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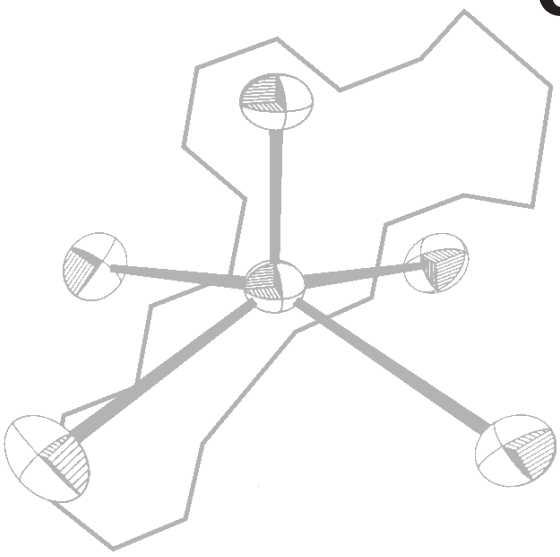

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Synthesis of Medium and Large Cyclic Amines in Rhodium-Catalysed Reactions of Aminoalkenes with H_2/CO[1]

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Rhodium-catalysed reactions of *N*-benzyl- or *N*-alkyl-aminoalkenes (6) with H_2/CO can give cyclic amines (7) (7–13 ring size) in good to excellent yields when BIPHEPHOS is used as a ligand. Hydrogenation of the aminoalkene becomes a competing reaction for the smaller rings but can be overcome by using a H_2/CO gas ratio of 1 : 5. Reactions of 2-alkenyloxybenzylamines (13) gave 9-, 12- and 17-membered rings (14) in 30–40% yield, but dimer formation (16) and/or hydrogenation were competing reactions. Similar reactions of alkenylamides and *ortho*-alkenylanilines gave only non-cyclized amino aldehydes as products in low isolated yields.

Keywords: Cyclic amines; rhodium catalysts; Biphepos.

Introduction

It has been shown[2–5] that metal-catalysed carbonylation reactions of unsaturated amines with H_2/CO can give 5- and 6-membered lactams in good yields. Carbonylation reactions were found to be favoured over hydroformylation reactions by using gas mixtures with a high CO content (typically H_2/CO, 1 : 9) and bulky phosphine ligands, e.g. tris(*o*-tolyl) phosphine.[6] Products arising from hydroformylation rather than carbonylation have been obtained, usually where the imine, iminium salt or enamine, arising from cyclization of the first formed amino aldehyde is either reduced to a cyclic amine[4,5,7,8] or trapped by intramolecular reaction with a pendant hydroxy group,[9] amine,[6,10,11] or amide.[10,12] In several of these publications initial coordination of the amine nitrogen to the rhodium metal has been suggested, and studies involving stoichiometric reactions of unsaturated amines with rhodium compounds have shown that such coordination is facile.[13,14] The catalytic systems referred to in most cases use very low ratios of rhodium to substrate, typically 1 : 200, and thus it appeared to us that only the newly created aldehyde would be in close proximity to the intramolecular coordinated nitrogen atom. Thus 'disguised high dilution' conditions[15] would be effectively established and the possibility of obtaining medium and large heterocycles from these reactions was investigated. Initial attempts involving rhodium-catalysed reactions of some alkenyloxybenzylamines with H_2/CO, in all cases, gave only polymeric material.[16] It thus appears that either polymerization is preferred to cyclization or that the initially formed cyclic imine, or iminium salt, is prone to polymerization under the reaction conditions. Support for the latter possibility comes from the reported successful syntheses of cyclic amines from amino aldehydes only when the initially formed cyclic species is reduced either with sodium borohydride[17] or by hydrogen over a palladium catalyst.[18]

It was thus decided to study the rhodium-catalysed reactions of unsaturated amines with H_2/CO and either first isolate but then immediately reduce the initially formed cyclic species or establish reaction conditions which would lead to their '*in situ*' reduction. In this paper we describe such reactions which have been shown to be successful for the synthesis of a range of cyclic amines.

Results and Discussion

Reactions of 10-Undecenamine

10-Undecenamine (1) was reacted with H_2/CO (1 : 1 or 1 : 9), $[Rh(OAc)_2]_2$ and PPh_3 as ligand (Scheme 1). No evidence for carbonylation products was obtained but the initial product showed peaks consistent with an imine N=CH group in both the ^1H and ^{13}C n.m.r. spectra. These peaks disappeared on standing, leading to only polymeric material. Immediate reduction of the product, presumably containing the cyclic imines (2) and (3) with sodium borohydride, followed by acetylation, led to isolation of a mixture of the N-acetyl-1-azacyclotridecane (4; R = Ac) and the N-acetyl-3-methyl-1-azacyclododecane (5; R = Ac) in modest yield (38%). The regioisomers (4) and (5) were in a ratio c. 2 : 1, reflecting an expected linear-to-branched initial hydroformylation ratio which had not been perturbed by amine coordination. The possibility that the imines (2) and (3) were arising via an initial carbonylation followed by reduction and elimination of water was excluded, as the 13-membered cyclic lactam (laurolactam) was shown to be inert under the reaction conditions.

Attempts to achieve '*in situ*' reduction by increasing the hydrogen partial pressure (H_2/CO, 9 : 1, 1200 psi) gave

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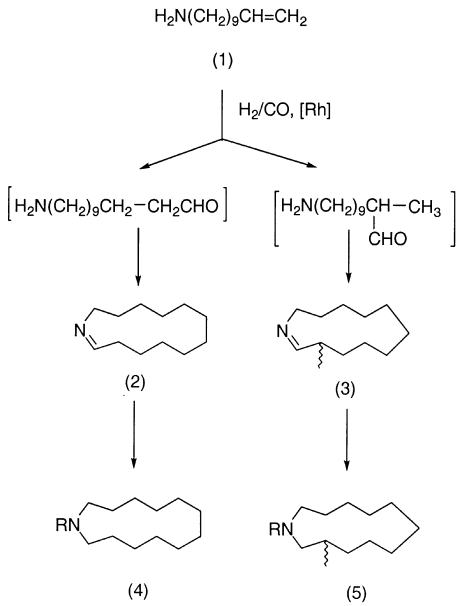
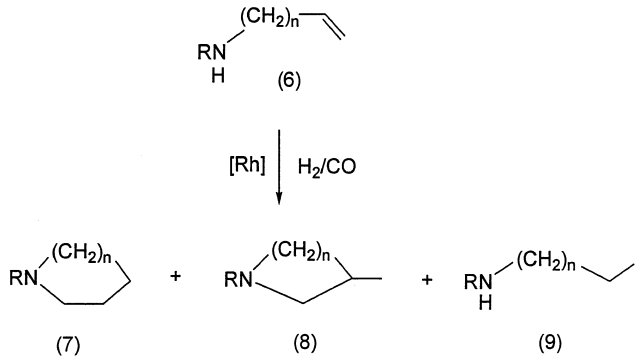


Scheme 1



Scheme 2

polymeric material together with some evidence for the formation of cyclic imines, while adding sodium borohydride[5] or sodium cyanoborohydride to the reaction mixture gave only recovered starting material. Only polymeric material was obtained when the zwitterionic catalyst, Rh(1,5-COD)BPh_4, which can function as a catalyst for both hydroformylation[5,19] and imine reduction, was used.[20]

Reactions of N-Substituted 10-Undecenamines (6a)

A reaction of *N*-benzyl-10-undecenamine (6a; R = Bn) with PPh_3 as ligand and a 1 : 1 ratio of H_2/CO directly gave the cyclic amines (7 and 8; R = Bn) in a ratio *c.* 2 : 1 in *c.* 25% isolated yield, together with polymeric material (Scheme 2, Table 1, entry 1) and a similar result was obtained for the *o*-tolylmethyl compound (6a; R = (*o*-Tol)CH_2) (entry 4).

Table 1. Rhodium-catalysed reactions of *N*-substituted undecenamines (6a) with H_2/CO

Reactions of (6a) were carried out for 20 h at 80° with an initial gas pressure (H_2 + CO) of 2.76 MPa (400 psi) with $[Rh(OAc)_2]_2$ and ligand in molar ratio 200 : 1 : 4

Entry	Reactant (6a) R	Ratio H_2/CO	Ligand	Product ratio[A] (7a)	(8a)	Isolated yield (%)[B] of (7a)
1	Bn	1 : 1	PPh_3	70	30	25
2	Bn	1 : 1	BIPHEPHOS	100	–	47
3	Bn	9 : 1	BIPHEPHOS	100	–	85
4	(o-Tol)CH2	1 : 1	PPh_3	85	15	22
5	(o-Tol)CH2	1 : 5	BIPHEPHOS	100	–	28
6	Bu	1 : 1	PPh_3			22[C]
7	Bu	1 : 1	BIPHEPHOS	100	–	40
8	Bu	9 : 1	BIPHEPHOS	100	–	82

[A] Estimated from ^1H and ^{13}C n.m.r. spectra of the total product.
[B] Material purified by selective extraction and/or chromatography.
[C] Isolated from complex mixture of products.

Cyclization of the secondary amine with an intermediate aldehyde must give an iminium salt or enamine and recent work has shown that enamines hydrogenate more rapidly than imines.[21] Use of BIPHEPHOS as ligand led to the expected improvement in regioselectivity[6,22,23] and only *N*-benzylazacyclotridecine (7a; R = Bn) was isolated (entries 2 and 3). The BIPHEPHOS/Rh system proved to be a more efficient hydrogenation system for iminium salts or enamines than the PPh_3/Rh system. A reaction using H_2/CO in the ratio 1 : 1 (entry 2) gave the cyclic amine (7a; R = Bn) in 47% isolated yield, and this was further improved to 85% when H_2/CO was used in the ratio 9 : 1 (entry 3). Very similar results were obtained for reactions of the *N*-butyl compound (6a; R=Bu) (entries 6–8), with a high yield (82%) of the azacyclotridecine (7a; R = Bu) being obtained when BIPHEPHOS was used as ligand together with a H_2/CO ratio of 9 : 1.

A reaction of *N*-phenylundec-10-enamine (6a; R = Ph), containing a weakly nucleophilic nitrogen atom, gave no cyclic material, and a mixture of amino aldehydes was isolated in low yield (24%) after chromatography. Surprisingly, the ratio of linear to branched compounds was *c.* 1 : 3, both in the crude product and in the isolated material, in contrast to the normal preference for linear product.[24]

Reactions of N-Substituted Aminoalkenes (6b–d)

The reaction conditions which led to high yields of the 13-membered cyclic amine (7a), i.e. use of BIPHEPHOS and a ratio of 9 : 1 H_2/CO, were applied to reactions for the shorter chain aminoalkenes (6b) and (6d) (Scheme 2; Table 2). Only modest yields (20–25%) of the 10- and 7-membered cyclic amines (7b) and (7d) were isolated, together with the aminoalkanes (9b,d) derived from hydrogenation of the starting alkene (35–40%) (Table 2, entries 10 and 12). The partial pressure of hydrogen in the H_2/CO was decreased to 1 : 1 and 1 : 5, in attempts to overcome the problem of alkene hydrogenation. No improvement was observed when a 1 : 1 gas ratio of H_2/CO was used for a reaction of (6b; R = Bn) (entry 9), but reaction of *N*-benzyl-5-hexenamine (6c; R = Bn) gave the 8-membered azocane (7c) in 43% yield (entry 11). A recent publication has recommended the use of even lower partial pressures of hydrogen to overcome this

Table 2. Rhodium-catalysed reactions of *N*-substituted aminoalkenes (6b–d) with H_2/CO and BIPHEPHOS as ligand
Reaction conditions and yields as for Table 1

Entry	Reactant	R	Ratio H_2/CO	Isolated yields (%) (7)	(9)
9	(6b)	Bn	1 : 1	25	35
10	(6b)	Bn	9 : 1	25	35
11	(6c)	Bn	1 : 1	43	–
12	(6d)	PhCH(Me)	9 : 1	20	40
13	(6d)	PhCH(Me)	1 : 5	60	–

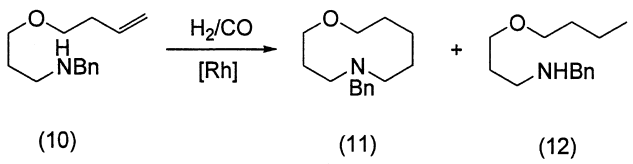
problem.[25] When a gas ratio of 1 : 5 H_2/CO was used for a reaction of (6d), the cyclic amine (7d) was obtained in 60% yield with no evidence for substrate hydrogenation (entry 13). A reaction of the substituted undecenamine (6a; R = (*o*-Tol)CH_2) under these conditions gave only a modest yield of the cyclic amine (7a; R = (*o*-Tol)CH_2) (Table 1, entry 5), lower than that obtained with the benzyl analogue (6a; R = Bn) by using a 1 : 1 gas ratio (Table 1, entry 2). Polymeric material was the only other product. It thus seems that the problem of olefin hydrogenation versus hydroformylation becomes more acute as the chain length of the aminoalkene decreases. Such an observation makes it even more difficult to predict the optimum pressure ratio of H_2 and CO to achieve high yields of cyclic amines with a minimum of polymerization and double bond hydrogenation.

