

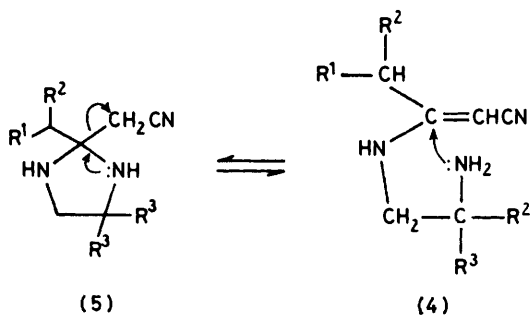
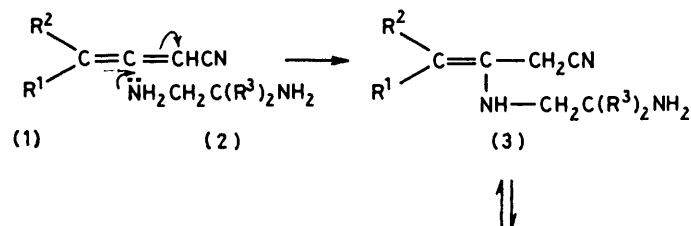
Allenes. Part 38.¹ Imidazolines, Benzimidazoles, and Hexahydrobenzimidazoles from 1,2-Diamines and Allenic or Acetylenic Nitriles

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The double Michael addition of 1,2-diamine to allenic or acetylenic nitriles has been shown to give imidazolines, benzimidazoles, or hexahydrobenzimidazoles in excellent yields *via* conjugated enaminic nitriles.

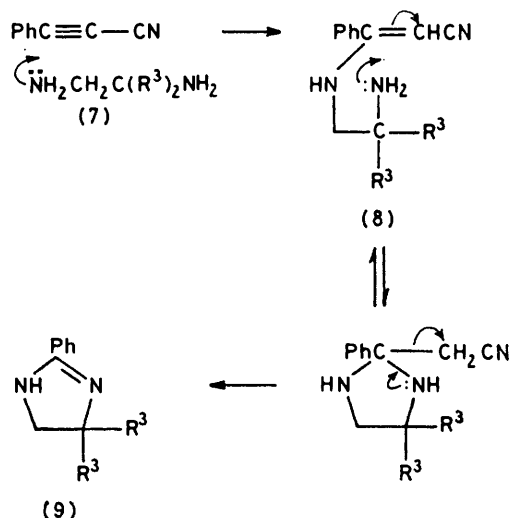
A NUMBER of pharmacologically active substances contain the imidazole or imidazoline ring system, for instance the natural amine histamine, 4-(2-aminoethyl)-imidazole, and the vasodilator drug, tolazoline (2-benzyl-imidazoline). Previously the Michael addition of amines to the central carbon atom of allenic nitriles had been investigated by us² and found to give excellent yields of enaminic nitriles so it was interesting to examine the reactions of 1,2-diamines to see if cyclic products could be obtained. In the event an unusual elimination of acetonitrile gave a new general synthesis of 2-substituted imidazoles³ of potential pharmaceutical interest.

Addition of the allenic nitrile (1) to a 1,2-diamino-



SCHEME 1 ($\text{R}^1 = \text{Me, Et, or Pr}$, $\text{R}^2 = \text{Me, Et, or H}$, and $\text{R}^3 = \text{H or Me}$)

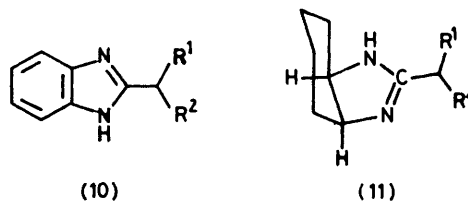
ethane (2) in ether gave, *via* the unconjugated adduct (3), a near quantitative yield of the conjugated enaminic nitrile (4) (see Scheme 1).



SCHEME 2 ($\text{R}^3 = \text{H or Me}$)

The conjugated enaminic nitriles had maximum absorption in the u.v. region at 260–262 nm (ϵ 15 000–20 000), which was similar to that recorded for conjugated enaminic nitriles derived from allenic nitriles and mono-functional primary amines in our previous work, λ_{max} 261–264 nm (ϵ 18 300–20 600).² The n.m.r. spectra showed a strongly shielded proton² near τ 6.3 (Table 4) for $=\text{CHCN}$ and intense bands in the i.r. spectra at 2 190 cm^{-1} for conjugated CN. When the conjugated adducts (4) were heated to 300 °C a second Michael addition effected ring closure to the unstable imidazolidine (5) which eliminated acetonitrile to give excellent yields of the 2-alkyl- or 2,4,4-trialkyl-substituted imidazolines (6).

