponding *N*-isopropyl derivative by the same method gave, respectively, an inseparable mixture of methylated products, and recovered starting material.

2-*Allyloxy*-N-*ethylacetanilide*.—Sodium hydride (50% suspension in oil) was added to a stirred solution of 2-allyloxyacetanilide[24] (3.82 g, 20 mmol) (itself prepared in 64% yield by reaction of 2-hydroxyacetanilide[25] with allyl bromide in dimethylformamide containing potassium carbonate) in tetrahydrofuran (50 ml) until the evolution of hydrogen had ceased. Ethyl bromide (4.36 g, 40 mmol) was then added dropwise, and the mixture was heated under reflux for 4.5 h. Methanol (20 ml) followed by water (60 ml) was added to the cooled solution, which was then extracted with ether (3 × 100 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated to give the *anilide* (70%) as an oil, b.p. 125—130 °C (0.1 Torr) (Found: C, 71.05; H, 8.05; N, 6.15. $C_{13}H_{17}NO_2$ requires C, 71.2; H, 7.8; N, 6.4%); $\delta_H$ 6.8—7.4 (4 H, m), 5.93 (1 H, m), 5.1—5.5 (2 H, m), 4.50 (2 H, m), 3.63 (2 H, m), 1.72 (3 H, s), and 1.10 (3 H, t); *m/z* 219 ($M^+$, 19%), 162 (20), 136 (100), and 43 (25).

2-*Allyloxy*-N,N-*diethylaniline*.—A solution of 2-allyloxy-*N*-ethylacetanilide (2.00 g, 9 mmol) in dry ether (30 ml) was added slowly to a stirred suspension of lithium aluminium hydride (1.14 g, 30 mmol) in dry ether (200 ml) under an atmosphere of dry nitrogen.[26] The mixture was heated under reflux for 1.5 h, and then cooled in ice. Wet ether, followed by water, and by aqueous potassium sodium tartrate (20%; 200 ml) was added and the ether layer was separated off. The aqueous layer was extracted with ether (2 × 150 ml), and the combined organic extracts were dried ($MgSO_4$) and concentrated to give the *aniline* (71%) as an oil, b.p. 95—100 °C (0.5 Torr); $\delta_H$ 6.8—7.3 (4 H, m), 6.07 (1 H, m), 5.1—5.5 (2 H, m), 4.59 (2 H, m), 3.18 (2 H, q), and 1.03 (3 H, t); $\delta_C$ 152.56 (q), 139.64 (q), 133.72, 122.13, 121.75, 120.69, 116.84, 113.61, 69.08, 45.77, and 12.07; *m/z* 205 ($M^+$, 34%), 164 (100), 148 (27), 136 (36), 120 (41), and 77 (18). This compound was characterised as a *picrate*, m.p. 94—95 °C (from ethanol) (Found: C, 52.15; H, 5.35; N, 13.1. $C_{19}H_{22}N_4O_7 \cdot H_2O$ requires C, 52.3; H, 5.5; N, 13.1%).

2-*Allyloxy*-N,N-*dimethylaniline*.—This compound was prepared in a similar manner to that described above for the *N,N*-diethyl derivative.

(*a*) 2-*Allyloxyformanilide*. This compound was obtained in 67% yield by alkylation of 2-hydroxyformanilide[25] using allyl bromide in dimethylformamide containing potassium carbonate; the *amide* had b.p. 135—140 °C (0.1 Torr) (Found: C, 67.5; H, 6.5; N, 7.7. $C_{10}H_{11}NO_2$ requires C, 67.8; H, 6.25; N, 7.9%); $\delta_H$ 8.39 (1 H, d), 8.20 (1 H, br s), 6.7—7.9 (3 H, m), 6.00 (1 H, m), 5.1—5.5 (2 H, m), and 4.49 (2 H, m); *m/z* 177 ($M^+$, 89%), 136 (82), 109 (25), 108 (100), and 80 (96).

(*b*) 2-*Allyloxy*-N-*methylformanilide*. Alkylation of the above amide using iodomethane in tetrahydrofuran containing sodium hydride yielded the N-*methylanilide* (69%), as a colourless oil, b.p. 125—135 °C (0.2 Torr) (Found: C, 68.95; H, 7.1; N, 7.1. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.85; N, 7.3%); $\delta_H$ 8.15 (1 H, s), 6.9—7.3 (4 H, m), 5.96 (1 H, m), 5.2—5.4 (2 H, m), 4.53 (2 H, m), and 3.18 (3 H, s); *m/z* 191 ($M^+$, 51%), 134 (32), 122 (100), 94 (53), and 77 (28).