Reactions of Some Amidoalkenes

Hydroformylation of some pent-4- and but-3-enamides has been shown to give 5- and 6-membered heterocycles in the presence of rhodium catalysts with or without added ligands at temperatures of 80–100° and with H_2/CO gas pressures of *c.* 8.2 MPa (1200 psi).[8b] The reactions of some undec-10-enamides were attempted under similar conditions to see if medium ring compounds would be formed. Reactions of undec-10-enamide with H_2/CO, 1 : 1, and PPh_3 as ligand, at 80° gave polymeric material. Reactions of the *N*-benzyl, *N*-butyl and *N*-aryl derivatives either with PPh_3 as ligand at 80° or by using $Rh_4(CO)_{12}$ with no added ligand at 100° with decreased pressures, 5.52 MPa (800 psi), of a mixture of H_2/CO, 1 : 3, gave no evidence for cyclic products. Starting amidoalkene was recovered from reactions of the *N*-phenyl compound, and in the other cases, linear and branched aldehydes resulting from hydroformylation were formed.

Reactions of Some Alkenyloxyamines

The possibility of introducing a second heteroatom into the heterocycles was briefly investigated. Reaction of *N*-benzyl-3-(but-3-enyloxy)propenamine (10) with BIPHEPHOS and a 9 : 1 H_2/CO gas ratio gave mainly the hydrogenated material (12) (46% isolated) together with a complex mixture of products (Scheme 3). Reduction of the hydrogen partial pressure to 1 : 1 H_2/CO, and use of PPh_3 as a ligand, gave the cyclic amine (11) in low yield (14%). The yield of amine thus paralleled that from the aminoalkene (6b; R = Bn) of the same chain length (Table 2, entries 9 and 10).



(10) (11) (12)

Scheme 3

Related studies were also carried out with a range of related 2-alkenyloxybenzylamines (13). Reactions of the primary amine (13a; Bn = H) under the usual conditions with 1 : 1 or 1 : 9 H_2/CO, or with $Rh_4(CO)_{12}$, were similar to those of undec-10-enamine (1), in that only polymeric material was obtained unless reaction products were immediately reduced as described above (Scheme 4). The cyclic amines were isolated as their *N*-acetyl derivatives (14a; Bn = Ac) and (15a; Bn = Ac) in 36% yield and *c.* equimolar ratio.

Reactions of the *N*-benzyl derivative (13a) gave a low isolated yield of cyclic product (14a) when PPh_3 was used as ligand (Table 3; entry 14) and this increased to 34% when BIPHEPHOS was used as ligand but, surprisingly, together with a significant yield of the dimer (16a) (entry 15). An increase in the hydrogen partial pressure gave a comparable yield of monomer (14a) but also increased the yield of the dimer (16a) (to 44%) together with some hydrogenated starting material (17a) (16%) (entry 16). A reaction using a gas mixture with a high CO partial pressure (1 : 5 H_2/CO) gave a similar ratio of products to the reaction with a H_2/CO ratio of 1 : 1, but in reduced yield (entry 17).

Reactions of the hexenyloxy homologue (13b) with either 1 : 1 or 9 : 1 H_2/CO gas ratios gave complex mixtures of products from which only small amounts (*c.* 20%) of the hydrogenated starting material (17b) could be isolated (Scheme 4; Table 3, entries 18 and 19). Use of the CO-rich gas mixture led to the isolation of the cyclic amines (14b) and (15b) in 30 and 10% yields, respectively. No hydrogenation product or dimer was detected (entry 20).

A reaction of the allyloxybenzylamine (13c) with 1 : 1 H_2/CO and BIPHEPHOS gave the cyclic benzoxazonine (14c) in 33% yield, together with the dimer (16c) (19%) and some deallylated starting materials (18%) (Scheme 4; Table 3, entry 21). A similar reaction but using PPh_3 was more complex, giving rise only to the phenol arising from deallylation (25%) and a benzoxazine (19%) arising from a previously noted rearrangement.[16]

The unpredictable formation of dimeric compounds in some cases mirrors other recent syntheses of medium and large heterocycles involving heterogeneous metal-catalysed hydrogenation cyclization of some nitroaldehydes.[26]

Experimental

All operations involving ligands, catalysts and hydride reagents were carried out under an atmosphere of dry nitrogen with dry solvents that were distilled prior to use. Flash chromatography was performed on E. Merck 230–400 mesh silica gel or alumina (basic, activity 1). 1H n.m.r. spectra were measured at 200, 300 or 400 MHz, 13C at 50 or 100 MHz. Mass spectra including accurate mass measurements were

obtained by electrospray mass spectroscopy (ESI) with a cone voltage of 25 V and with methanol as the mobile phase. Analytical gas–liquid chromatography was carried out by using a 1.8 m × 0.5 mm stainless steel column of 10% S.E. 30 on acid-washed DMCS chromosorb W 80/100.

Generally, combustion analysis gave errors >±0.4% even though ^{1}H and ^{13}C n.m.r. spectra suggested analytically pure material.

Materials

Rhodium(III) trichloride trihydrate ($RhCl_3.nH_2O$, $n \approx 3$) was supplied by Johnson Matthey Pty Ltd and converted into tetrakis (acetato)dirhodium(II), $[Rh(OAc)_2]_2$,[27] $Rh_4(CO)_{12}$[28] and 1,5-cyclooctadienetetraphenylboratorhodium, Rh(1,5-COD)(BPh_4).[29] BIPHEPHOS was prepared according to a literature procedure.[22] Light petroleum refers to the fraction of petroleum, b.p. 60–80°.

Alkenylamides were prepared by reactions of undec-10-enoyl chloride with the appropriate amine.

Undec-10-enamide was prepared as a cream solid (4.27 g, 86%), m.p. 84.5–86° (lit.[30] 88.5–89°). ^{13}C n.m.r. δ (50 MHz) 25.48, 28.82, 29.00, 29.15, 29.23 (C 3,4,5,6,7,8); 33.72 (C 9); 35.92 (C 2); 114.08 (C 11); 139.11 (C 10); 176.09 (CO).

N-Benzylundec-10-enamide was prepared as a cream solid (1.32 g, 36%), m.p. 57.5–59° (lit.[31] 60–61°). ^{13}C n.m.r. δ (50 MHz) 25.78, 28.90, 29.07, 29.30 (C 3,4,5,6,7,8); 33.80 (C 9); 36.78 (C 2); 43.63 (Ph**C**H_2N); 114.17 (C 11); 127.54 (C 4′); 127.85 (C 3′,5′); 128.73 (C 2′,6′); 138.36 (C 1′); 139.20 (C 10); 173.10 (C 1).

N-Butylundec-10-enamide was prepared as a low-melting solid (5.23 g, 81%), m.p. 35° (lit.[32] b.p. 195°/1.5 mm) (Found: *m/z* 240.2316. $(C_{15}H_{29}NO+H)^+$ requires *m/z* 240.2327). ^{13}C n.m.r. δ (50 MHz) 13.71 (C 4′); 20.03 (C 3′); 25.81, 26.47, 28.83, 29.01, 29.27 (C 3,4,5,6,7,8); 31.70 (C 2′); 33.73 (C 9); 36.82 (C 2); 39.12 (C 1′); 114.08 (C 11); 139.10 (C 10); 173.10 (C 1).

N-Phenylundec-10-enamide was prepared as a cream solid (1.77 g, 50%), m.p. 56–58° (lit.[31] 54–55°). ^{13}C n.m.r. δ (50 MHz) 25.80, 28.84, 29.03, 29.29 (C 3,4,5,6,7,8); 33.74 (C 9); 37.46 (C 2); 114.14 (C 11); 120.20 (C 3′,5′); 124.39 (C 4′); 128.87 (C 2′,6′); 137.76 (C 1′); 139.11 (C 10); 172.40 (C 1).

N-(3,5-Dimethoxyphenyl)undec-10-enamide was prepared as a brown solid (1.48 g, 43%) (Found: *m/z* 320.2224. $(C_{19}H_{29}NO_3+H)^+$ requires *m/z* 320.2226). ν_{max} (neat) 1660s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1.29, br s, 10H, H 4,5,6,7,8; 1.69, m, 2H, H 3; 1.98–2.07, m, 2H, H 9; 2.33, t, 2H, *J* 7.5 Hz, H 2; 3.75, s, 6H, OCH_3; 4.89–5.04, m, 2H, H 10; 5.80, ddt, 1H, *J* 16.8, 10.1, 6.6 Hz, H 11; 6.21, t, 1H, *J* 2.1 Hz, H 4′; 6.79, d, 2H, *J* 1.9 Hz, H 2′,6′; 7.56, br s, 1H, NH. ^{13}C n.m.r. δ (50 MHz) 25.52, 28.85, 29.04, 29.22, 29.29 (C 3,4,5,6,7,8); 33.74 (C 9); 37.81 (C 2); 55.30 (OCH_3); 96.51 (C 4′); 97.91 (C 2′6′); 114.12 (C 11); 139.13 (C 10); 139.82 (C 1′); 160.96 (C 3′,5′); 171.74 (C 1). Mass spectrum (ESI$^+$): *m/z* 320.3 $(M+H)^+$.

Table 3. Rhodium-catalysed reactions of *N*-benzyloxybenzylamines (13) with H_2/CO

Reaction conditions and yields as for Table 1

Entry	Reactant	Ratio H_2/CO	Ligand	Product yields (%) (14)	(15)	(16)	(17)
14	(13a)	1 : 1	PPh_3	10	–	–	–
15	(13a)	1 : 1	BIPHEPHOS	34	–	20	–
16	(13a)	9 : 1	BIPHEPHOS	38	–	44	16
17	(13a)	1 : 5	BIPHEPHOS	20	–	10	–
18	(13b)	1 : 1	BIPHEPHOS	–	–	–	20
19	(13b)	9 : 1	BIPHEPHOS	–		–	20
20	(13b)	1 : 5	BIPHEPHOS	30	10	–	–
21	(13c)	1 : 1	BIPHEPHOS	33	–	19	–[A]

A 2-Benzylaminomethylphenol (18%) was also isolated.

Primary Alkenylamines

Primary amines were prepared by reduction of the appropriate azide,[33] amide[34] or nitrile.[34]

Undec-10-enamine (1) was prepared as a clear oil (72–88%), b.p. (oven) 85°/0.1 mm (lit.[30,35] b.p. 80–82°/0.06 mm). ^{13}C n.m.r. δ (50 MHz) 26.78, 28.81, 29.01, 29.34, 29.38, 29.47 (C 3,4,5,6,7,8); 33.70, 33.77 (C 2,9); 42.16 (C 1); 113.98 (C 11); 139.04 (C 10).