In a similar manner 3-phenylpropynenitrile (7) reacted at the Michael position and gave first the 3-phenylenaminic nitriles (8) and then the 2-phenylimidazolines (9) by elimination of acetonitrile.

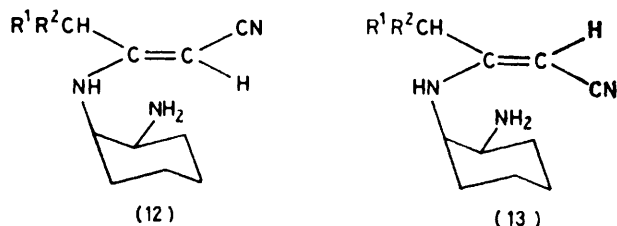


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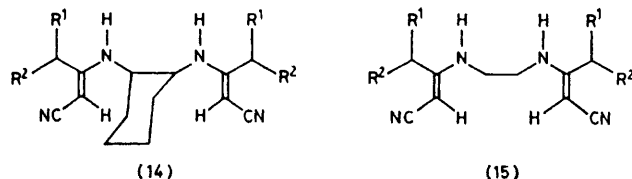
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When *o*-phenylenediamine was used in the reaction 2-alkylbenzimidazoles (10) were obtained. 1,2-Diaminocyclohexane similarly gave 2-alkylhexahydrobenzimidazoles (11) which on the basis of n.m.r. evidence and from mechanistic considerations, are thought probably to be *cis*-fused.

In the latter case the intermediate 2-enenitriles were a mixture of the *E* (12) and the *Z* (13) forms, detected by n.m.r. spectra which gave a singlet at *ca.* 6.23 (=CHCN) for the *E*-compounds and at τ *ca.* 6.10 (=CHCN) for the *Z*-compounds, in a ratio of 1 : 2.



During the preparation of these adducts, high-melting solids (*ca.* 10%) separated out of solution with *m/e* values corresponding to a ratio of allenic nitrile to diamine of 2 : 1, and with the probable structure (14). Bis-adducts of this type (15) could also be obtained by the addition of 1,2-diaminoethane to an excess of allenic nitrile and their exact structure and conditions of their formation are now being investigated and will be the subject of a future publication.



EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 257 spectrophotometer. U.v. spectra were obtained for ethanolic solutions with a Pye-Unicam 1800 spectrometer. N.m.r. spectra were determined with a Varian T60 spectrometer for solutions in deuteriochloroform, with tetramethylsilane as internal standard unless otherwise stated. Ethereal solutions were dried over $MgSO_4$. The allenic nitriles were prepared as previously reported.⁴

2-(1-Ethylpropyl)-2-imidazoline.— 4-Ethylhexa-2,3-dienitrile (3.6 g, 0.03 mol) dissolved in anhydrous diethyl ether (150 ml) was added dropwise with stirring at 0 °C to 1,2-diaminoethane (1.8 g, 0.03 mol) dissolved in diethyl ether (100 ml). The mixture was stirred at room temperature for 2 h, refluxed for 1 h, and left overnight. Removal of the ether by distillation at 760 mmHg and finally at 2 mmHg for 2 h gave crude 3-(2-aminoethyl)amino-4-ethylhex-2-enitrile in quantitative yield as a solid, m.p. 125–128 °C, ν_{max} 3 250 (NH), 2 150 (CN), 1 580 (conj. C=C), and 1 520 and 1 515 cm^{-1} (NH); λ_{max} 262 nm (ϵ 18 500). The crude adduct (5.4 g) was heated quickly to 300 °C in a distillation flask when acetonitrile (1.0 g, 81%) distilled off between 80 and 100 °C (spectroscopically identical with an authentic sample), followed by 2-(1-ethylpropyl)-2-imidazoline (5) (3.8

g, 90%), b.p. 242–243 °C). It solidified in the receiver and on recrystallisation (diethyl ether–petroleum) gave transparent prisms (3.4 g, 80%), m.p. 87–88 °C, ν_{max} (solid melt) 3 100 (NH str) and 1 590 cm^{-1} (NH def). Other data for this compound, (5), and for seven other imidazolines, (1)–(4) and (6)–(8), prepared as above, unless otherwise indicated, are given in Tables 1 and 2. Some of the intermediate enenitriles were characterised and data for these are given in Tables 3 and 4.

