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Synthesis and Thermolysis of 3-Azidoindolenines

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Several new 3-azidoindolenines have been synthesized in high yields (i) by the reaction of 2,3-disubstituted indoles with iodine azide or bromine azide, and (ii) by the reaction of 3-chloroindolenines with sodium azide in acetic acid. The 3-azidoindolenines undergo thermal rearrangement in variable yields and ratios to quinoxalines and quinazolines, along with the formation of the parent indoles. The ring-expansion of 3-azido-2,3-diphenylindolenine to 2,3-diphenylquinoxaline also occurs on treatment with acid but in much lower yield. Photolysis of the 3-azidoindolenines gives the parent indoles as major products.

Keywords——iodine azide; bromine azide; 3-haloindolenines; ring-expansion; quinoxalines; quinazolines; photolysis

The ring expansion of organic azides is a generally useful reaction[2] and has been applied to the synthesis of some nitrogen-containing heterocycles which include phenanthridines,[3] benz[*f*]-1,4-oxazepines,[4] dibenz[*b*,*f*]-1,4-oxazepines,[5] 2-azanaphthoquinones,[6] imidazolinones,[7] and azahomotriptycenes.[8] Recently we have described the synthesis of 3-azido-2,3-diphenyl- (**3a**) and 3-azido-3-methyl-2-phenyl-indolenines (**3b**), and their thermal rearrangement to quinoxaline and quinazoline ring systems.[9] The formation of the latter ring system is of particular interest because the reaction must occur with migration of an imino group to nitrogen. We now wish to report more detailed studies of the synthesis and ring-expansion reactions of the 3-azidoindolenines.

Synthesis

The synthesis of 3-azidoindolenines **3a** and **3b** was first achieved by treating indoles **1a**, **b** with 2 molar equiv. of iodine azide[10] prepared *in situ* in dry acetonitrile (Method A). This method was successfully applied to the synthesis of 5- and 6-substituted 3-azido-3-methyl-2-phenylindolenines (**3e—i**), 3-azido-3-ethyl- (**3c**) and 3-azido-3-*n*-propyl-2-phenylindolenines (**3d**), and 3-azido-2-ethoxycarbonyl-3-methylindolenine (**3j**), and the yields were generally high. However, this method failed with 2-acetyl-3-phenylindole, 2-benzoyl-3-methylindole, and dimethyl indole-2,3-dicarboxylate (**1k**). 2,3-Dimethylindole and 1,2,3,4-tetrahydrocarbazole did not give the corresponding 3-azidoindolenines but afforded 2-azidomethyl-3-methylindole and 1-azido-1,2,3,4-tetrahydrocarbazole, respectively. The details of the latter reaction

1) Location: *133–1, Yamada-kami, Suita, Osaka, 565, Japan.*
2) D.V. Banthorpe, "The Chemistry of the Azido Group," ed. by S. Patai, Interscience Publishers, London, 1971, p. 397.
3) *a*) C.L. Arcus and J.V. Evans, *J. Chem. Soc.*, **1958**, 789, and earlier papers; *b*) M.M. Cooms, *J. Chem. Soc.*, **1958**, 3454.
4) J.P. Le Roux, J.-C. Cherton, and P.-L. Desbene, *C. R. Acad. Sci.*, **278** (*C*), 1389 (1974).
5) R.H.B. Galt, J.D. Loudon, and A.D.B. Sloan, *J. Chem. Soc.*, **1958**, 1588.
6) H.W. Moore and D.S. Pearce, *Tetrahedron Lett.*, **1971**, 1621.
7) J.S. Millership and H. Suschitzky, *Chem. Commun.*, **1971**, 1496.
8) H. Quast and P. Eckert, *Angew. Chem. Int. Ed. Engl.*, **15**, 168 (1976).
9) M. Ikeda, F. Tabusa, Y. Nishimura, S. Kwon, and Y. Tamura, *Tetrahedron Lett.*, **1976**, 2347.
10) A. Hassner and F.W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968); *a*) Y. Tamura, M. W. Chun, K. Ohno, S. Kwon, and M. Ikeda, *Chem. Pharm. Bull.* (Tokyo), **26**, 2874 (1978).

