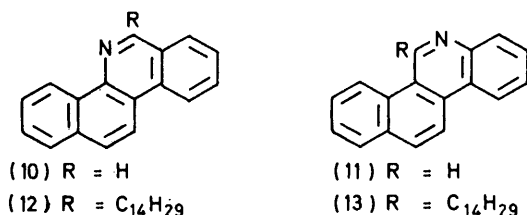
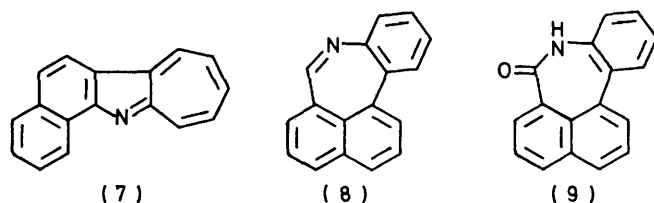
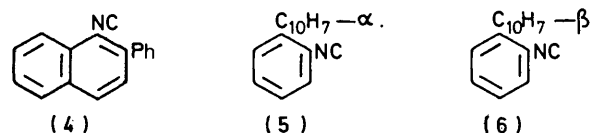
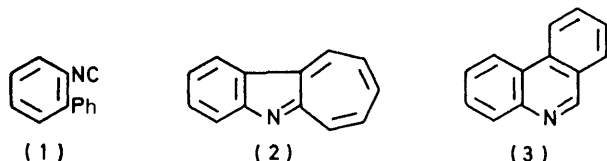


## Ring-closure Isomerisations for 1-Isocyano-2-phenyl-, 1-(2-Isocyano-phenyl)- and 2-(2-Isocyanophenyl)-naphthalene

By Joseph H. Boyer and Jayanti R. Patel, Department of Chemistry, University of Illinois, Chicago Circle Campus, Chicago, Illinois 60680, U.S.A.

Benzo[*g*]cyclohept[*b*]indole (7) and benzo[*e*]naphth[1,8-*cd*]azepine (8) were produced from 1-isocyano-2-phenylnaphthalene (4) and 1-(2-isocyanophenyl)naphthalene (5), respectively, upon irradiation at 254 nm in cyclohexane. Benzo[*c*]phenanthridine (10), the heterocycle (8), and benzo[*i*]phenanthridine (11) were produced from the isocyanides (4), (5), and 2-(2-isocyanophenyl)naphthalene (6), respectively, upon irradiation at 300 nm in methanol. Thermolysis isomerised each isocyanide into the corresponding aryl cyanide and the isocyanide (4) into the heterocycles (7) and (10). Solvent (tetradecane) participation accounted for the formation of 6-tetradecylbenzo[*c*]phenanthridines (12) and 5-tetradecylbenzo[*i*]phenanthridines (13) from the isocyanides (4) and (6), respectively. Irradiation slowly consumed 1-isothiocyano-2-phenylnaphthalene and 2-(2-isothiocyano-phenyl)naphthalene but desulphurisation into an isocyanide was not detected.

CYCLOHEPT[*b*]INDOLE (2) and phenanthridine (3) have been obtained from 2-isocyanobiphenyl (1) upon irradiation in cyclohexane or methanol.<sup>1,2</sup> Similar products were obtained by the thermolysis of 1-isocyano-2-phenylnaphthalene (4), 1-(2-isocyanophenyl)naphthalene (5), and 2-(2-isocyanophenyl)naphthalene (6).<sup>3</sup>



### RESULTS

Irradiation at 254 nm in cyclohexane left both 1-isothiocyano-2-phenylnaphthalene and 2-(2-isothiocyano-phenyl)naphthalene largely unconverted and gave no identifiable product.† Similar irradiation produced

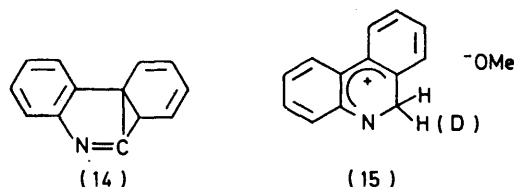
† Photo-desulphurisation of 2-isothiocyano-phenyl in cyclohexane has previously been reported.<sup>1</sup>

benzo[*g*]cyclohept[*b*]indole (7) (28%) from the isocyanide (4), benzo[*e*]naphth[1,8-*cd*]azepine (8) (5%) [isolated after chromatography as benzo[*e*]naphth[1,8-*cd*]azepin-7(8*H*)-one (9)] from the isocyanide (5) and intractable polymeric material from the isocyanides (5) and (6). Irradiation (254 nm) in methanol produced benzo[*c*]phenanthridine (10) (31%), the heterocycle (8) (5%), and benzo[*i*]phenanthridine (11) (44%) from the isocyanides (4), (5), and (6), respectively.