(*c*) 2-*Allyloxy*-N,N-*dimethylaniline*.—Lithium aluminium hydride reduction of the above anilide gave the *N,N*-dimethylaniline derivative[27] in 64% yield, b.p. 85—95 °C (0.2 Torr); $\delta_H$ 6.8—7.0 (4 H, m), 6.11 (1 H, m), 5.2—5.5 (2 H, m), 4.62 (2 H, m), and 2.82 (6 H, s); $\delta_C$ 150.94 (q), 142.50 (q), 133.40, 121.76, 120.90, 117.86, 116.94, 112.66, 68.79, and 42.99; *m/z* 177 ($M^+$, 28%), 136 (100), 120 (19), and 108 (19).

*Di-o-tolylethane*.—(*a*) *Bis*(o-*methylbenzyl*) *oxalate*. This compound was prepared in 81% yield by the method of Trahanovsky[8] from *o*-methylbenzyl alcohol (2.44 g, 20 mmol) and oxalyl chloride (0.9 ml, 10.3 mmol) in dry ether (100 ml) containing triethylamine (4.0 ml, 30 mmol); the *oxalate* had m.p. 62—64 °C (from ethanol) (Found: C, 72.3; H, 6.15. $C_{18}H_{18}O_4$ requires C, 72.45; H, 6.1%); $\delta_H$ 7.1—7.6 (8 H, m), 5.30 (4 H, s), and 2.34 (6 H, s); *m/z* 298 ($M^+$, 13%), 209 (31), 208 (96), 121 (65), 105 (100), and 91 (83).

(*b*) *Di-o-tolylethane*. The above oxalate (0.936 g, 3.14 mmol) was sublimed at 140 °C and $10^{-2}$—$10^{-3}$ Torr through the furnace tube (35 × 2.5 cm) which was maintained at 775 °C. After 2 h, the solid fraction of the pyrolysate (0.48 g) was recrystallised from ethanol to give di-*o*-tolylethane (0.336 g, 51%), m.p. 55—57 °C (lit.,[28] 66.5 °C); $\delta_H$ 7.26 (8 H, s), 2.98 (4 H, s), and 2.43 (6 H, s).

*Pyrolysis Experiments*.—These were carried out on a small scale (50—250 mg) as previously described.[29] In all cases, the products were identified by comparison [g.l.c. (5% Carbowax or 5% SE30) and g.l.c.–mass spectrometry] with authentic samples. Yields of major products were obtained directly from the $^1H$ n.m.r. spectra of the crude pyrolysates by use of cyclohexane as an integral standard. Approximate yields of minor products (usually less than 4%) were estimated by comparison of the areas of g.l.c. peaks with those of the major constituents without correction for detector response. Results are presented as follows: compound pyrolysed, quantity, inlet temperature, furnace temperature, pressure range, pyrolysis time, and products, with their yields and parent ions from g.l.c.–mass spectrometry.

*Phenyl* 2-(N,N-*dimethylamino*)*benzyl ether*, 0.060 g (0.264 mmol), 130 °C, 700 °C, 1—5 × $10^{-3}$ Torr, 10 min; phenol (65%), *m/z* 94; *o*-xylene (trace), *m/z* 106; *o*-toluidine (1%), *m/z* 107; anisole (trace), *m/z* 108; *o*-ethyltoluene (3%), *m/z* 120; *o*-tolualdehyde (2%), *m/z* 120; *N*-methylindoline (1%), *m/z* 133; and di-*o*-tolylethane (24%), *m/z* 210.

*Phenyl* 2-([$^2H_6$]-N,N-*dimethylamino*)*benzyl ether*, 0.086 g (0.37 mmol) 110 °C, 700 °C, 1—5 × $10^{-3}$ Torr, 20 min; the entire pyrolysate was dissolved in chloroform and analysed by $^2H$ n.m.r. spectroscopy $\delta(^2H)$ 4.71, 2.89, 2.36, and 2.29 p.p.m. The signals at δ 2.89 and 2.36 (integral ratio 1:2.3) were identified as due to labelled di-*o*-tolylethane, by comparison with an authentic $^1H$ n.m.r. spectrum.

2-*Allyloxy*-N,N-*diethylaniline*, 0.135 g (0.658 mmol), 70 °C, 750 °C, $10^{-2}$—$10^{-3}$ Torr, 10 min; *o*-hydroxystyrene (10%), *m/z* 120; phenol (3%), *m/z* 94; benzofuran (3%), *m/z* 118; benzoxazole (2%), *m/z* 119 and *o*-ethylphenol (6%), *m/z* 122.

2-*Allyloxy*-N,N-*diethylaniline*, 0.135 g (0.658 mmol), 70 °C, 750 °C, $10^{-2}$—$10^{-3}$ Torr, 10 min; *o*-cresol (19%), *m*/*z* 108; benzofuran (3%), *m*/*z* 118; benzoxazole (2%), *m*/*z* 119; *o*-hydroxystyrene (4%), *m*/*z* 120; *o*-ethylphenol (4%), *m*/*z* 122 and 2-methylbenzoxazole (trace), *m*/*z* 133.

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