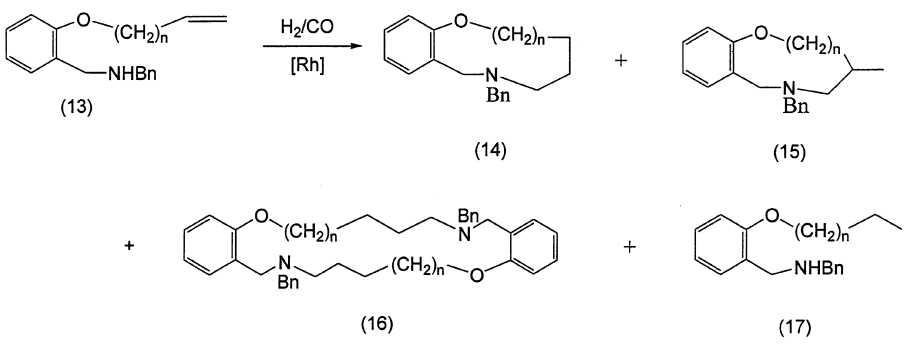
3-(But-3-enyloxy)propanamine. Reaction of 3-(but-3-enyloxy) propanenitrile[36] (5.00 g, 40.0 mmol) with $LiAlH_4$ (2.28 g, 60.0 mmol) in ether (50 ml) at reflux for 2 h gave the corresponding amine[37] as a clear oil (4.07 g, 79%) (Found: *m/z* 128.1067. $C_{17}H_{15}NO$ requires *m/z* 128.1075). ^{13}C n.m.r. δ (50 MHz) 32.75 (C 2); 33.61 (C 2′); 39.07 (C 1); 68.41 (C 3); 69.57 (C 1′); 115.64 (C 4′); 134.70 (C 3′).

Synthesis of Compounds (13a) and (13b)

The 2-substituted benzylamines were prepared from the corresponding 2-substituted benzonitriles as described below.

2-(Undec-10-enyloxy)benzonitrile

Reaction of 2-hydroxybenzonitrile (1.11 g, 9.3 mmol), undec-10-enyl mesylate (2.30 g, 9.3 mmol) and K_2CO_3 (1.92 g, 13.9 mmol) in dry acetone (50 ml) at reflux for 16 h gave *2-(undec-10-enyloxy)benzonitrile* after chromatography (silica, 20% EtOAc/light petroleum) as a clear oil (1.91 g, 73%) (Found: *m/z* 271.194. $(C_{18}H_{25}NO+H)^+$ requires *m/z* 271.194). ν_{max} (neat) 2228s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1.19–1.52, m, 12H, H 3,4,5,6,7,8; 1.77–1.91, m, 2H, H 2′; 1.99-2.08, m, 2H, H 9′; 4.05, t, 2H, *J* 6.5 Hz, H 1′; 4.89-5.05, m, 2H, H 11′; 5.81, ddt, 1H, *J* 16.9, 10.1, 6.6 Hz, H 10′; 6.92–7.00, m,



(a), n = 9; (b), n = 4; (c), n = 1

Scheme 4

2H, H 4,5; 7.46–7.56, m, 2H, H 3,6. ^{13}C n.m.r. δ (50 MHz) 25.78, 28.82, 29.02, 29.20, 29.32, 29.38 (C 2′,3′,4′,5′,6′,7′,8′); 33.72 (C 9′); 68.93 (C 1′); 101.92 (C 2); 112.11 (C 4); 114.03 (C 11′); 116.42 (CN); 120.41 (C 5); 133.64, 134.17 (C 3,6); 136.09 (C 10′); 160.74 (C 1). Mass spectrum (ESI$^+$): *m/z* 272.1 $(M+H)^+$.

2-(Undec-10-enyloxy)benzylamine (13a; Bn = H)

Reaction of the above nitrile (1.46 g, 5.4 mmol) with $LiAlH_4$ (0.25 g, 6.5 mmol) in ether (20 ml) at reflux for 2 h gave the *amine* (13a; Bn=H) as a clear oil (1.41 g, 95%) (Found: C, 78.7; H, 10.8; N, 5.0. $C_{18}H_{29}NO$ requires C, 78.5; H, 10.6; N, 5.1%). ^{1}H n.m.r. δ (200 MHz) 1.31–1.50, m, 12H, H 3′,4′,5′,6′,7′,8′; 1.71–1.86, m, 2H, H 2′; 1.98–2.08, m, 2H, H 9′; 2.15, br s, 2H, NH_2; 3.80, s, 2H, ArC**H**$_2$N; 3.97, t, 2H, *J* 6.3 Hz, H 1′; 4.89–5.04, m, 2H, H 11′; 5.80, ddt, 1H, *J* 16.9, 10.1, 6.7 Hz, H 10′; 6.81–6.92, m, 2H, and 7.17–7.26, m, 2H, ArH. ^{13}C n.m.r. δ (50 MHz) 26.11, 28.81, 29.02, 29.24, 29.34, 29.43 (C 2′,3′,4′,5′,6′,7′.8′); 33.71 (C 9′); 42.64 (Ar**C**H$_2$N); 67.61 (C 1′); 110.88 (C 4); 114.05 (C 11′); 120.21 (C 5); 127.98 (C 3,6); 131.41 (C 1); 139.05 (C 10′); 156.82 (C 2). Mass spectrum (ESI$^+$): *m/z* 276.2 $(M+H)^+$.

2-(Hex-5-enyloxy)benzonitrile

Reaction of 2-hydroxybenzonitrile (1.67 g, 14.0 mmol) and hex-5-enyl mesylate (2.50 g, 14.0 mmol) as described above gave *2-(hex-5-enyloxy)benzonitrile* as a clear oil (2.03 g, 72%) (Found: *m/z* 224.2037. $(C_{13}H_{15}NO+Na)^+$ requires *m/z* 224.1051). ν_{max} (neat) 2228s cm^{-1}. ^{1}H n.m.r. δ (200 MHz) 1.53–1.69, m, 2H, H 3′; 1.79–1.93, m, 2H, H 2′; 2.08–2.19, m, 2H, H 4′; 4.03, t, 2H, *J* 6.5Hz, H 1'; 4.94–5.09, m, 2H, H 6′; 5.82, ddt, 1H, *J* 16.8, 10.1, 6.6 Hz, H 5′; 6.93–7.02, m, 2H and 7.47–7.55, m, 2H, ArH. ^{13}C n.m.r. δ (50 MHz) 24.96 (C 3′); 28.15 (C 2′); 33.16 (C 4′); 68.67 (C 1′); 101.78 (C 1); 112.08 (C 3); 114.77 (C 6′); 116.16 (CN); 120.45 (C 5); 133.58, 134.21 (C 4,6); 138.17 (C 5′); 160.63 (C 2). Mass spectrum (ESI$^+$): *m/z* 201.6 $(M+H)^+$.

2-(Hex-5-enyloxy)benzylamine (13b; Bn = H)

Reaction of the above nitrile (1.95 g, 9.7 mmol) with $LiAlH_4$ (0.74 g, 19.4 mmol) as described above gave the *benzylamine* (13b; Bn = H) as a clear oil (1.61 g, 81%) (Found: *m/z* 206.1545. $(C_{13}H_{19}NO+H)^+$ requires *m/z* 206.1545). ^{1}H n.m.r. δ (200 MHz) 1.50–1.66, m, 2H, H 3′; 1.68, s, 2H, NH_2; 1.73-1.90, m, 2H, H 2′; 2.06–2.19, m, 2H, H 4′; 3.81, s, 2H, ArC**H**$_2$N; 3.98, t, 2H, *J* 6.2 Hz, H 1′; 4.94–5.09, m, 2H, H 6′; 5.82, ddt, 1H, *J* 16.9, 10.1, 6.6 Hz, H 5′; 6.81–6.93, m, 2H and 7.15–7.26, m, 2H, ArH. ^{13}C n.m.r. δ (50 MHz) 25.35 (C 3′); 28.65 (C 2′); 33.28 (C 4′); 42.69 (Ar**C**H$_2$N); 67.37 (C 1′); 110.84 (C 3); 114.71 (C 6′); 120.24 (C 5); 127.87, 128.30 (C 4,6); 131.80 (C 1); 138.30 (C 5′); 156.73 (C 2). Mass spectrum (ESI$^+$): *m/z* 206 $(M+H)^+$.

Secondary Alkenylamines

Secondary amines were generally prepared by reductive amination of the appropriate aromatic aldehyde and an alkenylamine,[38] by reductive amination of the appropriate alkenyl aldehyde and benzylamine, by $LiAlH_4$ reduction of the appropriate amide[34] or by alkylation of benzylamine with the appropriate alkenyl bromide or mesylate.

N-Benzylundec-10-enamine (6a; R = Bn)

Reaction of benzaldehyde (0.63 g, 5.9 mmol) with undec-10-enamine (1) (1.00 g, 5.9 mmol) in dry methanol (20 ml), followed by reduction with $NaBH_4$ (0.34 g, 8.9 mmol), gave the amine (6a; R = Bn)[31] as a clear, colourless oil (1.42 g, 93%). ^{13}C n.m.r. δ (50 MHz) 27.26, 28.83, 29.03, 29.35, 29.45, 30.02, 33.71 (C 2,3,4,5,6,7,8,9); 49.42 (C 1); 54.01 (Ph**C**H$_2$N); 114.02 (C 11); 126.70 (C 4′); 127.97, 128.22 (C 2′,6′,3′,5′); 139.03 (C 10); 140.47 (C 1′).

The amine was also prepared in 80% yield by the reaction of benzylamine (0.64 g, 5.9 mmol) and undec-10-enal (1.00 g, 5.9 mmol), followed by $NaBH_4$ reduction.

N-(2-Methylbenzyl)undec-10-enamine (6a; R = (o-Tol)CH$_2$)

Reaction of 2-methylbenzaldehyde (0.71 g, 5.9 mmol) with undec-10-enamine (1.00 g, 5.9 mmol), followed by $NaBH_4$ reduction, gave the *amine* (6a; R = (*o*-Tol)CH_2) as a clear oil (1.44 g, 89%) (Found: *m/z* 274.2536. $(C_{19}H_{31}N+H)^+$ requires *m/z* 274.2535). ^{1}H n.m.r. δ (200 MHz) 1.20–1.42, m, 12H, H 3,4,5,6; 1.45–1.54, m, 2H, H 2; 1.98–2.08, m, 2H, H 9; 2.33, s, 3H, CH_3; 2.65, t, 2H, *J* 7.0 Hz, H 1; 3.74, s, 2H, PhC**H**$_2$N; 4.88–5.04, m, 2H, H 11; 5.80, ddt, 1H, *J* 16.8, 10.1, 6.6 Hz, H 10; 7.13–7.18, m, 3H and 7.25–7.30, m, 1H, ArH. ^{13}C n.m.r. δ (50 MHz) 18.87 (CH_3); 27.32, 28.87, 29.07, 29.39, 29.51, 30.07 (C 2,3,4,5,6,7,8); 33.76 (C 9); 49.82 (C 1); 51.58 (Ph**C**H$_2$N); 114.06 (C 11); 125.80, 126.77 (C 4′,5′); 128.19, 130.13 (C 3′,6′); 136.07 (C 2′); 138.40 (C 1′); 140.00 (C 10). Mass spectrum (ESI$^+$): *m/z* 274.3 $(M+H)^+$.

N-Benzyloct-7-enamine (6b; R = Bn)

Reaction of benzylamine (2.74 g, 25.5 mmol) with 8-bromooctene (2.44 g, 12.8 mmol) and K_2CO_3 (3.53 g, 25.6 mmol) in dry acetone (50 ml) at reflux for 18 h gave a mixture of the mono- and di-alkylated products. Purification by flash chromatography (silica, 20% EtOAc/light petroleum) gave the *amine* (6b; R = Bn) as a beige oil (0.60 g, 22%) (Found: *m/z* 218.1903. $(C_{15}H_{23}N+H)^+$ requires *m/z* 218.1909). ^{1}H n.m.r. δ (200 MHz) 1.24–1.56, m, 8H, H 2,3,4,5; 1.98–2.08, m, 2H, H 6; 2.61, t, 2H, *J* 7.0 Hz, H 1; 3.77, s, 2H, PhC**H**$_2$N; 4.88–5.04, m, 2H, H 8; 5.80, ddt, 1H, *J* 16.9, 10.1, 6.6 Hz, H 7; 7.18–7.32, m, 5H, PhH. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 27.15, 28.80, 28.98, 30.01 (C 2,3,4,5); 33.68 (C 6); 49.43 (Ph**C**H$_2$N); 54.05 (C 1); 114.15 (C 8); 126.78 (C 4′); 128.04, 128.29 (C 2′,3′,5′,6′); 139.00 (C 7); 140.51 (C 1′). Mass spectrum (ESI$^+$): *m/z* 218 $(M+H)^+$.

