

## Allenes. Part 46.<sup>1</sup> Synthesis of 1,2-Dihydro-4*H*-3,1-benzoxazines, 4*H*-3,1-Benzoxazines, and 3-Cyanoquinolines from Allenic and Acetylenic Nitriles

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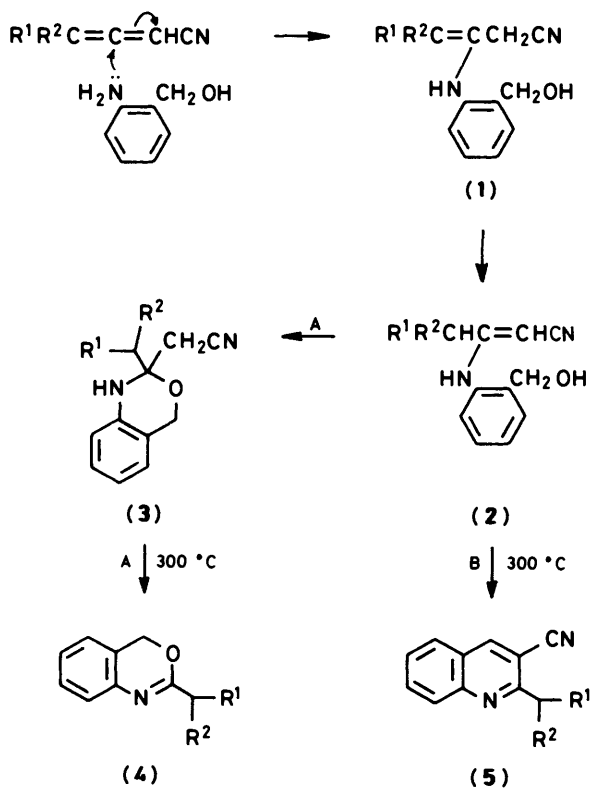
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Allenic nitriles or phenylpropynenitrile react in refluxing ethanol with *o*-aminobenzyl alcohol to give first enaminic nitriles (2) which slowly cyclise to dihydro-4*H*-3,1-benzoxazines (3). The latter eliminate acetonitrile on heating to give 4*H*-3,1-benzoxazines (4) whereas the enaminic nitriles under the same conditions give mainly 2-alkyl-3-cyanoquinolines (5). Mechanistic considerations and spectroscopic details are discussed.

Benzoxazines have been shown to possess interesting pharmacological properties.<sup>2-4</sup> We have investigated a possible synthetic route to the benzoxazines (4) from allenic nitriles and *o*-aminobenzyl alcohol as outlined in Scheme 1.



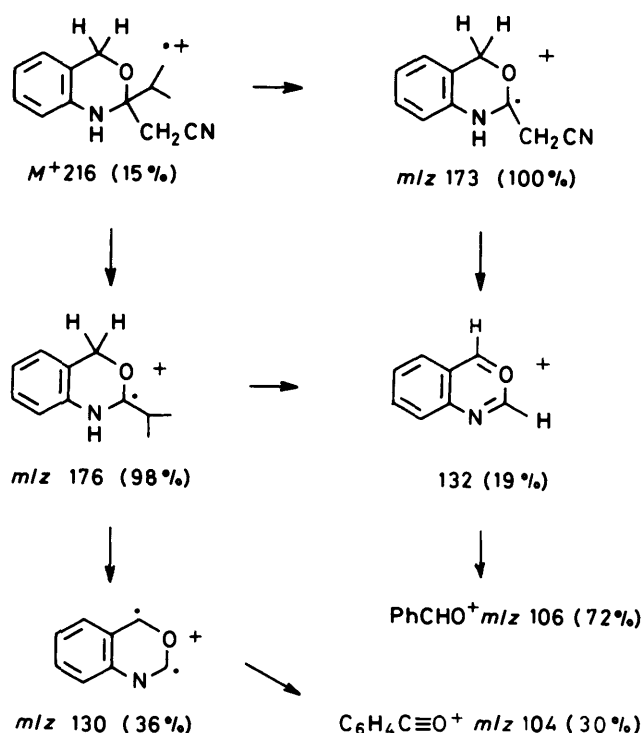
- a : R<sup>1</sup> = Pr, R<sup>2</sup> = H  
 b : R<sup>1</sup> = Me, R<sup>2</sup> = Me  
 c : R<sup>1</sup> = Me, R<sup>2</sup> = Et  
 d : R<sup>1</sup> = Et, R<sup>2</sup> = Et

Scheme 1.