2-(1-Methylpropyl)benzimidazole.— 4-Methylhexa-2,3-dienitrile (5.35 g, 0.05 mol) in super-dry ethanol (150 ml) was added dropwise with stirring during 2 h to *o*-phenylenediamine (5.4 g, 0.05 mol, twice recrystallised from water) in ethanol (150 ml) under reflux. After a further 2 h under reflux the mixture was left overnight at room temperature and the ethanol distilled off, finally on a rotary evaporator, to give 3-(2-aminoanilino)-4-methylhex-2-enitrile (9.1 g) 85%), m.p. 169–170 °C (recrystallisation, ethanol–water, (Found: C, 72.5; H, 7.8; N, 19.5). $C_{13}H_{17}N_3$ requires C, 72.6; H, 7.9; N, 19.5%), ν_{max} (Nujol) 3 400 and 3 200 (NH), 2 170 (C=N), 1 610 (C=C), and 1 560 cm^{-1} (NH def); λ_{max} 205 nm (ϵ 19 300), 240 (21 100), and 267 (18 100); 295sh (8 000), τ 8.90 (3 H, t, CH_3CH_2), 8.70 (3 H, d, CH_3CH), 8.47–8.13 (2 H, m, CH_3CH_2), 7.28–6.60 (1 H, m, EtCHMe), 6.27 (2 H, s, $PhNH_2$, disappears on deuteration), 6.15 (1 H, s, =CHCN), 4.43br (1 H, s, NH, disappears on deuteration), and 3.37–2.67 (4 H, m, ArH).

The enitrile (4.3 g, 0.02 mol) was heated to 300 °C and acetonitrile (0.5 g, 61%) distilled off in *ca.* 25 min. The residue solidified on cooling and gave 2-(1-methylpropyl)benzimidazole (2.6 g, 74%), m.p. 226–227 °C (recrystallised H_2O –EtOH)⁵ (Found: C, 75.8; H, 7.8; N, 16.5). $C_{11}H_{14}N_2$ requires C, 75.9; H, 8.0; N, 16.1%), ν_{max} (Nujol) 3 200–2 550br (NH) and 1 520 cm^{-1} (NH def); λ_{max} 207 nm (ϵ 49 500), 244 (9 000), 274 (9 000), and 281 (10 400); τ 9.03 (3 H, t, CH_3CH_2), 8.52 (3 H, d, CH_3CH), 8.37–7.70 (2 H, m, CH_3CH_2), 7.20–6.53 (1 H, m, EtCHMe), 2.87–2.60 (2 H, m, 5,6-ArH), 2.53–2.27 (2 H, m, 4,7-ArH), and 1.45br (1 H, s, NH, disappears on deuteration).

In a similar manner, 4-methylpenta-2,3-dienitrile and *o*-phenylenediamine in super-dry methanol gave, after chromatography on acid alumina (activity 2) and elution with 1 : 4 chloroform–petroleum (40–60 °C), 3-(2-aminoanilino)-4-methylpenta-2-enitrile (55%), m.p. 138–139 °C (recrystallised methanol–water) (Found: C, 71.6; H, 7.6; N, 20.8). $C_{12}H_{15}N_3$ requires C, 71.7; H, 7.5; N, 20.9%), ν_{max} 3 400, 3 200 (NH), 2 170 (CN), 1 605 (C=C), and 1 570 cm^{-1} (NH def); λ_{max} 205 (ϵ 20 500), 240 (21 000), 265 (18 000), and 295sh (9 300); τ 8.67 [6 H, d, $(CH_3)_2CH$], 7.07–6.47 [1 H, m, $(CH_3)_2CH$], 6.35 (2 H, s, $PhNH_2$, disappears on deuteration), 6.20 (1 H, s, =CHCN), 4.43br (1 H, s, NH, disappears on deuteration), and 3.40–2.70 (4 H, m, ArH). The enaminic nitrile as described above gave 2-isopropylbenzimidazole (67%), m.p. 210–212 °C (recrystallised H_2O –MeOH)⁶ (Found: C, 74.9; H, 7.6; N, 17.7). $C_{10}H_{12}N_2$ requires C, 75.0; H, 7.5; N, 17.5%), ν_{max} (Nujol) 3 200–2 550br (NH) and 1 520 cm^{-1} (NH def); λ_{max} 207 nm (ϵ 42 700), 245 (9 600), 274 (9 600), and 281 (10 600); τ 8.52 [6 H, d, $(CH_3)_2CH$], 7.07–6.40 [1 H, m, $(CH_3)_2CH$], 3.37br (1 H, s, NH, disappears on deuteration), 2.87–2.63 (2 H, m, 5,6-ArH), and 2.60–2.27 (2 H, m, 4,7-ArH).