A similar reaction in CH_3CN gave the title amine in 72% yield.

N-Benzylhex-5-enamine (6c; R = Bn)

Reaction of benzylamine (0.44 g, 4.1 mmol) with hex-5-enyl mesylate (0.50 g, 3.4 mmol) at 60° for 18 h gave the amine (6c; R = Bn)[39] after chromatography (silica, 30% EtOAc/light petroleum) as a clear, colourless oil (0.35 g, 54%). ^{13}C n.m.r. δ (50 MHz) 26.56, 29.51 (C 2,3); 33.58 (C 4); 49.22 (Ph**C**H$_2$N); 54.01 (C 1); 114.39 (C 6); 126.77 (C 4′); 128.01, 128.29 (C 2′,3′,5′,6′); 138.69 (C 5); 140.47 (C 1′).

N-Butylundec-10-enamine (6a; R = Bu)

Reaction of *N*-butylundec-10-enamide (2.0 g, 8.4 mmol) with $LiAlH_4$ (0.48 g, 12.6 mmol) in ether at reflux for 2 h gave the amine as a pale yellow oil (1.67 g, 89%), b.p. (oven) 85°/0.7 mm (lit.[32] 107–109°/0.8 mm) (Found: *m/z* 224.2358. $C_{15}H_{31}N^-$ requires *m/z* 224.2378). ^{13}C n.m.r. δ (50 MHz) 14.02 (C 4′); 20.52 (C 3′); 27.40, 28.90, 29.10, 29.28, 29.42, 29.53, 30.21 (C 2,3,4,5,6,7,8); 32.35 (C 2′); 33.78 (C 9); 49.84, 50.18 (C 1,1′); 114.06 (C 11); 139.18 (C 10).

N-Phenylundec-10-enamine (6a; R = Ph)

Reduction of the corresponding amide (0.65 g, 2.5 mmol) with $LiAlH_4$ (0.19 g, 5.0 mmol) gave the amine[31] as a pale yellow oil (0.53 g, 86%). ^{13}C n.m.r. δ (50 MHz) 27.09, 28.84, 29.04, 29.36, 29.46 (C 2,3,4,5,6,7,8); 33.73 (C 9); 43.85 (C 1); 112.54 (C 2′,6′); 114.07 (C 11); 116.90 (C 4′); 129.06 (C 3′,5′); 139.01 (C 10); 148.41 (C 1′).

N-Benzyl-3-(but-3-enyloxy)propanamine (10)

Reaction of benzaldehyde (1.65 g, 15.5 mmol) and 3-(but-3-enyloxy)propanamine (2.00 g, 15.5 mmol) in methanol (15 ml), followed by reduction with $NaBH_4$ (1.17 g, 31.0 mmol), gave the *amine* (10) as a clear oil (2.12 g, 62%) (Found: *m/z* 220.1696. $(C_{14}H_{21}NO+H)^+$ requires *m/z* 220.1701). ^{1}H n.m.r. δ (200 MHz) 1.80, p, 2H, *J* 6.5 Hz, H 2; 2.33, q, 2H, *J* 6.7 Hz, H 2′; 2.73, t, 2H, *J* 6.8 Hz, H 1; 3.47, t, 2H, *J* 6.7 Hz and 3.51, t, 2H, *J* 6.2 Hz, H 1′,3; 3.78, br s, 2H, PhC**H**$_2$N; 5.01–5.14, m, 2H, H 4′; 5.82, ddt, 1H, *J* 17.0, 10.2, 6.7 Hz, H 3′; 7.22–7.34, m, 5H, PhH. ^{13}C n.m.r. δ (50 MHz) 29.79 (C 2); 34.09 (C 2′); 46.81 (C 1); 53.90 (Ph**C**H$_2$N); 69.39 (C 3); 70.05 (C 1′); 116.18 (C 4′); 126.75 (C 4″); 128.00, 128.24 (C 2″,3″,5″,6″); 135.20 (C 3′); 140.27 (C 1″). Mass spectrum (ESI$^+$): *m/z* 219.8 $(M+H)^+$.

N-Benzyl-2-(undec-10-enyloxy)benzylamine (13a)

Reaction of benzaldehyde (0.39 g, 3.6 mmol) and 2-(undec-10-enyloxy)benzylamine (1.00 g, 3.6 mmol), followed by reduction with $NaBH_4$ (0.21 g, 5.5 mmol), gave the *amine* (13a) as a clear oil (1.13 g, 85%) (Found: C, 82.2; H, 9.8; N, 3.5. $C_{25}H_{35}NO$ requires C, 82.1; H, 9.7; N, 3.8%). ^{1}H n.m.r. δ (200 MHz) 1.28, br s, 12H, H 3′,4′,5′,6′,7′,8′; 1.69–1.83, m, 2H, H 2′; 1.99–2.09, m, 2H, H 9′; 2.27, br s, 1H, NH; 3.76, s, 2H, PhC**H**$_2$N; 3.81, s, 2H, ArC**H**$_2$N; 4.90–5.05, m, 2H, H 11′; 5.81, ddt, 1H, *J* 19.9, 10.1, 6.6 Hz, H 10′; 6.87, m, 2H, 7.17–7.27, m, 3H and 7.29–7.35, m, 4H, ArH. ^{13}C n.m.r. δ (50 MHz) 26.19, 28.89, 29.09, 29.32, 29.42, 29.50 (C 2′,3′,4′,5′,6′,7′,8′); 33.78 (C 9′); 49.06 (Ar**C**H$_2$N); 53.00 (Ph**C**H$_2$N); 67.74 (C 1′); 111.00 (C 3); 114.12 (C 11′); 120.13 (C 5); 126.71 (C 1); 126.76, 127.23, 128.16, 128.27, 128.34, 130.02 (C 4,6, PhCH); 139.14 (C 10′); 140.44 (C 1″); 157.22 (C 2). Mass spectrum (ESI$^+$): *m/z* 366.3 (M+H)$^+$.

N-Benzyl-2-(hex-5-enyloxy)benzylamine (13b)

Reaction of benzaldehyde (0.78 g, 7.3 mmol) and 2-(hex-5-enyloxy)benzylamine (1.50 g, 7.3 mmol), followed by $NaBH_4$ reduction as described above, gave the *benzylamin*e (13b) as a clear oil (1.78 g, 82%) (Found: *m/z* 296.1998. $(C_{20}H_{25}NO+H)^+$ requires *m/z* 296.2014). ^{1}H n.m.r. δ (200 MHz) 1.46–1.65, m, 2H, H 3′; 1.72–1.85, m, 2H, H 2′; 1.98, br s, 1H, NH; 2.05–2.15, m, 2H, H 4′; 3.76, s, 2H, and 3.82, s, 2H, ArC**H**$_2$N and PhC**H**$_2$N; 3.96, t, 2H, *J* 6.2 Hz, H 1′; 4.94–5.06, m, 2H, H 5′; 5.79, ddt, 1H, *J* 16.8, 10.2, 6.5 Hz, H 5′; 6.81–6.93, m, 2H and 7.16–7.33, m, 7H, ArH. ^{13}C n.m.r. δ (50 MHz) 25.41 (C 3′); 28.73 (C 2′); 33.35 (C 4′); 48.96 (Ar**C**H$_2$N); 53.03 (Ph**C**H$_2$N); 67.53 (C 1′); 110.99 (C 3); 114.76 (C 6′); 120.18 (C 5); 126.74, 128.03, 128.14, 128.26, (128.31(C 1)), 128.45, 129.96 (PhCH); 138.38 (C 5′); 140.50 (C 1″); 157.13 (C 2). Mass spectrum (ESI$^+$): *m/z* 296.2 (M+H)$^+$.

N-Benzyl-2-(prop-2-enyloxy)benzylamine (13c)

Reaction of 2-hydroxybenzaldehyde and 3-bromopropene gave 2-(prop-2-enyloxy)benzaldehyde[40] as a clear oil (48%). ^{13}C n.m.r. δ (50 MHz) 68.98 (C 1′), 112.72 (C 3); 117.86 (C 3′); 120.69 (C 4); 124.92 (C 1); 128.20 (C 5); 132.27 (C 2′); 135.72 (C 6); 160.79 (C 2); 189.50 (CHO).

Reaction of the aldehyde (1.00 g, 6.2 mmol) with benzylamine (0.66 g, 6.2 mmol), followed by $NaBH_4$ reduction, gave the *amine* (13c) as a clear oil (1.43 g, 92%) (Found: *m/z* 254.1543. $(C_{17}H_{19}NO+H)^+$ requires *m/z* 254.1545). ^{1}H n.m.r. δ (200 MHz) 3.77, s, 2H, PhC**H**$_2$N; 3.84, s, 2H, ArC**H**$_2$N; 4.53, dt, 2H, *J* 5.0, 1.5 Hz, H 1′; 5.22–5.43, m, 2H, H 3′; 6.03, ddt, 1H, *J* 17.3, 10.3, 5.1 Hz, H 2′; 6.84, d, 1H, *J* 8.2 Hz, H 3; 6.91, t, 1H, *J* 7.4 Hz, H 5; 7.16–7.36, m, 7H, ArH. ^{13}C n.m.r. δ (50 MHz) 48.78 (Ar**C**H$_2$N); 53.02 (Ph**C**H$_2$N); 68.58 (C 1′); 111.46 (C 3); 117.15 (C 3′); 120.55 (C 5); 126.77, 128.11, 128.17, 128.27, 128.51 (C 1), 130.03, 133.25 (ArCH); 140.43 (C 1″); 156.64 (C 2). Mass spectrum (ESI$^+$): *m/z* 254 (M+H)$^+$.

General Conditions for Reaction with H_2/CO

Reactions were carried out in a 100 ml Parr autoclave with a glass sleeve containing a stirrer bead. The substrate (0.1–0.3 g, *c.* 1 mmol), the rhodium catalyst precursor and the ligand (in the ratio 200 : 1 : 4) were placed in the autoclave under N_2 followed by deoxygenated solvent (10 ml).

The vessel was flushed and evacuated three times with 200 psi (1.38 MPa) of H_2/CO (1 : 1 molar mixture) and pressurized to 400 psi (2.76 MPa). Alternatively, it was flushed with H_2 and then pressurized to an initial pressure of 400, 800 or 1200 psi (2.76, 5.52 or 8.28 MPa) with the appropriate gas mixture. The reaction was kept at temperature for 20 h, the autoclave cooled, the gases released and the contents analysed as reported. In general, ratios of products including regioisomers were determined by relative peak areas of appropriate hydrogens in ^{1}H n.m.r. spectra and/or relative signal intensities of comparable carbons in ^{13}C n.m.r. spectra. Selective extraction of the total product with light petroleum gave in most cases n.m.r.-pure material in higher yields than chromatography on silica or alumina.

Unless otherwise stated, all reactions involved the use of $[Rh(OAc)_2]_2$ and were carried out in benzene at 80° for 20 h. Reactions involving the use of $[Rh(OAc)_2]_2$ and PPh_3 as the catalyst system at 80° with an initial pressure of 1 : 1 H_2/CO (400 psi, 2.76 MPa) are referred to as 'the usual conditions'.

Reactions leading to cyclized products were repeated at least once and gave product ratios with ±5% reproducibility.

1-Acetyl-3-methylazacyclododecane (5; R = Ac) and 1-Acetylazacyclotridecane (4; R = Ac)

Undec-10-enamine (1) (0.30 g, 1.8 mmol), $[Rh(OAc)_2]_2$ (3.9 mg, 8.9 μmol) and PPh_3 (9.3 mg, 35.5 μmol) were reacted under the usual conditions. Polymeric material lined the reaction vessel. Evaporation of the benzene solution gave a viscous oil (0.25 g) (^{1}H n.m.r. δ 5.76, t, *J* 7.2 Hz; ^{13}C n.m.r. δ 164.5, 167.7) which polymerized on standing.

