N-Substituted Lithium 2-Lithioallylamines: New Intermediates in Synthesis

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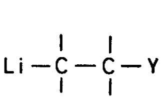
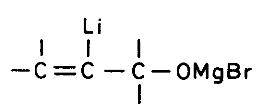
N-Phenyl or *N*-benzoyl 2-halogenoallylamines (**5**) or (**10**) react successively with phenyl-lithium and lithium naphthalenide at −78 °C to give the intermediates (**4**) or (**11**), which on reaction with electrophiles (water, deuterium oxide, dimethyl disulphide, aldehydes, ketones, or allyl bromide) yield functionalized allyl amines (**6**) and (**12**). The corresponding *N*-alkyl derivatives (**9**) afford prop-2-ynylamines (**8**) under the same reaction conditions.

β-Substituted organolithium compounds (**1**) are interesting in organic synthesis because on reaction with electrophiles they afford directly bifunctionalized organic systems.[1] The routes for preparing the dianions (**1**) are either through trans-metallation of β-substituted organomercury compounds[2] with lithium powder[3] or by lithiation of the corresponding chlorohydrins[4] or epoxides[5] using lithium naphthalenide, in both cases at low temperature (−78 °C). The intermediates (**1**) are very unstable species owing to their tendency to undergo β-elimination to yield olefins even at low temperatures; this process has been successfully employed in the regioselective synthesis of alkenes.[6] The stability of such intermediates can be strongly increased by attaching the metal to an sp^2-hybridized carbon atom; thus, the corresponding oxygenated dianions (**2**)[7] are typical organolithium derivatives stable at room temperature. We are aware of only one example of a nitrogenated monoanionic intermediate (**3**), used in the synthesis of bergamotenes through the corresponding cuprate.[8] For these reasons we have studied the preparation and reactivity of dianionic derivatives of the general type (**4**) or (**11**).

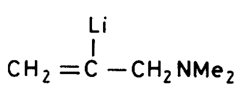


(**1**)

Y = OLi, PhNLi



(**2**)

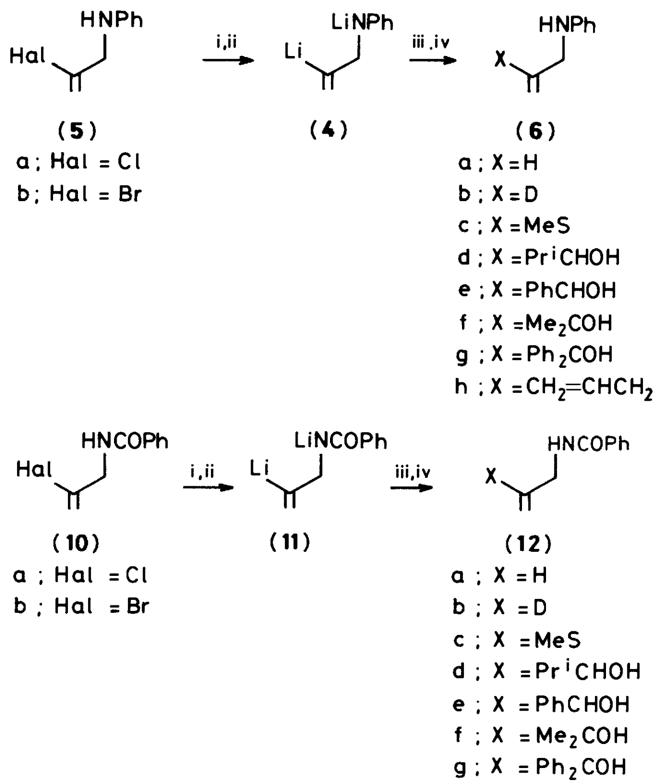


(**3**)

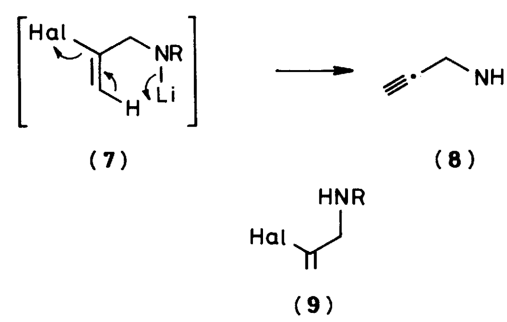
Results and Discussion

The successive reaction of 2-chloro- or 2-bromo-allylaniline (**5a**, **b**) [obtained from 2,3-dihalogenopropene (Hal = Cl, Br) and aniline[9]] with phenyl-lithium and lithium naphthalenide at −78 °C leads to the corresponding intermediate (**4**), which on treatment with different electrophiles (water, deuterium oxide, dimethyl disulphide, carbonyl compounds, or allyl bromide) affords the expected products (**6**) (Scheme 1). The preparation of the intermediate (**4**) has to be carried out at low temperature (−78 °C) in order to avoid the decomposition of the initially formed anion (**7**; R = Ph) by elimination of hydrogen halogenide to yield prop-2-ynylaniline (**8**; R = Ph) as the main reaction product (Scheme 2).