Similarly, hepta-2,3-dienitrile and *o*-phenylenediamine in super-dry ethanol gave, after chromatography (Woelm acid, activity 4), 3-(2-aminoanilino)-hept-2-enitrile (68%),

TABLE 1
 Preparation of 2-imidazolines

$$R^1R^2C=C=CHCN \xrightarrow{\text{diamine}} \overline{N:CR^1R^2 \cdot NH \cdot CH_2 \cdot CR^3_2} + MeCN$$

No.	R ¹	R ²	Diamine *	M.p. (°C)	Yield (%)	λ _{max} /nm	ε	Found (%)			Required (%)		
								C	H	N	C	H	N
(1)	Me	Me	(a)	(b.p. 202 °C) ^b	72 ^a	223	5 200	(m/e 112)			(m/e 112)		
(2)			(b)	98 ^d	76 ^e	220	5 200	68.5	11.2	20.2	68.6	11.4	20.0
(3)	Me	Et	(a)	~30	68 ^e			66.9	11.1	22.3	66.7	11.2	22.2
(4)			(b)	87 ^e	82 ^e	220	5 400	69.9	11.6	18.3	70.1	11.7	18.2
(5)	Et	Et	(a)	87	80	223	5 200	68.6	11.6	19.9	68.6	11.4	20.0
(6)			(b)	89 ^e	83 ^e	221	5 600	71.5	11.5	16.8	71.2	11.7	16.8
(7)	Pr	H	(a)	35	80	223	4 900	67.0	11.0	21.9	66.7	11.2	22.2
(8)			(b)	(b.p. 216 °C)	85 ^e	217	4 000	(m/e 154)			(m/e 154)		

* (a) = 1,2-Diaminoethane (R³ = H), (b) = 1,2-Diamino-2-methylpropane (R³ = Me).

^a Refluxed 2 h. ^b Chromatography gave a semi-solid product. ^c No ether used, addition was at 20 °C and intermediate enenitrile obtained after 15 min at 80 °C. ^d Recrystallised hexane-dichloromethane. ^e Recrystallised pentane-chloroform.

m.p. 132—134 °C, ν_{max} (melt) 3 250 (NH), 2 180 (C≡N), 1 640 (C=C), and 1 570 (NH def); λ_{max} 205 (ε 19 200), 240 (20 300), 265 (17 400), and 295 nm (9 100). The enenitrile without further purification and as described above, gave 2-butylbenzimidazole (71%), m.p. 150 °C [recrystallised CHCl₃-petroleum (b.p. 40—60 °C)],⁷ ν_{max} (Nujol) 3 400—2 600br (NH) and 1 510 cm⁻¹ (NH def); λ_{max} 207 (ε 48 000), 245 (9 800), 274 (9 800), and 281 (11 500); τ 9.12 (3 H, t, CH₃CH₂), 8.92—8.33 (2 H, m, CH₃CH₂), 8.30—7.88 (2 H, m, EtCH₂), 7.00 (2 H, t, CH₂C=N), 2.83—2.57 (2 H, m, 5,6-ArH), 2.53—2.25 (2 H, m, 4,7-ArH), 1.70br (1 H, s, NH, disappears on deuteration).

3-(2-Aminocyclohexylamino)-4-methylhex-2-enenitrile.— 4-Methylhex-2,3-dienenitrile (2.14 g, 0.02 mol) in dichloromethane (30 ml) was added dropwise with stirring to 1,2-diaminocyclohexane (2.3 g, 0.02 mol) in dichloromethane (40 ml) at 20 °C; the mixture was stirred for 6 h. A solid bis-adduct separated out and was filtered off (1.0 g), m.p. 254—256 °C, m/e 328 (C₂₀H₃₂N₄ requires 328). Re-

moval of solvent from the filtrate gave a mixture of conjugated and unconjugated nitriles, which on warming to 80 °C for 10 min gave a mixture of the conjugated *E*- and *Z*-3-(2-aminocyclohexylamino)-4-methylhex-2-enenitrile (3.4 g, 77%), ν_{max} 3 300 (NH), 2 190 (C≡N), 1 590 (C=C), and 1 530 cm⁻¹ (NH def); τ 9.08 (3 H, t, CH₃CH₂), 8.82 and 8.78 (3 H, overlapping d, CH₃CH, *E* and *Z* alkyl to CN), 8.62—8.17 [10 H, m, (CH₂)₄ and CH₃CH₂], 8.02 (2 H, s, NH₂, disappears on deuteration), 7.43—6.67 (3 H, m, HN-CH-CHNH₂ and CH₃CH), 6.23 (0.33 H, s, =CHCN, *cis* to alkyl), 6.10 (0.66 H, s, =CHCN, *trans*- to alkyl), 5.36 and 4.9br (1 H, s, NH, disappears on deuteration).