*o*-Aminobenzyl alcohol, in refluxing ethanol, added slowly to the central carbon of the allenic nitrile.<sup>5,6</sup> Examination of the crude product (by chromatography and spectroscopy) indicated that a mixture of the conjugated 2-enitrile (2) and the cyclised dihydro-4*H*-3,1-benzoxazine (3) had been formed in

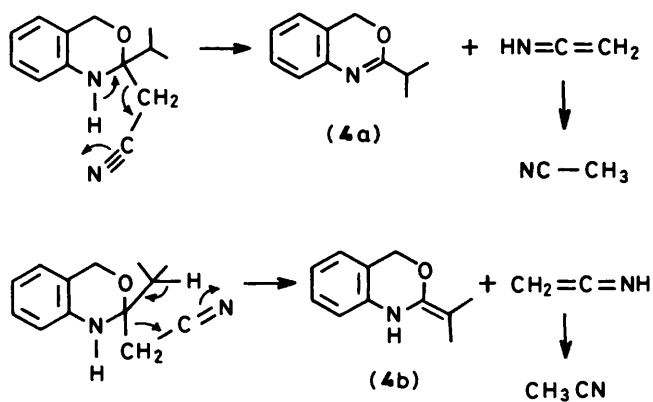
each case, the relative amount of the adduct (2) and heterocycle (3) varying with the time of reflux and the substituents on the allene. After 50–70 h reflux in ethanol, the principal product was the adduct (2), shorter times resulting in recovery of some starting material and traces of the unconjugated adduct (1). After 100 h the main product was the dihydro-oxazine (3) and this became the only product after reflux in ethanol for 8 days.<sup>7</sup> Cyclic intermediates such as (3), resulting from a double Michael addition of a dinucleophile to an allenic nitrile have been postulated by us as occurring in the synthesis of other heterocyclic systems but had hitherto not been isolated or identified.<sup>1,5,6,8,9</sup>

The isomeric enaminic adducts (2) and dihydrobenzoxazines (3) are readily distinguished by their spectroscopic data. The adducts (2) have twin peaks at *ca.* 3 260 and 3 380 cm<sup>-1</sup> for the NH and OH groups as well as an intense peak just below 2 200 cm<sup>-1</sup> for the conjugated nitrile (NH–CH=CH–CN) whereas the dihydrobenzoxazines (3) show a single peak at 3 250 cm<sup>-1</sup> for

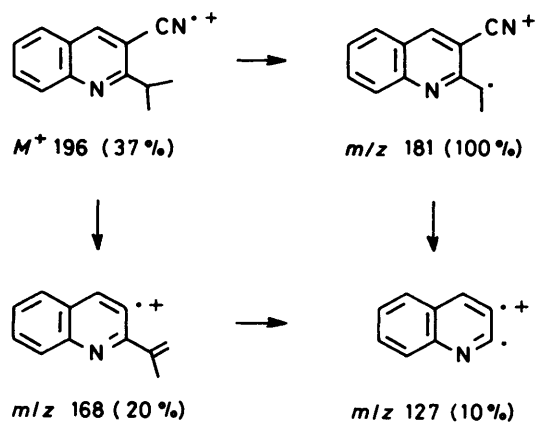


Scheme 2.

the NH group and a less intense peak at  $2250\text{ cm}^{-1}$  for the methylenitrile ( $\text{CH}_2\text{CN}$ ) in the i.r. spectrum. In the u.v. spectrum the maximum at longest wavelength for adducts (2) is an intense band at  $\lambda_{\text{max}}$ , 275 nm whereas the dihydrobenzoxazines show a broad, low intensity peak at ca. 300 nm with a minimum at ca. 270 nm. Diagnostic signals in the n.m.r. are a 1 H singlet for the shielded alkenic proton at about  $\delta$  4.20 typical of the *E*-isomer of the enaminic adduct (2)<sup>5</sup> and a 2 H singlet corresponding to  $\text{CH}_2\text{CN}$  at  $\delta$  2.62 in the dihydrobenzoxazine (3). The mass spectral fission pattern confirmed the structure of (3) (Scheme 2). The molecular ion (for the isopropyl side-chain  $m/z$  216, 15%) loses isopropyl to give the base peak ( $m/z$  173, 100%) or alternatively loses the acetonitrile radical to give the intense peak ( $m/z$  176, 98%). Both fragments degrade further by loss of the remaining side-chain to give peaks at  $m/z$  132 (19%) and 130 (36%). The intense peak at  $m/z$  106 (72%) could result from loss of HCN and transfer of hydrogen and this loses CO to give the benzene radical ion ( $m/z$  77, 35%). The dihydrobenzoxazines are readily converted into the corresponding benzoxazines (4) in about 80% yield on heating to 250–270 °C for 10 min followed by distillation. Elimination of acetonitrile by two competing, concerted mechanisms is possible (Scheme 3).<sup>1</sup> However we have no evidence that compound (4b) is present in the product.