When aliphatic amines of the type (**9**; R = Pr^i or Cy and Hal = Cl, Br) were used under the same reaction conditions as for (**4**) the reaction failed, the corresponding prop-2-ynylamines (**8**) being isolated as the main product. The elimination of hydrogen halogenide in the species of the type



Scheme 1. *Reagents and conditions:* i, PhLi, −78 °C; ii, $Li^+ C_{10}H_8^-$, −78 °C; iii, electrophile = H_2O, D_2O, Me_2S_2, Pr^iCHO, PhCHO, Me_2CO, Ph_2CO, $BrCH_2CH{=}CH_2$, −78 to 20 °C; iv, H_2O



Scheme 2.

Table. Reaction of intermediates (4) and (11) with electrophiles

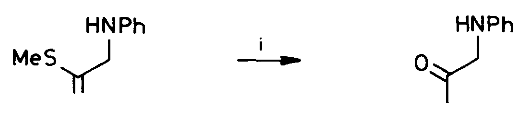
Starting Material	Intermediate	Electrophile	Product No.	Product Yield (%)[a]
(5a)	(4)	H_2O	**(6a)**	93
		D_2O	**(b)**	78
		Me_2S_2	**(c)**	90
		Pr^iCHO	**(d)**	75
		PhCHO	**(e)**	76
		Me_2CO	**(f)**	78
		Ph_2CO	**(g)**	77
(5b)		$BrCH_2CH{=}CH_2$	**(h)**	75
(10a)	**(11)**	H_2O	**(12a)**	91
(10b)		D_2O	**(b)**	84
		Me_2S_2	**(c)**	72
		Pr^iCHO	**(d)**	68
		PhCHO	**(e)**	70
		Me_2CO	**(f)**	69
		Ph_2CO	**(g)**	74

[a] Isolated yield based on the starting materials (**5**) or (**10**).

(**7**), formed in the first step of the process, is easier for aliphatic systems than for (**5**) owing to their higher basicity (Scheme 2).

This inconvenience, in the case of the primary amine derivative (**9**; R = H), has been overcome by using the corresponding benzoyl derivatives (**10**) as starting materials (obtained by benzoylation of the appropriate 2-halogenoallylamines); thus, the same sequence of reactions as used for (**4**) yields the intermediate (**11**), which on reaction with different electrophilic reagents (water, deuterium oxide, dimethyl disulphide, or carbonyl compounds) affords, after hydrolysis, the expected products (**12**) (Scheme 1).

Finally, we hydrolysed the sulphide (**6c**) to see whether, in general, α-amino ketones could be prepared by acid hydrolysis of the vinyl sulphides prepared; by this process the expected product (**13**) was isolated (Scheme 3).



(**6c**) (**13**)

Scheme 3. *Reagents:* i, HCl–H_2O

In the Table are summarized the products prepared by this new method, which in our opinion represents an adequate route for introducing the unit $CH_2{=}\bar{C}{-}CH_2NHR$ in an electrophilic reagent.

Experimental

General.—M.p.s are uncorrected and were measured on a Büchi-Tottoli capillary melting point apparatus. I.r. spectra were determined with a Perkin-Elmer 298 spectrometer. ^1H and ^{13}C N.m.r. spectra were recorded on a Varian FT-80 spectrometer with $SiMe_4$ as internal standard; when carbon tetrachloride was used as solvent or the sample was neat, a D_2O capillary was employed as lock reference. Mass spectra (electron impact) were recorded with a Hewlet-Packard 5987A spectrometer. The purity of volatile distilled products and the chromatographic analysis were determined with a g.l.c. Varian Aerograph 2800 instrument equipped with a OV-101 Chromosorb column. Elemental analysis was carried out with a Perkin-Elmer 240 Elemental Analyser. Starting reactants were of the best commercial grade available and were used without further purification. Phenyl-lithium[10] and lithium naphthalenide[11] were prepared as described earlier. Ether (referring to diethyl ether) was dried successively with anhydrous calcium chloride, sodium sulphate, sodium, and a K–Na (K_3Na) liquid alloy[12] under argon reflux, and was then distilled and stored under argon. Tetrahydrofuran (THF) was dried successively with anhydrous calcium chloride and sodium sulphate; it was then refluxed with potassium, distilled, and stored under argon. All reactions (except the preparation of the starting materials) were carried out under argon and the glassware was dried before use. Starting 2-chloro-[13] and 2-bromo-allylamine[14] were prepared according to the literature methods.