Thermolysis at 253 °C of each isocyanide in *n*-tetradecane produced the corresponding cyanide and also transformed the isocyanide (4) into heterocycles (7) (3%) and (10) (31%). Solvent participation accounted for formation of 6-tetradecylbenzo[*c*]phenanthridine (12) (trace) and 5-tetradecylbenzo[*i*]phenanthridine (13) (3%) from isocyanides (4) and (6), respectively.

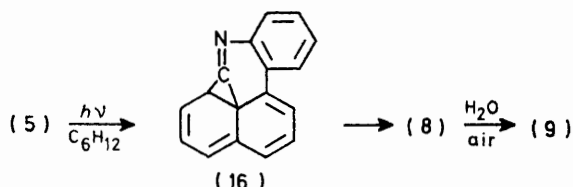
### DISCUSSION

The photo-isomerisation of 2-isocyanobiphenyl (1) in cyclohexane into cyclohept[*b*]indole (2) in high yield and into phenanthridine (3) (trace amount) was accounted for by the intermediacy of a cyclopropanonimine (14).<sup>1</sup> On the other hand photo-isomerisation of the isocyanide (1) in methanol gave phenanthridine (3) (28%) and the indole (2) (8%). The formation of [6-<sup>2</sup>H]- and [6-<sup>1</sup>H]-phenanthridine (1 : 1) in dry MeOD revealed solvent participation and was accounted for by a dissociation of methanol from an intermediate adduct (15).<sup>2</sup>



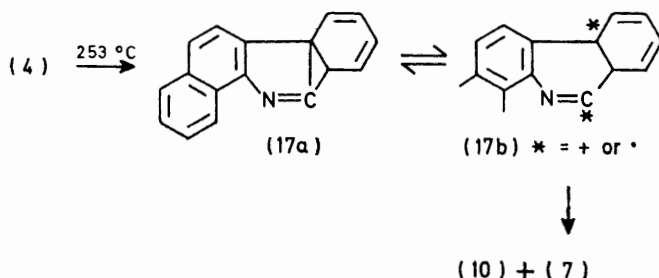
Similar explanations now account for the photo-isomerisation of the isocyanide (4) into the cycloheptindole (7) and the benzophenanthridine (10), the isocyanide (5) into the heterocycle (8), and the isocyanide (6) in methanol into the benzophenanthridine (11). Photo-polymerisation<sup>4</sup> of the isocyanide (5) in either cyclohexane or methanol and (6) in cyclohexane had no detectable competition from a structural iso-

merisation to a cycloheptindole.\* Since these cycloheptindoles would contain a photosensitive benzotropolidene structure, ready reversion of each into a cyclopropanimine, and then into the appropriate isocyanide, was expected.† The photo-isomerisation of the isocyanide (5) into the heterocycle (8) is assumed to proceed by either direct insertion into a C-H bond or by rearrangement of an intermediate cyclopropanimine (16). These pathways have not been differentiated; however, the latter may be less likely since it requires that both naphthalene rings become quinonoid.‡ Oxidation of the heterocycle (8) into the amide (9) is attributed to an attack by moist air during work-up.<sup>9</sup>



Thermolytic isomerisation of the isocyanide (4) in *n*-tetradecane at 253 °C to the cycloheptindole (7) provided the first example of a non-catalysed insertion of a ground-state isocyano-carbon atom into an arene C-C bond.§ Each thermolysis product (7) and (10) can be accounted for by a rearrangement of an intermediate cyclopropanimine (17a) or its ring-opened biradical or zwitterionic isomer (17b).¶

Two minor products from thermolysis have been tentatively identified as (a) tetradecylbenzo[*c*]phen-



anthridine(s) (12) from the isocyanide (4) and (b) tetradecylbenzo[*i*]phenanthridine(s) (13) from the isocyanide