Similarly, 4-ethylhexa-2,3-dienenitrile and 1,2-diaminocyclohexane in ether gave a solid bis-adduct, m.p. 299—301 °C, and *E*- and *Z*-3-(2-aminocyclohexylamino)-4-ethylhex-2-enenitrile (91%), ν_{max} 3 300 (NH), 2 190 (CN), 1 590 (C=C), and 1 525 cm⁻¹ (NH def); τ 9.05 [6 H, t, (CH₃CH₂)₂CH], 8.87—7.97 [12 H, m, (CH₂)₄ and (CH₃CH₂)₂], 7.80 (2 H, s, NH₂, disappears on deuteration), 7.63—6.67 (3 H, m, HN-CH-CH-NH₂ and Et₂CH), 6.02 (0.33 H, s, =CHCN *cis* to alkyl), 6.14 (0.66 H, s, =CHCN, *trans* to alkyl), 5.16br and 4.77br (1 H, s, NH, disappears on deuteration).

Similarly, 4-methylpenta-2,3-dienenitrile and 1,2-diaminocyclohexane in the absence of solvent, gave rise to an exothermic reaction (the temperature reaching 60 °C) resulting in a mixture of conjugated and unconjugated nitriles, which when heated at 80 °C for 15 min gave a mixture of conjugated *E*- and *Z*-3-(2-aminocyclohexylamino)-4-methylpent-2-enenitrile in quantitative yield, ν_{max} 3 320 (NH), 2 190 (CN), 1 595 (C=C), and 1 550 cm⁻¹ (NH def); τ 8.82—8.80 [2 H, overlapping d, (CH₃)₂CH], 8.57—7.67 [10 H, m, (CH₂)₄ and NH₂], 7.60—6.87 (3 H, m, NH-CH-CH-NH₂ and Me₂CH), 6.32 (0.33 H, s, =CHCN, *cis* to alkyl), 6.17 (0.66 H, s, =CHCN, *trans* to alkyl), 5.40br and 4.63br (1 H, s, NH, disappears on deuteration).

2-*s*-Butyl-4,5,6,7,8,9-hexahydrobenzimidazole.— 3-(2-Aminocyclohexylamino)-4-methylhex-2-enenitrile (3.1 g, 0.014 mol) was distilled at a bath temperature of 300—320 °C when acetonitrile (0.30 g, 52%) was collected, followed by 2-*s*-butyl-4,5,6,7,8,9-hexahydrobenzimidazole (1.65 g, 65%), m.p. 79—81 °C (Found: C, 73.3; H, 11.0; N, 15.7. C₁₁H₂₀N₂ requires C, 73.3; H, 11.1; N, 15.6%), ν_{max} 3 200 (NH) and 1 600 cm⁻¹ (C=N); λ_{max} 219 (ε 3 500); τ 9.03 (3 H, t, CH₃CH₂), 8.85 (3 H, d, CH₃CH), 8.72—7.97 [10 H, m, (CH₂)₄ and CH₃CH₂], 7.93—7.45 (1 H, m, CH₃CH), 7.03 (1 H, m, CH₂CH), and 6.33 (2 H, m, NH and CH₂CH, 1 H disappears on deuteration).

Similarly, 3-(2-aminocyclohexylamino)-4-ethylhex-2-ene-

TABLE 2

N.m.r. data for imidazolines (τ values)

