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The Stereochemistry of Organometallic Compounds. XLIII* Rhodium-Catalysed Reactions of 2-(Alkenyloxy)benzylamines and 2-(*N*-Allyl-*N*-benzylamino)benzylamine†

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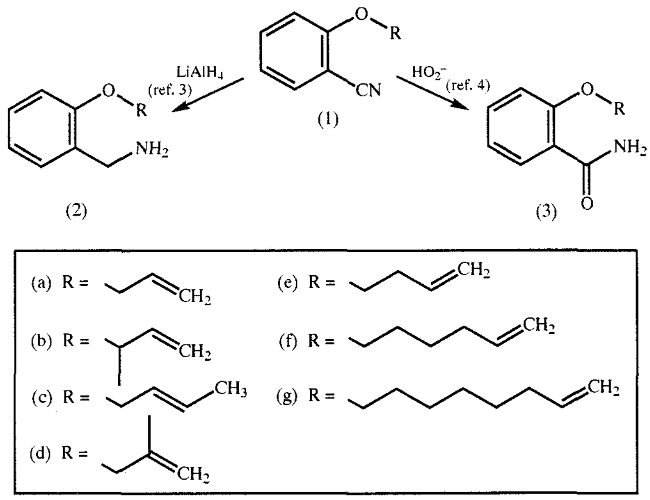
Reactions of 2-(allyloxy)benzylamines with H_2/CO in the presence of rhodium catalysts give 1,3-benzoxazines, and 2-(*N*-allyl-*N*-benzylamino)benzylamine gives a quinazoline. These reactions have been shown to involve allylic cleavage followed by regioselective carbonylation at the internal carbon atom as demonstrated by crossover experiments. Reactions of longer chain (alkenyloxy)benzylamines under similar conditions give polymeric material.

Introduction

We have recently described the preparation of quinazolines and quinazolinones by rhodium-catalysed reactions of *ortho*-alkenylbenzylamines or benzamides with H_2/CO.[2] These preparations apparently involved a second cyclization of an initially formed amino- or amido-substituted cyclic imine. In order to gain mechanistic information regarding these reactions, and in an attempt to devise rational syntheses of medium- and large-ring heterocycles, we have investigated the rhodium-catalysed reactions of some 2-(alkenyloxy)benzylamines, 2-(alkenyloxy)benzamides and 2-(*N*-allyl-*N*-benzylamino)benzylamine. In these compounds the possibility of a second cyclization to an intermediate cyclic imine is eliminated.



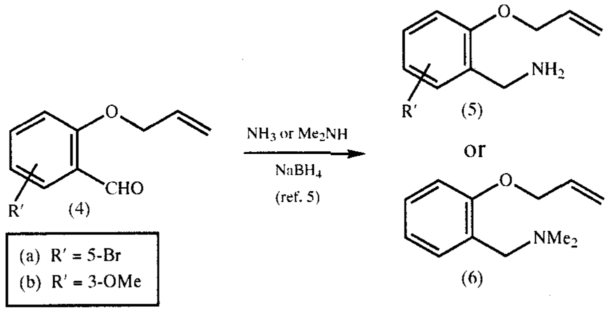
Scheme 1

Results and Discussion

Preparation of 2-(Alkenyloxy)benzylamines and Benzamides

The above compounds, (2) and (3), with no further substituents in the phenyl ring, were prepared by reduction or hydrolysis of the 2-(alkenyloxy)benzonitriles (1) by using standard literature methods[3,4] (Scheme 1).

Compounds with substituents in the benzene ring (5) or on the benzylamine nitrogen (6) were prepared from commercially available salicylaldehydes (4) by allylation and reductive amination[5] (Scheme 2).



Scheme 2

*Preparation of 2-(*N*-Allyl-*N*-benzylamino)-benzylamine (7)*

The preparation is outlined in Scheme 3 and involves monoallylation of 2-(*N*-benzylamino)benzonitrile and

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† Some of this work has appeared as a communication.[1]

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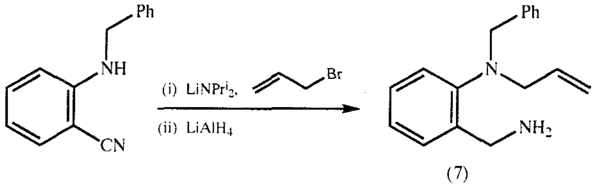
subsequent reduction of the nitrile with lithium aluminium hydride.

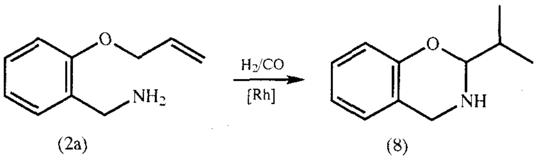


Scheme 3

Rhodium-Catalysed Reactions with H_2/CO

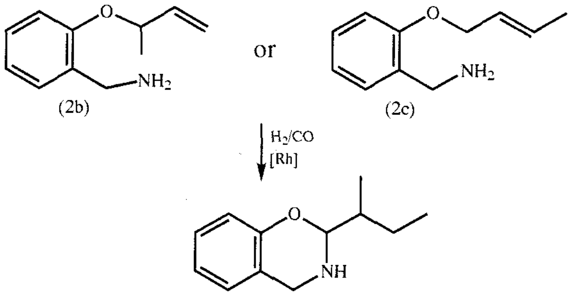
2-(Allyloxy)benzylamines

Reaction of (2a) with H_2/CO in ethyl acetate with rhodium(II) acetate dimer and PPh_3 as the catalyst precursor at 60° for 20 h gave the 1,3-benzoxazine (8) as the sole product in 90% isolated yield (Scheme 4). The same product was obtained in similar high yields under a variety of reaction conditions involving temperatures from 40–60°, benzene or ethyl acetate as solvent and $[Rh(OAc)_2]_2/PPh_3$ or $HRh(CO)(PPh_3)_3$ as catalyst. The structure of the product was deduced from spectroscopic data and confirmed by the preparation of an authentic sample by the condensation of 2-aminomethylphenol with 2-methylpropanal in the presence of molecular sieves.[6]



Scheme 4

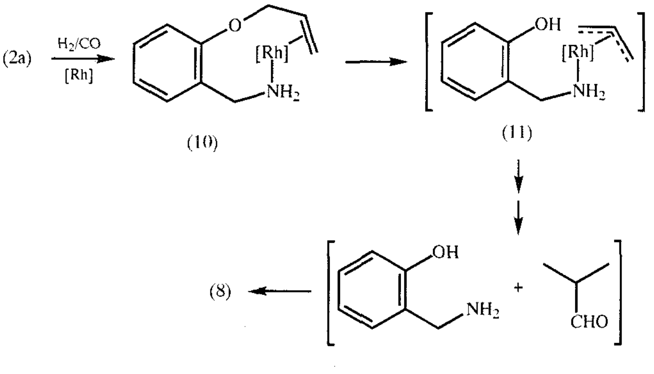
Reactions of aryl-substituted 2-(allyloxy)benzylamines (5) showed varying results. Reaction of the 5-bromo substituted compound (5a) gave a high isolated yield (90%) of the 6-bromo analogue of (8). In contrast, reaction of the 3-methoxy compound (5b) gave only polymeric material. It is possible that the 3-methoxy oxygen is involved in coordination to a rhodium intermediate, diverting the reaction from the rearrangement pathway (see later).



Scheme 5

Reactions of the methyl-substituted allyl systems (2b,c) gave in each case the s-butylbenzoxazine (9) in good to excellent yield [estimated 70% for (2b) and 90% for (2c); isolated yields for pure compounds, 56% for (2b) and 71% for (2c)] (Scheme 5). The formation of (9) from both (2b) and (2c) suggests that production of the 1,3-benzoxazines (8) and (9) involves cleavage of the allylic ether linkage, probably resulting in the formation of a π-allylrhodium species, e.g. (11) (Scheme 6).*

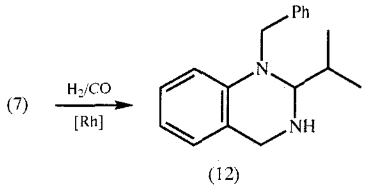
Carbonylation must occur at the internal carbon atom of the allylic system. This would result in the formation of a mixture of 2-aminomethylphenol and either 2-methylpropanal from (2a) or 2-methylbutanal from either (2b) or (2c). These may be free compounds or coordinated to rhodium. The free compounds on heating under these conditions readily form benzoxazines. Reaction of the 2-methylprop-2-enyloxy compound (2d) under the same reaction conditions led to the formation of polymeric material. In this case, whilst a rhodium–allyl compound corresponding to (11) could readily form, carbonylation on the central carbon atom is not possible.



Scheme 6

2-(N-Allyl-N-benzylamino)benzylamine (7)

Reaction of the *N*-benzyl analogue (7) of the (allyloxy)benzylamine (2a) under similar conditions but at a slightly higher temperature, 80°, followed a similar pathway leading to formation of the tetrahydroquinazoline (12) (Scheme 7). A small amount of another unidentified compound was detected in the reaction mixture. An authentic sample of (12) was prepared by the reaction of 2-(benzylamino)benzylamine with 2-methylpropanal in the presence of molecular sieves.[6]



Scheme 7

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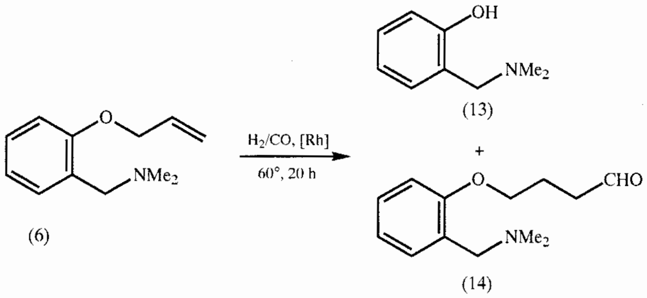
* An alternative mechanism for the formation of (8) involves initial formation of a branched aldehyde followed by formation of a π-allylrhodium species, hydride transfer, subsequent hemiaminal formation and dehydration. We thank Professor I. Ojima, State University of New York at Stony Brook for this suggestion.

Literature precedents for the migration of allyl species have recently been reported in rhodium-catalysed silylaminocarbonylations[7] and in palladium-catalysed allylation reactions.[8] Cleavage of an *N*-allyl substituent with formation of a π-allylcobalt species has been suggested to explain the formation of *N*-benzyl-2-pyrrolidone in the reaction of *N,N*-diallylbenzylamine with H_2/CO in the presence of $Co_2(CO)_8$.[9] Substitution of π-allylic metal complexes usually occurs preferentially at a terminal carbon atom,[10] but recently two reports of nucleophilic attack at the central carbon of π-allylplatinum complexes have been reported.[11,12] The reason for the regioselective attack on the central carbon atom in our reactions is not well understood. Equally puzzling is why the 2-methylallyl compound (2d) does not react at a terminal carbon leading to the formation of 3-methylbutanal; however, it may be relevant that the rate of hydroformylation of other 1,1-disubstituted alkenes, e.g. α-methylstyrene, is slow.

Crossover Experiments

The *N,N*-dimethyl analogue (6) of 2-(allyloxy)benzylamine (2a) was reacted under the standard reaction conditions to see if cleavage of the allylic group occurred. The products were a mixture of the phenol (13), resulting from allylic cleavage, and the linear aldehyde (14) in the ratio 55:45. No trace of the branched-chain aldehyde resulting from carbonylation at the internal alkene carbon atom was detected (Scheme 8).



Scheme 8

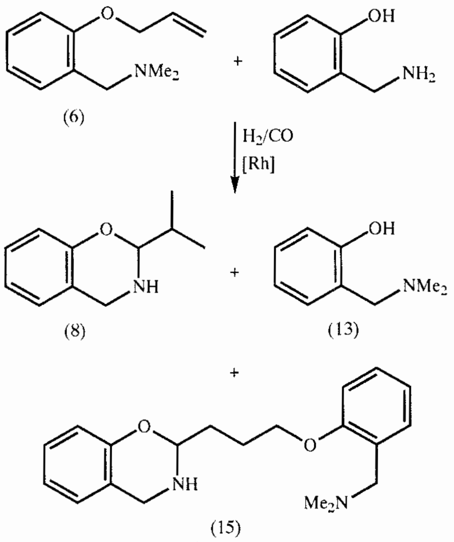
An equimolar mixture of the dimethyl compound (6) and 2-aminomethylphenol was reacted with H_2/CO in the presence of the catalyst system to see if a cleaved allylic fragment could be trapped. A mixture of the oxazine (8), presumably arising from allyl transfer to 2-aminomethylphenol, followed by carbonylation and cyclization, and the de-allylated phenol (13) was formed, together with the oxazine (15) (ratio *c.* 30:40:30) (Scheme 9). The oxazine (15) presumably arose from condensation of the terminal aldehyde (14) with 2-aminomethylphenol.

Allylic crossover was also observed in a similar reaction of an equimolar mixture of 2-aminomethylphenol and 2-(*N*-allyl-*N*-benzylamino)benzylamine (7), when both the oxazine (8) and the quinazoline (12) were obtained (Scheme 10).