Preparation of N-*Substituted 2-Halogenoallylamines* (**5**) *and* (**9**): *General Procedure.*—2,3-Dihalogenopropene (100 mmol) was added dropwise at 50—65 °C (bath temperature) over a period of 30 min, to a stirred mixture of the appropriate amine (200 mmol) in water (40 ml). Stirring was continued for 4 h at the same temperatures. Sodium hydroxide (10 g, 250 mmol) to the resulting mixture at 10 °C and stirring continued for 1 h the temperature being allowed to rise to 20 °C; the mixture was then extracted with ether (2 × 30 ml). The organic extract was dried (Na_2SO_4) and evaporated (15 mmHg) and the residue was distilled to afford compounds (**5**) and (**9**). N-(2-*Chloroallyl)aniline* (**5a**) (13.7 g, 82%), b.p. 69—71 °C (0.1 mmHg) [lit.,[15] 116—118 °C (2 mmHg)]; $\nu_{max.}$(neat) 3 410 (NH), 3 030, 1 640, 1 610, and 1 505 cm^{-1} (HC=C); δ_H($CDCl_3$) 3.5 (2 H, s, CH_2N), 3.6 (1 H, br s, NH), 5.0 and 5.1 (2 H, 2 s, CH_2=C), and 6.1—7.0 (5 H, m, ArH); δ_C(neat) 50.1 (CH_2N), 112.3 (CH_2=C), 113.1, 118.6, 129.8, 140.3, and 147.8 p.p.m. (ArC and C=CH_2); *m/z* 169 (M^+ + 2, 8%), 167 (M^+, 26), 132 (29), 130 (11), 117 (10), 106 (100), 77 (18), 65 (12), and 51 (11).

N-(2-*Bromoallyl)aniline* (**5b**)[16] (17.0 g, 80%), b.p. 84—86 °C (0.1 mmHg); $\nu_{max.}$(neat) 3 400 (NH), 3 025, 1 640, 1 610, and 1 510 cm^{-1} (HC=C); δ_H($CDCl_3$) 3.6 (1 H, br s, NH), 3.8 (2 H, s, CH_2N), 5.4 and 5.7 (2 H, 2 s, CH_2=C), and 6.2—7.2 (5 H, m, ArH); δ_C(neat) 52.2 (CH_2N), 117.1 (CH_2=C), 113.5, 118.6, 130.0, 132.1, and 147.8 p.p.m. (ArC and C=CH_2); *m/z* 213 (M^+ + 2, 22%), 211 (M^+, 22), 132 (35), 130 (15), 117 (14), 106 (100), 77 (19), and 65 (10).

N-(2-*Chloroallyl*)-N-*isopropylamine* (**9**; R = Pr^i; Hal = Cl) (10.1 g, 76%), b.p. 137—139 °C (760 mmHg) [lit.,[9] 138—140 °C (760 mmHg)]; $\nu_{max.}$(neat) 3 350 (NH), 3 020, and 1 630 cm^{-1} (HC=C); δ_H(CCl_4) 0.8 (6 H, d, *J* 6.5 Hz, 2 × Me), 1.5 (1 H, br s, NH), 2.65 (1 H, heptet, *J* 6.5 Hz, CH), 3.1 (2 H, s, CH_2N), and 5.0 and 5.15 (2 H, 2 s, CH_2=C); δ_C(neat) 22.1 (2 × Me), 40.7 (CH), 52.3 (CH_2N), 111.25 (CH_2=C), and 141.25 p.p.m. (C=CH_2); *m/z* 135 (M^+ + 2, 2%), 133 (M^+, 6), 120 (32), 118 (96), 86 (12), 84 (19), 77 (26), 75 (100), 56 (10), 49 (20), and 39 (10).

N-(2-*Bromoallyl*)-N-*isopropylamine* (**9**; R = Pr^i, Hal = Br) (13.9 g, 78%), b.p. 45—47 °C (15 mmHg) [lit.,[17] 64—67 °C (27 mmHg)]; $\nu_{max.}$(neat) 3 360 (NH), 3 010, and 1 630 cm^{-1} (HC=C); δ_H(CCl_4) 0.8 (6 H, d, *J* 6.5 Hz, 2 × Me), 1.8 (1 H, br s, NH), 2.6 (1 H, heptet, *J* 6.5 Hz, CH), 3.2 (2 H, s, CH_2N), and 5.3 and 5.6 (2 H, 2 s, CH_2=C); δ_C(neat) 22.6 (2 × Me), 46.1 (CH), 54.8 (CH_2N), 115.2 (CH_2=C), and 134.6 p.p.m. (C=CH_2); *m/z* 164 (M^+ + 2, 96%), 162 (M^+, 100), 121 (10), 119 (10), 83 (36), 82 (17), 68 (18), 56 (11), and 39 (10).

N-(2-*Chloroallyl*)-N-*cyclohexylamine* (**9**; R = c-C_6H_{11}, Hal = Cl) (13.5 g, 78%), b.p. 44—46 °C (0.1 mmHg) [lit.,[18] 83—84 °C (2 mmHg)]; $\nu_{max.}$(neat) 3 310 (NH), 3 010, and 1 625 cm^{-1} (HC=C); δ_H(CCl_4) 0.7—1.9 (11 H, m, 5 × ring CH_2 and NH), 2.4 (1 H, quintet, *J* 6.5 Hz, CH), 3.35 (2 H, s, CH_2N), and 5.2 and 5.3 (2 H, 2 s, CH_2=C); δ_C(neat) 24.9, 26.9, and 33.7 (5 × ring CH_2), 53.0 (CH), 55.5 (CH_2N), 111.7 (CH_2=C), and 143.2 p.p.m.