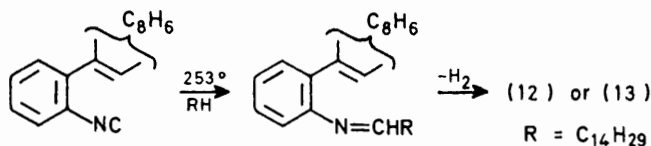
\* A slow photoconversion of cyclohept[b]indole (2) into intractable, presumably polymeric, material is believed to require initial isomerisation to the isocyanide (1) followed by  $\alpha$ -polymerisation; phenanthridine (3) was not detected.<sup>1</sup>

† Benzonorcaradiene structures are thermodynamically preferred to their benzo[1,2]- or benzo[2,3]-tropolidene isomers,<sup>5</sup> the photochemical reorganisation of benzo[1,2]- and benzo[3,4]-tropolidene into benzonorcaradienes having been reported.<sup>6</sup> The ready extrusion of an isocyanide when the incipient isocyano carbon atom is part of a 3-membered ring has been briefly reviewed.<sup>7</sup>

‡ Carde and Jones have described the first examples of intramolecular nitrene insertion into naphthalene C-C bonds.<sup>8</sup> They observed that the intermediate 1-(2-nitrobenzyl)naphthalene isomerised into indoloazepines when the non-expanding naphthalene ring remained fully aromatic throughout intermediate (and product) stages.

§ Brown *et al.* have reported the thermal transformation of 2-isocyanobiphenyl (1) at 800 °C into phenanthridine (3) in 0.6% yield.

(6). This is supported by the similarities in the u.v. spectra (Table) for the pairs of phenanthridines (10) and (12) and (11) and (13) and by the *m/e* (70 eV) peak at  $M^+ 425$  for each, and a series of peaks between *m/e* 410 and 256 corresponding to the loss of  $C_nH_{2n+1}$  ( $n = 1-11$ ). Each of these phenanthridines (12) and (13) can be produced by dehydrogenation after a thermal disrotatory



electrocyclisation from an imine produced by insertion of the carbon atom of an isocyano-group into a paraffinic C-H bond.\*\*

U.v. absorptions [ $\lambda$  (log  $\epsilon$ )] for benzophenanthridines (10)–(13) in ethanol

(10) <sup>a</sup>	360 (3.90), 343 (3.86), 310sh (4.09), 262 (5.04), 253 (4.90)
(11) <sup>b</sup>	358.5 (3.30), 352 (2.84), 343 (3.41), 326 (3.88), 313 (3.87), 298 (3.80), 266 (4.81), 256sh (4.62), 236 (4.08), 233 (4.36), 218 (4.34)
(12)	360 (3.44), 343 (3.47), 327sh (3.67), 264 (4.70), 254 (4.75), 240 (4.70), 212 (4.77)
(13)	360 (3.62), 340 (3.80), 329 (4.23), 310 (4.25), 266 (5.16), 255 (5.01), 221 (4.96), 215 (4.97)

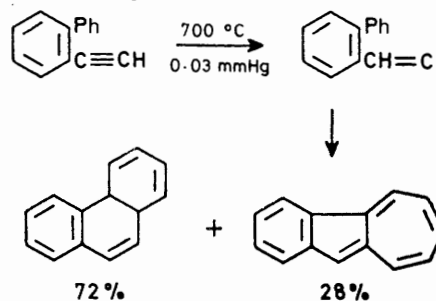
<sup>a</sup> For similar data see B. D. Tilak, T. Ravindranathan, and K. N. Subbaswami, *Indian J. Chem.*, 1968, **6**, 422. <sup>b</sup> For similar data see ref. 19.

#### EXPERIMENTAL

Instruments included Perkin-Elmer 237B and 521 grating i.r., Varian A-60 n.m.r., Perkin-Elmer 270 mass, A.E.I. MS30 double-beam mass, and Cary 14 spectrophotometers. Irradiations were carried out in a Rayonet RPR 100 photochemical chamber reactor (Southern New England Ultraviolet Co.) equipped with 16 low-pressure lamps having principal emission at 254, 300, or 350 nm. Before irradiation under nitrogen, solutions were flushed with nitrogen (prepurified grade) for 30 min. Cyclohexane and methanol were distilled from lithium aluminium hydride and Linde molecular sieves type 3A, respectively, directly into the reactor tube. Each known product was identical with an authentic sample. Yields were based on starting material consumed. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

1-Isocyano-2-phenylnaphthalene (4).—1-Amino-2-phenyl-

¶ Brown and his co-workers have reported the following conversion which is analogous to the conversion (4)  $\rightarrow$  (7) + (8).<sup>11</sup>