An identical result was obtained when using a H_2/CO gas mixture of 1 : 9. The benzene-soluble products from a repeat reaction were immediately added dropwise to a cooled suspension of $LiAlH_4$ (76 mg, 2.0 mmol) in dry benzene (10ml) and heated at reflux for 2 h. The reaction was quenched at 5° with $Na_2SO_4.10H_2O$, filtered, and the filtrate was reacted with acetic anhydride (36 g, 3.6 mmol) at reflux for 1 h. Water (1 ml) was added and reflux continued for a further 1 h. Concentration under reduced pressure gave an approximate 2 : 1 mixture (^{1}H n.m.r.) of linear and branched products as a brown oil (0.55 g). Column chromatography (basic alumina, EtOAc) gave a mixture of 1-acetyl-3-methylazacyclododecane (5; R = Ac) and 1-acetyl-azacyclotridecane (4; R = Ac) (0.15 g, 38%). ν_{max} (neat) 1654 cm^{-1}. Mass spectrum (ESI$^+$): *m/z* 226.1 (M+H)$^+$. For (5; R = Ac). ^{1}H n.m.r. δ (200 MHz) 1.09, d, 3H, *J* 7.0 Hz, CH_3; 1.28, m, 14H, H 4,5,6,7,8,9,10; 1.40–1.73, m, 4H, H 3,11; 1.97, s, 3H, $COCH_3$; 2.32–2.48, m, 1H, H 2; 3.16–3.26, m, 2H, H 12. ^{13}C n.m.r. δ (50 MHz) 13.15 (CH_3); 21.86 (CO**C**H$_3$); 26.74, 28.94, 29.18, 29.27, 30.36, 30.30 (C 3,4,5,6,7,8,9,10,11); 39.48 (C 12); 46.13 (C 2); 170.18 (CO). For (4; R = Ac). ^{1}H n.m.r. δ (200 MHz) 1.38, m, 16H, H 3,4,5,6,7,8,9,10; 1.66, m, 4H, H 11,2; 2.11, s, 3H, CH_3; 3.29, t, 2H, *J* 7.5 Hz and 3.35, t, 2H, *J* 7.5 Hz, H 2 and H 13. ^{13}C n.m.r. δ (50 MHz) 21.28 (CO**C**H$_3$); 24.10, 24.67, 25.04, 25.12, 25.20, 25.54, 25.66, 26.72, 29.29 (C 4,5,6,7,8,9,10,11,12); 47.16, 49.96 (C 2,13); 170.97 (CO).

An authentic sample of (4; R = Ac) was prepared by reduction of laurolactam with $LiAlH_4$ followed by acetylation to give a light brown oil which on distillation (b.p. (oven) 95° /0.5 mm) gave a white solid, m.p. 40–42°.

1-Benzylazacyclotridecane (7a; R = Bn)

Reaction of *N*-benzylundec-10-enamine (6a; R = Bn) (0.2 g, 0.8 mmol), $[Rh(OAc)_2]_2$ (1.7 mg, 3.8 μmol) and BIPHEPHOS (12.1 mg, 15.4 μmol) with 9 : 1 H_2/CO (400 psi) gave a brown oil (0.23 g), which on extraction with light petroleum gave 1-benzylazacyclotridecane (7a; R = Bn)[41] as a semisolid (0.18g, 85%). ^{1}H n.m.r. δ (200 MHz) 1.28, m, 16H, H 3,4,5,6,7,8,9,10; 1.38–1.45, m, 4H, H 2,11; 2.37, t, 4H, *J* 6.3 Hz, H 1,12; 3.52, s, 2H, PhC**H**$_2$N; 7.21–7.27, m, 1H, H 4′; 7.29–7.35, m, 4H, H 2′,3′,5′,6′. ^{13}C n.m.r. δ (50 MHz) 26.95, 29.32, 29.50, 29.56 (C 2,3,4,5,6,7,8,9,10,11); 53.08 (C 1,12); 59.02 (Ph**C**H$_2$N); 126.59 (C 4′); 128.04 (C 3′,5′); 128.89 (C 2′,6′); 140.24(C 1′). Mass spectrum (ESI$^+$): *m/z* 274.2 (M+H)$^+$.

An authentic sample was prepared by reaction of azacyclotridecane with benzyl chloride, b.p. 120°/0.1 mm (Found: C, 83.43; H, 11.50; N, 5.18. $C_{19}H_{31}N$ requires C, 83.45; H, 11.43; N, 5.12%).

Reactions using BIPHEPHOS or PPh_3 but with 1 : 1 H_2/CO at 80° led to isolation of the cyclic amine (7a; R = Bn) (47% and 25%, respectively) together with polymeric material. The n.m.r. spectra of the total non-polymeric product showed only the cyclic amine (7a; R = Bn) in the former case but suggested a ratio of 70 : 30 ((7a) : (8a)) in the latter case based on the benzyl signals at *c.* 3.5 and the CH_3 signal at *c.* 0.8 ppm in the ^{1}H n.m.r. spectra and the benzyl carbons in the 57–59 ppm region in the 13C n.m.r. spectra.

1-(2′-Methylbenzyl)azacyclotridecane (7a; R = (o-Tol)CH_2)

Reaction of *N*-(2-methylbenzyl)undec-10-enamine (6a; R = (*o*-Tol)CH_2) (0.30 g, 1.1 mmol) under the usual conditions gave an 85 : 15 mixture (n.m.r.) of linear and branched products as a brown oil (0.31 g). Column chromatography (silica; 5% EtOAc/light petroleum) gave only *1-(2′*-methylbenzyl)azacyclotridecane (7a; R = (*o*-Tol)CH_2) as a white solid (0.07 g, 22%). A portion of the solid was dissolved in CH_2Cl_2. Slow evaporation of solvent gave crystals, m.p. 97–99° (Found: C 83.60, H 11.71, N 4.62. $C_{20}H_{33}N$ requires C 83.55, H 11.58, N 4.87%). ^{1}H n.m.r. δ (200 MHz) 1.27, m, 16H, H 3,4,5,6,7,8,9,10; 1.37–1.43, m, 4H, H 2,11; 2.35–2.37, m, 7H, H 1,12, PhC**H**$_3$; 3.48, s, 2H, PhC**H**$_2$N; 7.12–7.17, m, 3H and 7.33, m, 1H, ArH. ^{13}C n.m.r. δ (50 MHz) 19.27 (Ph**C**H$_3$); 26.82, 27.48, 29.55, 29.64 (C 2,3,4,5,6,7,8,9,10,11); 53.85 (C 1,12); 57.06 (Ph**C**H$_2$N); 125.36, 126.54 (C 4′,5′); 129.60, 130.00 (C 3′,6′); 137.04, 138.02 (C 1′,2′). Mass spectrum (ESI$^+$): *m/z* 288.3 $(M+H)^+$.

A reaction using BIPHEPHOS and a H_2/CO ratio of 1 : 5 (400 psi) at 80° gave only (7a; R = *o*-(Tol)CH_2), which was isolated in 28% yield.

1-Butylazacyclotridecane (7a; R = Bu)

Reaction of *N*-butylundec-10-enamine (6a; R = Bu) (0.15 g, 0.7 mmol), $[Rh(OAc)_2]_2$ (1.5 mg, 3.3 μmol) and BIPHEPHOS (10.4 mg, 13.3 μmol) with 9 : 1 H_2/CO (400 psi) gave a brown oil (0.15 g) whose light petroleum extract gave *1-butylazacyclotridecane* (7a; R = Bu) as a waxy solid (0.13 g, 82%) (Found: *m/z* 240.2681. $(C_{16}H_{33}N+H)^+$ requires *m/z* 240.2691). ^{1}H n.m.r. δ (200 MHz) 0.84, t, 3H, *J* 6.8 Hz, H 4′; 1.19–1.38, m, 26H, H 3,4,5,6,7,8,9,10,11,12,2′,3′; 2.31, t, 4H, *J* 6.6 Hz, H 2,13,1′. ^{13}C n.m.r. δ (50 MHz) 14.04 (C 4′); 20.72 (C 3′); 26.76, 27.60, 29.18, 29.29, 29.58 (C 3,4,5,6,7,8,9,10,11,12,2′); 54.04 (C 2,13,1′). Mass spectrum (ESI$^+$): *m/z* 240.1 $(M+H)^+$.

An authentic sample, prepared from reaction of azatricyclodecane and butyl bromide had identical spectra, b.p. 100°/0.1 mm (Found: C, 80.08; H, 13.61; N, 6.14. $C_{16}H_{33}N$ requires C, 80.26; H, 13.89; N, 5.85%).

Reaction with 1 : 1 H_2/CO by using BIPHEPHOS or PPh_3 as ligands gave (7a; R = Bu) in 40 and 22% yield, respectively. The total product of the latter reaction was very complex and showed some evidence for lactam formation (^{13}C n.m.r. δ 172.9).

2-Methyl-11-phenylaminoundecanal and 12-Phenylaminoundecanal

Reaction of *N*-phenylundec-10-enamine (0.30 g, 1.2 mmol), $[Rh(OAc)_2]_2$ (2.7 mg, 6.1 μmol) and PPh_3 (6.4 mg, 24.5 μmol) under the usual conditions gave the linear and branched aldehyde isomers in the ratio 25 : 75 as a brown oil (0.37 g). Column chromatography (silica, 10% EtOAc/light petroleum) gave *2-methyl-11-phenylaminoundecanal* (0.06 g, 18%) (Found: *m/z* 551.4586. $(2(C_{18}H_{29}NO)+H)^+$ requires *m/z* 551.4576). ν_{max} (neat) 1714s cm^{-1}. ^{1}H n.m.r. δ (400 MHz) 1.08, d, 3H, *J* 7.0 Hz, CH_3; 1.29–1.37, m, 14H, H 3,4,5,6,7,8,9; 1.60, m, 2H, H 2; 2.29–2.33, m, 1H, H 2; 3.09, t, 2H, *J* 7.1 Hz, H 11; 6.59, dd, 1H, *J* 8.6, 1.1 Hz, H 4′; 7.16, dd, 2H, *J* 8.5, 7.3 Hz, H 3′,5′; 9.60, d, 1H, *J* 2.0 Hz, H 1. ^{13}C n.m.r. δ (100 MHz) 13.35 (CH_3); 26.92, 27.15, 29.38, 29.40, 29.48, 29.53, 30.54 (C 3,4,5,6,7,8,9,10); 43.99 (C 11); 46.31 (C 2); 112.69 (C 2′,6′); 117.07 (C 4′); 129.20 (C 3′,5′); 148.56 (C 1′); 205.29 (C 1). Mass spectrum (ESI$^+$): *m/z* 276.2 $(M+H)^+$.

Further elution gave 12-phenylaminoundecanal (0.02 g, 6%). ν_{max} (neat) 1713s cm^{-1}. ^{1}H n.m.r. δ (400 MHz) 1.23–1.39, m, 16H, H 3,4,5,6,7,8,9,10; 1.61, m, 2H, H 11; 2.41, td, 2H, *J* 7.3, 1.9 Hz, H 2; 3.10, t, 2H, *J* 7.1 Hz, H 12; 6.59, d, 2H, *J* 7.7 Hz, H 2′,6′; 6.68, t, 1H, *J* 7.3 Hz, H 4′; 7.16, dd, 2H, *J* 8.3, 7.4 Hz, H 3′,5′; 9.76, t, 1H, *J* 1.9 Hz, H 1. ^{13}C n.m.r. δ (100 MHz) 24.07, 28.73, 28.79, 28.96, 29.18, 29.68 (C 2,3,4,5,6,7,8,9,10,11); 44.03 (C 12); 112.72 (C 2′,6′); 117.11 (C 4′); 129.23 (C 3′,5′); 148.59 (C 1′); 202.87 (C 1). Mass spectrum (ESI$^+$): *m/z* 276.2 $(M+H)^+$.