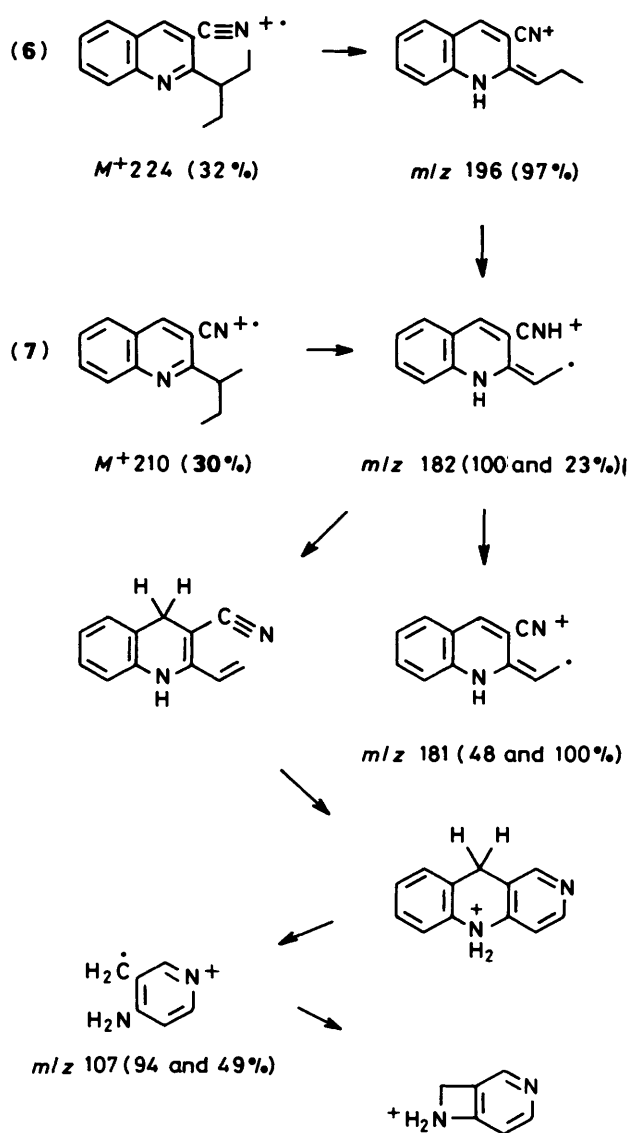
When the enaminic nitrile adducts (2) containing small quantities of the dihydrobenzoxazines (3) (from the reflux of ethanolic solutions of starting materials for 50–70 h) were heated at 300 °C and distilled, two products were obtained, the minor product being the benzoxazine (4). The major product showed a nitrile band in the i.r. near  $2220\text{ cm}^{-1}$  and an n.m.r.



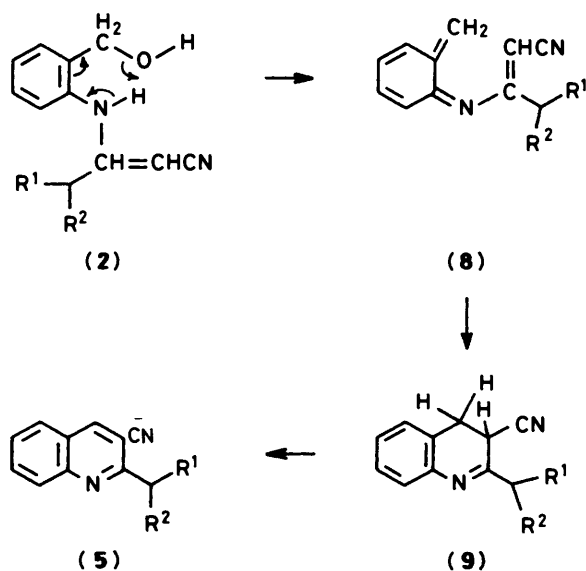
signal at  $\delta$  8.42 typical of a strongly deshielded proton at the 4-position of a 3-cyanoquinoline.<sup>10</sup> The mass spectra are rationalised as follows  $M^+$  (for an isopropyl side-chain) at  $m/z$  196 (37%) loses a methyl radical to give the base peak at  $m/z$  181 (100%). Alternatively,  $M^+$  196 gives  $m/z$  168 (20%) by elimination of HCN and  $\text{H}^\cdot$ , which loses the side-chain ( $-41$ ) to give  $m/z$  127 (10%) which also results from loss of ethene and HCN from  $m/z$  181. Finally the  $m/z$  127 fragment degrades to the phenylacetylene radical ( $m/z$  101, 5%) and then the benzene radical ion ( $m/z$  77, 7%). 2-(1-Methylpropyl) and 2-(1-ethylpropyl)-3-cyanoquinolines (7) and (6) give the expected McLafferty rearrangement followed by an unusual electrocyclic reaction, hydrogen transfer and loss of benzene to give the 4-amino-3-methylpyridine ion,  $m/z$  107.