\*\* A similar photochemical formation of (an) imine(s) from 4-isocyanobiphenyl was observed (J. H. Boyer, C. C. Lai, and T. Bauer, unpublished results).

naphthalene<sup>12</sup> (5.71 g, 0.026 mol) in 88% formic acid (35 ml) was heated at reflux for 6 h. Concentration under reduced pressure left a residue which was washed with water and dried. Recrystallisation from ethanol gave 1-formamido-2-phenylnaphthalene (6.06 g, 94.0%), m.p. 150–151°;  $\nu_{\max}$  (CHCl<sub>3</sub>) 3 400 (NH) and 1 690 cm<sup>-1</sup> (C=O);  $m/e$  (70 eV) 247 ( $M^+$ ) (Found: C, 82.15; H, 5.45; N, 5.5. C<sub>17</sub>H<sub>13</sub>NO requires C, 82.57; H, 5.30; N, 5.66%).

Triethylamine (28 ml, 0.2 mol) and 1-formamido-2-phenylnaphthalene (6.9 g, 0.027 mol) in methylene chloride (140 ml) was held at 0–4 °C as phosgene (8.3 g or 120 drops) was added dropwise. Stirring was continued for 4 h at 0 °C, the reaction mixture was washed with cold water, and the methylene chloride layer was dried (MgSO<sub>4</sub>), evaporated, and chromatographed on silica gel. n-Hexane (500 ml) eluted 3.82 g (59.7%) of 1-isocyano-2-phenylnaphthalene (4), m.p. 94.5–95.5°;  $m/e$  (70 eV) 229 ( $M^+$ );  $\nu_{\max}$  (CHCl<sub>3</sub>) 2 119 cm<sup>-1</sup> (–NC);  $\delta$  (CDCl<sub>3</sub>) 7.5 (m);  $\lambda_{\max}$  (cyclohexane) (log  $\epsilon$ ) 295 (4.15), 253 (4.70), 323.5 (4.65), and 213 nm (4.56);  $\lambda_{\max}$  (EtOH) (log  $\epsilon$ ) 297 (4.13), 252 (4.70), 228 (4.74), and 210 nm (4.483) (Found: C, 88.6; H, 5.05; N, 6.2. C<sub>17</sub>H<sub>11</sub>N requires C, 89.06; H, 4.84; N, 6.11%).

*Photolyses.* (a) A solution of 1-isocyano-2-phenylnaphthalene (4) (256 mg, 1.11 mmol) in cyclohexane (400 ml) was degassed by a stream of nitrogen for 12 h and then irradiated (254 nm) under nitrogen for 64 h. Cyclohexane was removed and the residue was chromatographed on silica gel. n-Hexane (200 ml) eluted starting material (153 mg, 59.8%), n-hexane–benzene (3 : 1; 200 ml) eluted a dark yellow oil (25 mg), and benzene (300 ml) eluted benzo[g]cyclohept[b]indole (7) as a purple solid (28 mg, 27.2%), m.p. 190–191° (lit.,<sup>13</sup> 190–191°),  $m/e$  229 ( $M^+$ ). A tar (26 mg) was eluted by benzene–chloroform (1 : 3; 400 ml) and chloroform (150 ml).

(b) A solution of 1-isocyano-2-phenylnaphthalene (4) (1.00 g, 0.004 mol) in methanol (400 ml) was degassed by a stream of nitrogen for 6 h and was irradiated (254 nm) under nitrogen for 70 h. Methanol was removed and the residue was chromatographed on silica gel. n-Hexane (200 ml) eluted starting material (0.50 g, 50%), n-hexane–benzene (3 : 1, 500 ml) eluted benzo[c]phenanthridine (10) (97 mg, 19.4% based on recovered starting material) as a pale yellow solid, m.p. 133–134° (from light petroleum) (lit.,<sup>14</sup> 135°). Benzene (500 ml) eluted 0.135 g and methyl alcohol eluted 0.237 g of unidentified material.