1-Benzylazecane (7b; R = Bn)

Reaction of *N*-benzyloct-7-enamine (6b; R = Bn) (0.20 g, 9.2 mmol), $[Rh(OAc)_2]_2$ (2.0 mg, 4.6 μmol) and BIPHEPHOS (14.4 mg, 18.4 μmol) with 9 : 1 H_2/CO (400 psi) gave a brown oil (0.20 g). Gradient elution column chromatography (alumina, 2–10% EtOAc/light petroleum) gave *1-benzylazecane* (7b; R = Bn) clear oil (0.05 g, 25%) (Found: *m/z* 232.2065. $(C_{16}H_{25}N+H)^+$ requires 232.2065). ^{1}H n.m.r. δ (200 MHz) 1.26–1.63, m, 14H, H 3,4,5,6,7,8,9; 2.37, t, 4H, *J* 6.2 Hz, H 2,10; 3.52, s, 2H, PhC**H**$_2$N; 7.21–7.36, 5H, ArH. ^{13}C n.m.r. δ (50 MHz) 26.82, 27.01, 29.14 (C 3,4,5,6,7,8,9); 52.88 (C 2,10); 59.38 (Ph**C**H$_2$N); 126.57 (C 4′); 128.03, 128.86 (C 2′,3′,5′,6′); 140.41 (C 1′). Mass spectrum (ESI$^+$): *m/z* 231.9 $(M+H)^+$.

Further elution gave N-*benzyloctylamine* as a yellow oil (0.07 g, 35%) (Found: *m/z* 232.2056. $(C_{16}H_{25}N+H)^+$ requires *m/z* 232.2065). ^{1}H n.m.r. δ (200 MHz) 0.88, t, 3H, *J* 6.1 Hz, H 8; 1.26–1.51, m, 12H, H 2,3,4,5,6,7; 2.38, t, 2H, *J* 7.5 Hz, H 1; 3.53, s, 2H, PhC**H**$_2$N; 7.29–7.31, m, 5H, ArH. ^{13}C n.m.r. δ (50 MHz) 14.14 (C 8); 22.71, 26.98, 27.48, 29.56, 29.69 (C 2,3,4,5,6); 31.95 (C 7); 49.48 (Ph**C**H$_2$N); 53.82 (C 1); 126.59 (C 4′); 128.04, 128.85 (C 2′,3′,5′,6′); 140.19 (C 1′). Mass spectrum (ESI$^+$): *m/z* 219.9 $(M+H)^+$.

A reaction using PPh_3 under otherwise identical conditions gave an almost identical result.

1-Benzylazocane (7c; R = Bn)

Reaction of *N*-benzylhex-5-enamine (6c; R = Bn) (0.15 g, 0.8 mmol), $[Rh(OAc)_2]_2$ (1.8 mg, 4.0 μmol) and BIPHEPHOS (16.6 mg, 15.9 μmol) under the usual conditions gave a brown oil (0.20 g). Column chromatography (alumina: 10% EtOAc/CH_2Cl_2) gave 1-benzylazocane (7c; R = Bn) as a clear oil (0.07 g, 43%). ^{1}H n.m.r. δ (200 MHz) 1.47–1.72, m, 10H, H 3,4,5,6,7; 2.55, t, 4H, *J* 6.0 Hz, H 2,8; 3.60, s, 2H, PhC**H**$_2$N; 7.22–7.40, m, 5H, ArH (in agreement with literature[42]). ^{13}C n.m.r. δ (50 MHz) 26.16, 27.82, 29.73 (C 3,4,5,6,7); 54.08 (C 2,8); 63.59 (Ph**C**H$_2$N); 126.65 (C 4′); 128.04, 128.95 (ArCH); C 1′ not observed. Mass spectrum (ESI$^+$): *m/z* 204.0 $(M+H)^+$.

N-(1-Phenylethyl)azepane (7d; R = PhCH(Me))

Reaction of *N*-(1-phenylethyl)pent-4-enamine (6d; R = PhCH(Me)) (0.25 g, 1.3 mmol), $[Rh(OAc)_2]_2$ (3.0 mg, 6.6 μmol) and BIPHEPHOS (10.0 mg, 13.2 μmol) by using 1 : 5 H_2/CO (400 psi) gave an oil (0.27 g) which on distillation gave the azepane (7d) as a clear oil (0.16 g, 60%), b.p. (oven) 130°/0.5 mm (lit.[43] b.p. (oven) 130°/0.4 mm) with identical spectral data to those described previously.

An identical reaction but using 9 : 1 H_2/CO gave an oil (0.3 g). Distillation gave a mixture of (7d) and hydrogenated starting material (9d) (0.15 g) in a 1 : 2 ratio. Chromtography (silica, 30% EtOAc/light petroleum) gave a sample of (9d). ^{1}H n.m.r. δ (200 MHz) 0.86, t, 3H, *J* 6.6 Hz, H 5: 1.17–1.57, m, 6H, H 2,3,4; 1.35, d, 3H, *J* 6.6 Hz, C**H**$_3$ CH; 2.33–2.55, m, 2H, H 1; 3.75, q, 1H, *J* 6.6 Hz,CH; 7.18–7.37, m, 5H, PhH. ^{13}C n.m.r. δ (50 MHz) 14.00 (C 5); 22.57 (C 4); 24.33 (**C**H$_3$CH); 29.53, 29.95 (C 2,3); 47.86 (C 1); 58.37 (CH); 126.50, 126.75, 128.34 (PhCH); 145.87 (C 1′). Mass spectrum (ESI$^+$) m/z 192.2 $(M+H)^+$.

An authentic sample of the alkane (9d) was prepared by hydrogenation of the alkene (6d; R = PhCH(Me)), b.p. (oven) 105°/0.5 mm.

N-Benzyl-11-formylundecanamide and N-Benzyl-10-formylundecanamide

Reaction of *N*-benzylundec-10-enamide (0.30 g, 1.1 mmol) and $Rh_4(CO)_{12}$ (2.1 mg, 2.7 μmol) with 1 : 3 H_2/CO, (800 psi) at 100° gave an approximately 55 : 45 mixture of the linear and branched aldehydes as a brown solid (0.37 g). Recrystallization from ether/light petroleum gave N-*benzyl-11-formylundecanamide* as a cream solid (0.13 g, 39%) (Found: *m/z* 304.2277. $(C_{19}H_{29}NO_2+H)^+$ requires *m/z* 304.2276). ν_{max} (Nujol) 1709w cm^{-1}. ^{1}H n.m.r. δ (400 MHz) 1.28, br s, 12H, H 4,5,6,7,8,9; 1.63, m, 4H, H 3,10; 2.20, t, 2H, *J* 7.5 Hz, H 2; 2.41, dt, 2H, *J* 1.9, 7.3 Hz, H 11; 4.43, d, 2H, *J* Hz, PhC**H**$_2$N; 5.75, br s, 1H, NH; 7.25–7.37, m, 5H, ArH; 9.75, t, 1H, *J* 1.9 Hz, CHO. ^{13}C n.m.r. δ (100 MHz) 22.08, 25.74, 29.13, 29.22, 29.28, 29.31, 29.35 (C 3,4,5,6,7,8,9,10); 36.80 (C 2); 43.62 (Ph**C**H$_2$N); 43.90 (C 11); 127.50, 127.84, 128.71 (ArCH); 138.47 (C 1′); 172.98 (C 1); 202.89 (CHO). Mass spectrum (ESI$^+$): *m/z* 304.2 $(M+H)^+$.

Concentration of the filtrate gave *N*-benzyl-10-formylundecanamide as a clear oil (0.12 g, 36%). ν_{max} (neat) 1712s, 1648s cm^{-1}. ^1H n.m.r. δ (200 MHz) 1.06, d, 3H, *J* 7.0 Hz, H 11; 1.27, br s, 10H, H 4,5,6,7,8; 1.57–1.71, m, 2H, H 3; 1.96–2.01, m, 2H, H 9; 2.18, t, 2H, *J* 7.5 Hz, H 2; 2.24–2.39, m, 1H, H 10; 4.36, d, 2H, *J* 5.7 Hz, PhC**H**$_2$N; 6.53, br s, 1H, NH; 7.21–7.34, m, 5H, ArH; 9.55, d, 1H, *J* 2.1 Hz, CHO. ^{13}C n.m.r. δ (50 MHz) 13.15 (C 11); 25.61, 26.72, 28.96, 29.09, 29.37, 30.29 (C 3,4,5,6,7,8,9); 36.41 (C 2); 43.25 (Ph**C**H$_2$N); 46.11 (C 10); 127.14, 127.52, 128.40 (ArCH); 138.39 (C 1′); 173.25 (C 1); 205.36 (CHO). Mass spectrum (ESI$^+$): *m/z* 304.3 $(M+H)^+$.

N-Butyl-11-formylundecanamide and N-Butyl-10-formylundecanamide

Reaction of *N*-butylundec-10-enamide (0.30 g, 1.3 mmol) and $Rh_4(CO)_{12}$ (2.3 mg, 3.1 μmol) with 1 : 3 H_2/CO (800 psi) in tetrahydrofuran gave a 55 : 45 mixture of linear and branched aldehydes as a brown solid (0.33 g). Recrystallization from ether/light petroleum gave *N*-butyl-11-formylundecanamide as a cream solid (0.11 g, 33%) (Found: *m/z* 270.2422. $(C_{16}H_{31}NO_2+H)^+$ requires *m/z* 270.2433). ν_{max} (Nujol) 1708m, 1639m cm^{-1}. ^1H n.m.r. δ (200 MHz) 0.92, t, 3H, *J* 7.0 Hz, H 4′; 1.28, br s, 12H, H 4,5,6,7,8,3′; 1.36-1.52, m, 2H, H 2′; 1.55–1.66, m, 4H, H 3,10; 2.15, t, 2H, *J* 7.5 Hz, H 2; 2.42, dt, 2H, *J* 7.3, 1.8 Hz, H 11; 3.25, q, 2H, *J*6.8 Hz, H 1′; 5.43, br s, 1H, NH; 9.76, t, 1H, *J* 1.8 Hz, CHO. ^{13}C n.m.r. δ (50 MHz) 13.77 (C 4′); 20.08 (C 3′); 24.69, 25.78, 28.90, 29.03, 29.16 (C 3,4,5,6,7,8,9); 31.73 (C 2′); 33.98 (C 10); 36.92 (C 2); 39.29 (C 1′); 173.06 (C 1); 202.70 (CHO). Mass spectrum (ESI$^+$): *m/z* 270.1 $(M+H)^+$.

Concentration of the filtrate gave *N*-butyl-10-formylundecanamide as a yellow oil (0.16 g, 47%). ν_{max} (neat) 1710s, 1644m cm^{-1}. ^1H n.m.r. δ (400 MHz) 0.92, t, 3H, *J* 7.3 Hz, H 4′; 1.09, d, 3H, *J* 7.0 Hz, H 11; 1.29–1.39, m, 12H, H 4,5,6,7,8,3′; 1.43–1.52, m, 2H, H 2′; 1.58–1.65, m, 4H, H 3,9; 2.17, t, 2H, *J* 7.5 Hz, H 2; 2.32, m, 1H, H 10; 3.23, q, 2H, *J* 7.1 Hz, H 1′; 6.23, br s, 1H, NH; 9.61, d, 1H, 2.0 Hz, CHO. ^{13}C n.m.r. δ (50 MHz) 13.61 (C 4′); 16.87 (C 11); 19.92 (C 3′); 25.71, 29.05 (C 3,4,5,6,7,8,9); 31.46 (C 2′); 36.53 (C 2); 39.17 (C 1′); 39.31 (C 10); 181.06 (CHO). Mass spectrum (ESI$^+$): *m/z* 270.3 $(M+H)^+$.

A reaction under the usual conditions gave the linear and branched aldehydes in a 70 : 30 ratio.

N-*(3,5-Dimethoxyphenyl)-11-formylundecanamide and* N-*(3,5-Dimethoxyphenyl)-10-formylundecanamide*

Reaction of *N*-(3,5-dimethoxyphenyl)undec-10-enamide (0.30 g, 0.9 mmol), under the usual conditions, gave a 2 : 1 mixture (^1H n.m.r.) of linear and branched aldehydes as a brown solid (0.33 g). Trituration with ether gave *N*-(3,5-dimethoxyphenyl)-11-formylundecanamide as a brown solid (0.15 g, 48%). ν_{max} (Nujol) 1721s, 1665s cm^{-1}. ^1H n.m.r. δ (200 MHz) 1.28, br s, 12H, H 4,5,6,7,8,9; 1.59–1.71, m, 4H, H 3,10; 2.34, t, 2H, *J* 7.6 Hz, H 2; 2.42, dt, 2H, *J* 7.2, 1.9 Hz, H 11; 3.77, 6H, OCH_3; 6.22, s, 1H, H 4′; 6.79, s, 2H, H 2′,6′; 7.31, br s, 1H, NH; 9.76, br s, 1H, CHO. ^{13}C n.m.r. δ (50 MHz) 22.05, 25.47, 29.10, 29.19, 29.29 (C 3,4,5,6,7,8,9,19); 37.87 (C 2); 43.92 (C 11); 55.38 (OCH_3); 96.56 (C 4′); 97.84 (C 2′,6′); 139.84 (C 1′); 161.03 (C 3′,5′); 171.55 (C 1); 203.11 (CHO).