(C=CH_2); m/z 175 (M^+ + 2, 4%), 173 (M^+, 13), 138 (16), 132 (27), 130 (100), 94 (15), 82 (23), and 39 (16).

N-(2-*Bromoallyl*)-N-*cyclohexylamine* (**9**; R = c-C_6H_{11}, Hal = Br) (16.8 g, 77%) (Found: C, 49.3; H, 7.5; N, 6.5. $C_9H_{16}BrN$ requires C, 49.55; H, 7.39; N, 6.42%), b.p. 61—63 °C (0.1 mmHg); $\nu_{max.}$(neat) 3 320 (NH), 3 010, and 1 630 cm^{-1} (HC=C); δ_H(CCl_4) 0.9—1.9 (11 H, m, 5 × ring CH_2 and NH), 2.35 (1 H, quintet, J 6.5 Hz, CH), 3.4 (2 H, s, CH_2N), and 5.5 and 5.8 (2 H, 2 s, CH_2=C); δ_C(neat) 25.8, 27.3, and 29.1 (5 × ring CH_2), 55.1 (CH), 55.2 (CH_2N), 116.8 (CH$_2$=C), and 135.9 p.p.m. (C=CH_2); m/z 219 (M^+ + 2, 13%), 217 (M^+, 14), 176 (94), 174 (100), 138 (31), 95 (17), 94 (18), 82 (35), 56 (11), 55 (12), 41 (17), and 39 (22).

Preparation of N-(2-*Halogenoallyl*)*benzamides* (**10**): *General Procedure.*—Benzoyl chloride (11.6 ml, 100 mmol) was added dropwise at 0 °C (bath temperature) over a period of 30 min to a mixture of the appropriate 2-halogenoallylamine (100 mmol), sodium hydroxide (5 g, 125 mmol), and water (50 ml). The mixture was then stirred for 2 h the temperature being allowed to rise to 20 °C. The resulting precipitate was filtered off, dried (0.1 mmHg), and recrystallized from ether. N-(2-*Chloroallyl*)*benzamide* (**10a**) (18.4 g, 94%), m.p. 94—96 °C (lit.,[19] 95 °C); $\nu_{max.}$(KBr) 3 300 (NH), 3 030, 1 540, and 1 500 (HC=C), and 1 630 cm^{-1} (C=O); δ_H($CDCl_3$) 4.2 (2 H, d, J 5 Hz, CH_2N), 5.35 and 5.4 (2 H, 2 s, CH_2=C), 6.8—7.1 (1 H, br signal, NH), and 7.4—8.1 (5 H, m, ArH); δ_C($CDCl_3$) 46.3 (CH_2N), 118.1 (CH$_2$=C), 127.8, 129.5, 132.7, 134.8, and 139.1 (ArC and C=CH_2), and 169.0 p.p.m. (C=O); m/z 160 (M^+ − Cl, 100%), 105 (86), 77 (52), and 51 (12).

N-(2-*Bromoallyl*)*benzamide* (**10b**) (22.8 g, 95%), m.p. 97—99 °C (lit.,[20] 97—98 °C); $\nu_{max.}$(KBr) 3 250 (NH), 3 025, 1 530, 1 500 (HC=C), and 1 625 cm^{-1} (C=O); δ_H($CDCl_3$) 4.3 (2 H, d, J 5.5 Hz, CH_2N), 5.6 and 5.9 (2 H, 2 s, CH_2=C), 6.6—6.9 (1 H, br signal, NH), and 7.2—7.9 (5 H, m, ArH); δ_C($CDCl_3$) 48.8 (CH_2N), 117.6 (CH$_2$=C), 128.1, 129.5, 130.6, 132.8, and 135.0 (ArC and C=CH_2), and 169.2 p.p.m. (C=O); m/z 160 (M^+ − Br, 88%), 105 (100), 77 (68), 51 (21), and 50 (10).

Preparation of Intermediates (**4**) *and* (**11**) *and Reaction with Electrophiles: General Procedure.*—A solution of phenyl-lithium (5 mmol) in ether at −78 °C was added to a solution of (**5**) or (**10**) (5 mmol) in tetrahydrofuran (20 ml) under argon, and stirring was continued for 30 min at the same temperature. To the resulting mixture was added a solution of lithium naphthalenide (11 mol) in THF and the mixture was stirred for 2 h at −78 °C. The appropriate electrophile (5 mmol) was added and the mixture was allowed to warm to room temperature overnight. It was then hydrolysed with water and extracted with ether (2 × 10 ml) and the organic extract was washed with water and dried (Na_2SO_4). The solvents were evaporated (15 mmHg), naphthalene was removed *in vacuo* (0.001 mmHg; 50 °C bath temperature), and the residue was distilled or recrystallized to afford the products (**6**) and (**12**). In the case of products (**6a**) and (**6b**) the separation of naphthalene was carried out by extraction and work-up. N-Allylaniline (**6a**), b.p. 62—63 °C (0.1 mmHg) [lit.,[21] 218—220 °C (760 mmHg)].