1-(2-Isocyanophenyl)naphthalene (5).—A solution of triethylamine (14 ml) and 1-(2-formamidophenyl)naphthalene<sup>15</sup> (3.84 g, 0.015 mol) in methylene chloride (70 ml) was cooled to 0 °C and phosgene (60 drops of 4.14 g) was introduced to the reaction mixture held at 0–4 °C. The mixture was stirred for a further 4 h at 0 °C, concentrated, washed with water, and chromatographed on silica gel. n-Hexane (500 ml) eluted the isocyanide (5) (3.06 g, 85.9%), m.p. 82.5–83 (from n-hexane);  $m/e$  (70 eV) 229 ( $M^+$ );  $\nu_{\max}$  (CHCl<sub>3</sub>) 2 119 cm<sup>-1</sup> (NC);  $\lambda_{\max}$  (EtOH) (log  $\epsilon$ ) 221 (4.85), 280 (3.80), 286 (3.54), and 291 nm (3.54),  $\lambda_{\max}$  (cyclohexane) (log  $\epsilon$ ) 222 (4.83), 282 (3.82), 287 (3.80), and 291 nm (3.90) (Found: C, 89.5; H, 4.75; N, 6.2. C<sub>17</sub>H<sub>11</sub>N requires C, 89.06; H, 4.84; N, 6.11%).

*Photolyses.* (a) A solution of 1-(2-isocyanophenyl)naphthalene (5) (0.24 g, 1.04 mmol) in cyclohexane (400 ml) was degassed for 6 h by a stream of nitrogen, and then irradiated (300 nm) for 50 h under nitrogen. The reaction mixture was concentrated and chromatographed on silica gel. n-Hexane (350 ml) eluted starting material (66 mg,

27.5%), n-hexane–benzene (4 : 1, 200 ml) eluted a yellow solid (18 mg; two spots on t.l.c.); bright yellow fluorescence) from which preparative t.l.c. (Kodak chromatogram) gave benzo[e]naphth[1,8-cd]azepin-7(8H)-one (9) (10 mg, 5.7%) as yellow needles, m.p. 230–234° from CHCl<sub>3</sub>;  $m/e$  (70 eV) 245 ( $M^+$ );  $\nu_{\max}$  (CHCl<sub>3</sub>) 3 420 (NH) and 1 710 cm<sup>-1</sup> (C=O) [lit.,<sup>9</sup> (hexachlorobutadiene mull) 3 300 cm<sup>-1</sup> (NH) and (Nujol mull) 1 660 cm<sup>-1</sup> (C=O)];  $\lambda_{\max}$  (EtOH) (log  $\epsilon$ ) 400 (3.46), 333 (3.89), 321 (3.86), 295 (4.27), 282 (4.29), 240 (4.11), 221 (4.21), and 217 nm (4.22). Benzene (500 ml) and ethyl acetate (300 ml) eluted polymeric material (0.013 and 0.047 g; t.l.c., several spots).

(b) A solution of 1-(2-isocyanophenyl)naphthalene (5) (0.250 g, 1.09 mmol) in methanol (400 ml) was degassed by a stream of nitrogen for 3 h and then irradiated (300 nm) under nitrogen for 24 h. The concentrated mixture was chromatographed on silica gel. n-Hexane–benzene (3 : 2) eluted the azepinone (9) (13 mg, 5.2%) as yellow needles, m.p. 230–234° (from CHCl<sub>3</sub>). Benzene and then methylene chloride eluted intractable oils (202 mg, many spots on t.l.c.).

2-(2-Isocyanophenyl)naphthalene (6).—A solution of 2-(2-aminophenyl)naphthalene<sup>12</sup> (3.9 g, 0.018 mol) in formic acid (88%; 25 ml) was refluxed for 6 h. Filtration separated 2-(2-formamidophenyl)naphthalene which recrystallised from benzene (4.3 g, 97.7%), m.p. 115–112°;  $\nu_{\max}$  (CHCl<sub>3</sub>) 3 400 (NH) and 1 690 cm<sup>-1</sup> (C=O);  $m/e$  (79 eV) 247 ( $M^+$ ) (Found: C, 82.75; H, 5.45; N, 5.3. C<sub>17</sub>H<sub>13</sub>NO requires C, 82.57; H, 5.30; N, 5.66%).