The 2-alkyl-3-cyanoquinolines are obtained in 60–70% yield, thus affording access to these little known heterocycles.

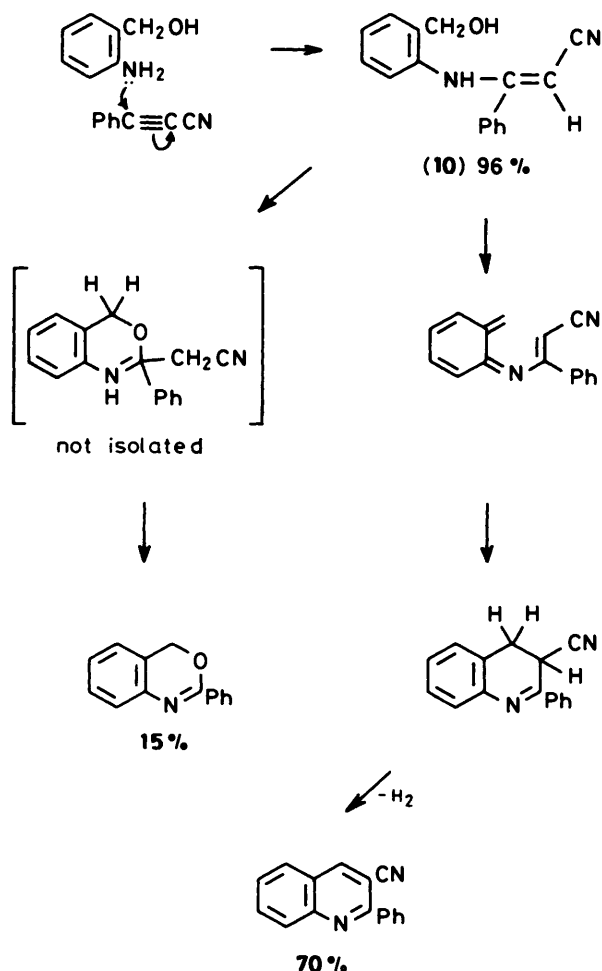
The reaction must proceed through three stages from the



adduct (2): (1) dehydration; (2) ring closure; and (3) dehydrogenation. A number of mechanistic schemes can be envisaged, the following (Scheme 4) being the most plausible, taking into consideration that we are dealing with a pyrolytic



conversion in the absence of a polar solvent. Dehydration of the enaminic nitrile (2) gives the unstable triene (8) which undergoes a fast thermal electrocyclic reaction (disrotatory) to the dihydroquinoline (9) and then a *cis*-elimination of hydrogen



Scheme 5.

to give the 2-alkyl-3-cyanoquinoline (5). The n.m.r. of the crude products shows the presence of some dihydroquinoline (9).

In order to investigate a similar reaction of acetylenic nitriles, phenylpropynenitrile was heated under reflux with *o*-aminobenzyl alcohol in alcoholic solution for 62 h which resulted in the crystalline adduct (10) in 96% yield. The adduct (10) was heated at 260–270 °C for 20 min and was distilled to yield 2-phenyl-4H-3,1-benzoxazine (15%) as an oil and 2-phenyl-3-cyanoquinoline (70%) as white crystals thus demonstrating the general applicability of this reaction sequence to acetylenic nitriles.\*

### Experimental

I.r. spectra were determined with a Perkin-Elmer 337 spectrophotometer. U.v. spectra were determined for ethanolic solutions with a Beckman 25 spectrophotometer. N.m.r. spectra were determined with a Perkin-Elmer R12A spectrophotometer for solutions in deuteriochloroform unless otherwise stated, with tetramethylsilane as the internal standard. The allenic nitriles and phenylpropyne nitrile were prepared as previously described.<sup>7</sup> Commercial 2-aminobenzyl alcohol was recrystallised from ethanol–methylene dichloride until it gave one spot on t.l.c.