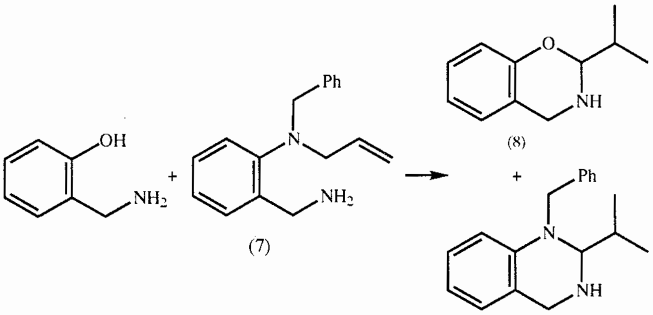
Reactions of Longer Chain Analogues of the Allylic Ether (2a)

Reactions of the but-3-enyl (2e), hex-5-enyl (2f) and oct-7-enyl (2g) compounds at various temperatures and times with either $[Rh(OAc)_2]_2$ or $Rh_4(CO)_{12}$ as precatalysts gave polymeric material in all cases. No evidence for alkenyl cleavage and/or transfer was obtained in keeping with the facile metal-catalysed cleavage of allylic bonds versus that of longer chain alkenyl species. The formation of polymers rather than heterocyclic compounds was disappointing, especially as the linear aldehyde from the octenyl compound (2g) should cyclize to a 14-membered ring, outside the difficult medium ring cyclizations. Modification of the steric and electronic properties of the benzylamine nitrogen by use of the *N*-methyl analogue (16) of (2e) still led to the formation of polymeric material.

The polymeric material was not characterized but was assumed to be a polyimine. Reactions of the

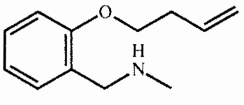


Scheme 9



Scheme 10

(12)

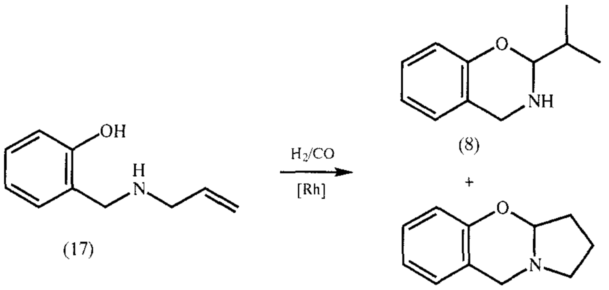


(16)

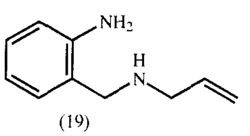
related unsaturated nitriles (1e,f) and the amide (3e) gave excellent yields of mixtures of linear and branched aldehydes in ratios *c.* 65 : 35, i.e. similar to those for other terminal alkenes under these reaction conditions. Reactions of the allylic nitrile (1a) and amide (3a) led to significant cleavage of the allyl group together with the formation of aldehydes. The amide (3a) interestingly only gave linear aldehyde, paralleling the reaction of the corresponding dimethylamino compound (6).

*Reaction of 2-(*N*-Allylaminomethyl)phenol (17)*

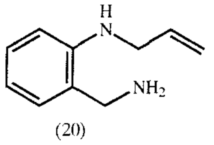
Reaction of this compound, differing from (2a) in that the allylic function had been moved from oxygen to nitrogen, gave a mixture of the oxazine (8) and the pyrrolo[2,1-*b*]benzoxazine (18) in the ratio 30 : 70 (Scheme 11). It should be noted that the amino analogues of both (17) and (2a), i.e. 2-amino-*N*-allylbenzylamine (19) and 2-(allylamino)benzylamine (20), gave only heterocyclic compounds arising from exclusive terminal hydroformylation.[2,13]



Scheme 11



(19)



(20)

Mechanistic Comment

The results described in this paper suggest that rhodium-catalysed reactions of 2-(allyloxy)benzylamines (2a–c) and the *N*-benzyl *N*-allyl compound (7) involve allyl cleavage with carbonylation of a resulting allylrhodium species exclusively on the central carbon. In contrast, closely related compounds (19) and (20), with the allyl on a benzylamino or anilino nitrogen, give single products which arise exclusively from terminal hydroformylation and cyclization of the resulting aldehyde.[2,13] 2-(*N*-Allylaminomethyl)phenol (17) gives products arising from a mixture of the above two reaction types. The subtle factors which control the regioselectivity of reactions of these closely related compounds are under further investigation.

Experimental

General conditions were as described previously.[14]

Preparation of 2-(Alkenyloxy)benzonitriles (1)

2-(Prop-2′-enyloxy)benzonitrile (1a)

The general procedure of Antonini *et al.*[15] was used. A mixture of 2-hydroxybenzonitrile (4·0 g, 34 mmol), 3-bromoprop-1-ene (8·13 g, 67 mmol) and powdered anhydrous potassium carbonate (4·65 g, 34 mmol) was heated to reflux for 6 h. Upon cooling, water was added (*c.* 30 ml) and the aqueous layer was extracted with ether (3×20 ml). The combined organic extracts were washed with 2% potassium hydroxide solution (10 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a light orange oil (5·32 g). Kugelrohr distillation afforded *2-(prop-2′-enyloxy)benzonitrile* (1a) as a clear and colourless liquid (5·12 g, 95%), b.p. (oven) 85°/0·19 mm (Found: C, 75·5; H, 5·7; N, 8·8. $C_{10}H_9NO$ requires C, 75·5; H, 5·7; N, 8·8%). ν_{max} 3082w, 2928w, 2874w, 2227s, 1648w, 1599s, 1574m, 1491s, 1450s, 1425m, 1290s, 1260s, 1235m, 1166m, 1110m, 1044m, 996s, 934m, 839w, 757s cm^{-1}. ^{1}H n.m.r. δ (300 MHz) 4·65, dt, *J* 5·1, 1·5 Hz, 2H, H1′; 5·30, dq, *J* 10·6, 1·4 Hz, 1H, H3′$_E$; 5·47, dq, *J* 17·2, 1·4 Hz, 1H, H3′$_Z$; 6·04, ddt, *J* 17·2, 10·7, 4·9 Hz, 1H, H2′; 6·98, m, 2H, H3,5; 7·52, m, 2H, H4,6. ^{13}C n.m.r. δ (50 MHz) 69·25 (C1′); 102·0 (C1); 112·5 (C3); 116·3 (CN); 118·1 (C3′); 120·76 (C5); 131·72, 133·6, 134·16 (C4,6,2′); 160·0 (C2). Mass spectrum: *m/z* 159 (M, 100%), 144 (5), 130 (13), 119 (70), 102 (12), 91 (97), 75 (29), 69 (12), 63 (41), 51 (11).

The Benzonitriles (1b–g)

The following compounds were prepared by the above method.[15]

2-(1′-Methylprop-2′-enyloxy)benzonitrile (1b) was obtained from 3-chlorobut-1-ene (3·04 g, 33·6 mmol) as a yellow oil (1·08 g). Kugelrohr distillation afforded a clear and colourless liquid (0·62 g, 21%), b.p. (oven) 75–80°/0·3 mm (Found: C, 76·1; H, 6·4; N, 7·9. $C_{11}H_{11}NO$ requires C, 76·3; H, 6·4; N, 8·1%). ν_{max} 3029m, 2922m, 2227s, 1599s, 1579m, 1491s, 1450s, 1289s, 1253s, 1230s, 1166m, 1111m, 1044m, 968s, 756s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·51, d, *J* 6·4 Hz, 3H, CH_3; 4·90, p, *J* 6·3 Hz, 1H, H1′; 5·22, dt, *J* 10·5, 1·2 Hz, 1H, H3′$_E$; 5·31, dt, *J* 17·3, 1·2 Hz, 1H, H3′$_Z$; 5·91, ddd, *J* 17·3, 10·5, 6·1 Hz, 1H, H2′; 6·93–7·01, m, 2H, H3,5; 7·43–7·57, m, 2H, H4,6. ^{13}C n.m.r. δ (50 MHz) 21·18 (CH_3); 76·22 (C1′); 102·74 (C1); 114·27 (C3); 116·45 (C3′); 116·55 (CN); 120·68 (C5); 133·66, 133·93 (C4,6); 137·82 (C2′); 159·78 (C2).

2-(But-2′-enyloxy)benzonitrile (1c) was obtained from 1-bromobut-2-ene (4·53 g, 33·6 mmol) as a light brown liquid (3·02 g). Kugelrohr distillation gave a clear and colourless liquid (2·75 g, 95%), b.p. (oven) 80°/0·1 mm (Found: C, 76·2; H, 6·5; N, 8·0. $C_{11}H_{11}NO$ requires C, 76·3; H, 6·4; N, 8·1%). ν_{max} 3028m, 2919m, 2227s, 1598s, 1579m, 1491s, 1450s, 1379m, 1289s, 1256s, 1231s, 1166m, 1110m, 1044m, 968s, 914w, 756s cm^{-1}. ^{1}H n.m.r.* δ (300 MHz) 1·76, dq, *J* 6·5, 1·3 Hz, 3H, CH_3; 4·58, dt, *J* 5·9, 1·2 Hz (4·73, dt, *J* 6·0, 1·2 Hz), 2H, H1′; 5·66–5·95, m, 2H, H2′,3′; 6·99, m, 2H, H3,5; 7·50, m, 2H, H4,6. ^{13}C n.m.r. δ (50 MHz) 17·72 (22·22) (CH_3); 69·63 (64·66) (C1′); 101·91 (C1); 112·51 (112·40) (C3); 116·45 (CN); 120·53 (120·59) (C5); 124·71 (124·36) (C3′); 130·69 (129·23) (C2′); 133·58, 134·11 (133·64) (C4,6); 160·27 (C2). Mass spectrum: *m/z* 173 (M, 10%), 172 (33), 119 (100), 91 (26), 63 (10), 55 (59).

2-(2′-Methylprop-2′-enyloxy)benzonitrile (1d) was obtained from 3-chloro-2-methylprop-1-ene (4·5 g, 33·3 mmol) as a brown oil (2·35 g). Kugelrohr distillation afforded a clear and colourless liquid (2·28 g, 52%), b.p. (oven) 100°/0·3–0·4 mm (Found: C, 76·2; H, 6·5; N, 7·8. $C_{11}H_{11}NO$ requires C, 76·3; H, 6·4; N, 8·1%). ν_{max} 3081m, 2976m, 2228s, 1659m,

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* Mixture of *Z* and *E* isomers in the ratio of 10 : 90 respectively. Data for ^{1}H and ^{13}C n.m.r. of minor isomer in parentheses where appropriate.

1599s, 1579s, 1491s, 1449s, 1378m, 1291s, 1257s, 1230s, 1166s, 1111s, 1049s, 1007s, 705s, 756s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·85, d, J 0·5 Hz, 3H, CH_3; 4·55, s, 2H, H 1′; 5·02, septet, J 1·4 Hz, 1H, H 3′$_Z$; 5·15, t, J 1·2 Hz, 1H, H 3′$_E$; 6·96, d, J 8·5 Hz, 1H, H 3; 7·00, td, J 7·6, 0·9 Hz, 1H, H 5; 7·47–7·57, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 19·10 (CH_3); 72·18 (C 1′); 101·98 (C 1); 112·53 (C 3); 113·24 (C 3′); 116·32 (CN); 120·75 (C 5); 113·58, 134·14 (C 4,6); 139·40 (C 2′); 160·21 (C 2). Mass spectrum: m/z 173 (M, 11%), 172 (14), 158 (2), 146 (3), 133 (3), 130 (3), 119 (14), 105 (4), 102 (5), 91 (12), 77 (4), 73 (12), 63 (7), 55 (100).

2-(But-3′-enyloxy)benzonitrile (1e) was prepared from 4-bromobut-1-ene (4·5 g, 33·3 mmol) as a brown oil (2·35 g). Kugelrohr distillation gave a clear and colourless liquid (2·28 g, 52%), b.p. (oven) 85°/0·15 mm (Found: C, 76·1; H, 6·6; N, 8·4. $C_{11}H_{11}NO$ requires C, 76·3; H, 6·4; N, 8·1%). ν_{max} 3300s, 3080w, 2227s, 1642w, 1599s, 1493s, 1469m, 1452s, 1389w, 1290s, 1261s, 1165m, 1111m, 1043m, 1021m, 995m, 921m, 846w, 756s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 2·61, qt, J 6·7, 1·3 Hz, 2H, H 2′; 4·11, t, J 6·7 Hz, 2H, H 1′; 5·18, m, 2H, H 4′; 5·93, ddt, J 17·2, 10·3, 6·8 Hz, 1H, H 3′; 7·00, m, 2H, H 3,5; 7·53, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 33·39 (C 2′); 68·33 (C 1′); 102·14 (C 1); 112·33 (C 3); 116·51 (CN); 117·82 (C 4′); 120·84 (C 5); 133·67, 133·88, 134·40 (C 3′,4,6); 160·64 (C 2). Mass spectrum: m/z 173 (M, 10%), 172 (36), 145 (5), 132 (7), 119 (61), 104 (3), 102 (15), 91 (39), 77 (3), 75 (7), 63 (10), 55 (100).

