

## Photolysis of Quinolyl and Isoquinolyl Azides in Primary and Secondary Aliphatic Amines: Synthesis of Bicyclic Azepines, Diazepines, and Quinolyl- and Isoquinolyl-diamines

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Photolysis of the title compounds in primary aliphatic amines gave in some cases bicyclic azepines and diazepines as well as *o*-diamines, while in secondary amines mainly the appropriate *o*-diamines are obtained. On the basis of the many examples studied guidelines are put forward to predict the nature of products from photolysis of bicyclic azides in primary and secondary amines and to obtain maximum yields.

We have noted in preliminary communications that photolysis of certain quinolyl azides in secondary aliphatic amines yields quinolyl-*o*-diamines,<sup>1</sup> whilst in primary amines they produce in some cases bicyclic azepines as well as *o*-diamines.<sup>2</sup> We now report an extension of this work that leads us to suggest criteria for predicting the nature of the photolytic products of (6-6) fused bicyclic azides in primary and secondary amines.

Quinolyl azides were prepared from the corresponding amines by diazotization followed by addition of sodium azide. Aminoquinolines were obtained by reduction of the appropriate nitroquinoline (made by a Skraup reaction) with iron and acetic acid.

Photolytic decomposition of these azides in a large excess of a secondary amine gave the corresponding diamines listed in Table 1 with details of yields and reaction conditions in Table 2. The main products of irradiation of 3-, 6-, 7-, and 8-quinolyl azides are quinolyl-*o*-diamines (Table 2) with attachment of the dialkyl-amino-group at the position originally occupied by the azido-function. We have attributed formation of these diamines to nucleophilic attack by amine on the appropriate tricyclic azirine [*i.e.* (14)] to form an aziridine [*e.g.* (15)] that undergoes re-aromatization<sup>2</sup> (1a) (*cf.* Scheme 1). Recently, tricyclic azirines have been observed directly by i.r. spectroscopy in the matrix photolysis of naphthyl azides,<sup>3</sup> which we have found<sup>2</sup> to give benzazepines or *o*-diamines on photolysis in amines. However, it should be noted that the naphthazirine produced in the matrix photolysis experiment rapidly interconverts to a more stable didehydrobenzazepine (16) or its isomer which might prove to be the species in this case (16a) that is intercepted by a nucleophile. Experimental evidence that allows a distinction between these two possibilities is lacking at present. Quinolyl-*o*-diamines were invariably accompanied by the corresponding quinolyl amine (the triplet derived product<sup>4</sup>) in these azide decompositions. By contrast, the 4- and the 5-quinolylamine were the only products character-

ised from photolysis of the respective azides in diethylamine or piperidine.

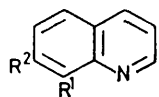
Photolysis of 8-azidoquinoline in diethylamine as solvent led to an 86% yield of diamine (1a) whereas use of hexahydroazepine, a much larger nucleophile, gave only 26% yield of (1e). This is thought to be due to steric hindrance exerted by the lone pair on the quinoline nitrogen towards attack on the *peri*-position (*i.e.* position 8) by the larger nucleophile on compound (14). Carrying out the latter reaction in the presence of co-solvents such as TMEDA (tetramethylethylenediamine) or dioxan resulted in double the yield of compound (1e). It is felt that these solvents stabilise the singlet nitrene<sup>5,6</sup> by co-ordination consequently suppressing singlet-triplet intersystem crossing thereby promoting azirine formation and making the azirine intermediate more available for nucleophilic attack by increasing its concentration.

It is noteworthy that the yield of *o*-diamines from photolysis of 6-quinolyl azide in the same series of secondary amines does not drop with increasing size of the nucleophile. Nucleophilic attack in this case is at a  $\beta$ -position (naphthalene nomenclature) in the azirine (12) to give aziridine (17) and steric effects are not important. Similarly, for photolysis of 7-quinolyl azide in diethylamine and piperidine little difference in the yield of diamines (1n) and (1g) was observed since nucleophilic attack takes place again at a  $\beta$ -position in compound (13). Higher yields of *o*-diamines (1f) 71% and (2e) 88% are obtained from photolysis of 8- and 6-quinolyl azides in morpholine compared with those obtained in piperidine (1d) 47% and (2c) 77% from the same azides. This might be accounted for by morpholine stabilizing the singlet nitrene like dioxan, and again the effect is greater for the 8-azido-isomer as might be expected.

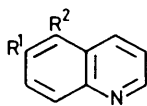
The structures of the *o*-diamines were established from spectroscopic data (i.r., m.s., n.m.r.) and by comparison with authentic materials where possible.

N.m.r. spectra (Table 6) of the *o*-diamines listed in Table 1, except 7-amino-8-pyrrolidinoquinoline (1c), contain nonequivalent  $\alpha$ -methylene protons in the dialkyl-amino-group indicating restricted rotation of the 8-substituent. The spectrum of 7-amino-8-piperidino-

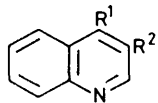
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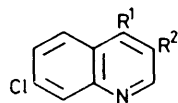
(1a - p)



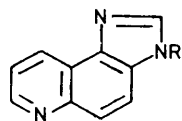
(2a - f)



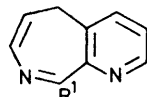
(3a)



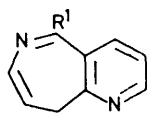
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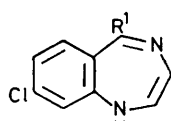
(5a - c)



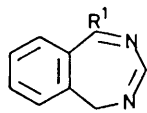
(6a - h)



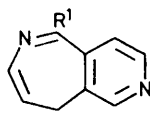
(7a - g)



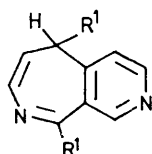
(8a - h)



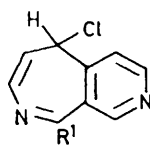
(9a - c)



(10a - c)



(11a)

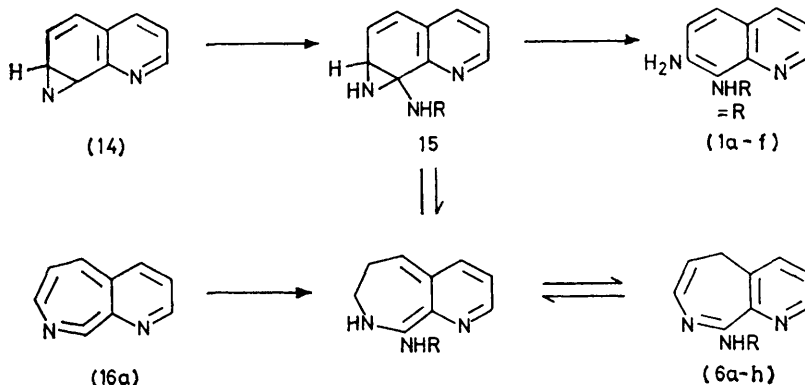


(11b)

quinoline was recorded at various temperatures and the two  $\alpha$ -methylene proton signals were found to coalesce at 110 °C as free rotation becomes possible.