**2-Butyl-2-cyanomethyl-1,2-dihydro-4H-3,1-benzoxazine (3a).**—(a) 2-Aminobenzyl alcohol (3.7 g, 30 mmol) and hepta-2,3-dienenitrile (3.2 g, 30 mmol) were dissolved in ethanol and refluxed with stirring for 100 h. A sample of the reaction was checked by t.l.c. which indicated traces of starting material and the formation of two new compounds. Removal of the solvent under reduced pressure gave a crude product (6.8 g) as an oil and part of this material (2.5 g) was chromatographed on alumina (300 g, activity 3). Elution with hexane–ethyl acetate (9:1) gave 2-butyl-2-cyanomethyl-1,2-dihydro-4H-3,1-benzoxazine (1.9 g, 76%) (Found: C, 73.0; H, 7.85; N, 12.25. C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 73.04; H, 7.82; N, 12.17%);  $\nu_{\max}$  3 250 (NH) and 2 260 cm<sup>-1</sup> (C≡N);  $\lambda_{\max}$  208, 246, and 298 nm ( $\epsilon$  22 800, 13 400, and 3 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>);  $\delta_{\text{H}}$  0.85 (3 H, t, MeCH<sub>2</sub>), 1.15–1.55 (4 H, m, MeCH<sub>2</sub>CH<sub>2</sub>), 1.52–1.82 (2 H, m, CH<sub>2</sub>C=), 2.62 (2 H, s, CH<sub>2</sub>CN), 4.25 (1 H, br s, NH, exchanges D<sub>2</sub>O), 4.75 (2 H, s, CH<sub>2</sub>O), and 6.50–7.15 (4 H, m, ArH).

Elution with hexane–ethyl acetate (8:2) gave (after rechromatography) 3-(2-hydroxymethyl-anilino)hept-2-enenitrile (2a) (0.5 g, 7%) (Found: C, 73.2; H, 7.7; N, 12.3. C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 73.04; H, 7.83; N, 12.17%);  $\nu_{\max}$  3 350–3 250 (OH, NH), 2190 (CN), and 1 590 cm<sup>-1</sup> (C=C);  $\lambda_{\max}$  205, 339, and 277 nm ( $\epsilon$  12 000, 9 000, and 8 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>);  $\delta_{\text{H}}$  0.80 (3 H, t, MeCH<sub>2</sub>), 1.10–1.70 (4 H, m, MeCH<sub>2</sub>CH<sub>2</sub>), 2.30 (2 H, t, CH<sub>2</sub>C=), 3.40 (1 H, br s, OH, disappears on deuteration), 4.20 (2 H, s, CH<sub>2</sub>OH), 4.60 (1 H, s, =CHCN), 6.20–7.20 (4 H, m, ArH), and 8.00 (1 H, s, NH, exchanges D<sub>2</sub>O).

(b) *o*-Aminobenzyl alcohol (0.62 g, 5 mmol) and hepta-2,3-dienenitrile (0.54 g, 5 mmol) were allowed to react as in (a) but for an extended reaction time of 150 h. Chromatography of the reaction product gave the dihydro-4H-3,1-benzoxazine (3a) (0.93 g, 80%) with identical spectroscopic properties to the compound obtained in (a).

**2-Butyl-4H-3,1-benzoxazine (4a).**—Part of the crude mixture (4.3 g) consisting mainly of 2-butyl-2-cyanomethyl-1,2-dihydro-4H-3,1-benzoxazine (3a) obtained above was heated at 300 °C. A distillate was collected which was dissolved in methylene

\* Acetylenic nitriles with different substituents give the same reactions as phenylpropynenitrile, S. R. Landor and R. Roberts, unpublished work.

dichloride (200 ml), washed with water (3 × 60 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent and distillation of the residue gave 2-butyl-4H-3,1-benzoxazine (2.7 g, 78%), b.p. 165 °C at 760 mmHg (Found: C, 75.95; H, 7.7; N, 7.25. C<sub>12</sub>H<sub>15</sub>NO requires C, 76.19; H, 7.93; N, 7.40%; v<sub>max</sub>, 1 620 cm<sup>-1</sup>; λ<sub>max</sub>, 206, 235, and 286 (ε 17 400, 10 900, and 1 900 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.92 (3 H, t, MeCH<sub>2</sub>), 1.2–1.8 (4 H, m, MeCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>), 2.22 (2 H, t, CH<sub>2</sub>CH<sub>2</sub>), 4.22 (2 H, s, CH<sub>2</sub>O), and 6.6–7.4 (4 H, m, ArH). A second fraction (0.4 g), which contained 2-butyl-3-cyanoquinoline and benzoxazine, was not purified further.