2-(Hex-5′-enyloxy)benzonitrile (1f) was obtained from 6-bromohex-1-ene (5·0 g, 30·7 mmol) as a brown oil (4·19 g). Kugelrohr distillation afforded a clear and colourless liquid (4·00 g, 79%), b.p. (oven) 90°/0·2 mm (Found: C, 77·4; H, 7·6; N, 6·9. $C_{13}H_{15}NO$ requires C, 77·6; H, 7·5; N, 7·0%). ν_{max} 3077m, 2942s, 1640m, 1599s, 1580m, 1494s, 1472m, 1451s, 1394w, 1290s, 1260s, 1166m, 1111m, 1043m, 997m, 949w, 913m, 756s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·62, m, 2H, H 3′; 1·86, m, 2H, H 2′; 2·14, qt, J 7·1, 1·3 Hz, 2H, H 4′; 4·07, t, J 6·4 Hz, 2H, H 1′; 4·94–5·09, m, 2H, H 6′; 5·82, ddt, J 17·1, 10·2, 6·6 Hz, 1H, H 5′; 6·97, m, 2H, H 3,5; 7·52, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 25·09 (C 3′); 28·29 (C 2′); 33·29 (C 4′); 68·79 (C 1′); 101·95 (C 1); 112·17 (C 3); 114·92 (C 6′); 116·51 (CN); 120·56 (C 5); 133·73, 134·29, 138·31 (C 4,6,5′); 160·75 (C 2). Mass spectrum: m/z 202 (M+1, 20%), 201 (M, 7), 173 (12), 120 (28), 119 (40), 102 (10), 91 (18), 83 (90), 67 (42), 55 (100).

2-(Oct-7′-enyloxy)benzonitrile (1g) was prepared from 8-bromooct-1-ene (5·0 g, 26·1 mmol) as a yellow liquid (7·43 g). Kugelrohr distillation afforded a clear and colourless liquid (5·86 g, 98%), b.p. (oven) 125–130°/0·2 mm (Found: C, 78·2; H, 8·3; N, 6·2. $C_{15}H_{19}NO$ requires C, 78·6; H, 8·4; N, 6·1%). ν_{max} 2931s, 2857m, 2228s, 1640m, 1599s, 1580m, 1494m, 1451s, 1290s, 1261s, 1165m, 1110m, 1043m, 998m, 912m, 756s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·42, m, 6H, 1·82, m, 2H, and 2·06, m, 2H, H 2′,3′,4′,5′,6′; 4·06, t, J 6·4 Hz, 2H, H 1′; 4·90–5·05, m, 2H, H 8′; 5·81, ddt, J 17·1, 10·2, 6·7 Hz, 1H, H 7′; 6·93–7·02, m, 2H, H 3,5; 7·47–7·55, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 25·60, 28·62, 28·73, 33·56 (C 2′,3′,4′,5′,6′); 68·84 (C 1′); 101·84 (C 1); 112·09 (C 3); 114·22 (C 8′); 116·40 (CN); 120·41 (C 5); 133·61, 134·18 (C 4,6); 138·82 (C 7′); 160·69 (C 2). Mass spectrum: m/z 229 (M, 2%), 228 (2), 200 (4), 186 (7), 172 (4), 146 (2), 132 (6), 119 (69), 102 (17), 91 (22), 81 (22), 69 (100), 55 (72).

Preparation of 2-(Alkenyloxy)benzylamines[3]

2-(Prop-2′-enyloxy)benzylamine (2a)

A solution of 2-(prop-2′-enyloxy)benzonitrile (1a) (2·0 g, 12·6 mmol) in anhydrous ether (12 ml) was added dropwise to a suspension of lithium aluminium hydride (0·76 g, 19·0 mmol) in anhydrous ether (12 ml). The resulting mixture was heated to reflux for 2 h, cooled and syringed into a saturated solution of Rochelle salt (40 ml). The aqueous layer was extracted with ether (3×30 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a light yellow oil (1·50 g). Kugelrohr distillation gave *2-(prop-2′-enyloxy)benzylamine* (2a) as a clear and colourless liquid (1·42 g, 70%), b.p. (oven) 48°/0·19 mm (Found: C, 73·9; H, 8·0; N, 8·3. $C_{10}H_{13}NO$ requires C, 73·6; H, 8·0; N, 8·6%). ν_{max} 3650m, 3377m, 1648w, 1600s, 1588s, 1490s, 1453s, 1423m, 1288m, 1239s, 1189m, 1047m, 1021s, 998s, 927s, 754s cm^{-1}. ^{1}H n.m.r. δ (300 MHz) 1·55, br s, 2H, NH_2; 3·85, s, 2H, Ph$\mathbf{CH_2}$; 4·57, dt, J 5·0, 1·6 Hz, 2H, H 1′; 5·27, dq, J 10·6, 1·6 Hz, 1H, H 3′$_E$; 5·41, dq, J 17·4, 1·6 Hz, 1H, H 3′$_Z$; 6·09, ddt, J 17·4, 10·6, 5·0 Hz, 1H, H 2′; 6·83–6·94, m, 2H, H 3,5; 7·17–7·25, m, 2H, H 4,6. ^{13}C n.m.r. δ (75 MHz) 42·74 ($PhCH_2$); 68·54 (C 1′); 111·54 (C 3); 117·11 (C 3′); 120·71 (C 5); 127·90, 128·49 (C 4,6); 132·18 (C 1); 133·26 (C 2′); 156·33 (C 2). Mass spectrum: m/z 163 (M, 11%), 162 (21), 146 (62), 131 (24), 122 (100), 107 (38), 95 (50), 77 (93), 66 (27), 51 (36).

The Benzylamines (2b–g)

The above reduction procedure[3] was used to prepare the following amines.

2-(1′-Methylprop-2′-enyloxy)benzylamine (2b). This was a clear, colourless liquid (78%), b.p. (oven) 95°/0·07 mm (Found: C, 74·4; H, 8·8; N, 8·1. $C_{11}H_{15}NO$ requires C, 74·5; H, 8·5; N, 7·9%). ν_{max} 3375m, 3075m, 2978s, 2931s, 1638m, 1600s, 1588s, 1488s, 1455s, 1421w, 1373m, 1287m, 1237s, 1147m, 1104m, 1057m, 990m, 929s, 753s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·45, d, J 6·5 Hz, 3H, CH_3; 1·72, br s, 2H, NH_2; 3·82, s, 2H, $\mathbf{CH_2}NH_2$; 4·04, p, J 6·2 Hz, 1H, H 1′; 5·16, dt, J 10·5, 1·3 Hz, 1H, H 3′$_E$; 5·26, dt, J 17·3, 1·3 Hz, 1H, H 3′$_Z$; 5·92, ddd, J 17·3, 10·5, 5·7 Hz, 1H, H 2′; 6·84–6·93, m, 2H, H 3,5; 7·12–7·22, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 21·30 (CH_3); 42·87 (CH_2NH_2); 74·40 (C 1′); 113·03 (C 3); 115·41 (C 3′); 120·46 (C 5); 127·69, 128·46 (C 4,6); 132·50 (C 1); 139·02 (C 2′); 155·68 (C 2). Mass spectrum: m/z 177 (M, 18%), 162 (28), 160 (15), 145 (19), 123 (56), 122 (93), 106 (100), 91 (29), 78 (67), 77 (44), 70 (19), 56 (36), 55 (90).

2-(But-2′-enyloxy)benzylamine (2c). This was a clear, colourless liquid (80%), b.p. (oven) 90°/0·05 mm (Found: C, 74·6; H, 8·2; N, 8·2. $C_{11}H_{15}NO$ requires C, 74·5; H, 8·5; N, 7·9%). ν_{max} 3378m, 3301w, 3023m, 2917m, 2858m, 1600s, 1588s, 1490s, 1453s, 1378m, 1288m, 1236s, 1007s, 966s, 891m, 752s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·67–1·77, m, 3H, CH_3; 3·81, s, 2H, $\mathbf{CH_2}NH_2$; 4·48, dd, J 5·5, 1·1 Hz, 2H, H 1′; 5·63–5·93, m, 2H, H 2′,3′; 6·81–6·94, m, 2H, H 3,5; 7·15–7·25, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 17·71 (CH_3); 42·60 (CH_2NH_2); 68·35 (C 1′); 111·32 (C 3); 120·41 (C 5); 126·02, 127·82, 128·38, 129·60 (C 2′,3′,4,6); 131·81 (C 1); 156·42 (C 2). Mass spectrum: m/z 177 (M, 5%), 176 (5), 162 (20), 160 (23), 145 (21), 122 (87), 106 (100), 95 (17), 78 (60), 77 (38), 70 (16), 65 (11), 55 (92).

2-(2′-Methylprop-2′-enyloxy)benzylamine (2d). The reaction was worked up by using the method of Treasurywala[16] to give a clear oil. Kugelrohr distillation gave *2-(2′-methylprop-2′-enyloxy)benzylamine* (2d) as a clear and colourless liquid (75%), b.p. (oven) 100–102°/0·4 mm (Found: C, 74·1; H, 8·6; N, 8·3. $C_{11}H_{15}NO$ requires C, 74·5; H, 8·5; N, 7·9%). ν_{max} 3378m, 3076m, 2918m, 2855m, 1656w, 1600s, 1588s, 1491s, 1452s, 1376w, 1286w, 1237s, 1189w, 1108m, 1059m, 1018s, 900s, 753s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·66, br s, 2H, NH_2; 1·83, d, J 0·5 Hz, 3H, CH_3; 3·84, s, 2H, $\mathbf{CH_2}NH_2$; 4·43, s, 2H, H 1′; 4·98, q, J 1·3 Hz, 1H, H 3′$_Z$; 5·10, q, J 0·8 Hz, 1H, H 3′$_E$; 6·81–6·94, m, 2H, H 3,5; 7·14–7·26, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 19·25 (CH_3); 42·51 (CH_2NH_2); 71·13 (C 1′); 111·09 (C 3); 112·14 (C 3′); 120·43 (C 5); 127·72, 128·23 (C 4,6); 131·80 (C 1); 140·54 (C 2′); 156·20 (C 2). Mass spectrum: m/z 177 (M, 18%), 160 (12), 145 (48), 121 (90), 107 (67), 95 (21), 77 (49), 70 (16), 65 (13), 55 (100).

2-(But-3′-enyloxy)benzylamine (2e). This was obtained as a clear and colourless liquid (85%), b.p. (oven) 65°/0·25 mm (Found: C, 74·8; H, 8·7; N, 8·1. $C_{11}H_{15}NO$ requires C, 74·5; H, 8·5; N, 7·9%). ν_{max} 3375m, 3075m, 2926s, 1642m, 1600s, 1492s, 1454s, 1384m, 1289m, 1240s, 1151m, 1103m, 1047s, 991m, 916s, 753s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·73, br s, 2H, NH_2; 2·57, qt, *J* 6·5, 1·3 Hz, 2H, H 2′; 3·80, s, 2H, $\mathbf{CH_2}NH_2$; 4·05, t, *J* 6·4 Hz, 2H, H 1′; 5·14, m, 2H, H 4′; 5·91, ddt, *J* 17·1, 10·2, 6·7 Hz, 1H, H 3′; 6·90, m, 2H, H 3,5; 7·23, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 33·79 (C 2′); 42·93 (CH_2NH_2); 66·78 (C 1′); 110·98 (C 3); 117·18 (C 4′); 120·5 (C 5); 128·03, 128·56 (C 4,6); 131·97 (C 1); 134·66 (C 3′); 156·73 (C 2). Mass spectrum: *m/z* 177 (M, 10%), 176 (67), 160 (8), 147 (20), 133 (52), 122 (100), 106 (50), 95 (19), 77 (49), 65 (9), 55 (47).

2-(Hex-5′-enyloxy)benzylamine (2f). Kugelrohr distillation gave a clear and colourless liquid (87%), b.p. (oven) 87°/0·26 mm (Found: C, 75·9; H, 9·6; N, 6·9. $C_{13}H_{19}NO$ requires C, 76·1; H, 9·3; N, 6·8%). ν_{max} 3377m, 3301w, 3074m, 2938s, 2864m, 1639m, 1600m, 1588m, 1493s, 1454s, 1388w, 1288m, 1240s, 1046m, 996m, 911s, 752s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·51–1·90, m, 6H, H 2′,3′, NH_2; 2·14, q, *J* 7·1 Hz, 2H, H 4′; 3·82, s, 2H, $\mathbf{CH_2}NH_2$; 4·00, t, *J* 6·3 Hz, 2H, H 1′; 5·00, m, 2H, H 6′; 5·83, ddt, *J* 17·1, 10·2, 6·6 Hz, 1H, H 5′; 6·88, m, 2H, H 3,5; 7·21, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 25·41, 28·72, 33·34 (C 2′,3′,4′); 42·77 (CH_2NH_2); 67·45 (C 1′); 110·93 (C 3); 114·77 (C 6′); 120·32 (C 5); 127·95, 128·38 (C 4,6); 131·90 (C 1); 138·38 (C 5′); 156·81 (C 2). Mass spectrum: *m/z* 205 (M, 3%), 204 (7), 188 (8), 173 (2), 162 (5), 147 (8), 134 (22), 122 (100), 106 (51), 95 (18), 78 (43), 67 (12), 55 (44), 51 (11).