N-(2-*Deuterioallyl*)*aniline* (**6b**), b.p. 62—63 °C (0.1 mmHg); $\nu_{max.}$(neat) 3 400 (NH) and 3 050, 1 600, and 1 500 cm^{-1} (HC=C); δ_H(CCl_4) 3.6 (2 H, s, CH_2N), 3.4 (1 H, br s, NH), 4.9—5.2 (2 H, m, CH_2=C), and 6.3—7.1 (5 H, m, ArH); δ_C(neat) 46.5 (CH_2N), 116.1 (CH$_2$=C), 114.2, 117.6, 129.8, and 149.2 (ArC), and 135.9 p.p.m. (t, J_{CD} 23 Hz, CD); m/z 134 (M^+, 94%), 133 (86), 118 (21), 106 (100), 92 (11), 79 (13), 77 (36), and 65 (12).

N-(2-*Methylthioallyl*)*aniline* (**6c**) (Found: C, 67.2; H, 7.2; N, 7.9. $C_{10}H_{13}NS$ requires C, 67.00; H, 7.31; N, 7.81%), b.p. 103—104 °C (0.1 mmHg); $\nu_{max.}$(neat) 3 400 (NH) and 3 110, 3 040, 1 600, and 1 500 cm^{-1} (HC=C); δ_H(CCl_4) 2.0 (1 H, br s, NH), 2.2 (3 H, s, Me), 3.7 (2 H, s, CH_2N), 4.6 and 5.1 (2 H, 2 s, CH_2=C), and 6.3—7.3 (5 H, m, ArH); δ_C(neat) 14.8 (Me), 49.1 (CH_2N), 105.0 (CH$_2$=C), and 113.0, 117.6, 129.6, 145.3, and 148.4 p.p.m. (ArC and C=CH_2); m/z 179 (M^+, 35%), 132 (10), 130 (21), 106 (100), 105 (13), 79 (11), and 77 (31).

2-*Anilinomethyl*-4-*methylpent*-1-*en*-3-*ol* (**6d**) (Found: C, 76.0; H, 9.5; N, 6.7. $C_{13}H_{19}NO$ requires C, 76.06; H, 9.33; N, 6.82%), b.p. 84—86 °C (0.001 mmHg); $\nu_{max.}$(neat) 3 400 (OH and NH) and 3 040, 1 640, 1 600, and 1 500 cm^{-1} (HC=C); δ_H($CDCl_3$) 0.8 and 0.9 (6 H, 2 d, J 6.5 Hz, 2 × Me), 1.75 (1 H, m, CHC), 2.5 (2 H, br s, OH and NH), 3.8 (2 H, s, CH_2N), 3.85 (1 H, d, J 7 Hz, CHO), 5.1 and 5.15 (2 H, 2 s, CH_2=C), and 6.5—7.4 (5 H, ArH); δ_C($CDCl_3$) 18.4 and 20.2 (2 × Me), 31.9 (CHMe), 46.1 (CH_2N), 80.6 (CHO), 112.5 (CH$_2$C=C), and 113.2, 118.1, 129.9, 148.1, and 149.5 p.p.m. (ArC and C=CH_2); m/z 205 (M^+, 14%), 144 (13), 141 (21), 130 (29), 129 (20), 128 (20), 106 (100), 94 (20), 93 (37), 77 (22), 71 (18), and 43 (12).

2-*Anilinomethyl*-1-*phenylprop*-2-*en*-1-*ol* (**6e**) (Found: C, 80.4; H, 7.0; N, 5.7. $C_{16}H_{17}NO$ requires C, 80.30; H, 7.16; N, 5.85%), b.p. 132—134 °C (0.001 mmHg); $\nu_{max.}$(neat) 3 400 (OH and NH) and 3 010, 1 640, 1 600, and 1 500 cm^{-1} (HC=C); δ_H(CCl_4) 3.3 (2 H, br s, OH and NH), 3.5 (2 H, s, CH_2N), 4.7 (1 H, s, CH), 5.05 and 5.15 (2 H, 2 s, CH_2=C), and 6.2—7.5 (10 H, m, ArH); δ_C($CDCl_3$) 46.8 (CH_2N), 77.0 (CH), 112.9 (CH$_2$=C), and 114.1, 118.6, 127.2, 128.0, 129.1, 130.2, 141.6, 143.8, and 149.3 p.p.m. (ArC and C=CH_2); m/z 239 (M^+, 32%), 221 (15), 220 (51), 146 (36), 145 (55), 131 (26), 130 (17), 129 (21), 117 (20), 116 (15), 115 (21), 106 (82), 105 (40), 104 (32), 94 (100), 93 (49), 91 (17), 79 (21), 78 (13), 77 (87), 65 (14), and 51 (18).