**2-Cyanomethyl-2-isopropyl-1,2-dihydro-4H-3,1-benzoxazine (3b).**—2-Aminobenzyl alcohol (4.92 g, 0.04 mol) and 4-methylpenta-2,3-dienitrile (3.72 g, 0.04 mol) in ethanol (165 ml) heated under reflux for 144 h and evaporated to dryness. A portion (3 g) was chromatographed on silica gel (125 g) and eluted with hexane-chloroform (9:1) to give 2-cyanomethyl-2-isopropyl-1,2-dihydro-4H-3,1-benzoxazine (2.34 g, 78%), m.p. 57–58 °C (Found: C, 72.2; H, 7.5; N, 12.75. Calc. for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O: C, 72.22; H, 7.40; N, 12.96%; v<sub>max</sub>, 3 250 (NH) and 2 260 cm<sup>-1</sup> (C≡N); λ<sub>max</sub>, 209, 246, and 298 nm (ε 21 600, 11 200, and 2 400 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 1.06 (6 H, d, Me<sub>2</sub>CH), 2.23 (1 H, septet, Me<sub>2</sub>CH), 2.73 (2 H, s, CH<sub>2</sub>CN), 4.21 (1 H, br s, NH, exchanges D<sub>2</sub>O), 4.75 (2 H, s, CH<sub>2</sub>O), and 6.5–7.2 (4 H, m, ArH).\*

**2-Isopropyl-4H-3,1-benzoxazine (4b) and 3-Cyano-2-isopropylquinoline (5b).**—The crude mixture (5.3 g, obtained above) was distilled slowly, bath temp. 300–320 °C, to give 2-isopropyl-4H-3,1-benzoxazine (3.4 g, 80%), b.p. 130 °C at 760 mmHg (Found: C, 75.8; H, 7.2; N, 7.7. C<sub>11</sub>H<sub>13</sub>NO requires C, 75.42; H, 7.42; N, 7.40%; λ<sub>max</sub>, 205, 235, and 286 nm (ε 16 200, 11 300, and 2 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 1.19 (6 H, d, Me<sub>2</sub>CH), 2.3 (1 H, septet, CHMe<sub>2</sub>), 4.85 (2 H, s, CH<sub>2</sub>O), and 6.6–7.4 (4 H, m, ArH). Also isolated as a white crystalline solid in the condenser was 3-cyano-2-isopropylquinoline (0.7 g, 13%), m.p. 96–98 °C (Found: C, 79.6; H, 5.9; N, 14.4. C<sub>13</sub>H<sub>12</sub>N<sub>2</sub> requires C, 79.59; H, 6.12; N, 14.29%; v<sub>max</sub>, 2 200 cm<sup>-1</sup> (C≡N); λ<sub>max</sub>, 214, 241, and 280 nm (ε 30 500, 24 000, and 4 200 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 1.13 (6 H, d, Me<sub>2</sub>CH), 3.64 (1 H, septet, CHMe<sub>2</sub>), 7.3–8.2 (4 H, m, ArH), and 8.45 (1 H, s, N=C–C=CH).

**2-(1-Methylpropyl)-4H-3,1-benzoxazine (4c) and 3-Cyano-2-(1-methylpropyl)quinoline (5c).**—2-Aminobenzyl alcohol (4.92 g, 0.04 mol) and 4-methylpenta-2,3-dienitrile (4.28 g, 0.04 mol) in ethanol (80 ml) were heated under reflux for 66 h to give, after chromatography, recovered allenic nitrile (0.4 g, 9%), impure 2-cyanomethyl-2-(1-methylpropyl)-2,3-dihydro-4H-3,1-benzoxazine (3c) [contaminated by the adduct (2c)] (2.7 g, 27%) and 3-(2-hydroxymethylanylino)-4-methylhex-2-enitrile (2c) (5.85 g, 64%) (Found: C, 73.21; H, 8.04; N, 12.11. C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 73.04; H, 7.83; N, 12.17%; v<sub>max</sub>, 3 400 (OH) and 3 280 cm<sup>-1</sup> (NH); λ<sub>max</sub>, 207, 244, and 274 nm (ε 15 500, 8 400, and 8 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.98 (3 H, t, MeCH<sub>2</sub>), 1.4 (3 H, d, CHMe), 1.59 (2 H, quintet, CHCH<sub>2</sub>Me), 2.80 (1 H, br s, OH), 2.86 (1 H, sextet, CH<sub>2</sub>CHMe), 4.30 (1 H, s, =CH), 4.51 (2 H, s, CH<sub>2</sub>OH), 7.2 (1 H, br s, NH, exchanges D<sub>2</sub>O), 6.7–7.3 (4 H, m, ArH); m/z 230 (M<sup>+</sup>). The crude mixture (7 g) was distilled (bath temp. 300–310 °C) to give 2-(1-methylpropyl)-4H-3,1-benzoxazine (4c) (1.8 g, 31%), b.p. 158 °C at 760 mmHg (Found: C, 76.45; H, 8.25; N, 7.8. C<sub>12</sub>H<sub>15</sub>NO requires C, 76.19; H, 7.93;