2-(Oct-7′-enyloxy)benzylamine (2g). Kugelrohr distillation gave a clear and colourless liquid (100%), b.p. (oven) 115°/0·2 mm (Found: C, 77·0; H, 10·2; N, 6·0. $C_{15}H_{23}NO$ requires C, 77·2; H, 9·9; N, 6·0%). ν_{max} 3379m, 3303w, 2929s, 2858s, 1640s, 1600s, 1589m, 1492s, 1473m, 1454s, 1388w, 1288m, 1240s, 1047m, 1026m, 996m, 909s, 752s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·30–1·55, m, 8H, 1·80, m, 2H, and 2·06, m, 2H, H 2′,3′,4′,5′,6′, NH_2; 3·81, s, 2H, $\mathbf{CH_2}NH_2$; 3·97, t, *J* 6·3 Hz, 2H, H 1′; 4·90–5·05, m, 2H, H 8′; 5·81, ddt, *J* 17·1, 10·4, 6·7 Hz, 1H, H 7′; 6·81–6·92, m, 2H, H 3,5; 7·15–7·25, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 25·95, 28·69, 29·17, 33·57 (C 2′,3′,4′,5′,6′); 42·75 (CH_2NH_2); 67·51 (C 1′); 110·83 (C 3); 114·20 (C 8′); 120·17 (C 5); 127·82, 128·25 (C 4,6); 131·88 (C 1); 138·80 (C 7′); 156·76 (C 2). Mass spectrum: *m/z* 233 (M, 4%), 232 (10), 133 (10), 122 (100), 107 (43), 106 (54), 95 (13), 77 (27), 67 (16), 55 (27).

N,N-*Dimethyl-2-(prop-2′-enyloxy)benzylamine (6)*

2-(Prop-2′-enyloxy)benzaldehyde (4; R′ = H) was prepared as a clear liquid, b.p. (oven) 60°/0·05 mm (lit.[17] 135°/10 mm). An aqueous solution of dimethylamine (10 ml, 26% w/v, 56·5 mmol) was added to a stirred mixture of this aldehyde (1·50 g, 9·2 mmol) in methanol (22 ml). The resulting yellow solution was stirred for 1 h at ambient temperature, then sodium borohydride (2·00 g, 52·9 mmol) was added portionwise and the mixture allowed to stir for a further 1 h. Dilute HCl (2 M) was added until the mixture was acidic and the mixture was extracted with ether (2×20 ml) to remove any starting material. The aqueous extracts were made basic with concentrated NaOH solution and extracted again with ether (2×50 ml). The ethereal extracts were dried ($MgSO_4$) and the solvent was removed under vacuum to give a clear liquid (1·20 g). Kugelrohr distillation gave N,N-*dimethyl-2-(prop-2′-enyloxy)benzylamine* (6) as a clear and colourless oil (1·05 g, 60%), b.p. (oven) 75–80°/0·07 mm (Found: $M^{+\bullet}$ 191·131±0·001. $C_{12}H_{17}NO$ requires $M^{+\bullet}$ 191·131). ν_{max} 2974m, 2941s, 2854m, 2816s, 2768s, 1601m, 1588m, 1491s, 1453s, 1364m, 1240s, 1107m, 1023s, 999m, 927m, 834w, 754s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 2·27, s, 6H, CH_3; 3·50, s, 2H, CH_2N; 4·54, dt, *J* 5·0, 1·6 Hz, 2H, H 1′; 5·26, dq, *J* 10·5, 1·6 Hz, 1H, H 3′$_E$; 5·43, dq, *J* 17·3, 1·6 Hz, 1H, H 3′$_Z$; 6·06, ddt, *J* 17·3, 10·5, 5·0 Hz, 1H, H 2′; 6·82–6·96, m, 2H, H 3,5; 7·11–7·33, m, 2H, H 4,6. ^{13}C n.m.r. δ (50 MHz) 45·42 (CH_3); 57·44 (CH_2N); 68·68 (C 1′); 111·64 (C 3); 116·77 (C 3′); 120·35 (C 5); 127·13 (C 1); 127·92, 130·75, 133·44 (C 4,6,2′); 156·69 (C 2). Mass spectrum: *m/z* 191 (M, 8%), 190 (9), 176 (5), 164 (5), 148 (40), 145 (47), 134 (21), 131 (29), 117 (14), 107 (28), 91 (43), 77 (29), 58 (100), 51 (12).

5-Bromo-2-(prop-2′-enyloxy)benzylamine (5a)

5-Bromo-2-(prop-2′-enyloxy)benzaldehyde (4a) was first prepared by heating a mixture of 5-bromo-2-hydroxybenzaldehyde (8·45 g, 42·0 mmol), 3-bromoprop-1-ene (15 ml, 172 mmol) and powdered anhydrous K_2CO_3 (1·00 g, 7·24 mmol) under reflux for 24 h. Isolation in ether gave a light brown solid (9·30 g). Recrystallization from light petroleum and charcoal gave the aldehyde (4a) as a white solid (8·64 g, 85%), m.p. 37–38° (Found: C, 50·0; H, 3·8. $C_{10}H_9BrO_2$ requires C, 49·8; H, 3·8%). ν_{max} 1676s, 1590m, 1479m, 1463m, 1391m, 1365w, 1272m, 1237m, 1184m, 1124m, 996m, 938m, 886m, 804m, 670m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 4·64, dt, *J* 5·1, 1·5 Hz, 2H, H 1′; 5·32–5·50, m, 2H, H 3′; 6·06, ddt, *J* 17·2, 10·5, 5·5 Hz, 1H, H 2′; 6·88, d, *J* 8·9 Hz, 1H, H 3; 7·59, dd, *J* 8·9, 2·6 Hz, 1H, H 4; 7·90, d, *J* 2·6 Hz, 1H, H 6; 10·43, s, 1H, CHO. ^{13}C n.m.r. δ (50 MHz) 69·41 (C 1′); 113·51 (C 5); 114·85 (C 3); 118·42 (C 3′); 126·18 (C 3); 130·81, 131·81 (C 4,6); 138·09 (C 2′); 159·70 (C 2); 188·17 (CHO). Mass spectrum: *m/z* 242 (M, ^{81}Br, 10%), 240 (M, ^{79}Br, 11), 200·9 (24), 198·9 (22), 197·9 (18), 144·9 (17), 143 (18), 132·1 (19), 119 (9), 105·1 (8), 77·1 (9), 63·1 (100), 53·1 (19), 50·1 (20).

Ammonia solution (28%, 10 ml) was added to a stirred solution of the aldehyde (4a) (1·00 g, 4·15 mmol) in methanol (30 ml) and the mixture was allowed to stir for 1 h. Sodium borohydride (2·00 g, 54·1 mmol) was added portionwise to the mixture and the resulting solution was stirred for a further 1 h. Concentrated HCl (32%) was added dropwise to destroy excess $NaBH_4$ and the mixture was extracted with ether (3×15 ml). The aqueous extracts were made basic with NaOH solution (50%) and extracted with ether (3×30 ml). The ethereal extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a light brown oil (0·80 g). Kugelrohr distillation gave *5-bromo-2-(prop-2′-enyloxy)benzylamine* (5a) as a clear and colourless liquid (0·60 g, 60%), b.p. 95–97°/0·1 mm (Found: $M^{+\bullet}$ 241·011±0·002. $C_{10}H_{12}BrNO$ requires $M^{+\bullet}$ 241·010). ν_{max} 3379s, 3296s, 2920s, 2865s, 1648m, 1594s, 1484s, 1451s, 1299m, 1239s, 1019s, 996s, 842m, 655m, 621m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·55, br s, 2H, NH_2; 3·80, s, 2H, $\mathbf{CH_2}NH_2$; 4·52, dt, *J* 5·0, 1·5 Hz, 2H, H 1′; 5·28, dq, *J* 10·5, 1·5 Hz, 1H, H 3′$_E$; 5·39, dq, *J* 17·3, 1·6 Hz, 1H, H 3′$_Z$; 6·02, ddt, *J* 17·3, 10·5, 5·0 Hz, 1H, H 2′; 6·69, d, *J* 8·6 Hz, 1H, H 3; 7·27, dd, *J* 8·6, 2·5 Hz, 1H, H 4; 7·35, d, *J* 2·5 Hz, 1H, H 6. ^{13}C n.m.r. δ (50 MHz) 41·91 (CH_2NH_2); 68·61 (C 1′); 112·76 (C 5); 112·94 (C 3); 117·34 (C 3′); 130·18, 130·95 (C 4,6); 132·63 (C 2′); 134·15 (C 1); 155·14 (C 2). Mass spectrum: *m/z* 243 (M, ^{81}Br, 10%), 241 (M, ^{79}Br, 10), 226 (14), 224 (14), 211 (12), 209 (12), 202 (32), 200 (37), 185 (20), 173 (15), 162 (31), 145 (100), 127 (29), 121 (64), 94 (83), 85 (13), 77 (51), 65 (66), 56 (83).

3-Methoxy-2-(prop-2′-enyloxy)benzylamine (5b)

3-Methoxy-2-(prop-2′-enyloxy)benzaldehyde (4b) was prepared, b.p. (oven) 97–98°/0·05 mm (lit.[18] 93–95°/0·01 mm). Reductive amination as described above gave a light brown oil which on Kugelrohr distillation gave *3-methoxy-2-(prop-2′-enyloxy)benzylamine* (5b) as a clear liquid (1·33 g, 66%), b.p. (oven) 107–110°/0·1 mm (Found: C, 68·6; H, 7·8. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8%). ν_{max} 3342m, 2937s, 2837s, 1646w, 1585s, 1279s, 1356w, 1274s, 1209s, 1183m, 1072s, 989s, 928m, 777m, 748s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 3·81, s, 2H, CH_2NH_2; 3·84, s, 3H, CH_3; 4·48, dt, *J* 5·9, 1·3 Hz, 2H, H 1′; 5·17, dq, *J* 10·4, 1·2 Hz, 1H, H $3'_E$; 5·30, dq, *J* 17·2, 1·5 Hz, 1H, H $3'_Z$; 6·02, ddt, *J* 17·2, 10·3, 5·9 Hz, 1H, H 2′; 6·82, dd, *J* 7·5, 2·2 Hz, 1H, H 4; 6·92–7·05, m, 2H, H 5,6. ^{13}C n.m.r. δ (50 MHz) 48·22 (CH_2NH_2); 55·65 (CH_3); 73·85 (C 1′); 111·14 (Ar **CH**); 117·26 (C 3′); 121·62, 123·76 (2×Ar **CH**); 134·28 (C 1); 134·31 (C 2′); 146·01, 152·51 (C 2,3). Mass spectrum: *m*/*z* 193 (M, 11%), 192 (77), 177 (23), 161 (22), 151 (45), 137 (100), 121 (53), 117 (47), 106 (47), 93 (50), 77 (42), 65 (86), 56 (70).

2-(But-3′-enyloxy)-N-*methylbenzylamine (16)*

2-(But-3′-enyloxy)-N-*benzylformamide* was prepared according to the general procedure of Rouot.[19] A solution of formic anhydride in acetic acid was prepared by heating acetic anhydride (1·25 ml, 13·2 mmol) with formic acid (0·60 ml, 15·9 mmol) at 50° for 25 min. The solution was cooled to 0° in an ice–water bath and 2-(but-3′-enyloxy)benzylamine (2e) (0·67 g, 3·78 mmol) was added in one portion. The mixture was heated to 50° for 8 h and the resultant solution was evaporated to dryness under vacuum to give an orange-brown oil (0·70 g). Purification by Kugelrohr distillation gave the amide as a yellow liquid (0·61 g, 78%), b.p. (oven) 115°/0·19 mm (Found: C, 70·0; H, 7·5; N, 6·8. $C_{12}H_{15}NO_2$ requires C, 70·2; H, 7·4; N, 6·8%). ν_{max} 3293bs, 3072m, 2927m, 2870m, 1665s, 1602m, 1494s, 1455s, 1384m, 1245s, 1119m, 1032m, 992w, 919m, 754s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 2·58, qt, *J* 6·3, 1·3 Hz, 2H, H 2′; 4·08, t, *J* 6·2 Hz, 2H, H 1′; 4·45, d, *J* 6·1 Hz, 2H, CH_2NH; 5·12–5·26, m, 2H, H 4′; 5·91, ddt, *J* 17·1, 10·2, 6·7 Hz, 1H, H 3′; 6·37, br s, 1H, NH; 6·83–6·94, m, 2H, H 3,5; 7·20–7·28, m, 2H, H 4,6; 8·13, d, *J* 0·9 Hz, 1H, CHO.