The products listed in Table 3 were obtained by photolysis of quinolyl azides in a large excess of primary amines. The 6-, 7-, and 8-quinolyl and 7-chloro-4-quinolyl azides yield *o*-diamine as with secondary amines, but the two last azides also undergo ring expansion to give bicyclic azepines. In the case of the 5-quinolyl azide, the bicyclic azepines (7a—g) were obtained but *o*-diamines could not be detected. Optimum conditions for azepine formation were established<sup>2</sup> for the decomposition of 8-quinolyl azide in cyclohexylamine and TMEDA as for most of the decompositions reported in Table 2. In separate experiments, irradiation of 9-cyclohexylamino-5*H*-pyrido[2,3-*c*]azepine (6c) in cyclohexylamine, or dioxan, gave 7-amino-8-cyclohexylaminoquinoline (11) quantitatively, but under the optimum photolysis conditions the azepine (6c) to diamine (11) ratio did not alter significantly on extended irradiation, possibly because the polymeric by-products formed act as a u.v. filter and prevent interconversion.

The structures assigned to the azepines and diamines (Table 3) are based on spectroscopic data. For instance, 9-*n*-hexylamino-5*H*-pyrido[2,3-*c*]azepine (6h) has i.r. absorptions at 3 280 (NH) and 1 605  $\text{cm}^{-1}$  (C=N). Signals in the n.m.r. at  $\delta$  3.47 (N-CH<sub>2</sub>), 1.5-1.8 (broad multiplet) (CH<sub>2</sub>)<sub>4</sub>, 1.0 (triplet) (CH<sub>3</sub>), and 6.0 (exchanges with D<sub>2</sub>O) (NH) indicate incorporation of the *n*-hexylamino-group. The aromatic region shows doublets at  $\delta$  8.5, 7.3 and 7.45 which are assigned to the 2-, 3-, and 4-protons in the pyridine ring respectively. Protons in the azepine ring appear as doublets at  $\delta$  6.65 (7-H), 5.15 (6-H), and 3.02 (CH<sub>2</sub>), and irradiation at  $\delta$  5.15 reduces the doublets at  $\delta$  6.65 and 3.02 to singlets. The mass spectrum gave the correct molecular ion  $M^+$  243 (base peak 173). The 8-*n*-hexylamino-7-quinolylamine (1m; R<sup>1</sup>=*n*-C<sub>6</sub>H<sub>13</sub>NH, R<sup>2</sup>=NH<sub>2</sub>) has i.r. absorptions at 3 450 and 3 350 (NH<sub>2</sub>) and 3 250  $\text{cm}^{-1}$  (NH-hexyl). The aromatic region of the n.m.r. shows doublets at  $\delta$  8.7 (2-H), 7.2 (3-H), and 7.87 (4-H), and doublets at 7.2 (5-H) and 6.95 (6-H). Incorporation of *n*-hexyl is established by the appearance of a triplet at  $\delta$  3.1 (N-CH<sub>2</sub>), a multiplet  $\delta$  1.35—1.6 [(CH<sub>2</sub>)<sub>4</sub>], and a triplet at  $\delta$  0.9 (CH<sub>3</sub>). A broad singlet at  $\delta$  4.5 (3H) (NH<sub>2</sub> and NH-



## SCHEME

TABLE I

Products from quinolyl azide photolysis in secondary amines

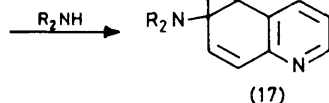
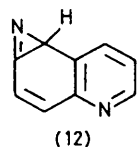
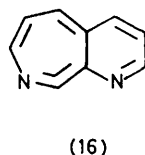
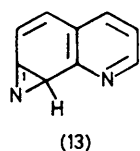
R <sup>1</sup>	R <sup>2</sup>	M.p. (°C) [B.p. °C/Torr]	Molecular formula	Elemental analysis or molecular ion Required (Found)		
				C	H	N
<i>(a) o-Diamines</i>						
(1a) (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	NH <sub>2</sub>	95	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub>	72.5 (72.8)	8.0 (8.1)	19.5 (19.7)
(1b) (n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> N	NH <sub>2</sub>	[168/1.7]	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub>	74.1 (74.4)	8.7 (8.9)	17.3 (17.1)
(1c) C <sub>4</sub> H <sub>9</sub> N	NH <sub>2</sub>	93	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub>	73.2 (73.1)	7.1 (7.1)	19.7 (19.9)
(1d) C <sub>5</sub> H <sub>10</sub> N	NH <sub>2</sub>	102	C <sub>14</sub> H <sub>17</sub> N <sub>3</sub>	74.0 (74.2)	7.5 (7.6)	18.5 (18.4)
(1e) C <sub>6</sub> H <sub>12</sub> N	NH <sub>2</sub>	88—90	C <sub>15</sub> H <sub>19</sub> N <sub>3</sub>	74.7 (74.8)	7.9 (8.0)	17.4 (17.6)
(1f) $\overline{\text{O}}\cdot[\text{CH}_2]_2\cdot\text{N}\cdot[\text{CH}_2]_2$	NH <sub>2</sub>	170—172	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> O	68.1 (68.3)	6.6 (6.6)	18.3 (18.6)
(1g) i-C <sub>3</sub> H <sub>7</sub> NH	NH <sub>2</sub>	159	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> ·2HCl * (201.1)	M+ 201.1265 (M+ 201.1265)		
(1h) t-C <sub>4</sub> H <sub>9</sub> NH	NH <sub>2</sub>	168	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> ·2HCl * (215.1)	M+ 215.1421 (M+ 215.1420)		
(1i) n-C <sub>4</sub> H <sub>9</sub> NH	NH <sub>2</sub>	162	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> ·2HCl * (215.1)	(M+ 215.1420)		
(1j) i-C <sub>3</sub> H <sub>7</sub> NH	NH <sub>2</sub>	170	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> ·2HCl * (215.14)	(M+ 215.1420)		
(1k) s-C <sub>4</sub> H <sub>9</sub> NH	NH <sub>2</sub>	165	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> ·2HCl * (215.14)	54.17 (54.04)	6.62 (6.66)	14.57 (14.49)
(1l) C <sub>6</sub> H <sub>11</sub> NH	NH <sub>2</sub>	68 <sup>2</sup>				
(1m) n-C <sub>6</sub> H <sub>13</sub> NH	NH <sub>2</sub>	160	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub> ·2HCl	56.96 (56.75)	7.33 (7.33)	13.29 (12.91)
(1n) NH <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	36	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub>	72.5 (72.8)	8.0 (8.0)	19.5 (19.4)
(1o) NH <sub>2</sub>	C <sub>5</sub> H <sub>10</sub> N	65 (lit., <sup>a</sup> m.p. 65)				
(1p) NH <sub>2</sub>	C <sub>6</sub> H <sub>11</sub> NH	47	C <sub>15</sub> H <sub>19</sub> N <sub>3</sub>	74.7 (74.7)	7.9 (7.9)	17.4 (17.4)
(2a) (C <sub>3</sub> H <sub>6</sub> ) <sub>2</sub> N	NH <sub>2</sub>	63	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub>	72.5 (56.75)	8.0 (7.33)	19.5 (12.91)
(2b) C <sub>4</sub> H <sub>9</sub> N	NH <sub>2</sub>	123 (lit., <sup>a</sup> m.p. 123)				
(2c) C <sub>5</sub> H <sub>10</sub> N	NH <sub>2</sub>	166 (lit., <sup>a</sup> m.p. 166)				
(2d) C <sub>6</sub> H <sub>12</sub> N	NH <sub>2</sub>	122 (lit., <sup>a</sup> m.p. 124)				
(2e) $\overline{\text{O}}\cdot[\text{CH}_2]_2\cdot\text{N}\cdot[\text{CH}_2]_2$	NH <sub>2</sub>	165 (lit., <sup>a</sup> m.p. 166)				
(2f) C <sub>6</sub> H <sub>11</sub> NH	NH <sub>2</sub>	118	C <sub>15</sub> H <sub>19</sub> N <sub>3</sub>	74.7 (74.7)	7.9 (7.9)	17.4 (17.4)
(3a) NH <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	134	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub>	72.5 (72.8)	8.0 (8.1)	19.5 (19.3)
(4a) i-C <sub>3</sub> H <sub>7</sub> NH	NH <sub>2</sub>	132	C <sub>13</sub> H <sub>13</sub> ClN <sub>3</sub>	61.2 (61.0)	6.0 (5.7)	17.8 (17.5)
(4b) n-C <sub>3</sub> H <sub>7</sub> NH	NH <sub>2</sub>	154	C <sub>12</sub> H <sub>13</sub> ClN <sub>3</sub>	61.2 (61.1)	6.0 (5.8)	17.8 (17.5)
(4c) C <sub>6</sub> H <sub>11</sub> NH	NH <sub>2</sub>	138	C <sub>16</sub> H <sub>13</sub> ClN <sub>3</sub>	65.3 (65.0)	6.5 (6.2)	15.3 (15.0)
(4d) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH	NH <sub>2</sub>	139	C <sub>16</sub> H <sub>13</sub> ClN <sub>3</sub>	66.3 (66.0)	5.2 (4.9)	15.5 (15.3)
<i>(b) Azepines, diazepines, and imidazoles</i>						
(5a) i-C <sub>3</sub> H <sub>7</sub>		73—74	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> ·H <sub>2</sub> O	68.1 (68.0)	6.6 (6.95)	18.3 (18.2)
(5b) n-C <sub>4</sub> H <sub>9</sub>		68—69	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub>	74.64 (74.48)	6.71 (6.77)	18.65 (18.39)
(5c) n-C <sub>6</sub> H <sub>13</sub>		69—70	C <sub>16</sub> H <sub>19</sub> N <sub>3</sub>	78.85 (75.90)	7.56 (7.46)	16.59 (16.63)
(6a) n-C <sub>3</sub> H <sub>7</sub> NH		58	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> (201.3)	71.61 (71.7)	7.51 (7.5)	20.88 (21.0)
(6b) i-C <sub>3</sub> H <sub>7</sub> NH		86	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> (201.3)	(71.59)		(20.69)
(6c) C <sub>6</sub> H <sub>11</sub> NH		91 <sup>2</sup>	C <sub>15</sub> H <sub>19</sub> N <sub>3</sub> (241.3)			
(6d) n-C <sub>4</sub> H <sub>9</sub> NH		63	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub>	72.52 (72.38)	7.96 (8.02)	19.52 (19.38)