N, 7.40%; λ<sub>max</sub>, 203, 234, and 284 nm (ε 17 300, 11 800, and 2 600 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.90 (3 H, t, MeCH<sub>2</sub>), 1.14 (3 H, d, CHMe), 2.1 (1 H, sextet, CH<sub>2</sub>CHMe), 4.40 (2 H, s, CH<sub>2</sub>OH), and 6.6–7.4 (4 H, m, ArH). A second fraction, 3-cyano-2-(2-methylpropyl)quinoline (5c), was also obtained (3.7 g, 58%), b.p. 180 °C at 760 mmHg (Found: C, 79.9; H, 6.6; N, 13.6. C<sub>14</sub>H<sub>14</sub>N<sub>2</sub> requires C, 80.0; H, 6.67; N, 13.33%; v<sub>max</sub>, 2 215 cm<sup>-1</sup> (C≡N); λ<sub>max</sub>, 214, 243, and 280 nm (ε 21 800, 27 800, and 3 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.92 (3 H, t, MeCH<sub>2</sub>), 1.42 (3 H, d, CHMe), 1.85 (2 H, quintet, MeCH<sub>2</sub>), 3.55 (1 H, sextet, CH<sub>2</sub>CHMe), 7.3–8.2 (4 H, m, ArH), and 8.44 (1 H, s, N≡C–C≡CH).

**2-Cyanomethyl-2-(1-ethylpropyl)-1,2-dihydro-4H-3,1-oxazine (3d).**—2-Aminobenzyl alcohol (3.69 g, 0.03 mol) and 4-ethylhexa-2,3-dienitrile (3.63 g, 0.03 mol) in ethanol (100 ml) refluxed for 50 h gave, after chromatography, 3-ethyl-3-(2-hydroxymethylanylino)hex-2-enitrile (2d) (5.56 g, 76%), m.p. 122 °C (Found: C, 73.5; H, 8.1; N, 11.25. C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O requires C, 73.77; H, 8.20; N, 11.47%; v<sub>max</sub>, 3 360 (OH), 3 250 (NH), and 2 190 cm<sup>-1</sup> (CN); λ<sub>max</sub>, 207, 238, and 276 nm (ε 10 900, 7 500, and 10 200 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.99 (6 H, t, 2 × MeCH<sub>2</sub>), 1.59 (4 H, quintet, 2 × CH<sub>2</sub>Me), 2.40 (1 H, s, OH, exchanges D<sub>2</sub>O), 2.78 (1 H, quintet, CH<sub>2</sub>CHCH<sub>2</sub>), 4.48 (1 H, s, C=CH), 4.57 (2 H, s, CH<sub>2</sub>OH), and 6.8–7.4 (5 H, m, ArH and NH; latter exchanges D<sub>2</sub>O).

**3-Ethyl-3-(2-hydroxymethylanylino)hex-2-enitrile (2d)** (1.22 g, 5 mmol) refluxed for 140 h in ethanol (10 ml) gave, after chromatography of the reaction product, 2-cyanomethyl-2-(1-ethylpropyl)-1,2-dihydro-4H-3,1-benzoxazine (3d) (1.0 g, 82%), m.p. 42 °C (Found: C, 73.8; H, 8.15; N, 11.68. C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O requires C, 73.77; H, 8.20; N, 11.47%; v<sub>max</sub>, 3 250 (NH) and 2 250 cm<sup>-1</sup> (CN); λ<sub>max</sub>, 210, 246, and 298 (ε 23 400, 13 800 and 3 100 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.94 (6 H, t, 2 × MeCH<sub>2</sub>), 1.40 (4 H, quintet, 2 × MeCH<sub>2</sub>), 2.15 (1 H, quintet, CH<sub>2</sub>CHCH<sub>2</sub>), 2.60 (2 H, s, CH<sub>2</sub>CN), 4.35 (1 H, br s, NH, exchanges D<sub>2</sub>O), 4.75 (2 H, s, CH<sub>2</sub>O), and 6.5–7.2 (4 H, m, ArH).