3-*Anilinomethyl*-2-*methylbut*-3-*en*-2-*ol* (**6f**) (Found: C, 75.3; H, 9.1; N, 7.2. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%), b.p. 62—64 °C (0.001 mmHg); $\nu_{max.}$(neat) 3 450 (OH and NH), 3 050, 1 650, 1 600, and 1 500 cm^{-1} (HC=C); δ_H(CCl_4) 1.3 (6 H, s, 2 × Me), 2.6 (2 H, br s, OH and NH), 3.7 (2 H, s, CH_2N), 5.05 and 5.1 (2 H, 2 s, CH_2=C), and 6.4—7.3 (5 H, m, ArH); δ_C($CDCl_3$) 30.5 (2 × Me), 46.2 (CH_2N), 73.7 (CH), 110.1 (CH$_2$=C), 113.9, 123.0, 130.6, 149.1, and 153.8 p.p.m. (ArC and C=CH_2); m/z 191 (M^+, 19%), 173 (10), 172 (10), 158 (11), 106 (100), and 77 (18).

2-*Anilinomethyl*-1,1-*diphenylprop*-2-*en*-1-*ol* (**6g**) an oil; $\nu_{max.}$(neat) 3 410 (OH and NH) and 3 010, 1 640, 1 600, and 1 500 cm^{-1} (HC=C); δ_H($CDCl_3$) 3.5 (2 H, br s, OH and NH), 3.85 (2 H, s, CH_2N), 4.75 and 5.4 (2 H, 2 s, CH_2=C), and 6.5—7.7 (15 H, m, ArH); δ_C($CDCl_3$) 48.9 (CH_2N), 83.6 (CO), 117.3 (CH$_2$=C), 114.7, 119.2, 127.9, 128.6, 128.8, 130.4, 145.8, 149.1, and 151.3 p.p.m. (ArC and C=CH_2); m/z 315 (M^+, 42%), 298 (19), 297 (91), 296 (100), 221 (12), 220 (69), 206 (13), 205 (31), 204 (15), 193 (16), 192 (24), 191 (32) 183 (11), 130 (14), 106 (82), 105 (73), 104 (20), 93 (21), 77 (88), and 51 (17).

2-*Methylene*-N-*phenylpent*-4-*en*-1-*amine* (**6h**) (Found: C, 83.1; H, 8.8; N, 8.0. $C_{12}H_{15}N$ requires C, 83.19; H, 8.73; N, 8.08%), b.p. 42—44 °C (0.001 mmHg); $\nu_{max.}$(neat) 3 390 (NH), 3 060, 1 630, 1 610, and 1 500 cm^{-1} (HC=C); δ_H(CCl_4) 3.3 (1 H, br s, NH), 3.6 (2 H, d, J 5 Hz, CH_2C), 3.8 (2 H, s, CH_2N), 5.0—5.3 (4 H, m, 2 × CH_2=C), 5.55—5.85 (1 H, m, CH), and 6.3—7.2 (5 H, m, ArH); δ_C(CCl_4) 47.0 (CH$_2$C), 53.1 (CH_2N), 113.1 and 118.1 (2 × CH_2=C), 114.2, 116.9, 130.8, 137.7, and 149.2 (ArC and C=CH_2), and 135.2 p.p.m. (CH); m/z 173 (M^+, 74%), 172 (12), 146 (88), 144 (21), 132 (22), 131 (14), 130 (53), 118 (13), 117 (21), 105 (29), 104 (68), 77 (100), 51 (28), 41 (33), and 39 (19).

N-*Allylbenzamide* (**12a**), b.p. 82—84 °C (0.001 mmHg) [lit.,[19] 173—174 °C (14 mmHg)]; $\nu_{max.}$(neat) 3 310 (NH), 3 030, 1 600, 1 520, and 1 490 (HC=C), and 1 640 cm^{-1} (C=O); δ_H(CCl_4) 3.9 (2 H, d, J 5 Hz, CH_2N), 4.9 and 5.1 (2 H, 2 d, J 8 and 12 Hz, CH_2=C), 5.7 (1 H, m, CH), 6.3—6.6 (1 H, br signal, NH), and 7.1—8.0 (5 H, m, ArH); δ_C(neat) 42.8 (CH_2N), 115.9 (CH_2=CH), 127.5, 128.7, 132.0, and 135.2 (ArC), 135.1 (CH), and 168.2 p.p.m. (C=O); *m/z* 161 (M^+, 9%), 105 (100), 77 (51), and 51 (11).

N-(2-*Deuterioallyl*)*benzamide* (**12b**), b.p. 82—84 °C (0.001 mmHg); $\nu_{max.}$(neat) 3 310 (NH), 3 030, 1 600, 1 530, 1 500 (HC=C), and 1 640 cm^{-1} (C=O); δ_H($CDCl_3$) 4.1 (2 H, d, *J* 6 Hz, CH_2N), 5.1 and 5.25 (2 H, 2 s, CH_2=C), 6.25—6.55 (1 H, br signal, NH), and 7.2—8.0 (5 H, m, ArH); δ_C(neat) 42.8 (CH_2N), 115.9 (CH_2=C), 127.5, 128.7, 132.0, and 135.2 (ArC), 134.8 (t, J_{CD} 23 Hz, CD), and 168.2 p.p.m. (C=O); *m/z* 162 (M^+, 8%), 105 (100), 77 (46), and 51 (14).