TABLE 1 (continued)

R <sup>1</sup>	R <sup>2</sup>	M.p. (°C) [B.p. °C/Torr]	Molecular formula	Elemental analysis or molecular ion Required (Found)		
				C	H	N
(b) Azepines, diazepines, and imidazoles (continued)						
(6e) i-C <sub>4</sub> H <sub>9</sub> NH		[73/0.2]		(72.73)	(7.97)	(19.24)
(6f) s-C <sub>4</sub> H <sub>9</sub> NH		[85/0.2]		(72.38)	(7.82)	(19.70)
(6g) t-C <sub>4</sub> H <sub>9</sub> NH		62		(72.57)	(7.87)	(19.42)
(6h) n-C <sub>6</sub> H <sub>13</sub> NH		[120/0.2]	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub>	74.04 (74.08)	8.70 (9.02)	17.26 (16.96)
(7a) n-C <sub>3</sub> H <sub>7</sub> NH		98	C <sub>12</sub> H <sub>16</sub> N <sub>3</sub> (201.?)	71.61 (71.6)	7.51 (7.6)	20.88 (21.1)
(7b) i-C <sub>3</sub> H <sub>7</sub> NH		154		(71.23)	(7.73)	(20.48)
(7c) C <sub>6</sub> H <sub>11</sub> NH		125	C <sub>15</sub> H <sub>19</sub> N <sub>3</sub>	74.7 (74.8)	7.9 (8.0)	17.4 (17.3)
(7d) n-C <sub>4</sub> H <sub>9</sub> NH		100	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> (215.?)	72.52 (72.44)	7.96 (8.06)	19.52 (19.65)
(7e) i-C <sub>4</sub> H <sub>9</sub> NH		98		(72.45)	(7.81)	(19.53)
(7f) t-C <sub>4</sub> H <sub>9</sub> NH		108		(72.67)	(8.29)	(19.16)
(7g) n-C <sub>6</sub> H <sub>13</sub> NH		92	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub> (M <sup>+</sup> 243.1734) (243.17) (M <sup>+</sup> 243.1733)	74.03 (74.61)	8.70 (8.28)	17.27 (17.11)
(8a) n-C <sub>3</sub> H <sub>7</sub> NH		119	C <sub>12</sub> H <sub>13</sub> ClN <sub>3</sub> (233)	61.2 (61.0)	6.0 (5.7)	17.8 (18.0)
(8b) i-C <sub>3</sub> H <sub>7</sub> NH		136		(61.5)	(5.6)	(17.4)
(8c) C <sub>6</sub> H <sub>11</sub> NH		126	C <sub>15</sub> H <sub>17</sub> ClN <sub>3</sub> (273)	65.3 (64.9)	6.5 (6.4)	15.3 (15.7)
(8d) n-C <sub>4</sub> H <sub>9</sub> NH		150	C <sub>13</sub> H <sub>15</sub> ClN <sub>3</sub> (247)	62.5 (62.0)	6.5 (6.5)	16.8 (16.9)
(8e) t-C <sub>4</sub> H <sub>9</sub> NH		110	C <sub>13</sub> H <sub>15</sub> ClN <sub>3</sub> (247)	62.0 (62.0)	6.2 (6.2)	17.0 (17.0)
(8f) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH		142	C <sub>16</sub> H <sub>13</sub> ClN <sub>3</sub>	66.3 (66.0)	5.2 (4.8)	15.5 (15.4)
(8g) (CH <sub>3</sub> ) <sub>2</sub> N[CH <sub>2</sub> ] <sub>2</sub> NH		132	C <sub>13</sub> H <sub>16</sub> ClN <sub>4</sub> (58.7)	58.9 (58.7)	6.5 (6.1)	21.1 (21.2)
(8h) (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N[CH <sub>2</sub> ] <sub>2</sub> NH		114	C <sub>15</sub> H <sub>20</sub> ClN <sub>4</sub> (64.3)	64.6 (64.3)	8.1 (7.9)	16.7 (16.4)
(9a) C <sub>6</sub> H <sub>11</sub> NH		98	C <sub>16</sub> H <sub>19</sub> N <sub>3</sub>	74.7 (74.7)	7.9 (8.0)	17.4 (17.3)
(9b) n-C <sub>3</sub> H <sub>7</sub> NH		89	C <sub>12</sub> H <sub>14</sub> N <sub>3</sub>	71.6 (71.4)	7.5 (7.3)	20.8 (20.6)
(9c) i-C <sub>3</sub> H <sub>7</sub> NH		91	C <sub>12</sub> H <sub>14</sub> N <sub>3</sub>	(71.4)	(7.4)	(20.8)
(10a) C <sub>6</sub> H <sub>11</sub> NH		102	C <sub>16</sub> H <sub>19</sub> N <sub>3</sub>	74.7 (74.6)	7.9 (8.0)	17.4 (17.0)
(10b) n-C <sub>3</sub> H <sub>7</sub> NH		108	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub>	71.6 (71.8)	7.5 (7.8)	20.8 (20.6)
(10c) i-C <sub>3</sub> H <sub>7</sub> NH		136–138	C <sub>12</sub> H <sub>16</sub> N <sub>3</sub>	(71.4)	(7.3)	(20.7)
(11a) C <sub>6</sub> H <sub>11</sub> NH		134	C <sub>21</sub> H <sub>30</sub> N <sub>4</sub>	74.6 (74.5)	8.9 (9.1)	16.6 (16.4)
(11b) C <sub>6</sub> H <sub>11</sub> NH		126	C <sub>16</sub> H <sub>18</sub> ClN <sub>3</sub>	65.3 (64.9)	6.6 (6.3)	15.2 (15.0)