Triethylamine (18 ml) was added to a solution of 2-(2-formamidophenyl)naphthalene (4.3 g, 0.0174 mol) in methylene chloride (90 ml). The mixture was held at 0–40° while phosgene (5.4 g or 76 drops) was introduced dropwise. Stirring was continued for 4 h at 0 °C, the reaction mixture was washed by cold water, and the methylene chloride layer was dried (MgSO<sub>4</sub>), evaporated, and chromatographed from silica gel. n-Hexane eluted the isocyanide (6) (0.906 g, 22.8%), m.p. 116–117°;  $m/e$  (70 eV) 229 ( $M^+$ );  $\nu_{\max}$  (CHCl<sub>3</sub>) 2 132 cm<sup>-1</sup> (–NC);  $\lambda_{\max}$  (cyclohexane) (log  $\epsilon$ ) 282 (3.85), 255 (3.95), 246 (3.95), 224 (4.30), and 218 nm (4.25),  $\lambda_{\max}$  (EtOH) 282 (3.85), 255 (3.95), 246.5 (4.00), 226 (4.37), and 219 nm (4.32) (Found: C, 88.9; H, 4.9; N, 6.0. C<sub>17</sub>H<sub>11</sub>N gives C, 89.06; H, 4.84; N, 6.11%).

*Photolyses.* (a) A solution of 2-(2-isocyanophenyl)naphthalene (6) (150 mg, 0.65 mmol) in methanol (250 ml) was degassed by a stream of nitrogen for 3 h and then irradiated (254 nm) under nitrogen for 30 h. The solvent was removed and the residue chromatographed on silica gel. n-Hexane eluted starting material (11 mg, 7.3%) and n-hexane–benzene (2 : 1) eluted benzo[i]phenanthridine as a yellow solid (66 mg, 47.5%), m.p. 179–180° (lit.,<sup>16</sup> 181–182°);  $m/e$  (70 eV) 229 ( $M^+$ ). Methylene chloride and methanol eluted a tar (60 mg).

*Pyrolysis of 1-Isocyano-2-phenylnaphthalene (4).*—A mixture of 1-isocyano-2-phenylnaphthalene (4) (0.250 g, 1.1 mmol) and n-tetradecane (4 ml,  $n_D^{25}$  1.428) was heated at reflux (253 °C) for 35 min. After 35 min absorption at  $\nu_{\max}$  2 119 cm<sup>-1</sup> (isocyanide) had disappeared. The mixture was chromatographed on silica gel. Light petroleum eluted n-tetradecane (14 mg), and n-hexane eluted first 1-cyano-2-phenylnaphthalene (86 mg, 34.5%), m.p. 118–119°

\* The amide (9) has also been prepared from 1-(2-formamidophenyl)naphthalene in phosphorus oxychloride and stannic chloride (J. H. Boyer and J. R. Patel, unpublished results).

(n-hexane);  $\nu_{\max}$  (CHCl<sub>3</sub>) 2 228 cm<sup>-1</sup> (CN);  $m/e$  (70 eV) 229 ( $M^+$ ) (Found: C, 89.1; H, 5.0; N, 5.9. C<sub>17</sub>H<sub>11</sub>N requires C, 89.06; H, 4.84; N, 6.11%). Further elution with n-hexane gave benzo[*c*]phenanthridine (77 mg, 30.8%), m.p. 130–133°.

Benzene-hexane (3 : 1) eluted an orange oil (155 mg) purified by elution with hexane from a silica gel column and tentatively identified as 6-tetradecylbenzo[*c*]phenanthridines (106 mg);  $\nu_{\max}$  (CHCl<sub>3</sub>) 2 870 and 2 950 (aliphatic CH), and 3 050 cm<sup>-1</sup> (aromatic CH),  $\lambda_{\max}$  (ethanol) (log  $\epsilon$ ) 360 (3.44), 343 (3.47), 327sh (3.67), 264 (4.70), 254 (4.75), 240 (4.70), and 212 nm (4.77);  $m/e$  (70 eV) 425 ( $M^+$ , 1.4%), 424 ( $M^+$  - H, 1.4), 410 ( $M^+$  - CH<sub>2</sub>, trace), 396 ( $M^+$  - C<sub>2</sub>H<sub>5</sub>, trace), 382 ( $M^+$  - C<sub>3</sub>H<sub>7</sub>, 1.4), 368 ( $M^+$  - C<sub>4</sub>H<sub>9</sub>, 1.4), 354 ( $M^+$  - C<sub>5</sub>H<sub>11</sub>, 1.4), 340 ( $M^+$  - C<sub>6</sub>H<sub>13</sub>, 2.8), 326 ( $M^+$  - C<sub>7</sub>H<sub>15</sub>, 2.8), 312 ( $M^+$  - C<sub>8</sub>H<sub>17</sub>, 2.8), 298 ( $M^+$  - C<sub>9</sub>H<sub>19</sub>, 2.8), 284 ( $M^+$  - C<sub>10</sub>H<sub>21</sub>, 2.8), 270 ( $M^+$  - C<sub>11</sub>H<sub>23</sub>, 2.8), 256 ( $M$  - C<sub>12</sub>H<sub>25</sub>, 7.1), 255 ( $M^+$  - C<sub>12</sub>H<sub>25</sub>, 20), 245 ( $M^+$  - C<sub>13</sub>H<sub>27</sub>, 100), 243 ( $M$  - C<sub>13</sub>H<sub>27</sub>, 7.1), 230 ( $M^+$  - C<sub>14</sub>H<sub>29</sub>, 5.7), 229 ( $M^+$  - C<sub>14</sub>H<sub>29</sub>, 2.8), 228 ( $M^+$  - C<sub>14</sub>H<sub>29</sub>, 2.8), 219 (22.8), 217 (25.7), 202 (2.8), 201 (2.1), 189 (5.7), and 108.5 (10).