N-(2-*Methylthioallyl*)*benzamide* (**12c**) (Found: C, 63.6; H, 6.4; N, 6.8. $C_{11}H_{13}NOS$ requires C, 63.74; H, 6.32; N, 6.76%), m.p. 105—106 °C (hexane–$CHCl_3$); $\nu_{max.}$(KBr) 3 290 (NH), 3 010, 1 600, 1 540, 1 500 (HC=C), and 1 640 cm^{-1} (C=O); δ_H($CDCl_3$) 2.2 (3 H, s, Me), 4.2 (2 H, d, *J* 6 Hz, CH_2N), 4.8, 5.3 (2 H, 2 s, CH_2=C), 6.25—6.55 (1 H, br signal, NH), and 7.3—7.9 (5 H, m, ArH); δ_C($CDCl_3$) 15.4 (Me), 45.5 (CH_2N), 106.8 (CH_2=C), 127.7, 129.3, 132.8, 135.7, and 146.1 (ArC and C=CH_2), and 169.2 p.p.m. (C=O); *m/z* 207 (M^+, 2%), 160 (61), 105 (100), 77 (47), and 51 (10).

N-(3-*Hydroxy*-4-*methyl*-2-*methylenepentyl*)*benzamide* (**12d**) (Found: C, 72.1; H, 8.2; N, 6.1. $C_{14}H_{19}NO_2$ requires C, 72.07; H, 8.21; N, 6.00%), m.p. 114—116 °C (hexane–$CHCl_3$); $\nu_{max.}$(KBr) 3 400 (OH and NH), 3 010, 1 590, 1 520, and 1 500 (HC=C), and 1 640 cm^{-1} (C=O); δ_H($CDCl_3$) 0.85 and 1.0 (6 H, 2 d, *J* 6.5 Hz, 2 × Me), 1.9 (1 H, octet, *J* 6.5 Hz, CHC), 2.2 (1 H, br s, OH), 3.95 (1 H, d, *J* 6.5 Hz, CHO), 4.2 (2 H, d, *J* 6 Hz, CH_2N), 5.2 (2 H, s, CH_2=C), 6.7—7.0 (1 H, br signal, NH), and 7.3—8.0 (5 H, m, ArH); δ_C($CDCl_3$) 18.6 and 19.8 (2 × Me), 31.9 (CHMe), 42.0 (CH_2N), 81.3 (CHO), 114.7 (CH_2=C), 127.1, 128.8, 132.0, 135.9, and 147.4 (ArC and C=CH_2), and 168.3 p.p.m. (C=O); *m/z* 233 (M^+, 2%), 190 (16), 162 (11), 160 (12), 106 (14), 105 (100), and 77 (24).

N-(3-*Hydroxy*-2-*methylene*-3-*phenylpropyl*)*benzamide* (**12e**) an oil; $\nu_{max.}$(neat) 3 390 (OH and NH), 3 040, 1 590, 1 530, 1 490 (HC=C), and 1 650 cm^{-1} (C=O); δ_H($CDCl_3$) 3.7 (1 H, br s, OH), 3.9 (2 H, d, *J* 6 Hz, CH_2N), 5.1 (1 H, s, CH), 5.15 and 5.3 (2 H, 2 s, CH_2=C), 6.35—6.65 (1 H, br signal, NH), and 7.2—7.8 (10 H, m, ArH); δ_C($CDCl_3$) 42.2 (CH_2N), 76.5 (CH), 114.1 (CH_2=C), 127.6, 128.1, 129.1, 129.3, 130.3, 132.7, 135.5, 143.7, and 148.2 (ArC and C=CH_2), and 168.1 p.p.m. (C=O); *m/z* 267 (M^+, 3%), 162 (11), 160 (20), 105 (100), 77 (44), and 51 (10).

N-(3-*Hydroxy*-3-*methyl*-2-*methylenebutyl*)*benzamide* (**12f**) (Found: C, 71.3; H, 7.7; N, 6.3. $C_{13}H_{17}NO_2$ requires C, 71.20; H, 7.82; N, 6.39%), b.p. 134—136 °C (0.001 mmHg); $\nu_{max.}$(neat) 3 400 (OH and NH), 3 030, 1 580, 1 520, and 1 490 (HC=C), and 1 640 cm^{-1} (C=O); δ_H($CDCl_3$) 1.4 (6 H, s, 2 × Me), 1.5 (1 H, br s, OH), 4.1 (2 H, d, *J* 5 Hz, CH_2N), 5.0 and 5.15 (2 H, 2 s, CH_2=C), 6.9—7.2 (1 H, br signal, NH), and 7.2—7.9 (5 H, m, ArH); δ_C($CDCl_3$) 30.2 (2 × Me), 41.8 (CH_2N), 73.0 (CO), 111.6 (CH_2=C), 127.1, 129.0, 132.6, 135.0, and 152.4 (ArC and C=CH_2), and 168.6 p.p.m. (C=O); *m/z* 219 (M^+, 2%), 160 (22), 105 (100), 77 (42), and 51 (10).