\* Satisfactory analyses were not obtained owing to the hygroscopic nature of these compounds.

† H. Suschitzky and M. E. Sutton, *J. Chem. Soc. C*, 1968, 3058.



hexyl) undergoes exchange with D<sub>2</sub>O. The mass spectrum gave the correct molecular ion M<sup>+</sup> 243 (base peak 124).

Diamines formed on photolysis of 6-quinolyl azide in isopropyl-, n-butyl-, and n-hexyl-amines are very unstable so they were cyclised to the corresponding imidazoles (5a–c) by heating the residue obtained after evaporation of the photolysis solvent, with formic acid at reflux. The 3-isopropylimidazo[4,5-f]quinoline (5a) has an i.r. absorption at 1 580 cm<sup>-1</sup> (imidazole C=N) and an n.m.r. signal at δ 8.1 (s, imidazole CH) while the quinoline ring appears at δ 8.95 (2 H and 4 H), 7.5 (3 H), 7.75 (7 H), 8.0 (8 H) and the isopropyl group at 4.66 and 1.6. The mass spectrum gave the correct molecular ion M<sup>+</sup> 211.

The formation of singlet-derived products in the bicyclic azide series appears to be promoted by a combination of internal and external factors. (1) Azides with an electron-withdrawing group in the second (fused) ring give the best yield as instanced by comparing the pho-

TABLE 2  
Yields of products from photolysis of quinolyl azides in secondary amines

Azide (RN <sub>3</sub> )	Photolysis solvent	Apparatus	Products	
			(%) <i>o</i> -Diamines	(%) Quinolylamine
8-Quinolyl-	Diethylamine	Q <sup>a</sup>	(1a) (86)	8-, (12)
8-Quinolyl-	Diethylamine	P <sup>a</sup>	(1a) (74)	8-, (12)
8-Quinolyl-	Diethylamine	S <sup>b</sup>	(1a) (88)	8-, (4)
8-Quinolyl	<i>n</i> -Propylamine	Q	(1b) (54)	8-, (trace)
8-Quinolyl-	Pyrrolidine	Q	(1c) (36)	8-, (15)
8-Quinolyl-	Pyrrolidine	P	(1c) (33)	8-, (46)
8-Quinolyl-	Pyrrolidine : TMEDA (3 : 1) <sup>c</sup>	P	(1c) (36)	8-, (40)
8-Quinolyl-	Pyrrolidine : dioxan (1 : 1)	P	(1c) (42)	8-, (26)
8-Quinolyl-	Piperidine	Q	(1d) (47)	8-, (29)
8-Quinolyl-	Piperidine	P	(1d) (47)	8-, (29)
8-Quinolyl-	Piperidine : TMEDA (3 : 1)	P	(1d) (56)	8-, (34)
8-Quinolyl-	Piperidine : dioxan (1 : 1)	P	(1d) (62)	8-, (13)
8-Quinolyl-	Piperidine : dioxan (3 : 1)	P	(1d) (70)	8-, (6)
8-Quinolyl-	Hexahydroazepine	Q	(1e) (27)	8-, (20)
8-Quinolyl-	Hexahydroazepine	P	(1e) (26)	8-, (38)
8-Quinolyl-	Hexahydroazepine TMEDA (3 : 1)	P	(1e) (49)	8-, (37)
8-Quinolyl-	Hexahydroazepine dioxan (1 : 1)	P	(1e) (56)	8-, (26)
8-Quinolyl-	Morpholine	Q	(1f) (71)	8-, (trace)
8-Quinolyl-	Morpholine	P	(1f) (74)	8-, (trace)
8-Quinolyl-	Morpholine	S	(1f) (70)	8-, (trace)
7-Quinolyl-	Diethylamine	Q	(1n) (74)	7-, (14)
7-Quinolyl-	Piperidine	P	(1o) (60)	7-, (trace)
6-Quinolyl-	Diethylamine	Q	(2a) (92)	6-, (4)
6-Quinolyl-	Diethylamine	S	(2a) (85)	6-, (trace)
6-Quinolyl-	Pyrrolidine	P	(2b) (56)	6-, (20)
6-Quinolyl-	Pyrrolidine : TMEDA (3 : 1)	P	(2b) (58)	6-, (23)
6-Quinolyl-	Piperidine	P	(2c) (77)	6-, (12)
6-Quinolyl-	Piperidine : TMEDA (3 : 1)	P	(2c) (82)	6-, (trace)
6-Quinolyl-	Hexahydroazepine	P	(2d) (70)	6-, (9)
6-Quinolyl-	Hexahydroazepine TMEDA (3 : 1)	P	(2d) (76)	6-, (trace)
6-Quinolyl-	Morpholine	Q	(2e) (88)	6-, (trace)
5-Quinolyl-	Diethylamine	P		5-, (60)
5-Quinolyl-	Diethylamine : dioxan (3 : 1)	P		5-, (36)
5-Quinolyl-	Piperidine	P		5-, (53)
5-Quinolyl-	Piperidine : dioxan (3 : 1)	P		5-, (40)
4-Quinolyl-	Diethylamine	Q		4-, (27)
3-Quinolyl-	Diethylamine	Q	(3a) (83)	3-, (trace)

<sup>a</sup> Irradiation with a medium-pressure mercury lamp in a quartz (Q) or Pyrex (P) vessel. <sup>b</sup> Irradiation with sunlight in a Pyrex vessel. <sup>c</sup> TMEDA = tetramethylethylenediamine.