A solution of 2-(but-3′-enyloxy)-*N*-benzylformamide (0·50 g, 2·44 mmol) in anhydrous ether (10 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0·14 g, 3·69 mmol) in anhydrous ether (10 ml). Workup as described previously and Kugelrohr distillation gave *2-(but-3′-enyloxy)*-N-*methylbenzylamine* (16) as a clear and colourless liquid (0·37 g, 80%), b.p. (oven) 60°/0·18 mm (Found: C, 75·5; H, 9·0; N, 7·2. $C_{12}H_{17}NO$ requires C, 75·4; H, 9·0; N, 7·3%). ν_{max} 3333bs, 3075m, 2933s, 1641m, 1601s, 1493s, 1472s, 1454s, 1382m, 1292m, 1241s, 1107m, 1035s, 916m, 753s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·82, br s, 1H, NH; 2·38, s, 3H, CH_3; 2·55, qt, *J* 6·6, 1·3 Hz, 2H, H 2′; 3·73, s, 2H, CH_2NH; 4·03, t, *J* 6·4 Hz, 2H, H 1′; 5·08–5·23, m, 2H, H 4′; 5·86, ddt, *J* 17·1, 10·2, 6·7 Hz, 1H, H 3′; 6·81–6·93, m, 2H, H 3,5; 7·16–7·26, m, 2H, H 4,6.

*2-[*N-*(Prop-2′-enyl)aminomethyl]phenol (17)*

A mixture of 2-hydroxybenzaldehyde (3·66 g, 30 mmol), prop-2-en-1-amine (4·5 ml, 60 mmol) and methanol was stirred at room temperature for 1 h. Sodium borohydride (2·75 g, 73·0 mmol) was added portionwise and the mixture was stirred for a further 1 h. Dilute HCl (2 M) solution was added dropwise to destroy excess $NaBH_4$, the mixture was made neutral (pH 7–8) and the organic layer was extracted with ether (3×30 ml). The ethereal extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a brown liquid (4·32 g). Kugelrohr distillation gave the *phenol* (17) as a clear and colourless liquid (3·30 g, 67%), b.p. (oven) 90°/0·07 mm (Found: $M^{+\bullet}$ 163·100±0·001. $C_{10}H_{13}NO$ requires $M^{+\bullet}$ 163·100). ν_{max} 3300m, 3076m, 2849s, 1644w, 1613m, 1590s, 1491s, 1474s, 1411s, 1258s, 1186w, 1151w, 1091s, 1036w, 927m, 755s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 3·27, dt, *J* 6·0, 1·4 Hz, 2H, H 1′; 3·97, s, 2H, $PhCH_2N$; 5·12–5·25, m, 2H, H 3′; 5·88, ddt, *J* 17·1, 10·2, 6·0 Hz, 1H, H 2′; 6·72–6·84, m, 2H, H 4,6; 6·95, dd, *J* 7·4, 1·8 Hz, 1H, H 3; 7·15, td, *J* 8·0, 1·8 Hz, 1H, H 5. ^{13}C n.m.r. δ (50 MHz) 50·69, 51·70 (C 1′, Ph**C**H_2N); 116·27 (C 6); 117·16 (C 3′); 118·92 (C 4); 122·27 (C 2); 128·29, 128·60 (C 3,5); 134·87 (C 2′); 158·15 (C 1). Mass spectrum: *m*/*z* 163 (M, 50%), 162 (39), 148 (13), 131 (22), 121 (18), 107 (100), 91 (8), 77 (53), 70 (31), 56 (76), 51 (15).

Preparation of 2-(Alkenyloxy)benzamides (3)

2-(Prop-2′-enyloxy)benzamide (3a)

Hydrogen peroxide (30%, 1·4 ml) and a catalytic amount of anhydrous K_2CO_3 (0·15 g, 1·09 mmol) were added to a stirred solution of 2-(prop-2′-enyloxy)benzonitrile (1a) (1·00 g, 6·28 mmol) according to the procedure of Katritzky *et al.*[4] The mixture was allowed to warm to room temperature and after a short induction period (*c.* 15 min) a strong exothermic reaction was observed. After 5 min distilled water (50 ml) was added, cooling applied, and the product isolated by filtration. The product was washed with cold water and allowed to dry to give a white solid (0·94 g, 84%), m.p. 89–90° (lit.[20] 93–94°). ν_{max} (Nujol) 3404s, 3172s, 1628s, 1598s, 1571m, 1486m, 1460m, 1397m, 1275m, 1241s, 1166m, 1113m, 1047w, 996m, 912m, 840w, 758s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 4·66, d, *J* 5·5 Hz, 2H, H 1′; 5·35, dd, *J* 10·4, 1·0 Hz, 1H, H $3'_E$; 5·48, dd, *J* 17·5, 1·2 Hz, 1H, H $3'_Z$; 6·08, ddt, *J* 17·5, 10·4, 5·5 Hz, 1H, H 2′; 6·72, br s, 1H, NH; 6·97, d, *J* 8·3 Hz, 1H, H 3; 7·07, t, *J* 7·5 Hz, 1H, H 5; 7·45, td, *J* 8·4, 1·8 Hz, 1H, H 4; 7·83, br s, 1H, NH; 8·22, dd, *J* 7·8, 1·7 Hz, 1H, H 6. ^{13}C n.m.r. δ (50 MHz) 69·85 (C 1′); 112·68 (C 3); 118·23 (C 1); 119·32 (C 3′); 121·33 (C 5); 132·05, 132·48 (C 4,6); 133·23 (C 2′); 156·93 (C 2); 167·36 ($CONH_2$). Mass spectrum: *m*/*z* 177 (M, 12%), 160 (29), 148 (12), 133 (28), 121 (100), 105 (53), 92 (51), 77 (12), 65 (24), 57 (50), 51 (10).

2-(But-3′-enyloxy)benzamide (3e)

This compound was prepared from (1e) by the above method as a white *solid* (0·41 g, 37%), m.p. 83–84° (Found: C, 69·0; H, 6·5; N, 7·6. $C_{11}H_{13}NO_2$ requires C, 69·1; H, 6·8; N, 7·3%). ν_{max} (Nujol) 3443m, 3322w, 3162m, 1667s, 1643w, 1597m, 1270m, 1242m, 1164m, 1090w, 1022m, 936m, 834w, 753m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 2·64, qt, *J* 6·3, 1·3 Hz, 2H, H 2′; 4·20, t, *J* 6·3 Hz, 2H, H 1′; 5·17, dq, *J* 10·2, 1·3 Hz, 1H, H $4'_E$; 5·23, dq, *J* 17·2, 1·6 Hz, 1H, H $4'_Z$; 5·91, ddt, *J* 17·2, 10·2, 6·7 Hz, 1H, H 3′; 6·01, br s, 1H, NH; 6·97, dd, *J* 8·4, 0·8 Hz, 1H, H 3; 7·07, td, *J* 7·4, 1·0 Hz, 1H, H 5; 7·46, ddd, *J* 8·3, 7·3, 1·8 Hz, 1H, H 4; 7·83, br s, 1H, NH; 8·22, dd, *J* 7·8, 1·8 Hz, 1H, H 6. ^{13}C n.m.r. δ (50 MHz) 33·68 (C 2′); 67·81 (C 1′); 112·08 (C 3); 117·94 (C 4′); 120·79 (C 1); 121·18 (C 5); 132·59, 133·28, 134·35 (C 4,6,3′); 157·12 (C 2); 167·12 ($CONH_2$). Mass spectrum: *m*/*z* 191 (M, 1%), 161 (22), 150 (9), 146 (10), 137 (61), 120 (100), 105 (6), 92 (23).

Preparation of 2-[*N*-Benzyl-*N*-(prop-2′-enyl)amino]benzylamine (7)

2-(Benzylamino)benzonitrile

2-Aminobenzonitrile (2·00 g, 17·0 mmol) and benzaldehyde (2·69 g, 25·0 mmol) were heated at 100° for 2 h. Methanol (20 ml) was added; this caused the imine to crystallize. The colourless needles were collected, washed with two portions of cold saturated sodium metabisulphite solution and one portion of cold water, then dried to give the Schiff base as crystals (2·98 g, 85%), m.p. 111·5–112·5° after recrystallization from methanol.

A stirred solution of the Schiff base (4·77 g, 23·2 mmol) in methanol (145 ml) was heated to 40°. Sodium borohydride (1·31 g, 34·7 mmol) was added proportionwise over 10 min, and the solution was heated at reflux for 2 h. Water (30 ml) was added and the solution allowed to cool to give 2-(benzylamino)benzonitrile (4·36 g, 90%). Crystallization from aqueous methanol gave colourless crystals, m.p. 115·5–116·5° (lit.[21] 113–114°). ν_{max} (Nujol) 3376s, 2216s, 1603m, 1576m, 1523m, 1466m, 1332m, 754m cm^{-1}. ^{1}H n.m.r. δ (200 MHz)

4·43, d, J 5·60 Hz, 2H, **C**H$_2$Ph; 5·03, br s, 1H, NH; 6·63, d, J 8·4 Hz, 1H, H3; 6·69, t, J 7·5 Hz, 1H, H5; 7·35, m, 7H, H4,5 and ArH. ^{13}C n.m.r. δ (50 MHz) 47·46 (**C**H$_2$Ph); 95·70 (C1); 111·03 (C3); 116·86 (C5); 117·90 (CN); 127·17, 127·65, 128·87 (Ar **C**H); 132·76, 134·28 (C4,6); 137·70 (Ar **C**); 150·05 (C2). Mass spectrum: m/z 208 (M, 39%), 207 (11), 91 (100).

*2-[*N*-Benzyl-*N*-(prop-2′-enyl)amino]benzonitrile*

A stirred solution of the above benzonitrile (2·0 g, 9·60 mmol) in tetrahydrofuran (6 ml) was cooled to −78°. A lithium diisopropylamide solution (9·6 ml, 9·60 mmol) was added dropwise and the solution allowed to warm to 0°. A solution of 3-bromoprop-1-ene (1·16 g, 9·6 mmol) in tetrahydrofuran (2 ml) was added dropwise, the mixture was warmed to room temperature and then was refluxed for 21 h. The reaction mixture was quenched with water (20 ml), extracted with dichloromethane (3×40 ml) and dried (MgSO$_4$). The solvent was removed under reduced pressure and diisopropylamine removed by radial chromatography (silica, 10% ethyl acetate/light petroleum) to give the allylated product as an oil (1·95 g, 98%). Kugelrohr distillation gave the benzonitrile as a clear *oil*, b.p. (oven) 210°/0·4 mm (Found: C, 82·3; H, 6·5; N, 11·4. $C_{17}H_{16}N_2$ requires C, 82·2; H, 6·5; N, 11·3%). ν_{max} 3065m, 3029m, 2219s, 1596s, 1559m, 1488s, 1446s, 1418m, 1361m, 1286m, 1221m, 927m, 750s, 698s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 3·94, dt, J 5·9, 1·2 Hz, 2H, H1′; 4·50, s, 2H, **C**H$_2$Ph; 5·13–5·24, m, 2H, H3′; 5·92, ddt, J 16·7, 10·7, 5·9 Hz, 1H, H2′; 6·90, m, 2H, H3,5; 7·20–7·40, m, 6H, H4 and ArH; 7·55, d, J 7·5, 1·8 Hz, 1H, H6. ^{13}C n.m.r. δ (50 MHz) 55·57 (**C**H$_2$Ph, C1′); 104·00 (C1); 118·38 (C3′); 119·26 (CN); 120·11, 120·68 (C3,5); 127·38, 127·94, 128·61 (Ar **C**H); 133·37, 133·91 (C4,6); 134·99 (C2′); 137·44 (C1′); 153·69 (C2). Mass spectrum: m/z 249 (M+1, 2%), 248 (M, 13), 247 (4), 205 (3), 171 (7), 157 (14), 129 (12), 91 (100).

*2-[*N*-Benzyl-*N*-(prop-2′-enyl)amino]benzylamine (7)*

The procedure described previously[3] being followed, the above benzonitrile (0·54 g, 2·18 mmol) in dry ether (5 ml) was added dropwise to a suspension of lithium aluminium hydride (0·124 g, 3·27 mmol) in dry ether (5 ml). The mixture was heated at reflux for 2 h. Workup as before gave the benzylamine (7) as an *oil* (0·39 g, 71%), b.p. (oven) 175°/0·4 mm (Found: C, 80·7; H, 8·3; N, 11·1. $C_{17}H_{20}N_2$ requires C, 80·9; H, 8·0; N, 11·1%). ν_{max} 3373bs, 1640w, 1597m, 1490s, 1451s, 1209m, 919m, 767m, 728m, 699m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·61, br s, 2H, NH$_2$; 3·52, dt, J 6·3, 1·2 Hz, 2H, H1′; 3·94, br s, 2H, CH$_2$NH$_2$; 4·09, s, 2H, CH$_2$Ph; 5·06–5·18, m, 2H, H3′; 5·80, ddt, J 17·1, 10·2, 6·3 Hz, 1H, H2′; 7·04–7·33, m, 9H, H3,4,5,6 and ArH. ^{13}C n.m.r. δ (50 MHz) 56·63 (C1′, **C**H$_2$Ph); 58·30 (**C**H$_2$NH$_2$); 117·74 (C3′); 123·16, 124·48 (C3,5); 127·00, 127·10, 128·20, 128·44, 128·80 (C4,6 and Ar **C**H); 134·75 (C2′); 138·43 (Ar **C**); 149·31 (C2). Mass spectrum: m/z 252 (M, 5%), 234 (7), 223 (17), 194 (50), 161 (25), 144 (94), 91 (100).