**2-(1-Ethylpropyl)-4H-3,1-benzoxazine (4d).**—2-Cyanomethyl-2-(1-ethylpropyl)-1,2-dihydro-4H-3,1-benzoxazine (0.9 g) was distilled at 250 °C to give 2-(1-ethylpropyl)-4H-3,1-benzoxazine (0.6 g, 80%), b.p. 165 °C at 760 mmHg (Found: C, 76.7; H, 8.6; N, 7.2. C<sub>13</sub>H<sub>17</sub>NO requires C, 76.84; H, 8.37; N, 6.90%; v<sub>max</sub>, 204, 230, and 284 (ε 15 000, 13 000, and 2 800 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.82 (6 H, t, 2 × MeCH<sub>2</sub>), 1.85 (4 H, quintet, MeCH<sub>2</sub>CH), 2.11 (1 H, quintet, CH<sub>2</sub>CHCH<sub>2</sub>), 4.04 (2 H, s, CH<sub>2</sub>O), and 6.5–7.3 (4 H, m, ArH).

**3-Cyano-2-(1-ethylpropyl)quinoline (5d).**—4-Ethyl-3-(2-hydroxymethylanylino)hex-2-enitrile (4.8 g, 0.019 mol) was heated at bath temp. 300–310 °C and distilled to give first benzoxazine (1.2 g, 30%) and secondly 3-cyano-2-(1-ethylpropyl)quinoline (2.9 g, 66%), b.p. 184 °C at 760 mmHg (Found: C, 80.1; H, 7.0; N, 12.3. C<sub>15</sub>H<sub>16</sub>N<sub>2</sub> requires C, 80.35; H, 7.14; N, 12.50%; v<sub>max</sub>, 2 220 cm<sup>-1</sup>; λ<sub>max</sub>, 215, 243, and 280 (ε 22 700, 29 000, and 3 100 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 0.84 (6 H, t, 2 × MeCH<sub>2</sub>), 1.88 (4 H, quintet, 2 × MeCH<sub>2</sub>), 3.25 (1 H, quintet, CH<sub>2</sub>CHCH<sub>2</sub>), 7.1–8.2 (4 H, m, ArH), and 8.44 (1 H, s, N=C–C=CH).

**2-Phenyl-4H-3,1-benzoxazine and 3-Cyano-2-phenylquinoline.**—2-Aminobenzyl alcohol (3.69 g, 0.03 mol) and 3-phenylpropynitrile (3.81 g, 0.03 mol) refluxed in ethanol (125 ml) for 62 h gave crystalline 3-(2-hydroxymethylanylino)-3-phenylprop-2-enitrile (10) (7.2 g, 96%), m.p. 137 °C (Found: C, 76.75; H, 5.3; N, 11.15; M<sup>+</sup>, 250. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O requires C, 76.80; H, 5.60; N, 11.20%; M<sup>+</sup>, 250; v<sub>max</sub>, 3 400 (OH), 3 210 (NH), and 2 195 cm<sup>-1</sup> (CN); λ<sub>max</sub>, 203, 240, and 300 (ε 29 800, 13 700, and 5 900); δ(Me<sub>2</sub>SO–CDCl<sub>3</sub>) 2.70 (1 H, br s, OH,

\* The diastereotopic methyl groups and protons in this chiral 1,2-dihydro-4H-3,1-benzoxazine do not show non-equivalence on the 60 MHz n.m.r. spectrum as the shielding effect of the oxygen and nitrogen are nearly equivalent<sup>1</sup> and both differential chemical shifts and coupling constants are too small for resolution.

exchanges D<sub>2</sub>O), 4.38 (1 H, s, =CHCN), 5.57 (2 H, s, CH<sub>2</sub>OH), 7.0—7.8 (4 H, m, ArH), and 7.70 (1 H, br s, NH).

3-(2-Hydroxymethylanilino)-3-phenylprop-2-enenitrile (5.2 g, 0.02 mol) heated for 20 min and distilled at 260—270 °C gave 2-phenyl-4H-3,1-benzoxazine (0.6 g, 14%), b.p. 206 °C at 760 mmHg (Found: C, 79.2; H, 5.6; N, 6.3. C<sub>14</sub>H<sub>11</sub>NO requires C, 80.40; H, 5.26; N, 6.70%); δ 4.05 (2 H, s, CH<sub>2</sub>O) and 6.50—7.70 (9 H, m, ArH) and 3-cyano-2-phenylquinoline (3.4 g, 74%), m.p. 186 °C (Found: C, 83.55; H, 4.5; N, 12.35. C<sub>16</sub>H<sub>10</sub>N<sub>2</sub> requires C, 83.47; H, 4.43; N, 12.17%); ν<sub>max.</sub> 2 220 cm<sup>-1</sup> (CN); λ<sub>max.</sub> 213, 241, and 260 nm (ε 29 000, 34 900, and 35 400 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); δ 7.2—8.3 (9 H, m, ArH), and 8.62 (1 H, s, N=C=CH).

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