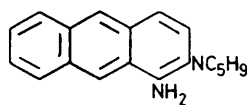
tolysis yields of 5-quinolyl and 1-naphthyl azide under identical conditions in cyclohexylamine yielding 42 and 12%<sup>2</sup> of the respective azepines. A similar effect on yields (*cf.* both azepine and diamine) is exerted by an ethoxycarbonyl group on azide photolyses in the benzo-*[b]*thiophen and indole series.<sup>4</sup>

(2) Yields as expected are highest for the strongest nucleophiles attacking at the least hindered positions. (3) In the case of weaker nucleophiles for attack at a hindered position the choice of a co-solvent often proves crucial to the success of a reaction. Solvents able to co-ordinate a singlet nitrene and thereby to retard singlet-triplet intersystem crossing significantly increase yields of singlet products (*i.e.* azepine and diamine). Such beneficial solvents are for instance tetrahydrofuran, TMEDA, methylene chloride, and dioxan.

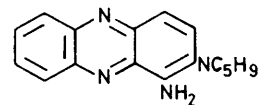
The nature of the singlet-derived products obtained from photolysis of the 1- and 2-naphthyl- and the 3-, 7-chloro-4-, 5-, 6-, 7- and 8-quinolyl azides are listed in Table 4. This shows that photolysis of  $\alpha$ -bicyclic azides in *primary* amines leads generally to azepines (and *o*-diamines for 8-quinolyl azide and for some 7-chloro-4-quinolyl azides) whilst  $\beta$ -bicyclic azides in

*secondary* amines yields *o*-diamines. A mechanistic rationale for this behaviour has already been proposed.<sup>4</sup> Since azepines are considered to be the product of kinetic and diamines that of thermodynamic control, structural features that stabilize azepines should also tend to favour their formation as reaction products. These structural features include: (1) an amidine system, (2) a re-aromatized ring annelated to the azepine, and (3) the sp<sup>3</sup> carbon (CH<sub>2</sub>) adjacent to the ring junction in the final azepine.

We tested the predicative powers of the above observations on a series of isoquinolyl azides as well as on two examples from azides quoted in the literature (*cf.* Table 5). As the reaction products obtained accord with prediction we feel that the above criteria provide useful guidelines for synthetic approaches to azepines or *o*-diamines from aromatic and heteroaromatic azides.



(18)



(19)

TABLE 3  
Yields of products from photolysis of quinolyl azides in primary amines

Azide (RN <sub>3</sub> )	Photolysis solvent	Apparatus (cf. Table 2)	Products		
			(%) Azepine	(%) <i>o</i> -Diamine	(%) Quinolylamine
8-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	P	(6c) (40)	(1l) (20)	
8-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> : TMEDA (15 : 1)	P	(6c) (57)	(1l) (27)	8-, (6)
8-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> : TMEDA (15 : 1)	Q	(6c) (65)	(1l) (20)	8-, (6)
8-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> : TMEDA (1 : 1)	P	(6c) (49)	(1l) (26)	
8-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> : TMEDA (1 : 15)	P	(6c) (26)	(1l) (49)	8-, (7)
8-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> : TMEDA (1 : 15)	Q	(6c) (33)	(1l) (43)	8-, (7)
8-Quinolyl-	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>	P	(6a) (42)		
8-Quinolyl-	i-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(6b) (43)	(1g) (15)	8-, (17)
8-Quinolyl-	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(6d) (47)	(1i) (20)	8-, (12)
8-Quinolyl-	i-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(6e) (56)	(1j) (12)	8-, (7)
8-Quinolyl-	s-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(6f) (17)	(1k) (23)	8-, (9)
8-Quinolyl-	t-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(6g) (46)	(1h) (32)	8-, (10)
8-Quinolyl-	n-C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(6h) (32)	(1m) (37)	8-, (18)
7-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	Q		(1p) (57)	7-, (29)
6-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	Q		(2f) (67)	6-, (7)
6-Quinolyl-	i-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q		(5a) (75) <sup>a</sup>	<i>b</i>
7-Quinolyl	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q		(5b) (71) <sup>a</sup>	<i>b</i>
6-Quinolyl-	n-C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q		(5c) (71) <sup>a</sup>	<i>b</i>
5-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	Q	(7c) (42)		
5-Quinolyl-	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>	Q	(7a) (43)		
5-Quinolyl-	i-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(7b) (53)		5-, (20)
5-Quinolyl-	n-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(7d) (60)		5-, (15)
5-Quinolyl-	i-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(7e) (37)		5-, (22)
5-Quinolyl-	t-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(7f) (32)		5-, (23)
5-Quinolyl-	n-C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub> : TMEDA (3 : 1)	Q	(7g) (56)		5-, (13)
7-Chloro-4-quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8c) (40)	(4c) (15)	17, (2)
7-Chloro-4-quinolyl-	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8a) (42)	(4b) (20)	(4a, R <sup>1</sup> = NH <sub>2</sub> R <sup>2</sup> = H) (5)
7-Chloro-4-quinolyl-	i-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8b) (35)	(4a) (20)	(4a, R <sup>1</sup> = NH <sub>2</sub> R <sup>2</sup> = H) (2)
7-Chloro-4-quinolyl-	n-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8d) (45)		(4a, R <sup>1</sup> = NH <sub>2</sub> R <sup>2</sup> = H) (10)
7-Chloro-4-quinolyl-	t-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8e) (35)		(4a, R <sup>1</sup> = NH <sub>2</sub> R <sup>2</sup> = H) (10)
7-Chloro-4-quinolyl-	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8f) (55)	(4d) (25)	(4a, R <sup>1</sup> = NH <sub>2</sub> R <sup>2</sup> = H) (5)
7-Chloro-4-quinolyl-	(CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8g) (15)		(4a, R <sup>1</sup> = NH <sub>2</sub> R <sup>2</sup> = H) (10)
7-Chloro-4-quinolyl-	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> : TMEDA (14 : 1)	P	(8h) (20)		(4a, R <sup>1</sup> = NH <sub>2</sub> R <sup>2</sup> = H) (10)
3-Quinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	P			3-, (78)

<sup>a</sup> Isolated as imidazole derivatives. <sup>b</sup> Not determined.

TABLE 4

Types of products formed on photolysis of  $\alpha$ -<sup>a</sup> and  $\beta$ -<sup>a</sup>-6,6 fused bicyclic aromatic azides in amines

	Reactants		Singlet-derived products	
	Azide	Amine	Azepine	Diamine
$\alpha$ -Type				
1-Naphthyl-		Primary	✓	—
		Secondary	—	✓
7-Chloro-4-quinolyl-		Primary	✓	✓
		Secondary	—	—
5-Quinolyl-		Primary	✓	—
		Secondary	—	—
8-Quinolyl-		Primary	✓	✓
		Secondary	—	✓
$\beta$ -Type				
2-Naphthyl-		Primary	—	—
		Secondary	—	✓
3-Quinolyl-		Primary	—	—
		Secondary	—	✓
6-Quinolyl-		Primary	—	✓
		Secondary	—	✓
7-Quinolyl-		Primary	—	✓
		Secondary	—	✓

<sup>a</sup> Naphthalene nomenclature.

## EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer, <sup>1</sup>H N.m.r. spectra on a Perkin-Elmer R32 90 MHz spectrometer, and mass spectra on an A.E.I. MS12 or MS9 instrument.

*Quinolyl Azides*.—The 3-, 5-, 6-, 7-, and 8-isomers were prepared from the corresponding amines by diazotization followed by addition of sodium azide. All are known compounds and their physical properties were in agreement with those reported in the literature. Aminoquinolines (except for the 3-isomer which was obtained from the Aldrich Chemical Co.) were obtained by reduction of the appropriate nitroquinoline (made by the Skraup reaction) with iron and acetic acid.

*4-Quinolyl Azide*.—This compound was prepared from the corresponding hydrazine (obtained by a known sequence of reactions<sup>7</sup>) by diazotization followed by addition of sodium azide.

*7-Chloro-4-quinolyl Azide*.—4,7-Dichloroquinoline (12 g, 0.06 mol) and sodium azide (7 g, 0.1 mol) in DMSO (200 ml) were stirred at 60 °C for 3 h. The mixture was poured into water (200 ml) and extracted with chloroform. The chloroform layer was washed with water (5 × 100 ml) and dried

TABLE 5  
Photolysis products of aromatic and heteroaromatic azides in amines

Azide (RN <sub>3</sub> )	Photolysis solvent	Singlet-derived products		
		(%) Azepine	R <sup>1</sup>	(%) <i>o</i> -Diamine
4-Isoquinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	(9a) (32)	C <sub>6</sub> H <sub>11</sub> NH	
	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>	(9b) (28)	n-C <sub>3</sub> H <sub>7</sub> NH	
	i-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>	(9c) (25)	i-C <sub>3</sub> H <sub>7</sub> NH	
5-Isoquinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	(10a) (50)	C <sub>6</sub> H <sub>11</sub> NH	
	n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>	(10b) (28)	n-C <sub>3</sub> H <sub>7</sub> NH	
	i-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>	(10c) (35)	i-C <sub>3</sub> H <sub>7</sub> NH	
5-Chloro-8-isoquinolyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> (4h)	(11a) (30)	C <sub>6</sub> H <sub>11</sub> NH	
		(11b) (20)		
2-Anthracenyl-	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> (8h)	(11a) (42)	C <sub>6</sub> H <sub>11</sub> NH	(18) (50) <sup>a</sup>
2-Phenaziny-	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH			(19) (23) <sup>b</sup>
	C <sub>5</sub> H <sub>9</sub> NH <sub>2</sub>			

<sup>a</sup> J. Rigaudy, C. Icier, and J. Barcelo, *Tetrahedron Lett.*, 1975, 3845. <sup>b</sup> G. F. Bettinetti, E. Fasani, G. Minoli, and S. Pietra, *Gazz. Chim. Ital.*, 1980, **110**, 135.

TABLE 6  
I.r. and <sup>1</sup>H n.m.r. spectroscopic data for *o*-diamines

I.r. (cm <sup>-1</sup> ) in Nujol	2-H	<i>J</i>	3-H	<i>J</i>	4-H	<i>J</i>	5-H	<i>J</i>	6-H	N.O.E. enhance- ment *	NH <sub>2</sub>	R <sup>1</sup>	N.m.r. of R <sup>1</sup>
(1a) 3 410, 3 300	8.65dd	(5)	6.95dd	(8)	7.84dd	(2)	7.35d	(8)	6.99d	27	4.68s	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	3.42q, 0.95t
(1b) 3 450, 3 340	8.65dd	(5)	6.92dd	(8)	7.78dd	(2)	7.25d	(8)	6.90d		4.70s	(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> N	3.3q, 8.6sex, 0.90t
(1c) 3 420, 3 280	8.60dd	(5)	6.87dd	(8)	7.80dd	(2)	7.30d	(8)	6.95d	19	4.50s	C <sub>4</sub> H <sub>9</sub> N	3.3t, 1.9qu
(1d) 3 460, 3 350	8.65dd	(5)	6.99dd	(8)	7.85dd	(2)	7.35d	(8)	7.05d	21	4.55s	C <sub>6</sub> H <sub>10</sub> N	3.85d, 2.85d, 1.65bs
(1e) 3 475, 3 355	8.65dd	(5)	6.95dd	(8)	7.85dd	(2)	7.30d	(8)	7.03d	23	4.55s	C <sub>6</sub> H <sub>12</sub> N	3.60bd, 3.10bd, 1.75bs
(1f) 3 450, 3 340	8.77dd	(5)	6.97dd	(8)	7.89dd	(2)	7.39d	(8)	7.00d	21	4.50s	O-[CH <sub>2</sub> ] <sub>2</sub> -N-[CH <sub>2</sub> ] <sub>2</sub>	4.10d, 3.80d, 2.50bs
(1g) 3 450, 3 350	8.68dd	(6)	7.22dd	(8)	7.95dd	(2)	7.30d	(8)	7.00d		4.28bs	i-C <sub>3</sub> H <sub>7</sub> N	3.3m, 1.2d
(1h) 3 450, 3 350	8.70dd	(6)	7.2dd	(8)	7.93dd	(2)	7.30d	(8)	7.00d		4.40bs	t-C <sub>4</sub> H <sub>9</sub> N	1.25s
(1i) 3 450, 3 350	8.57dd	(6)	7.22d	(8)	7.88dd	(2)	7.30d	(8)	7.00d		4.24bs	n-C <sub>4</sub> H <sub>9</sub> N	3.35t, 1.8--1.2m, 0.9t
(1j) 3 450, 3 350	8.67dd	(6)	7.20dd	(8)	7.90dd	(2)	7.28d	(8)	7.00d		4.4bs	i-C <sub>4</sub> H <sub>9</sub> N	3.20d, 1.9m, 0.9d
(1k) 3 450, 3 350	8.70dd	(6)	7.20dd	(8)	8.0dd	(2)	7.30d	(8)	7.00d		4.25bs	s-C <sub>4</sub> H <sub>9</sub> N	3.50m, 1.7--1.1m, 1.0t
(1m) 3 450, 3 350, 3 250	8.70dd	(5)	7.00dd	(8)	7.87dd	(2)	7.20d	(7)	6.95d		4.5bs	n-C <sub>6</sub> H <sub>13</sub> N	3.10t, 1.6--1.35m, 0.9t
(1n) 3 460, 3 310	8.65d	(5)	7.05dd	(8)	7.85dd	(2)	7.35dd	(8)	7.15d		5.27s	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	2.95q, 0.93t
(1p) 3 400, 3 320	8.80dd	(5)	7.00dd	(8)	8.00dd	(2)	7.30d	(8)	7.10d		4.20s	C <sub>6</sub> H <sub>11</sub> N	3.40bs, 2.2--1.0m
(2a) 3 410, 3 180	8.55dd	(5)	7.30dd	(8)	8.18dd	(2)	7.53s		7.53s		4.7s	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	3.0q, 0.99t
(2b) 3 405, 3 185	8.79dd	(5)	7.24dd	(8)	8.14dd	(2)	7.53s		7.53s		4.5s	C <sub>4</sub> H <sub>9</sub> N	3.1m, 1.95m
(2c) 3 405, 3 185	8.76dd	(5)	7.20dd	(8)	8.20dd	(2)	7.50bs		7.50bs		4.7s	C <sub>6</sub> H <sub>10</sub> N	2.9t, 1.68t
(2d) 3 475, 3 360	8.76dd	(5)	7.18dd	(8)	8.10dd	(2)	7.51s		7.51s		4.68bs	C <sub>6</sub> H <sub>12</sub> N	3.03t, 1.73s
(2e) 3 475, 3 360	8.85dd	(5)	7.3dd	(8)	8.20dd	(2)	7.63d	(8)	7.50d		4.8s	O-[CH <sub>2</sub> ] <sub>2</sub> -N-[CH <sub>2</sub> ] <sub>2</sub>	2.95t, 3.9t
(2f) 3 450, 3 350	8.60dd	(5)	7.1dd	(7)	8.0dd	(2)	7.6d	(8)	7.2d		4.0bs		3.2bs, 2.1--0.7m