Concentration of the filtrate gave *N*-(3,5-dimethoxyphenyl)-10-formylundecanamide as a yellow oil (0.05 g, 16%). ν_{max} (neat) 1721s, 1665s cm^{-1}. ^1H n.m.r. δ (200 MHz) 1.08, d, 3H, *J* 7.0 Hz, H 11; 1.28, br s, 10H, H 4,5,6,7,8; 1.58–1.71, m, 4H, H 3,9; 2.28–2.37, m, 3H, H 2,10; 3.74, s, 6H, OCH_3, 6.21, t, 1H, *J* 2.2 Hz, H 4′; 6.81, d, 2H, *J* 2.2 Hz, H 2′,6′; 8.09, br s, 1H, NH; 9.60, d, 1H, *J* 2.0 Hz, CHO. ^{13}C n.m.r. δ (50 MHz) 13.19 (C 11); 25.42, 26.74, 28.96, 29.13, 29.18, 29.39, 29.56, 30.31 (C 3,4,5,6,7,8,9); 37.54 (C 2); 46.18 (C 10); 55.17 (OCH_3); 96.32 (C 4′); 97.95 (C 2′,6′); 139.86 (C 1′); 160.80 (C 3′,5′); 172.03 (C 1); 205.68 (CHO).

5-Benzyl-1,5-oxazecane (11)

Reaction of *N*-benzyl-3-(but-3-enyloxy)propanamine (10) (0.20 g, 0.9 mmol) under the usual conditions gave a yellow oil which on chromatography (alumina, 5% EtOAc/CH_2Cl_2) gave *5-benzyl-1,5-oxazecane* (11) (0.03 g, 14%) (Found: *m/z* 234.1853. $(C_{15}H_{23}NO+H)^+$ requires *m/z* 234.1858). ^1H n.m.r. δ (400 MHz) 1.49–1.60, m, 4H and 1.62–1.74, m, 4H, H 3,7,8,9; 2.41, t, 2H, *J* 5.4 Hz, H 6; 2.52, t, 2H, *J* 6.1 Hz, H 4; 3.49, s, 2H, PhC**H**$_2$N; 3.63-3.66, m, 4H, H 2,10; 7.21–7.25, m, 1H and 7.26–7.37, m, 4H, ArH. ^{13}C n.m.r. δ (100 MHz) 26.12 (C 7); 27.17 (C 3,8,9); 48.46 (C 4); 55.05 (C 6); 61.09 (Ph**C**H$_2$N); 66.45 (C 2); 72.61 (C 10); 126.71 (C 4′); 128.06, 129.33 (C 2′,3′,5′,6′); 140.31 (C 1′). Mass spectrum (ESI$^+$): *m/z* 234.1 $(M+H)^+$.

A reaction using BIPHEPHOS under standard conditions gave a mixture of products. Chromatography (alumina, 50% EtOAc/light petroleum) gave only hydrogenated starting material, N-*benzyl-3-butyloxypropanamine* (12) (0.14 g, 46%) (Found: *m/z* 222.1846. $(C_{14}H_{23}NO+H)^+$ requires *m/z* 222.1858). ^1H n.m.r. δ (400 MHz) 0.82, t, 3H, *J* 7.3 Hz, H 4′; 1.23–1.29, m, 2H, H$_3$′; 1.41–1.48, m, 2H, H 2′; 1.68, t, 2H, *J* 6.7 Hz, H 2; 2.62, t, 2H, *J* 6.9 Hz, H 1; 3.30, t, 2H, *J* 6.6 Hz, H 3; 3.38, t, 2H, *J* 6.3 Hz, H 1′; 3.66, s, 2H, PhC**H**$_2$N; 7.19–7.26, m, 5H, PhH. ^{13}C n.m.r. δ (100 MHz) 13.84 (C 4′); 19.29 (C 3′); 29.92 (C 2); 31.75 (C 2′); 46.87 (C 1); 53.93 (Ph**C**H$_2$N); 69.35, 70.66 (C 1′,3); 126.78 (C 4″); 128.02, 128.31 (C 2″,3″,5″,6″); 140.33 (C 1″). Mass spectrum (ESI$^+$): *m/z* 221.9 $(M+H)^+$.

*14-Acetyl-2,3,4,5,6,7,8,9,10,11,12,13,14,15-tetradecahydro-1,14-benzoxazacycloheptadecine (14a; Bn = Ac) and 13-Acetyl-11-methyl-3,4,5,6,7,8,9,10,11,12,13,14-dodecahydro-2*H*-1,13-benzoxazacyclohexadecine (15a; Bn = Ac)*

The product from a reaction of 2-(undec-10-enyloxy)benzylamine (13a; Bn = H). (0.30 g, 1.1 mmol) under the usual conditions was reduced with $NaBH_4$ and acetylated as described above. The ^1H and ^{13}C n.m.r. spectra indicated an equimolar mixture of linear and branched products (14a; Bn = Ac) and (15a; Bn = Ac). Chromatography (alumina, EtOAc) gave the mixture of *N*-acetyl compounds as a clear oil (0.13 g 36%) (Found: *m/z* 332.2586. $(C_{21}H_{33}NO_2+H)$+ requires *m/z* 332.2589). Further chromatography (20% EtOAc/light petroleum) allowed partial separation for spectral assignment. 14-Acetyl-2,3,4,5,6,7,8,9,10, 11, 12, 13, 14, 15-tetradecahydro-1, 14-benzoxazacycloheptadecine (14a; Bn = Ac): ^1H n.m.r. δ (200 MHz) 0.81, m, 2H and 1.15–1.5, m, 18H, H 3,4,5,6,7,8,9,10,11,12; 1.74–1.87, m, 2H, H 13; 1.97, s, 3H, $COCH_3$; 3.86–3.96, m, 2H, H 2; 4.38–4.57, m, 2H, H 15; 6.74-6.93, m, 3H and 7.13–7.21, m, 1H, H 16,17,18,19. 13-Acetyl-11-methyl-3,4,5,6,7,8,9,10,11,12,13,14-dodecahydro-*2H*-1,13-benzoxa-zacyclohexadecine (15a; Bn = Ac): ^1H n.m.r. δ (200 MHz) 0.86, d, 3H, *J* 6.6 Hz, CH_3; 1.16–1.51, m, 14H and 1.54–1.65, m, 2H, H 3,4,5,6,7,8,9,10; 1.74–1.84, m, 2H, H 2; 3.22–3.37, m, 1H, H 11; 3.97–4.67, 2H, H 2; 4.55–4.68, m, 2H, H 14; 6.82–7.02, m, 3H and 7.11–7.28, m, 1H, H 15,16,17,18.

14-Benzyl-2,3,4,5,6,7,8,9,10,11,12,13,14,15-tetradecahydro-1,14-benzoxazacycloheptadecine (14a) and 6,25-Dibenzyl-5,6,7,8,9,10,11,12, 13,14,15,16,17,18,24,25,26,27,28,29,30,31,32,33,34,35,36,37-octaicosahydrodibenzo[b,s][1,18,5,22]dioxadiazacyclotetratriacontine (16a)

A reaction of *N*-benzyl-2-(undec-10-enyloxy)benzylamine (13a) (0.30 g, 0.8 mmol) under the usual conditions gave a brown oil (0.30 g) whose ^1H n.m.r. spectrum indicated only a small amount of branched chain product (15a) (δ 0.96, d, *J* 6.8 Hz). Column chromatography (silica, 10% EtOAc/light petroleum) gave *14-benzyl-2,3,4,5,6,7,8,9,10,11,12, 13,14,15-tetradecahydro-1,14-benzoxazacycloheptadecine* (14a) as a clear oil (0.03 g, 10%) (Found: C, 82.1; H, 10.1; N, 4.0. $C_{26}H_{37}NO$ requires C, 82.3; H, 9.8; N, 3.7%) (Found: *m/z* 380.2921. $(C_{26}H_{37}NO+H)^+$ requires *m/z* 380.2953). ^1H n.m.r. δ (200 MHz) 1.15–1.35, m, 14H, H 5,6,7,8,9,10,11; 1.40–1.50, m, 4H, H 4,12; 1.66–1.75, m, 2H, H 3; 2.43, t, 2H, *J* 7.5 Hz, H 13; 3.57, s, 2H and 3.63, s, 2H, H 15 and PhC**H**$_2$N; 3.91, t, 2H, *J* 5.5 Hz, H 2; 6.72–6.86, m, 2H, H 17,19; 7.05–7.39, m, 7H, H 16,18, PhH. ^{13}C n.m.r. δ (50 MHz) 24.74, 25.51, 25.86, 26.27, 26.65, 26.94, 27.27, 27.47, 29.16 (C 3,4,5,6,7,8,9,10,11,12); 51.72, 53.40, 58.04 (C 13, Ph**C**H$_2$N, C 15); 67.59 (C 2); 110.93 (C 19); 119.97 (C 17); 126.56 (C 4′); 127.42, 128.11, 128.62, 129.88 (C 16,18,2′,3′,5′,6′); 140.52 (C 1′); 157.25 (C 19a) (C 15a not observed). Mass spectrum (ESI$^+$): *m/z* 380.3 $(M+H)^+$.

A reaction of the amine (0.2 g, 0.6 mmol) under the usual conditions but with BIPHEPHOS gave a brown oil (0.24 g). The light petroleum extract of the oil was chromatographed (silica, 10% EtOAc/light petroleum) to give (14a) as a semisolid (0.07 g, 34%). The light petroleum insoluble material was the dimeric compound 6,25-dibenzyl-5,6,7,8,9,10,11,12,13,14,15,16,17,18,24,25,26,27,28,29,30,31,32,33,34,35,36,37-octaicosahydrodibenzo[b,s][1,18,5,22]dioxadiazacyclotetratriacontine (16a) (0.04 g, 20%), m.p. 111–113° (Found: m/z 759.5794. $(C_{52}H_{74}N_2O_2+H)^+$ requires m/z 759.5828). ^{1}H n.m.r. δ (200 MHz) 1.22–1.50, m, 28H, H 9,10,11,12,13,14,15,28,29,30,31,32,33,34; 1.75–1.79, m, 8H, H 8,16,25,27; 2.44, t, 4H, J 7.2 Hz, H 7,26; 3.61, s, 4H and 3.68, s, 4H, H 5,24, PhC**H**$_2$N; 3.95, t, 4H, J 5.8 Hz, H 18,37; 6.80–6.93, m, 4H, H 1,3,20,22; 7.14–7.51, m, 14H, H 2,4,21,23, PhH. ^{13}C n.m.r. δ (50 MHz) 26.52, 27.42, 29.54, 29.78 (C 8,9,10,11,12,13,14,15,16,17,27,28,29,30,31,32,33,34,35,36); 51.50,53.63, 58.63 (Ph**C**H$_2$N, C 5,7,24,26); 68.01 (C 18,37); 111.17 (C 1,20); 120.08 (C 3,22); 126.70 (C 4′); 128.11, 128.84, 130.80 (C 2,4,21,23, PhCH); 157.44 (C 19a,38a) (C 4a,23a, C 1′ not observed). Mass spectrum (ESI$^+$): m/z 759.6 ((M+H)$^+$.

A reaction of the amine (0.10 g, 0.3mmol) by using BIPHEPHOS as above with 1 : 5 H_2/CO gave, after chromatography (silica, 5–10% EtOAc/light petroleum), the cyclic amine (14a) (0.02 g, 20%) followed by the dimer (16a) (0.01 g, 10%).