Benzene and benzene-chloroform (1 : 1) eluted a tar (52 mg; t.l.c. several spots). Chloroform eluted benzo[*g*]cyclohept[*b*]indole (7) (7 mg, 3%), m.p. 189–191°.

*Pyrolysis of 2-(2-Isocyanophenyl)naphthalene (6).*—A mixture of 2-(2-isocyanophenyl)naphthalene (6) (0.104 g, 0.45 mmol) and n-tetradecane (3 ml) was heated at reflux (253 °C) for 1.5 h until absorption at  $\nu_{\max}$  2 132 cm<sup>-1</sup> (isocyanato) had disappeared. The reaction mixture was chromatographed on silica gel. n-Hexane eluted n-tetradecane; hexane-benzene (4 : 1) eluted a lemon-yellow liquid (56 mg), tentatively identified as 5-tetradecylbenzo[*i*]phenanthridines. It showed a light green fluorescence similar to that for benzo[*i*]phenanthridine;<sup>16</sup>  $m/e$  (70 eV) 425 ( $M^+$ , 1.3%), 424 ( $M^+$  - H, 1.8), 410 ( $M^+$  - CH<sub>3</sub>, trace), 396 ( $M^+$  - C<sub>2</sub>H<sub>5</sub>, 5), 382 ( $M^+$  - C<sub>3</sub>H<sub>7</sub>, 7.5), 381 ( $M^+$  - C<sub>3</sub>H<sub>8</sub>, 3.8), 368 ( $M^+$  - C<sub>4</sub>H<sub>9</sub>, 3.8), 354 ( $M^+$  - C<sub>5</sub>H<sub>11</sub>, 3.8), 340 ( $M^+$  - C<sub>6</sub>H<sub>13</sub>, 2.5), 326 ( $M^+$  - C<sub>7</sub>H<sub>15</sub>, 2.5), 312 ( $M^+$  - C<sub>8</sub>H<sub>17</sub>, 2.5), 298 ( $M^+$  - C<sub>9</sub>H<sub>19</sub>, 3.8), 284 ( $M^+$  - C<sub>10</sub>H<sub>21</sub>, 2.5), 270 ( $M^+$  - C<sub>11</sub>H<sub>23</sub>, 7.5), 256 ( $M^+$  - C<sub>12</sub>H<sub>25</sub>, 43.8), 244 ( $M^+$  - C<sub>13</sub>H<sub>27</sub>, 25), 243 ( $M^+$  - C<sub>13</sub>H<sub>27</sub>, 100), 242 ( $M^+$  - C<sub>13</sub>H<sub>27</sub>, 92.50), 241 ( $M^+$  - C<sub>13</sub>H<sub>28</sub>, 20), 229 ( $M^+$  - C<sub>14</sub>H<sub>29</sub>, 10.25), 228 ( $M^+$  - C<sub>14</sub>H<sub>29</sub>, 8.8), 227 ( $M^+$  - C<sub>14</sub>H<sub>30</sub>, 6.25), 217 (5), 202 (3.8), 201 (3.8), 189 (2.5), 149 (2.5), and 108.5 (trace). Further elution with hexane-benzene (9 : 1) gave 2-(2-cyanophenyl)naphthalene (16 mg, 15.4%), m.p. 110–112°;  $\nu_{\max}$  (CHCl<sub>3</sub>) 2 227 cm<sup>-1</sup> (-CN);  $m/e$  (70 eV) 229 ( $M^+$ );  $\lambda_{\max}$  (ethanol) (log  $\epsilon$ ) 286 (3.96), 275 (3.97), 257sh (4.40), 248 (4.45), 222 (4.69), and 220 nm (4.70),