Reactions of 2-(Alkenyloxy)benzylamines with H$_2$/CO

The general conditions for reactions were as described previously.[12]

Reaction of 2-(Prop-2′-enyloxy)benzylamine (2a)

A mixture of 2-(prop-2′-enyloxy)benzylamine (2a) (0·30 g, 1·84 mmol), rhodium(II) acetate dimer (0·0053 g, 0·0012 mmol) and triphenylphosphine (0·0101 g, 0·0385 mmol) in deoxygenated ethyl acetate (10 ml) was reacted with H$_2$/CO (1 : 1 molar mixture, 400 psi) at 60° for 20 h. The solvent was removed under vacuum. ^{1}H and ^{13}C n.m.r. spectroscopy indicated that 2-(1′-methylethyl)-3,4-dihydro-2*H*-1,3-benzoxazine (8) was the only product present. Purification by Kugelrohr distillation gave (8) as a clear liquid (0·24 g, 74%), b.p. 80°/0·05 mm (lit.[6] 72–75°/0·04–0·05 mm). ν_{max} 3322m, 2961s, 2876m, 1678w, 1608m, 1584s, 1488s, 1458s, 1390m, 1263s, 1251s, 1224s, 1107m, 1033m, 985m, 967m, 922s, 793m, 753s, 657m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·03, d, J 6·8 Hz, 3H, CH$_3$; 1·05, d, J 6·8 Hz, 3H, CH$_3$; 1·98, qqd, J 6·8, 6·8, 5·2 Hz, 1H, H1′; 3·88, d, J_{AB} 16·9 Hz, 1H, and 4·09, d, J_{AB} 16·9 Hz, 1H, H4; 4·47, d, J 5·2 Hz, 1H, H2; 6·80, m, 3H, H5,6,8; 7·08, t, J 7·3 Hz, 1H, H7. ^{13}C n.m.r. δ (50 MHz) 17·21 (CH$_3$); 17·44 (CH$_3$); 32·46 (C1′); 44·48 (C4); 91·05 (C2); 116·88 (C8); 119·86 (C6); 122·04 (C4a); 126·01, 127·52 (C5,7); 154·77 (C8a). Mass spectrum: m/z 177 (M, 18%), 162 (4), 145 (3), 134 (91), 107 (100), 77 (27), 71 (10), 63 (2), 51 (11). This spectroscopic data was consistent with literature[6] values and with data obtained from an authentic sample.[6]

Similar reactions in ethyl acetate at 50 or 40°, or in benzene at 60°, gave an identical result. However, no reaction occurred at 25° in ethyl acetate. Reaction of (2a) (0·20 g, 1·23 mmol) with H$_2$/CO in the presence of HRh(CO)(PPh$_3$)$_3$ (0·0113 g, 0·012 mmol) at 60° also gave an excellent yield of the oxazine (8); however, similar reactions with H$_2$/N$_2$ (400 psi, 1 : 1) or under N$_2$ at 60° gave recovered (2a).

Reaction of (2a) (0·25 g) with [Rh(OAc)$_2$]$_2$/PPh$_3$ as above with D$_2$/CO (400 psi) in ethyl acetate gave a deuterated oxazine (0·25 g, 97%). Analysis of the crude reaction mixture by ^{1}H and ^{13}C n.m.r. spectroscopy indicated that there was 75% incorporation of deuterium on the alkyl substituent and 100% incorporation at C2. There was no evidence to suggest substitution of deuterium for the aromatic or benzylic protons. ν_{max} 3319w, 3039s, 2929s, 2471m, 2163m, 1972m, 1651s, 1601s, 1584s, 1486s, 1454s, 1242s, 1114m, 1047s, 924s, 753s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·02, br s, 0·75H, CH$_3$; 1·05, br s, 0·75H, CH$_3$; 2·06, br d, J 3·5 Hz, 0·25H, H1′; 3·88, d, J_{AB} 16·9 Hz, 1H and 4·09, d, J_{AB} 16·9 Hz, 1H, H4; 6·75–6·93, m, 3H and 7·04–7·20, m, 1H, ArH. ^{13}C n.m.r. δ (50 MHz) 17·19 (CH$_3$); 44·25 (C4); 116·78 (C8); 119·26 (C6); 121·97 (C4a); 125·95, 126·88 (C5,7); 154·70 (C8a).

Reaction of 2-(But-2′-enyloxy)benzylamine (2c)

The reaction of (2c) (0·30 g, 1·69 mmol) at 80° gave a crude product whose ^{1}H and ^{13}C n.m.r. spectra indicated that *2-(1′-methylpropyl)-3,4-dihydro-2*H*-1,3-benzoxazine* (9) was the only product present, existing as a mixture of diastereoisomers in the ratio of 1 : 1. Purification by Kugelrohr distillation gave (9) as a clear and colourless liquid (0·23 g, 71%), b.p. (oven) 95°/0·05 mm (Found: M$^{+\bullet}$ 191·131±0·001. $C_{12}H_{17}NO$ requires M$^{+\bullet}$ 191·131). ν_{max} 3320m, 2959s, 2876m, 1677w, 1602m, 1584s, 1489s, 1458m, 1263s, 1251s, 1226s, 1107m, 1032s, 967m, 922s, 793m, 752s, 657m cm^{-1}. ^{1}H n.m.r.* δ (200 MHz) 0·83–1·10, m, 6H, H3′ and CH$_3$; 1·13–1·45, m, 2H, H2′; 1·55–1·82, m, 1H, H1′; 3·93, d, J_{AB} 17·0 Hz, 1H, and 4·13, d, J_{AB} 17·0 Hz, 1H, H4; 4·59, d, J 4·0 Hz and 4·60, d, J 4·7 Hz, 1H, H2; 6·75–6·95, m, 2H, H6,8; 7·05–7·09, m, 1H, H5; 7·09–7·14, m, 1H, H7. ^{13}C n.m.r. δ (50 MHz) 11·54, 11·64 (C3′); 13·45, 13·73 (CH$_3$); 24·44, 24·88 (C2′); 38·92, 39·16 (C1′); 44·57, 44·66 (C4); 89·97, 90·14 (C2); 116·91, 116·97 (C8); 119·90 (C6); 122·09 (C4a); 126·05, 127·55 (C5,7); 154·88 (C8a). Mass spectrum: m/z 191 (M, 20%), 176 (9), 162 (31), 134 (59), 121 (13), 107 (100), 77 (37), 70 (17), 57 (23). Spectroscopic data were identical with those of an authentic sample prepared by stirring a mixture of 2-aminomethylphenol (0·50 g, 4·06 mmol) and 2-methylbutanal (0·87 ml, 8·12 mmol) in benzene (30 ml) over 4 Å molecular sieves for 3 h at ambient temperature as described by McDonagh

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* ^{1}H and ^{13}C n.m.r. data obtained on a 1 : 1 mixture of diastereoisomers.

and Smith.[6] The sieves were filtered off, washed with benzene and the filtrate was evaporated under reduced pressure to give a dark brown liquid. Kugelrohr distillation gave the benzoxazine (9) as a clear liquid (0·63 g, 81%), b.p. 55°/0·01 mm.

Reaction of 2-(1′-Methylprop-2′-enyloxy)benzylamine (2b)

Reaction of the benzylamine (2b) (0·20 g, 1·13 mmol) at 60° gave a crude product whose ^{1}H and ^{13}C n.m.r. spectra indicated that 2-(1′-methylpropyl)-3,4-dihydro-2*H*-1,3-benzoxazine (9) was present as a mixture of diastereoisomers in the ratio of 1 : 1, with small amounts of unidentified material. Purification by Kugelrohr distillation gave the benzoxazine (9) as a clear and colourless liquid (0·12 g, 56%). The spectroscopic data were consistent with those reported above.

Reactions of 2-(2′-Methylprop-2′-enyloxy)benzylamine (2d), 2-(But-3′-enyloxy)benzylamine (2e), 2-(Hex-5′-enyloxy)benzylamine (2f) and 2-(Oct-7′-enyloxy)benzylamine (2g)

Reactions of each of these compounds (*c.* 2 mmol) in ethyl acetate at 60 or 80° for 5–20 h in all cases gave polymeric material with m.p. >300°, insoluble in a wide range of solvents.

Reaction of 5-Bromo-2-(prop-2′-enyloxy)benzylamine (5a)

Reaction of the benzylamine (5a) (0·30 g, 1·24 mmol) at 60° gave a product whose ^{1}H and ^{13}C n.m.r. spectra indicated that *6-bromo-2-(1′-methylethyl)-3,4-dihydro-2*H*-1,3-benzoxazine* was the only product present. Purification by Kugelrohr distillation gave the benzoxazine as a clear and colourless liquid (0·25 g, 80%), b.p. (oven) 105°/0·05 mm (Found: $M^{+\bullet}$ 255·026±0·003. $C_{11}H_{14}BrNO$ requires $M^{+\bullet}$ 255·026). ν_{max} 3322m, 3058m, 2960s, 1673s, 1592m, 1576m, 1485s, 1244s, 1120m, 1046m, 811m, 754m, 694m, 642m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·03, d, *J* 6·8 Hz, 3H, CH$_3$; 1·05, d, *J* 6·8 Hz, 3H, CH$_3$; 1·89–2·06, m, 1H, H1′; 3·88, d, J_{AB} 13·2 Hz, 1H, and 4·04, d, J_{AB} 13·2 Hz, 1H, H4; 4·65, dd, *J* 12·6, 5·1 Hz, 1H, H2; 6·65, d, *J* 8·7 Hz, 1H, H8; 7·05, d, *J* 2·4 Hz, 1H, H5; 7·17, dd, *J* 8·7, 2·4 Hz, H7. ^{13}C n.m.r. δ (50 MHz) 17·18, 17·39 (2×CH$_3$); 32·36 (C1′); 44·09 (C4); 91·34 (C2); 111·73 (C6); 118·68 (C8); 123·71 (C4a); 128·63, 130·31 (C5,7); 153·86 (C8a). Mass spectrum: *m/z* 257 (M, ^{81}Br, 14%), 255 (M, ^{79}Br, 14), 214 (58), 212 (61), 187 (61), 185 (65), 158 (12), 106 (11), 88 (10), 77 (57), 71 (100), 56 (32), 51 (38).

Reaction of 3-Methoxy-2-(prop-2′-enyloxy)benzylamine (5b)

The benzylamine (5b) (0·30 g, 1·55 mmol) was reacted with H$_2$/CO at 60°. The crude product coated the glass sleeve of an autoclave and appeared to be polymeric in nature. Attempts to dissolve the crude material in a range of solvents proved unsuccessful. The melting point of the material was greater than 300°.

Reaction of N,N*-Dimethyl-2-(prop-2′-enyloxy)benzylamine (6)*

Reaction of the benzylamine (6) (0·3 g, 1·57 mmol) at 60° gave a crude product whose ^{1}H and ^{13}C n.m.r. spectra indicated that 2-[(dimethylamino)methyl]phenol (13) and 4-(2′-[(dimethylamino)methyl]phenoxy)butanal (14) were present in the ratio of 55 : 45. The products were separated from spent catalyst by column chromatography (silica, 50% ethyl acetate/light petroleum) to give the products as a brown liquid (0·30 g). Attempts to separate the two products by distillation and chromatography were unsuccessful. The data obtained are of the 'purified' mixture. ν_{max} 3040m, 2949s, 2860s, 2781s, 1724m, 1589s, 1490s, 1454s, 1362m, 1259s, 1181w, 1106m, 1041m, 1016s, 973m, 838m, 754s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 2·11–2·25, m, 2H, H3 of (14); 2·27, s, 6H, NMe$_2$ of (14); 2·31, s, 6H, NMe$_2$ of (13); 2·78, td, *J* 7·1, 1·2 Hz, 2H, H2 of (14); 3·44, s, 2H, CH$_2$N of (14); 3·63, s, 2H, CH$_2$N of (13); 4·00, t, *J* 6·0 Hz, H4 of (14); 6·72–6·96, m, 4H, ArH; 7·11–7·31, m, 4H, ArH; 9·84, t, *J* 1·2 Hz, 1H, CHO of (14). ^{13}C n.m.r. δ (50 MHz) 22·00 (C3 of (14)); 40·65 (C2 of (14)); 44·38 (CH$_3$ of (13)); 45·39 (CH$_3$ of (14)); 57·43 (CH$_2$N of (14)); 62·75 (CH$_2$N of (13)); 66·72 (C4 of (14)); 111·25, 115·90, 118·80, 120·38 (Ar **CH**); 121·86, 126·81 (Ar **C**); 128·10, 128·17, 128·58, 130·81 (Ar **CH**); 156·79, 158·00 (Ar **C**); 201·72 (CHO of (14)).