A reaction of the amine (0.11 g, 0.3 mmol) by using BIPHEPHOS with 9 : 1 H_2/CO gave a brown oil (0.14 g). Column chromatography (silica, 10% EtOAc/light petroleum) of the light petroleum extract gave the cyclic amine (14a) (0.04 g, 38%), followed by impure (17a) (0.02 g, 16%). Mass spectrum (ESI$^+$): *m/z* 368.3 (M+H)$^+$. The light petroleum insoluble material was the dimer (16a) (0.05 g, 44%).

8-Benzyl-6-methyl-2,3,4,5,6,7,8,9-octahydro-1,8-benzoxazacycloundecine (15b) and 9-Benzyl-3,4,5,6,7,8,9,10-octahydro-2H-1,9-benzoxazacyclododecine (14b)

Reaction of *N*-benzyl-2-(hex-5-enyloxy)benzylamine (13b) (0.1 g, 0.3 mmol) with BIPHEPHOS and 1 : 5 H_2/CO gave a brown oil (0.11 g), showing (14b) and (15b) in a ratio of 70 : 30. Column chromatography (silica, 1% ether/light petroleum) gave *8-benzyl-6-methyl-2,3,4,5,6,7,8,9-octahydro-1,8-benzoxazacycloundecine* (15b) as a clear oil (0.01 g, 10%) (Found: *m/z* 310.2169. $(C_{21}H_{27}NO+H)^+$ requires *m/z* 310.2171). ^{1}H n.m.r. δ (400 MHz) 0.66, m, 1H, H 5$_A$; 0.77, d, 3H, *J* 6.4 Hz, CH_3; 1.45–1.54, m, 1H, H 4$_A$; 1.70–1.83, m, 2H, H 4$_B$,3$_A$; 1.99, m, 1H, H 3$_B$; 2.09–2.17, m, 2H, H 5$_B$,7A; 2.23, dd, 1H, *J* 12.0, 4.6 Hz, H 7$_B$; 2.32–2.40, m, 1H, H 6; 3.02, d, 1H, *J* 13.1 Hz, H 9$_A$; 3.40, d, 1H, *J* 13.6 Hz and 3.77, d, 1H, *J* 13.6 Hz, PhC**H**$_2$N; 3.78–3.83, m, 1H, H 2$_A$; 4.09, d, 1H, *J* 13.1 Hz, H 9$_B$; 4.24–4.27, m, 1H, H 2$_B$; 6.81, d, 1H, *J* 8.4 Hz, H 13; 6.82, dt, 1H, *J* 8.6, 1.0 Hz, H 11; 7.09, dd, 1H, *J* 7.1, 1.7 Hz, H 10; 7.14–7.25, m, 6H, H 12, PhH. ^{13}C n.m.r. δ (100 MHz) 17.80 (CH_3); 24.58 (C 4); 25.42 (C 3); 26.80 (C 6); 31.67 (C 5); 52.59 (C 9); 59.29 (Ph**C**H$_2$N); 60.44 (C 7); 68.00 (C 2); 110.16 (C 13); 119.20 (C 11); 126.43 (C 5′); 127.79, 128.27 (C 12); 128.40 (C 9a); 129.06 (PhCH); 130.73 (C 10); 140.23 (C 1′); 157.68 (C 13a). Mass spectrum (ESI$^+$): *m/z* 310.3 (M+H)$^+$.

Further elution (silica, 1% EtOAc/light petroleum) gave *9-benzyl-3,4,5,6,7,8,9,10-octahydro-2H-1,9-benzoxazacyclododecine* (14b) as a clear oil (0.03 g, 30%) (Found: *m/z* 310.2164. $(C_{21}H_{27}NO+H)^+$ requires *m/z* 310.2171). ^{1}H n.m.r. δ (400 MHz) 1.43, m, 4H, H 5,6; 1.60, m, 2H, H 7; 1.67, p, 2H, *J* 6.1 Hz, H 4; 1.89, p, 2H, *J* 5.6 Hz, H 3; 2.39, m, 2H, H 8; 3.57, s, 2H, and 3.64, s, 2H, H 10, PhC**H**$_2$N; 4.09, t, 2H, *J* 5.5 Hz, H 2; 6.87, t, 1H, *J* 7.4 Hz, H 14; 6.91, d, 1H, *J* 8.1 Hz, H 12; 7.18–7.31, m, 7H, H 11,13, PhH. ^{13}C n.m.r. δ (100 MHz) 22.73 (C 4,7); 24.47 (C 5 or 6); 27.02 (C 3); 29.40 (C 5 or 6); 51.84, 52.54, 58.60 (C 8,10, Ph**C**H$_2$N); 67.34 (C 2); 112.10 (C 14); 119.96 (C 12); 126.58, 127.99, 128.37, 129.05, 132.47 (C 11,13, PhCH); 158.12 (C 14a) (C 10a and C 1′ not observed). Mass spectrum (ESI$^+$): *m/z* 310.3 (M+H)$^+$.

Reactions of the amine (0.3 g, 1.0 mmol) with BIPHEPHOS and 1 : 1 or 9 : 1 H_2/CO gave in each case a mixture of products. Only N-*benzyl-2-(hexyloxy)benzylamine* (17b) was isolated from the light petroleum extract (0.06 g, 20%) (Found: *m/z* 298.2171. $(C_{20}H_{27}NO+H)^+$ requires *m/z* 298.2171). ^{1}H n.m.r. δ (200 MHz) 0.81, t, 3H, *J* 6.8 Hz, H 6′; 1.18–1.43, m, 6H, H 3′,4′,5′; 1.62–1.72, m, 2H, H 2′; 3.68, s, 2H and 3.73, s, 2H, ArC**H**$_2$N, PhC**H**$_2$N; 3.88, t, 2H, *J* 6.4 Hz, H 1′; 6.74–6.85, m, 2H, H 3,5; 7.10–7.25, m, 7H, H 4,6, PhH. ^{13}C n.m.r. δ (50 MHz) 14.02 (C 6′); 22.56, 25.87, 29.12 (C 3′,4′,5′); 31.52 (C 2′); 49.02 (Ar**C**H$_2$N); 53.00 (Ph**C**H$_2$N); 67.77 (C 1′); 111.01 (C 3); 120.12 (C 5); 126.76, 128.17, 128.27, 130.00 (C 4,6, PhCH); 140.45 (C 1″); 157.23 (C 2). Mass spectrum (ESI$^+$): *m/z* 298.1 (M+H)$^+$.

6-Benzyl-2,3,4,5,6,7-hexahydro-1,6-benzoxazonine (14c), 6,17-Dibenzyl-5,6,7,8,9,10,16,17,18,19,20,21-dodecahydrodibenzo[b,k][1,10,5,14]dioxadiazacyclooctadecine (16c) and 3-Benzyl-2-(1′-methylethyl)-3,4-dihydro-2H-1,3-benzoxazine

Reaction of *N*-benzyl-2-(propenyloxy)benzylamine (13c) (0.2 g, 0.7 mmol) by using BIPHEPHOS under standard conditions gave a yellow oil (0.22 g). Column chromatography (silica, 10% EtOAc/light petroleum) first gave *6-benzyl-2,3,4,5,6,7-hexahydro-1,6-benzoxazonine* (14c) as a yellow oil (0.07 g, 33%) (Found: *m/z* 268.1695. $(C_{18}H_{21}NO+H)^+$ requires *m/z* 268.1701). ^{1}H n.m.r. δ (200 MHz) 1.59–1.82, m, 4H, H 3,4; 2.93, t, 2H, *J* 6.0 Hz, H 5; 3.70, s, 2H and 3.75, s, 2H, H 7, PhC**H**$_2$N; 4.35, t, 2H, *J* 5.6 Hz, H 2; 6.78–7.36, m, 9H, H–8,9,10,11, PhH. ^{13}C n.m.r. δ (50 MHz) 24.31 (C 3); 26.97 (C 4); 54.17, 54.65 (C 7, Ph**C**H$_2$N); 58.97 (C 5); 74.45 (C 2); 119.45 (C 7a); 121.23, 123.01, 126.70, 128.06, 128.30, 128.89, 130.08 (C 8,9,10,11, PhCH); 138.97 (C 1′) 159.05 (C 11a). Mass spectrum (ESI$^+$): *m/z* 268 (M+H)$^+$.

The second fraction was the dimer *6,17-dibenzyl-5,6,7,8,9,10,16,17,18,19,20,21-dodecahydrodibenzo[*b,k*][1,10,5,14] dioxadiazacyclooctadecine* (16c) as a yellow oil (0.04 g, 19%). Trituration of the oil with ether gave a beige solid, m.p. 85–90° (Found: *m/z* 535.3330. $(C_{36}H_{42}N_2O_2+H)^+$ requires *m/z* 535.3324). ^{1}H n.m.r. δ (200 MHz) 1.78, m, 8H, H 8,9,19,20; 2.56, t, 4H, *J* 7.3 Hz, H 7,18; 3.64, s, 4H and 3.76, s, 4H, H 5,16, PhC**H**$_2$N; 3.91, t, 4H, *J* 5.0 Hz, H 10,21; 6.76, d, 2H, *J* 8.2 Hz, H 1,12; 6.90, dt, 2H, *J* 7.4, 0.9 Hz, H 3,14; 7.13–7.43, m, 14H, H 2,4,13,15, PhH. ^{13}C n.m.r. δ (50 MHz) 22.41 (C 9,20); 27.07 (C 8,19); 51.52, 52.63 (C 5,16, Ph**C**H$_2$N); 58.08 (C 7,18); 67.70 (C 10,21); 110.99 (C 1,12); 119.45 (C 4a,15a); 119.98 (C 3,14); 126.66, 127.80, 128.16, 128.68, 130.47 (C 2,4,13,15, PhCH); 138.95 (C 1′); 157.38 (C 11a,22a). Mass spectrum (ESI$^+$): *m/z* 535.2 (M+H)$^+$.

The third fraction was 2-(*N*-benzylaminomethyl)phenol[44] (0.03 g, 18%) (Found: *m/z* 214.1222. $(C_{14}H_{15}NO+H)^+$ requires *m/z* 214.1232). ^{13}C n.m.r. δ (50 MHz) 51.78 (Ar**C**H$_2$N); 52.49 (Ph**C**H$_2$N); 116.36 (C 6); 119.05 (C 4); 122.18 (C 2); 127.53 (C 4′); 128.33, 128.47, 128.64, 128.76 (C 3,5,2′,3′,5′,6′); 138.29 (C 1′); 158.15 (C 1).

A reaction of the amine (0.3 g, 0.8 mmol) under the usual conditions gave a yellow oil (0.32 g). Column chromatography (silica, 2% EtOAc/light petroleum) gave *3-benzyl-2-(1′-methylethyl)-3,4-dihydro-2H-1,3-benzoxazine* as a clear oil (0.06 g, 19%) (Found: *m/z* 268.1695. $(C_{18}H_{21}NO+H)^+$ requires *m/z* 268.1701). ^{1}H n.m.r. δ (400 MHz) 1.05, d, 3H, *J* 6.7 Hz, CH_3; 1.09, d, 3H, *J* 6.5 Hz, CH_3; 2.10–2.18, m, 1H, H 1′; 3.74, d, 1H, *J* 18.1 Hz, H 4$_A$; 3.75, d, 1H, *J* 13.8 Hz and 3.91, d, 1H, *J* 14.0 Hz, PhC**H**$_2$N; 3.93, d, 1H, *J* 18.0 Hz, H 4$_B$; 4.36, d, 1H, *J* 9.7 Hz, H 2; 6.81–6.90, m, 3H, H 5,6,8; 7.11-7.15, m, 1H, H 7; 7.25–7.27, m, 1H and 7.31–7.37, m, 4H, PhH. ^{13}C n.m.r. δ (100 MHz) 18.29, 19.51 (CH_3); 29.90 (C 1′); 46.55 (C 4); 54.03 (Ph**C**H$_2$N); 96.62 (C 2); 116.53 (C 8); 119.56 (C 4a); 120.14 (C 6); 127.05 (C 4′); 127.62, 127.66 (C 5.7); 128.36, 128.52 (PhCH); 139.06 (C 1′); 153.64 (C 8a). Mass spectrum (ESI$^+$): *m/z* 267 (M+H)$^+$.

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