No.	R ¹	R ²	R ³	τ values
(1)	Me	Me	H	8.79 [6 H, d, (CH ₃) ₂ CH], 7.43 [1 H, m, CH(CH ₃) ₂], 6.41 (4 H, s, CH ₂ CH ₂), and 5.20 (1 H, s, NH)
(2)	Me	Me	Me	8.83 [6 H, d, (CH ₃) ₂ CH], 8.78 [6 H, s, (CH ₃) ₂ C], 7.50 [1 H, m, CH(CH ₃) ₂], 6.68 (2 H, s, Me ₂ CCH ₂), and 6.12 (1 H, s, NH)
(3)	Me	Et	H	9.10 (3 H, t, CH ₃ CH ₂), 8.85 (3 H, d, CH ₃ CH), 8.72—8.0 (2 H, m, Me, CH ₂ CH), 7.62 (1 H, sextet, CH ₂ CHCH ₃), 6.38 (4 H, s, CH ₂ CH ₂), and 5.05 (1 H, s, NH)
(4)	Me	Et	Me	9.08 (3 H, t, CH ₃ CH ₂), 8.90 (3 H, d, CH ₃ CH), 8.76 [6 H, s, (CH ₃) ₂ C], 8.47 (2 H, m, CH ₃ CH ₂ CH), 7.68 (1 H, sextet, CH ₂ CHCH ₃), 6.67 (2 H, s, Me ₂ CCH ₂), and 6.35 (1 H, s, NH)
(5)	Et	Et	H	9.02 (6 H, t, CH ₃ CH ₂), 8.63—8.17 (4 H, m, CH ₃ CH ₂), 8.03—7.73 (1 H, m, Et ₂ CH), 6.37 (4 H, s, CH ₂ CH ₂), and 5.45 (1 H, s, NH)
(6)	Et	Et	Me	9.08 (6 H, t, CH ₃ CH ₂), 8.75 [6 H, s, (CH ₃) ₂ C], 8.68—8.22 (4 H, m, CH ₃ CH ₂), 8.12—7.67 (1 H, m, Et ₂ CH), 6.70 (2 H, s, Me ₂ CCH ₂), and 6.00 (1 H, s, NH)
(7)	Pr	H	H	9.05 (3 H, t, CH ₃ CH ₂), 8.83—9.17 [4 H, m, CH ₃ (CH ₂) ₂], 7.75 (2 H, t, CH ₂ C=N), 6.37 (4 H, s, CH ₂ CH ₂), and 5.23 (1 H, s, NH)
(8)	Pr	H	Me	9.05 [3 H, t, CH ₃ (CH ₂) ₃], 8.78 [6 H, s, (CH ₃) ₂ C], 8.78—7.92 [4 H, m, CH ₃ (CH ₂) ₂], 7.67 (2 H, t, CH ₂ C=N), 6.63 (2 H, s, Me ₂ CCH ₂), and 5.77 (1 H, s, NH)

TABLE 3

Data for intermediate enenitriles $R^1R^2CHC(:CHCN)\cdot NH\cdot CH_2\cdot CR_2^3\cdot NH_2$

No.	R ¹	R ²	R ³	M.p. (°C)	$\lambda_{max.}/nm$	ϵ	Found (%)			Required (%)		
							C	H	N	C	H	N
(9)	Me	Me	H		263	15 000 ^a						
(11)	Me	Et	H	71 ^b	261	17 600	64.6	10.3	25.0	64.7	10.2	25.2
(12)	Me	Et	Me	62 ^c	260	18 000						
(13)	Et	Et	H	128	262	18 500						
(14)	Et	Et	Me	41 ^d	260	16 000	63.9	10.6	19.1	63.8	10.6	18.6
(15)	Pr	H	H		261	20 000	64.3	10.0	25.1	64.7	10.2	25.2

^a Eluted from alumina with light petroleum–diethyl ether. ^b Eluted from alumina with pentane–chloroform. ^c Recrystallised hexane–dichloromethane. ^d Recrystallised pentane–chloroform.

nitrile at 300–350 °C gave acetonitrile (75%), and 2-(1-ethylpropyl)-4,5,6,7,8,9-hexahydrobenzimidazole (63%), m.p. 102–104 °C (Found: C, 74.4; H, 10.9; N, 14.4. $C_{12}H_{22}N_2$ requires C, 74.2; H, 11.3; N, 14.4%), $\nu_{max.}$ 3 130 (NH) and 1 600 cm^{-1} (C=N); $\lambda_{max.}$ 221 (ϵ 4 100); τ 9.05 (6 H, t, CH_3CH_2), 8.77–8.12 [12 H, m, $(CH_2)_4$ and $(CH_3CH_2)CH$], 8.05–7.60 (1 H, m, Et_2CH), 7.07 (1 H, m, CH_2CH_2CH), 6.75br (1 H, s, NH, disappears on deuteration), and 6.32 (1 H, m, CH_2CH_2CH).

Similarly, 3-cyclohexylamino-4-methylpent-2-enenitrile at 300–340 °C gave acetonitrile (70%), and 2-isopropyl-4,5,6,7,8,9-hexahydrobenzimidazole (60%), m.p. 93–95 °C (Found: C, 72.1; H, 10.7; N, 16.8. $C_{10}H_{18}N_2$ requires C, 72.4; H, 10.8; N, 16.8%), $\nu_{max.}$ 3 220 (NH) and 1 660 cm^{-1} (C=N); $\lambda_{max.}$ 220 nm (ϵ 3 300); τ 8.82 [6 H, d, $(CH_3)_2CH$], 8.63–8.00 [8 H, m, $(CH_2)_4$], 7.87–7.33 (1 H, m, Me_2CH),

7.07 (1 H, m, CH_2CH_2CH), 6.33 (1 H, m, CH_2CH_2CH), and 6.00br (1 H, s, NH, disappears on deuteration).