*Reaction of 2-[*N*-Benzyl-*N*-(prop-2′-enyl)amino]benzylamine (7)*

Reaction of the benzylamine (7) (0·72 g, 2·81 mmol) with H$_2$/CO in ethyl acetate (10 ml) at 80° for 20 h gave an oil (0·76 g). The ^{1}H and ^{13}C n.m.r. spectra indicated that the major product (80–90%) was *1-benzyl-2-(1′-methylethyl)-1,2,3,4-tetrahydroquinazoline* (12). A pure sample was obtained by radial chromatography and distillation (b.p. (oven) 210°/0·05 mm) which was identical with an authentic sample (see below) (Found: $M^{+\bullet}$ 266·178±0·003. $C_{18}H_{21}N_2$ requires $M^{+\bullet}$ 266·178). ν_{max} 3328w(br), 2956m, 2927m, 2868m, 1603s, 1578w, 1500s, 1452s, 1347m, 745s, 699m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 0·92, d, *J* 6·7 Hz, 3H, CH$_3$; 0·97, d, *J* 6·8 Hz, 3H, CH$_3$; 2·06, m, 1H, H1′; 3·86, d, *J* 7·0 Hz, 1H, H2; 3·92, d, *J* 16·75 Hz, 1H, and 4·02, d, *J* 16·75 Hz, 1H, H4; 4·36, d, *J* 16·86 Hz, 1H, and 4·64, d, *J* 16·86 Hz, 1H, CH$_2$Ph; 6·60–6·68, m, 2H, H6,8; 6·93, m, 1H, H5; 7·02, m, 1H, H7; 7·21–7·35, m, 5H, ArH. ^{13}C n.m.r. δ (50 MHz) 17·21, 19·82 (CH$_3$); 29·71 (C1′); 43·36 (C4); 55·08 (**CH$_2$**Ph); 77·66 (C2); 114·01, 116·62 (C6,8); 122·76 (C4a); 125·52, 126·71 (C5,7); 126·80, 127·29, 128·36 (Ar **CH**); 139·15 (Ar **C**); 144·55 (C8a). Mass spectrum: *m/z* 266 (M, 2%), 223 (100), 194 (22), 131 (22), 118 (30), 91 (90).

An authentic sample of (12) was prepared as described below. Reduction of 2-(benzylamino)benzonitrile (1·52 g, 7·29 mmol) with LiAlH$_4$ (1·67 g, 7·32 mmol) in dry ether (20 ml) under reflux for 2 h, followed by workup with Glauber's salt as described above, gave an oil (1·30 g) which was distilled (b.p. (oven) 150°/0·1 mm) to give pale yellow crystals. An analytical sample of *2-(benzylamino)benzylamine* was obtained by recrystallization from ethanol/water as colourless crystals, m.p. 42·5° (Found: C, 79·0; H, 7·2; N, 13·2. $C_{14}H_{18}N_2$ requires C, 79·2; H, 7·6; N, 13·2%). ν_{max} (Nujol) 3265w, 1603m, 1506m, 1309w, 1169w, 700m. ^{1}H n.m.r. δ (200 MHz) 1·4, br s, 2H, NH$_2$; 3·89, s, 2H, **CH$_2$**NH$_2$; 4·35, s, 2H, **CH$_2$**Ph; 6·3, br s, 1H, NH; 6·59, d, *J* 8·0 Hz, 1H, H3; 6·63, td, *J* 7·3, 1·0 Hz, 1H, H5; 7·02, dd, *J* 7·2, 1·6 Hz, 1H, H6; 7·11, td, *J* 7·7, 1·6 Hz, 1H, H4; 7·23–7·40, m, 5H, ArH. ^{13}C n.m.r. δ (50 MHz) 45·49 (**CH$_2$**NH$_2$); 47·55 (**CH$_2$**Ph); 110·59 (C3); 116·35 (C5); 125·52 (C1); 126·80, 127·24, 128·38, 128·42, 128·79 (C4,6 and Ar **CH**); 139·79 (Ar **C**); 147·72 (C2). Mass spectrum: *m/z* 212 (M, 18%), 195 (73), 194 (63), 121 (66), 118 (85), 106 (20), 94 (32), 91 (100), 77 (35), 65 (50).

A solution of this benzylamine (0·60 g, 2·8 mmol) and 2-methylbutanal (1·54 ml, 17·0 mmol) in benzene (50 ml) was stirred over 4 Å molecular sieves (dried at 100°/15 mm) at ambient temperature overnight.[6] The product was obtained as a brown oil (0·86 g), from which a pure sample of the quinazoline (12) was obtained by chromatography. A small amount of another product whose structure was tentatively assigned as 1-benzyl-2-(1′-methylethyl)-3-(2″-methylprop-1″-enyl)-1,2,3,4-tetrahydroquinazoline was present in the crude mixture. This quinazoline was obtained as the sole product (82%) from a reaction with molecular sieves which had been dried for 5 h at 250°/0·01 mm. Preparative chromatography on silica (ethyl acetate/light petroleum) gave an oil, b.p. (oven) 220°/0·05 mm (Found: $M^{+\bullet}$ 320·224±0·002. $C_{22}H_{28}N_2$ requires $M^{+\bullet}$ 320·225). ν_{max} 2958s, 2869s, 1668m, 1603s, 1576m, 1495s, 1452s, 1348m, 1120m, 745s, 700s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·01, d, *J* 6·7 Hz, 3H and 1·15, d, *J* 6·7 Hz, 3H, CH$_3$CH; 1·58, d, *J* 0·67 Hz, 3H and 1·74, d, *J* 0·68 Hz, 3H, CH_3C=; 2·04, m, 1H, H 1′; 3·69, d, *J* 17·3 Hz, 1H, H 4; 3·75, d, *J* 9·3 Hz, 1H, H 2; 4·38, d, *J* 16·25 Hz, 1H, C**H**$_2$Ph; 4·43, d, *J* 17·3 Hz, 1H, H 4; 4·71, d, *J* 16·25 Hz, 1H, C**H**$_2$Ph; 5·67, m, 1H, H 1″; 6·56–6·63, m, 2H, H 6,8; 6·94, m, 1H and 7·20–7·48, m, 6H, H 5,7 and ArH. ^{13}C n.m.r. δ (50 MHz) 17·58, 19·62 (**C**H$_3$CH); 20·15, 22·42 (**C**H$_3$C=); 32·70 (C 1′); 49·10 (C 4); 55·55 (**C**H$_2$Ph); 84·20 (C 2); 113·05, 116·72 (C 6,8); 119·97 (C 2″); 121·55 (C 4a); 127·40, 127·64, 128·27, 128·85, 128·95 (C 5,7 and Ar **C**H); 135·57 (C 1″); 140·14 (Ar **C**); 143·53 (C 8a). Mass spectrum: *m/z* 320 (M, <1%), 277 (15), 224 (28), 223 (100), 221 (21), 196 (17), 194 (46), 131 (21), 118 (23), 91 (70).

Crossover Reactions

Reaction of a Mixture of N,N-*Dimethyl-2-(prop-2′-enyloxy)-benzylamine (6) and 2-Aminomethylphenol with H_2/CO*

A mixture of the benzylamine (6) (0·30 g, 1·57 mmol), 2-aminomethylphenol (0·19 g, 1·57 mmol), rhodium(II) acetate dimer (0·007 g, 0·0158 mmol) and triphenylphosphine (0·0164 g, 0·0625 mmol) in deoxygenated ethyl acetate (20 ml) was reacted with H_2/CO (1:1 molar mixture, 400 psi) at 60° for 24 h. ^{1}H and ^{13}C n.m.r. spectroscopy indicated that 2-(dimethylaminomethyl)phenol (13), 2-(1′-methylethyl)-3,4-dihydro-2*H*-1,3-benzoxazine (8) and 2-(3′-[2″-(dimethylaminomethyl)phenoxy]propyl)-3,4-dihydro-2*H*-1,3-benzoxazine (15), were present in the ratio of 40:31:29. Attempted separation of the mixture by chromatography and distillation proved unsuccessful. The following data obtained are on the mixture. ^{1}H n.m.r. δ (200 MHz) 1·03, d, *J* 6·8 Hz, 3H, CH_3 of (8); 1·05, d, *J* 6·8 Hz, 3H, CH_3 of (8); 1·94–2·10, m, 5H, H 1′ of (8), H 1′,2′ of (15); 2·27, s, 6H, NMe_2 of (15); 2·30, s, 6H, NMe_2 of (13); 3·51, s, 2H, C**H**$_2$NMe$_2$ of (15); 3·62, s, 2H, C**H**$_2$NMe$_2$ of (13); 3·86–4·17, m, 6H, H 4 of (8), H 4,3′ of (13); 4·47, d, *J* 5·2 Hz, 1H, H 2 of (8); 4·79, t, *J* 5·5 Hz, 1H, H 2 of (15); 6·72–6·96, m, 8H and 7·06–7·23, 4H, ArH. ^{13}C n.m.r. δ (50 MHz) 17·19, 17·43 (2×CH_3 of (8)); 24·63 (C 2′ of (15)); 31·95 (C 1′ of (15)); 32·45 (C 1′ of (8)); 44·18 (C 4 of (15)); 44·38 (NMe_2 of (13)); 44·49 (C 4 of (8)); 45·15 (NMe_2 of (15)); 57·15 (CH_2N of (15)); 62·43 (CH_2N of (13)); 67·43 (C 3′ of (15)); 86·82 (C 2 of (15)); 91·08 (C 2 of (8)); 111·23, 115·91, 116·86, 118·81, 119·86, 120·17 (Ar **C**H); 121·86, 122·06 (Ar **C**); 126·06, 126·10 (Ar **C**H); 126·31 (Ar **C**); 127·51, 128·18, 128·60, 130·91 (Ar **C**H); 154·75, 157·10, 158·00 (Ar **C**).

*Reaction of a Mixture of 2-[*N*-Benzyl-*N*-(prop-2′-enyl)amino]-benzylamine (7) and 2-Aminomethylphenol with H_2/CO*

A mixture of the benzylamine (7) (0·11 g, 0·518 mmol) and 2-aminomethylphenol (0·064 g, 0·518 mmol) was reacted as above at 80° for 20 h to give an oil (0·21 g). The ^{1}H and ^{13}C n.m.r. spectra showed a mixture of the quinazoline (12) and the oxazine (8), together with some 2-(benzylamino)benzylamine. ^{13}C n.m.r. δ (50 MHz), for (12) 29·80 (**C**HCH$_3$); 77·79 (C 2). For (8) 32·47 (**C**HCH$_3$); 91·10 (C 2).

*Reaction of 2-[*N*-(Prop-2′-enyl)aminomethyl]phenol (17) with H_2/CO*

Reaction of the benzylamine (17) (0·30 g, 1·84 mmol) with H_2/CO at 80° for 20 h gave a crude product whose ^{1}H and ^{13}C n.m.r. spectra indicated that 2-(1′-methylethyl)-3,4-dihydro-2*H*-1,3-benzoxazine (8) and 1,2,3,3a-tetrahydro-9*H*-pyrrolo[2,1-*b*][1,3]benzoxazine (18) were present in the ratio 30:70. Products were separated by column chromatography (alumina, 50% ethyl acetate/light petroleum) for analysis.

*1,2,3,3a-Tetrahydro-9*H*-pyrrolo[2,1-*b*][1,3]benzoxazine* (18) (Found: $M^{+\bullet}$ 175·100±0·001. $C_{11}H_{13}NO$ requires $M^{+\bullet}$ 175·100). ν_{max} 3041s, 2960s, 2847s, 1610m, 1585s, 1485s, 1457s, 1355m, 1255s, 1220s, 1180m, 1084m, 952s, 887s, 753s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·65–2·25, m, 4H, H 2,3; 2·80–3·10, m, 2H, H 1; 3·81, d, J_{AB} 17·0 Hz, 1H and 3·35, J_{AB} 17·0 Hz, 1H, H 9; 5·05, dd, *J* 3·4, 1·5 Hz, 1H, H 3a; 6·68–6·85, m, 2H, H 5,7; 6·90–7·20, m, 2H, H 6,8. ^{13}C n.m.r. δ (50 MHz) 21·34 (C 2); 32·21 (C 3); 46·41, 49·14 (C 1,9); 90·72 (C 3a); 116·72, 120·38 (C 5,7); 122·64 (C 8a); 127·28, 127·51 (C 6,8); 158·15 (C 4a). Mass spectrum: *m/z* 175 (M, 100%), 174 (29), 158 (12), 146 (16), 132 (23), 118 (20), 107 (27), 91 (10), 78 (39), 69 (43).

2-(1′-Methylethyl)-3,4-dihydro-2*H*-1,3-benzoxazine (8) was identified by comparison with the spectroscopic data of an authentic sample.

Reaction of 2-(Alkenyloxy)benzamides

Reaction of 2-(Prop-2′-enyloxy)benzamide (3a)

Reaction of the benzamide (3a) (0·30 g, 1·69 mmol) with H_2/CO at 60° for 20 h gave a crude product whose ^{1}H and ^{13}C n.m.r. spectra indicated the presence of a mixture of 2-hydroxybenzamide and 2-(3′-formylpropyloxy)benzamide in the ratio 80:20 respectively. Column chromatography (alumina, 50% ethyl acetate/light petroleum) gave *2-(3′-formylpropyloxy)benzamide* (Found: $M^{+\bullet}$ 207·090±0·001. $C_{11}H_{13}NO_3$ requires $M^{+\bullet}$ 207·090). ν_{max} (Nujol) 3395m, 3168m, 1720s, 1675s, 1629s, 1589m, 1449s, 1376m, 1252m, 750s, 650m cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 2·19, apparent p, *J* 6·8 Hz, 2H, H 2′; 2·72, apparent q, *J* 7·9 Hz, 2H, H 3′; 4·12, t, *J* 6·8 Hz, 2H, H 1′; 6·80–7·00, m, 2H, H 3,5; 7·64, td, *J* 7·9, 1·2 Hz, 1H, H 4; 8·16, d, *J* 7·8 Hz, 1H, H 6; 9·82, t, *J* 7·5 Hz, 1H, CHO. Mass spectrum: *m/z* 207 (M, 10%), 191 (10), 149 (14), 137 (31), 120 (100), 105 (10), 92 (80), 80 (12), 77 (12), 71 (82), 65 (31).