TABLE 6 (continued)

	I.r. (cm <sup>-1</sup> ) in Nujol		5-H	<i>J</i>	6-H	7-H	8-H	NH <sub>2</sub>	NH	R <sup>1</sup>	N.m.r. of R <sup>1</sup>
	<i>ν</i> <sub>NH<sub>2</sub></sub>	2-H	←————— 8—7.37 —————→								
(3a)	3 400, 3 280	8.57s						5.35s		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N	3.05q, 1.03t
(4a)	3 500, 3 150	8.3s	7.7d		7.4dd		7.99dd	4.8s	7.5	<i>i</i> -C <sub>3</sub> H <sub>7</sub> N	4.0m, 1.6s
(4b)	3 500, 3 150	8.5s	7.7d		7.4dd		8.1d	4.8bs	7.8	<i>n</i> -C <sub>3</sub> H <sub>7</sub> N	3.9m, 1.3—1.6m
(4c)	3 500, 3 150	8.6s	7.7d		7.3dd		7.8d	6.5bs	7.2	C <sub>6</sub> H <sub>11</sub> N	4.2m, 1.2—2.3m
(4d)	3 500, 3 200	8.6s	7.6d		7.3m		7.8d	6.2s	7.0	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N	4.8d, 7.3m

\* Refers to increase of 6-H on irradiation of the NH<sub>2</sub>-group.

TABLE 7

I.r. and <sup>1</sup>H n.m.r. spectroscopic data for azepino[*b*]pyridines

	I.r. (cm <sup>-1</sup> ) in Nujol		2-H	<i>J</i>	3-H	<i>J</i>	4-H	<i>J</i>	CH <sub>2</sub>	6-H	7-H	R <sup>1</sup>	N.m.r. of R <sup>1</sup>
	<i>ν</i> <sub>NH</sub> <i>ν</i> <sub>O=N</sub>												
(6a)	3 300, 1 600	8.55dd	(5)	7.3dd	(6)	7.5dd	(2)	3.0d	(7)	5.2q	(10)	6.7d	<i>n</i> -C <sub>3</sub> H <sub>7</sub> 6.0d, 3.5q, 1.7sex, 1.0t
(6b)	3 285, 1 595	8.45dd	(6)	7.38dd	(8)	7.45dd	(2)	3.0d	(7)	5.12q	(7)	6.61d	<i>i</i> -C <sub>3</sub> H <sub>7</sub> 5.75, 4.25m, 1.3d
(6c)	3 280, 1 602	8.5dd	(5)	7.3dd	(6)	7.45dd	(2)	3.0d	(7)	5.1q	(7)	6.6d	C <sub>6</sub> H <sub>11</sub> 5.8bs, 3.0bd, 2.1—1.3
(6d)	3 285, 1 595	8.45dd	(6)	7.28dd	(8)	7.46dd	(2)	3.0d	(7)	5.14q	(7)	6.65d	<i>n</i> -C <sub>4</sub> H <sub>9</sub> 6.0bs, 3.48q, 1.8—1.3m, 1.0t
(6e)	3 285, 1 600	8.42dd	(6)	7.15dd	(8)	7.38dd	(2)	2.98d	(7)	5.05q	(7)	6.59d	<i>i</i> -C <sub>4</sub> H <sub>9</sub> 5.88bs, 3.3t, 1.92m, 1.0d
(6f)	3 285, 1 595	8.48dd	(6)	7.28dd	(8)	7.45dd	(2)	2.9d	(7)	5.1q	(7)	6.6d	<i>s</i> -C <sub>4</sub> H <sub>9</sub> 5.80bs, 4.17m, 1.8—0.9m
(6g)	3 280, 1 600	8.44dd	(6)	7.28dd	(8)	7.42dd	(2)	2.96d	(7)	5.09q	(7)	6.57d	<i>t</i> -C <sub>4</sub> H <sub>9</sub> 5.65bs, 1.5s
(6h)	3 280, 1 605	8.5dd	(5)	7.3dd	(6)	7.45dd	(2)	3.02d	(7)	5.15q	(7)	6.65d	<i>n</i> -C <sub>6</sub> H <sub>13</sub> 6.0bs, 3.47q, 1.8—1.5m, 1.0t
(7a)	3 215, 1 595	8.5dd	(5)	7.2dd	(6)	7.8dd	(2)	3.2d	(8)	5.10q	(7)	6.6d	(7) <i>n</i> -C <sub>3</sub> H <sub>7</sub> 5.0bd, 3.4t, 1.6sex, 0.9t
(7b)	3 200, 1 595	8.54dd	(6)	7.2dd	(8)	7.78dd	(2)	3.26d	(7)	5.14q	(7)	6.55d	(7) <i>i</i> -C <sub>3</sub> H <sub>7</sub> 4.3bs, 1.27d
(7c)	3 215, 1 595	8.5dd	(5)	7.2dd	(6)	7.8dd	(2)	3.3d	(7)	5.1q	(7)	6.6d	(8) C <sub>6</sub> H <sub>11</sub> 5.3bs, 4.0bd, 2.1—1.0m
(7d)	3 200, 1 590	8.5dd	(6)	7.2dd	(8)	7.8dd	(2)	3.25d	(7)	5.15q	(7)	6.58d	(7) <i>n</i> -C <sub>4</sub> H <sub>9</sub> 4.7bs, 3.5t, 1.8—1.3m
(7e)	3 215, 1 595	8.55dd	(6)	7.24dd	(8)	7.84dd	(2)	3.25d	(7)	5.15q	(7)	6.57d	(7) <i>i</i> -C <sub>4</sub> H <sub>9</sub> 2.0m, 1.0d
(7f)	3 200, 1 595	8.5dd	(6)	7.2dd	(8)	7.76dd	(2)	3.25d	(7)	5.10q	(7)	6.55d	(7) <i>t</i> -C <sub>4</sub> H <sub>9</sub> 4.2bs, 1.5
(7g)	3 200, 1 590	8.55dd	(6)	7.2dd	(8)	7.8dd	(2)	3.26d	(7)	5.15q	(7)	6.6d	(7) <i>n</i> -C <sub>6</sub> H <sub>13</sub> 4.55bs, 3.45t, 1.8—1.2m, 0.9t