3-Phenylpropynenitrile⁸ (with P. M. GREAVES).—1-Bromophenylacetylene (18.1 g, 0.1 mol) was added to a stirred suspension of anhydrous copper(I) cyanide (10 g, 0.11 mol) in dry *NN*-dimethylformamide (50 ml) and the temperature was kept at 50 °C. The mixture was stirred at 50 °C for 1.5 h, cooled, ether added, and the whole poured with vigorous stirring into water (500 ml). The solid was filtered off, washed with ether, and after separation the filtrate was extracted with ether (3 × 20 ml). The combined ethereal extracts were washed with water and dried. Distillation gave 3-phenylpropynenitrile (9.0 g, 70%), b.p. 65 °C at 1 mmHg, $\nu_{max.}$ 2 290 (CN) and 2 155 cm^{-1} (C≡C); $\lambda_{max.}$ 207 (ϵ 22 600), 211 (22 300), 249 (13 900), 262 (21 900), and 275 nm (15 800); and 1,4-diphenylbuta-1,3-diyne (2 g, 16%), b.p. 85–90 °C at 0.3 mmHg, m.p. 84–85 °C (recrystallised from petroleum) (Found: C, 94.9; H, 4.9. $C_{16}H_{10}$ requires C, 95.0; H, 5.0%), $\nu_{max.}$ 2 170 (C≡C); $\lambda_{max.}$ 204 (ϵ 42 800), 218 (32 300), 228 (28 700), 248 (27 500), 260 (27 100), 288 (21 000), 297 (17 200), 306 (31 500), 317 (13 300), and 327 nm (29 500).⁹

2-Phenyl-2-imidazoline.—3-Phenylpropynenitrile (3.8 g, 0.03 mol) in super-dry ethanol (100 ml) was added dropwise to stirred 1,2-diaminoethane (1.8 g, 0.03 mol) in ethanol (150 ml). The mixture was stirred under reflux for 3 h and left overnight. The solvent was removed on a rotary evaporator under reduced pressure and gave a crude product (2.9 g, 66%) which had no band at 2 190 cm^{-1} (CN). Chromatography on alumina (Woelm acid, activity 3) and elution with petroleum–chloroform (3:2) gave 2-phenyl-2-imidazoline¹⁰ (2.6 g, 60%), m.p. 100–101 °C (Found: C, 74.0; H, 6.8; N, 19.2%), $\nu_{max.}$ 3 200–3 100 (NH) and 1 570 cm^{-1} (NH); $\lambda_{max.}$ 205 (ϵ 13 400), 226 (18 300), and 275 nm (6 600); $\tau(CCl_4)$ 6.37 [4 H, s, $(CH_2)_2$], 4.57 (1 H, s, NH, disappears on deuteration), 2.83–2.50 (3 H, m, ArH, 3, 4, and 5), and 2.40–2.10 (2 H, m, ArH, 2 and 6).

2-Phenyl-4,4-dimethyl-2-imidazoline.—3-Phenylpropynenitrile (2.54 g, 0.02 mol) was added dropwise with vigorous shaking and cooling to 1,2-diamino-2-methylpropane (1.76 g, 0.02 mol). The mixture was warmed to 60 °C for 15 min and gave *E*- and *Z*-3-(2-amino-3-methylpropylamino)-3-phenylprop-2-enenitrile (3.4 g, 79.0%), m.p. 60–61 °C (recrystallised from *n*-pentane–chloroform), $\nu_{max.}$ 3 260 (NH), 2 190 (CN), 1 610 (C=C), and 1 560 cm^{-1} (NH def); $\lambda_{max.}$ 223 (ϵ 25 000) and 278 nm (13 000); $\tau(CCl_4)$ 8.88 and 9.02 (2 H, two s, NH_2 of *cis* and *trans* enes, disappear on deuteration), 8.85 [6 H, s, $(CH_3)_2C$], 7.20 (1.5 H, d, $NHCH_2$ *trans* to CN), 6.77 (0.5 H, d, $NHCH_2$ *cis* to CN), 6.13 (1 H, s, =CHCN), 4.71br (1 H, s, NH, disappears on deuteration), and 2.60 (5 H, m, ArH). The mixture of *cis*- and *trans*-enenitriles (3.0 g, 0.014 mol) on heating to 330–350 °C gave acetonitrile (0.39 g, 68%) followed by 2-phenyl-4,4-dimethyl-