This was followed by 2-hydroxybenzamide, m.p. 139–142° (lit.[22] 136–138°). ^{1}H n.m.r. δ (200 MHz) ((D$_6$)acetone) 6·82–6·93, m, 2H, H 3,5; 7·23, br s, 1H, NH; 7·43, td, *J* 7·1, 1·3 Hz, 1H, H 4; 7·84, dd, *J* 7·8, 1·3 Hz, 1H, H 6; 7·96, br s, 1H, NH. ^{13}C n.m.r. δ (50 MHz) ((D$_6$)acetone) 114·74 (C 1); 118·59, 119·12 (C 3,5); 128·27 (C 4); 135·10 (C 6); 163·10 (C 2); 173·83 (C=O). Mass spectrum: *m/z* 137 (M, 23%), 119 (78), 91 (100), 71 (22), 63 (27). The spectroscopic data were identical to those of an authentic sample of 2-hydroxybenzamide.

Reaction of 2-(But-3′-enyloxy)benzamide (3e)

Reaction of the benzamide (3e) (0·21 g, 1·10 mmol) with H_2/CO at 60° gave a mixture (by ^{1}H and ^{13}C n.m.r.) of *2-(4′-formylbutyloxy)benzamide* (A) and *2-(3′-formylbutyloxy)benzamide* (B) in the ratio 60:40. The products were separated from spent catalyst by column chromatography (silica, 100% ethyl acetate). The aldehydes could not be separated from one another by chromatography and the data obtained are on the purified mixture (Found: $M^{+\bullet}$ 221·105±0·001. $C_{12}H_{15}NO_3$ requires $M^{+\bullet}$ 221·105). ν_{max} 3457s, 3326m, 2939s, 2880m, 1721s, 1664s, 1598s, 1569m, 1491m, 1454s, 1390m, 1290s, 1260m, 1237s, 1164m, 1045m, 757s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·22, d, *J* 7·3 Hz, 3H, H 4′ of (B); 1·72–1·97, m, 6H, H 2′,3′ of (A) and H 2′ of (B); 2·30, qd, *J* 7·0, 7·0 Hz, 1H, H 3′ of (B); 2·56, td, *J* 6·8, 1·0 Hz, 2H, H 4′ of (A); 4·11, t, *J* 6·3 Hz, 2H, H 1′ of (A); 4·18, t, *J* 6·6 Hz, 2H, H 1′ of (B); 6·83, br s, 2H, NH of (A),(B); 6·93–7·09, m, 4H, H 3,5 of (A),(B); 7·39–7·52, m, 2H, H 4 of (A),(B); 7·83, br s, 2H, NH of (A),(B); 8·14–8·21, m, 2H, H 6 of (A),(B); 9·68, d, *J* 1·1 Hz, 1H, CHO of (B); 9·79, t, *J* 1·1 Hz, 1H, CHO of (A). ^{13}C n.m.r. δ (50 MHz) 13·07 (C 4′ of (B)); 18·08 (C 3′ of (A)); 28·04 (C 2′ of (A)); 29·09 (C 2′ of (B)); 42·68 (C 4′ of (A)); 42·80 (C 3′ of (B)); 66·15 (C 1′ of (B)); 68·89 (C 1′ of (A)); 111·86, 120·51 (C 3,5); 120·71 (C 1); 131·42, 132·84 (C 4,6); 156·49 (C 2 of (B)); 156·61 (C 2 of (A)); 167·13 (CONH$_2$); 201·48 (CHO of (A)); 203·64 (CHO of (B)). Mass spectrum: *m/z* 221 (M, 8%), 193 (5), 176 (7), 137 (37), 120 (100), 101 (41), 92 (35), 85 (14), 77 (14), 65 (20), 55 (46).

Reaction of 2-(Alkenyloxy)benzonitriles

Reaction of 2-(Prop-2′-enyloxy)benzonitrile (1a)

The benzonitrile (1a) (0·35 g, 2·20 mmol) was reacted with H_2/CO at 80° for 20 h. The ^{1}H and ^{13}C n.m.r. spectra of the total product indicated the presence of 2-hydroxybenzonitrile, *2-(3′-formylpropyloxy)benzonitrile* (A) and *2-(2′-formylpropyloxy)benzonitrile* (B) in the approximate ratio of 66 : 15 : 19 respectively. The aldehydes (A) and (B), were separated from the phenol by preparative radial chromatography (silica, 50% ether/light petroleum). The aldehydes could not be separated and were analysed as the mixture, b.p. (oven) 100°/0·2 mm (Found: C, 69·6; H, 5·5; N, 7·5. $C_{11}H_{11}NO_2$ requires C, 69·8; H, 5·9; N, 7·4%). ν_{max} 2227s, 1721s, 1599s, 1579m, 1493s, 1472m, 1451s, 1394w, 1291s, 1260s, 1166m, 1111m, 1044m, 1014m, 988m, 757s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·37, d, J 7·4 Hz, 3H, H 3′ of (B); 2·20, p, J 6·1 Hz, 2H, H 2′ of (A); 2·80, td, J 6·1, 1·0 Hz, 2H, H 3′ of (A); 2·99, dq apparent as a sextet, J 6·9 Hz, 1H, H 2′ of (B); 4·13, t, J 6·1 Hz, 2H, H 1′ of (A); 4·22, dd, J 9·3, 6·0 Hz, 1H, and 4·32, dd, J 9·3, 6·0 Hz, 1H, H 1′ of (B); 6·90–7·07, m, 2H, H 3,5; 7·48–7·57, m, 2H, H 4,6; 9·84, d, J 0·5 Hz, 1H, CHO of (B); 9·87, t, J 1·0 Hz, 1H, CHO of (A). ^{13}C n.m.r. δ (50 MHz) 10·58 (C 3′ of (B)); 21·42 (C 2′ of (A)); 40·10 (C 3′ of (A)); 45·74 (C 2′ of (B)); 67·42 (C 1′ of (A)); 68·15 (C 1′ of (B)); 100·85 (C 1 of (B)); 101·02 (C 1 of (A)); 112·11 (C 3 of (A)); 112·21 (C 3 of (B)); 116·35 (CN of (B)); 116·62 (CN of (A)); 120·89 (C 5 of (A)); 121·23 (C 5 of (B)); 133·50, 133·65, 134·52, 134·71 (C 4,6 of (A),(B)); 160·24 (C 2 of (A)); 160·31 (C 2 of (B)); 202·53 (CHO of (B)); 203·12 (CHO of (A)).

Reaction of the benzonitrile (1a) at 60° gave identical results to those above but at 40° no reaction was observed.

Reaction of 2-(But-3′-enyloxy)benzonitrile (1e)

The benzonitrile (1e) (0·30 g, 17·3 mmol) was reacted at 80°. The ^{1}H and ^{13}C n.m.r. spectra of the crude reaction mixture indicated the presence of the two isomeric aldehydes *2-(4′-formylbutyloxy)benzonitrile* and *2-(3′-formylbutyloxy)benzonitrile* in the approximate ratio of 60 : 40. The aldehydes were separated from spent catalyst by column chromatography (silica, 50% ethyl acetate/light petroleum) and distilled for analysis, b.p. (oven) 80°/0·2 mm (Found: C, 70·8; H, 6·6; N, 7·2. $C_{12}H_{18}NO_2$ requires C, 70·9; H, 6·5; N, 6·9%). The isomeric aldehydes were separated by radial chromatography (silica, 50% ethyl acetate/light petroleum).

2-(4′-Formylbutyloxy)benzonitrile had ν_{max} 2945s, 2879s, 2726s, 2225s, 1728s, 1597s, 1579s, 1490s, 1450s, 1391s, 1294s, 1252s, 1111s, 1043s, 1007s, 754s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·83, m, 4H, H 2′,3′; 2·59, td, J 6·9, 1·5 Hz, 2H, H 4′; 4·09, t, J 5·7 Hz, 2H, H 1′; 6·94–7·04, m, 2H, H 3,5; 7·49–7·58, m, 2H, H 4,6; 9·81, t, J 1·5 Hz, 1H, CHO. ^{13}C n.m.r. δ (50 MHz) 18·43 (C 3′); 28·01 (C 2′); 43·14 (C 4′); 68·31 (C 1′); 101·60 (C 1); 111·96 (C 3); 116·26 (CN); 120·57 (C 5); 133·46, 134·21 (C 4,6); 160·31 (C 2); 202·01 (CHO). Mass spectrum: m/z 203 (M, >1%), 175 (7), 146 (8), 132 (7), 119 (82), 102 (13), 91 (59), 85 (100), 67 (18), 55 (40).

2-(3′-Formylbutyloxy)benzonitrile had ν_{max} 2968m, 2937m, 2227s, 1725s, 1599s, 1580m, 1493s, 1473m, 1452s, 1397w, 1291s, 1261s, 1166m, 1111m, 1044m, 758s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·23, d, J 7·3 Hz, 3H, H 4′; 1·93, dq, J 14·5, 6·2 Hz, 1H, and 2·33, dq, J 14·5, 6·2 Hz, 1H, H 2′; 2·76, tqd, J 7·2, 7·2, 1·3 Hz, 1H, H 3′; 4·16, t, J 6·1 Hz, 2H, H 1′; 6·95–7·07, m, 2H, H 3,5; 7·31–7·59, m, 2H, H 4,6; 9·75, d, J 1·3 Hz, 1H, CHO. ^{13}C n.m.r. δ (50 MHz) 13·36 (C 4′); 29·41 (C 2′); 43·07 (C 3′); 66·11 (C 1′); 101·81 (C 1); 112·05 (C 3); 116·16 (CN); 120·84 (C 5); 133·57, 134·27 (C 4,6); 160·13 (C 2); 203·88 (CHO). Mass spectrum: m/z 203 (M, >1%), 174 (3), 146 (6), 119 (60), 101 (100), 91 (41), 83 (11), 73 (16), 64 (14), 55 (51).

Reaction of 2-(Hex-5′-enyloxy)benzonitrile (1f)

Reaction of the benzonitrile (1f) (0·40 g, 20·40 mmol) with H_2/CO at 60° gave a crude product whose ^{1}H and ^{13}C n.m.r. spectra indicated the presence of the two isomeric aldehydes, *2-(6′-formylhexyloxy)benzonitrile* (A) and *2-(5′-formylhexyloxy)benzonitrile* (B) in the approximate ratio of 70 : 30 respectively. The aldehydes were separated from spent catalyst by preparative radial chromatography (silica, 100% ether) and distilled for analysis to give a clear and colourless liquid (0·25 g, 55%), b.p. (oven) 100°/0·3 mm (Found: C, 72·4; H, 7·6; N, 5·9. $C_{14}H_{17}NO_2$ requires C, 72·7; H, 7·4; N, 6·1%). ν_{max} 2950s, 2880s, 2226s, 1724s, 1598s, 1579m, 1492s, 1472, 1449m, 1290s, 1261s, 1166m, 1111m, 756s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1·13, d, J 7·1 Hz, 3H, H 6′ of (B); 1·37–1·92, m, 8H, H 2′,3′,4′,5′ of (A) and 6H, H 2′,3′,4′ of (B); 2·43, tqd apparent as a sextet of doublets, J 7·1, 1·8 Hz, 1H, H 5′ of (B); 2·47, td, J 7·2, 1·7 Hz, 2H, H 6′ of (A); 4·07, t, J 6·3 Hz, 2H, H 1′ of (A); 4·08, t, J 6·2 Hz, 2H, H 1′ of (B); 6·94–7·04, m, 4H, H 3,5 of (A),(B); 7·48–7·56, m, 4H, H 4,6 of (A),(B); 9·65, d, J 1·8 Hz, 1H, CHO of (B); 9·78, t, J 1·7 Hz, 1H, CHO of (A). ^{13}C n.m.r. δ (50 MHz) 13·31 (C 6′ of (B)); 21·86, 25·70, 28·63, 28·73 (C 2′,3′,4′,5′ of (A)); 23·43, 28·87, 29·99 (C 2′,3′,4′ of (B)); 43·74 (C 6′ of (A)); 46·19 (C 5′ of (B)); 68·61 (C 1′ of (B)); 68·80 (C 1′ of (A)); 101·95 (C 1 of (A),(B)); 112·19 (C 3 of (A),(B)); 116·52 (CN of (A),(B)); 120·61 (C 5 of (A)); 120·70 (C 5 of (B)); 133·73, 134·32 (C 4,6 of (A),(B)); 160·73 (C 2 of (A),(B)); 202·73 (CHO of (A)); 205·03 (CHO of (B)).

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