N-(3-*Hydroxy*-2-*methylene*-3,3-*diphenylpropyl*)*benzamide* (**12g**) (Found: C, 80.4; H, 6.2; N, 4.0. $C_{23}H_{21}NO_2$ requires C, 80.44; H, 6.16; N, 4.08%), m.p. 132—134 °C (hexane–$CHCl_3$); $\nu_{max.}$(KBr) 3 350 (OH and NH), 3 110, 1 590, 1 550, and 1 490 (HC=C), and 1 640 cm^{-1} (C=O); δ_H($CDCl_3$) 1.8 (1 H, br s, OH), 4.2 (2 H, d, *J* 6.5 Hz, CH_2N), 4.75 and 5.4 (2 H, 2 s, CH_2=C), 6.3—6.6 (1 H, br signal, NH), and 7.1—7.7 (15 H, m, ArH); δ_C($CDCl_3$) 43.3 (CH_2N), 82.8 (CO), 118.6 (CH_2=C), 127.2, 127.3, 128.2, 128.4, 129.0, 132.1, 134.7, 146.9, and 151.6 (ArC and C=CH_2), and 169.1 p.p.m. (C=O); *m/z* 343 (M^+, 3%), 266 (10), 222 (11), 204 (13), 161 (16), 160 (45), 105 (100), and 77 (32).

Acid Hydrolysis of Compound (**6c**)*: Isolation of Anilinoacetone* (**13**).—A mixture of *N*-(2-methylthioallyl)aniline (**6c**) (1.7 g, 10 mmol) and 12M hydrochloric acid (5 ml, 60 mmol) was stirred overnight. The reaction mixture was then basified with aqueous 2M sodium hydroxide and extracted with ether (2 × 10 ml). The organic layer was washed with water, dried (Na_2SO_4), and evaporated (15 mmHg). The resulting residue was recrystallized to give the product (**13**) (1.31 g, 88%), m.p. 57—59 °C (hexane–$CHCl_3$) (lit.,[22] 59.5—60.5 °C); $\nu_{max.}$(KBr) 3 390 (NH), 3 020, 1 595, 1 490 (HC=C), and 1 715 cm^{-1} (C=O); δ_H(CCl_4) 2.1 (3 H, s, Me), 3.7 (2 H, s, CH_2), 4.0 (1 H, br s, NH), and 6.3—7.4 (5 H, m, ArH); δ_C($CDCl_3$) 27.5 (Me), 53.8 (CH_2), 112.9, 117.6, 129.9, and 148.1 (ArC), and 205.8 p.p.m. (C=O); *m/z* 149 (M^+, 20%), 106 (100), 79 (15), 77 (25), and 51 (10).

Attempt to Prepare Aliphatic Dianions of the Type (**4**) *and Isolation of Prop-2-ynylamines* (**8**)*: General Procedure*.—The reaction was carried out as described for (**4**) and (**11**) without adding the corresponding electrophile. N-*Isopropyl*-N-*prop*-2-*ynylamine* (**8**; R = Pr^i) (0.29 g, 60%), b.p. 108—110 °C (760 mmHg) [lit.,[9] 110—111 °C (760 mmHg)]; $\nu_{max.}$(neat) 3 380 (NH) and 2 100 cm^{-1} (C≡C); δ_H($CDCl_3$) 0.8 (6 H, d, *J* 7 Hz, 2 × Me), 1.8 (1 H, t, *J* 2 Hz, HC≡C), 2.75 (1 H, heptet, *J* 7 Hz, CHN), 3.1 (2 H, d, *J* 2 Hz, CH_2), and 4.3 (1 H, br s, NH); δ_C(neat) 22.3 (2 × Me), 36.5 (CH_2), 46.8 (CHN), 77.1 (HC≡C), and 82.6 p.p.m. (C≡CH); *m/z* 97 (M^+, 5%), 82 (100), and 42 (10).

N-*Cyclohexyl*-N-*prop*-2-*ynylamine* (**8**; R = c-C_6H_{11})[23] (0.43 g, 63%), b.p. 32—34 °C (0.1 mmHg); $\nu_{max.}$(neat) 3 385 (NH) and 2 120 cm^{-1} (C≡C); δ_H($CDCl_3$) 0.9—1.9 (11 H, m, 5 × ring CH_2 and NH), 2.1 (1 H, t, *J* 2.5 Hz, HC≡C), 2.6 (1 H, quintet, *J* 6.5 Hz, CHN), and 3.4 (2 H, d, *J* 2.5 Hz, CH_2N); δ_C(neat) 25.1, 27.3, and 33.5 (5 × ring CH_2), 36.2 (CH_2N), 55.1 (CHN), 71.8 (HC≡C), and 83.2 p.p.m. (C≡CH); *m/z* 137 (M^+, 13%), 94 (100), 93 (10), 81 (14), and 80 (41).

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