TABLE 8

I.r. and <sup>1</sup>H n.m.r. spectroscopic data for benzodiazepines

	I.r. (cm <sup>-1</sup> ) in Nujol		N'-H	2-H	3-H	6-H	7-H	9-H	NH	R'	N.m.r. of R <sup>1</sup>
	<i>ν</i> <sub>NH</sub> <i>ν</i> <sub>O=N</sub>										
(8a)	3 200, 1 605			7.44dd	6.7d	8.2d	7.9dd	8.4d		<i>n</i> -C <sub>3</sub> H <sub>7</sub>	3.6m, 2.3—1.0bm
(8b)	3 150, 1 605			7.5dd	6.7d	7.9d	7.7br	8.6d		<i>i</i> -C <sub>3</sub> H <sub>7</sub>	4.0m, 1.5s
(8c)	3 200, 1 605			7.3dd	6.7d	7.8d	7.7dd	8.6d		C <sub>6</sub> H <sub>11</sub>	4.2m, 2.0—1.0bm
(8d)	3 200, 1 605			7.4dd	6.7d	8.2d	7.8dd	8.4d		<i>n</i> -C <sub>4</sub> H <sub>9</sub>	3.6m, 2.2—1.4bm
(8e)	3 200, 1 605			7.4dd	6.7d	8.2d	7.8dd	8.4d		<i>t</i> -C <sub>4</sub> H <sub>9</sub>	2.0—1.8s
(8f)	3 200, 1 605			← 7.3—6.9m →		7.6dd	7.3—6.9m	8.6d		C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub>	7.3—6.9m, 4.8d
(8g)	3 200, 1 605			7.3dd	6.7d	7.9d	7.6dd	8.4d		(CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub>	2.7bm, 2.2s
(8h)	3 200, 1 605			7.4dd	6.6d	8.4d	7.9dd	8.7d		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub>	3.2q, 2.5bm, 1.5t
(9a)	3 150, 1 605	5.5s	8.6s				← 7.4—7.0m →		5.0br	C <sub>6</sub> H <sub>11</sub>	2.2—1.1bm
(9b)	3 150, 1 605	5.4s	8.5s				← 7.4—7.0m →		4.4br	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	3.8br, 2.2—1.0m
(9c)	3 150, 1 605	5.5s	8.5s				← 7.4—7.0m →		5.0br	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	4.2m, 1.5s



TABLE 9  
I.r. and  $^1\text{H}$  n.m.r. spectroscopic data for azepino[*c*]pyridines

	I.r. ( $\text{cm}^{-1}$ ) in Nujol		1-H	3-H	4-H	7-H	8-H	$\text{CH}_2$	NH	$\text{R}^1$	
	$\nu_{\text{NH}}$	$\nu_{\text{C=N}}$									
(10a)	3 200, 1 605		8.5s	8.4d	7.3d	6.5d	5.2q	3.0d	4.0br	$\text{C}_6\text{H}_{11}$	4.0br, 1.0br
(10b)	3 200, 1 604		8.4s	8.3d	7.4d	6.5d	5.2q	3.1d	4.1br	$n\text{-C}_3\text{H}_7$	4.7m, 1.8—1.6br
(10c)	3 200, 1 605		8.5s	8.4d	7.4d	6.5d	5.2q	3.0d	4.0br	$i\text{-C}_8\text{H}_7$	4.7m, 1.5s
							6-H	5-H			
(11a)	3 200, 1 605		9.6s	8.6d	7.2d	6.8d	7.0dd	4.0d	5.0br	$\text{C}_6\text{H}_{11}$	2.2—1.1br
(11b)	3 200, 1 605		9.5s	8.7d	7.2d	6.8d	7.1d	4.0d	5.0br	$(\text{C}_6\text{H}_{11})_2$	2.2—1.1br

( $\text{MgSO}_4$ ). Chromatography on alumina with chloroform-light petroleum (1:1) gave the azide 10.9 g (90%), m.p. 118 °C,  $\nu_{\text{max}}$  2 200 ( $\text{N}_3$ ) and 1 605  $\text{cm}^{-1}$  ( $\text{C=N}$ );  $\delta(\text{CDCl}_3)$  7.8 (1 H, d, 3-H), 8.0 (1 H, dd, 6-H), 8.4 (1 H, d, 5-H), 8.5 (1 H, d, 8-H), and 9.3 (1 H, d, 2-H) (Found: C, 52.6; H, 2.4; N, 27.2.  $\text{C}_9\text{H}_5\text{ClN}_4$  requires C, 52.8; H, 2.5; N, 27.4).

*Isoquinolyl Azides*.—The isomeric 4- (m.p. 64 °C; 82%) and 5- (m.p. 70—72 °C; 86%) isoquinolyl azides were prepared by the method below described for 5-chloro-8-isoquinolyl azide from the corresponding, known amines. They were purified by chromatography (alumina type H) and characterised by i.r. and n.m.r. spectroscopy.

*5-Chloroisoquinolyl Azide*.—Sodium nitrite solution (1.4 g, 0.02 mol, 10 ml) was added dropwise to a solution of 5-chloro-8-quinolylamine (2.5 g, 0.015 mol) in concentrated hydrochloric acid (10 ml) whilst the temperature was maintained below 5 °C. This solution was added to a solution of sodium azide (2.5 g, 0.04 mol) and sodium acetate (5.1 g, 0.08 mol) in water (50 ml). The product was extracted with chloroform and the extract concentrated under reduced pressure; crystallisation of the residue from light petroleum (b.p. 160—180 °C) gave the azide 1.5 g (50%), m.p. 123 °C,  $\nu_{\text{max}}$  2 300 ( $\text{N}_3$ ) and 1 605  $\text{cm}^{-1}$  ( $\text{C=N}$ ) (Found: C, 52.5; H, 2.4; N, 27.2.  $\text{C}_9\text{H}_5\text{ClN}_4$  requires C, 52.8; H, 2.5; N, 27.4).

*Photolysis of Azides in Amines: General Procedure*.—A solution of the azide (1 g) in the amine (100 ml) or amine and co-solvent, was purged with nitrogen for at least 10 min prior to photolysis. The stirred solution was irradiated at

room temperature under nitrogen, using a water-cooled immersion well containing a medium-pressure mercury arc (*cf.* Table). Each reaction was monitored by observing the disappearance of the azide i.r. band. After the azide peak had disappeared the amine was distilled off under reduced pressure and the residue chromatographed on alumina (type H), to yield the products.

We thank S.R.C. for studentships (B. N. and F. H.) and the University for a demonstratorship (Z. U. K.).

[1/835 Received, 27th May, 1981]

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