$\lambda_{\max}$  (cyclohexane) (log  $\epsilon$ ) 286 (4.00), 273 (4.04), 254sh (4.48), 247 (4.53), 225 (4.79), and 221 nm (4.79) (Found: C, 88.95; H, 5.15; N, 5.85. C<sub>17</sub>H<sub>11</sub>N requires C, 89.06; H, 4.84; N, 6.11%). Hexane-benzene (1 : 1) eluted an unidentified clear orange liquid (53 mg; t.l.c. several spots). Benzene eluted an oil (10 mg) which showed a light green fluorescence (t.l.c.) and was chromatographed (Kodak chromatogram) to give benzo[*i*]phenanthridine (3 mg, 2.9%), m.p. 178–180°.

*Pyrolysis of 1-(2-Isocyanophenyl)naphthalene (5).*—A mixture of 1-(2-isocyanophenyl)naphthalene (5) (0.125 g, 0.54 mmol) and n-tetradecane (6 ml) was heated at reflux (253 °C) for 10 min. As the mixture became dark yellow, the absorption at  $\nu_{\max}$  2 119 cm<sup>-1</sup> (-NC) disappeared and one at  $\nu_{\max}$  2 227 cm<sup>-1</sup> (-CN) developed. The mixture was chromatographed on silica gel. Petroleum ether eluted n-tetradecane; n-hexane eluted 1-(2-cyanophenyl)naphthalene (0.070 g, 56%); m.p. 122–123° (from light petroleum);  $m/e$  (70 eV) 229 ( $M^+$ ) (Found: C, 89.22; H, 4.97; N, 5.80. C<sub>17</sub>H<sub>11</sub>N requires C, 89.06; H, 4.84; N, 6.11%). Benzene eluted a dark yellow liquid (10 mg), and a tar (18 mg) was eluted by methanol.

[8/677 Received, 11th April, 1978]

#### REFERENCES

- 1 J. De Jong and J. H. Boyer, *J. Org. Chem.*, 1972, **37**, 3571.
- 2 J. De Jong and J. H. Boyer, *Chem. Comm.*, 1971, 961.
- 3 J. H. Boyer and J. R. Patel, *J.C.S. Chem. Comm.*, 1977, 855.
- 4 T. Saegusa and Y. Ito, 'Simple  $\alpha$ -Additions,' in I. Ugi, 'Isonitrile Chemistry,' Academic Press, London, 1971, p. 65.
- 5 W. Kirmse, 'Carbene Chemistry,' Academic Press, London, 1971, 2nd edn., pp. 381–406; M. Pomerantz, A. S. Ross, and G. W. Gruber, *J. Amer. Chem. Soc.*, 1972, **94**, 1403; M. Pomerantz and A. S. Ross, *ibid.*, 1975, **97**, 5850.
- 6 M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, 1971, **93**, 6615.
- 7 J. H. Boyer and K. G. Srinivasan, *J.C.S. Perkin I*, 1976, 1583.
- 8 R. N. Carde and G. Jones, *J.C.S. Perkin I*, 1974, 2066.
- 9 J. R. Craig and A. D. Woolhouse, *Austral. J. Chem.*, 1971, **24**, 835.
- 10 R. F. C. Brown, M. Butcher, and R. A. Fergie, *Austral. J. Chem.*, 1973, **26**, 1319.
- 11 R. F. C. Brown, K. J. Harrington, and G. L. McMullen, *J.C.S. Chem. Comm.*, 1974, 123; R. F. C. Brown, F. W. Eastwood, K. J. Harrington, and G. L. McMullen, *Austral. J. Chem.*, 1974, **27**, 2393.
- 12 D. H. Hey and S. E. Lawton, *J. Chem. Soc.*, 1940, 374.
- 13 C. W. Muth and E. S. Hanrahana, *J. Org. Chem.*, 1958, **23**, 395.
- 14 E. Ritchie, *J. Proc. Roy. Soc. N.S. Wales*, 1944, **78**, 173.
- 15 B. Mills and K. Schofield, *J. Chem. Soc.*, 1956, 4213.
- 16 C. E. Louder and C. J. Timmons, *J. Chem. Soc. (C)*, 1967, 1457.