TABLE 4

N.m.r. data for intermediate enenitriles $R^1R^2CH\cdot C(:CHCN)\cdot NH\cdot CH_2\cdot CR_2^3\cdot NH_2$ (τ values)

No.	R ¹	R ²	R ³	τ values
(9)	Me	Me	H	8.82 [6 H, d, $(CH_3)_2CH$], 8.42 (2 H, s, NH_2), ^a 7.12–6.62 (5 H, m, Me_2CH and CH_2CH_2), 6.30 (1 H, s, =CHCN), 4.75br (1 H, s, NH) ^b
(10)	Me	Me	Me	8.83 [6 H, s, $(CH_3)_2C$], 8.80 [6 H, d, $(CH_3)_2CH$], 8.47 (2 H, s, NH_2), ^a 7.32–6.83 (3 H, m, CH_3CH and CH_2NH), 6.30 (1 H, s, =CHCN), and 4.73br (1 H, s, NH) ^b
(11)	Me	Et	H	9.07 (3 H, t, CH_3CH_2), 8.83 (3 H, d, CH_3CH), 8.63–8.03 (4 H, m, CH_3CH_2 and NH_2), ^a 7.43–6.77 (5 H, m, CH_3CH and CH_2CH_2), 6.28 (1 H, s, =CHCN) and 4.77br (1 H, s, NH) ^b
(12)	Me	Et	Me	9.05 (3 H, t, CH_3CH_2), 8.81 (3 H, d, CH_3CH), 8.80 [6 H, s, $(CH_3)_2C$], 8.70–8.10 (4 H, m, CH_3CH_2 and NH_2), ^a 7.33–6.72 (3 H, m, CH_3CH and CH_2NH), 6.28 (1 H, s, =CHCN), and 4.83br (1 H, s, NH) ^b
(13)	Et	Et	H	9.08 [6 H, t, $(CH_3CH_2)_2$], 8.65–8.05 [6 H, m, $(CH_3CH_2)_2$ and NH_2], ^a 7.45–6.86 (5 H, m, CH_2CH and CH_2CH_2), 6.21 (1 H, s, =CHCN), and 4.84br (1 H, s, NH) ^b
(14)	Et	Et	Me	9.08 [6 H, t, $(CH_3CH_2)_2$], 8.85 [6 H, s, $(CH_3)_2C$], 8.70–8.17 [6 H, m, $(CH_3)_2CH_2$ and NH_2], ^a 7.43–6.90 (3 H, m, Et_2CH and CH_2NH), 6.22 (1 H, s, =CHCN), and 4.85br (1 H, s, NH) ^b
(15)	Pr	H	H	9.07 (3 H, t, CH_3CH_2), 8.80–8.09 (6 H, m, $CH_3CH_2CH_2$ and NH_2), ^a 7.98–7.33 (2 H, m, $CH_2C=$), 6.23 (1 H, s, =CHCN), and 4.77br (1 H, s, NH) ^b
(16)	Pr	H	Me	9.07 (3 H, t, CH_3CH_2), 8.83 [6 H, s, $(CH_3)_2C$], 8.75–8.17 (4 H, m, $CH_3CH_2CH_2$ and NH_2), ^a 7.90–7.43 (2 H, m, $CH_2C=$), 7.28 (2 H, d, CH_2NH), 6.30 (1 H, s, =CHCN), and 4.83 (1 H, s, NH) ^b

^a 2 H exchange with D_2O . ^b 1 H exchanges with D_2O .

2-imidazoline (1.8 g, 75%), m.p. 96—97 °C (recrystallised from hexane-dichloromethane) (Found: C, 76.0; H, 7.9; N, 15.9. $C_{11}H_{14}N_2$ requires C, 75.9; H, 8.1; N, 16.1%), ν_{\max} 3 140 (NH) and 1 560 (NH def); λ_{\max} 224 (ϵ 19 000) and 265 nm (6 000); $\tau(CCl_4)$ 8.77 [6 H, s, $(CH_3)_2C$], 6.65 (2 H, s, CH_2CMe_2), 4.85br (1 H, s, NH, disappears on deuteration), 2.73 (3 H, m, ArH, 3, 4, and 5), and 2.23 (2 H, m, ArH, 2 and 6); m/e 174 ($C_{11}H_{14}N_2$ requires 174).

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