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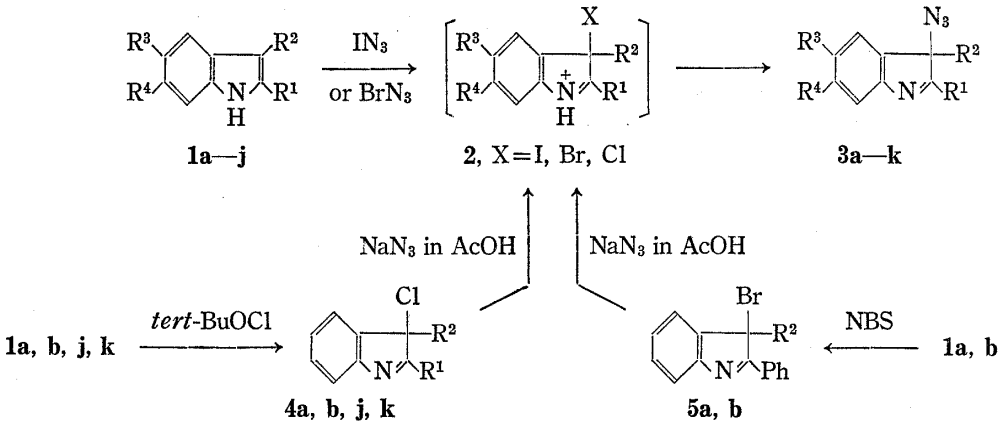
will be reported in a subsequent paper.[10a] Bromine azide[11] prepared *in situ* in methylene chloride could also be used for the conversion of **1a** and **1b** to **3a, b.**

Alternatively, the formation of 3-azidoindolenines **3a, b, j, k** was accomplished in excellent yields by reaction of the readily accessible 3-chloroindolenines **4a, b, j, k** with sodium azide in acetic acid (Method B).[12] Similar treatment of 3-bromoindolenines **5a** and **5b** also gave **3a, b** in quantitative yield.



a : $R^1=R^2=Ph$, $R^3=R^4=H$; **b** : $R^1=Ph$, $R^2=Me$, $R^3=R^4=H$;
c : $R^1=Ph$, $R^2=Et$, $R^3=R^4=H$; **d** : $R^1=Ph$, $R^2=n$-Pr $R^3=R^4=H$;
e : $R^1=Ph$, $R^2=R^3=Me$, $R^4=H$; **f** : $R^1=Ph$, $R^2=Me$, $R^3=Cl$, $R^4=H$;
g : $R^1=Ph$, $R^2=Me$, $R^3=NO_2$, $R^4=H$; **h** : $R^1=Ph$, $R^2=R^4=Me$, $R^3=H$;
i : $R^1=Ph$, $R^2=Me$, $R^3=H$, $R^4=Br$; **j** : $R^1=CO_2Et$, $R^2=Me$, $R^3=R^4=H$;
k : $R^1=R^2=CO_2Me$, $R^3=R^4=H$

Chart 1

The structures of 3-azidoindolenines **3a—k** were assigned on the basis of the spectral and chemical evidence; for example, compound **3b** showed a strong azide band at 2100 cm^{-1} in the infrared (IR) spectrum and ultraviolet (UV) absorption of a typical indolenine structure.[13] The nuclear magnetic resonance (NMR) spectrum of **3b** showed a 3-methyl singlet at δ 1.60. Reduction of **3a** and **3b** either by catalytic hydrogenation over 5% palladium carbon or with lithium aluminum hydride in ether reverted to the parent indoles **1a, b** in high yields.

The fact that reaction of 3-haloindolenines **4** and **5** with sodium azide proceeds only in acidic medium[14] strongly suggests the intermediacy of 3-haloindoleninium ions **2**, which are attacked by azide anion. The reaction of **1** with iodine azide or bromine azide is also considered to proceed *via* 3-haloindoleninium ions **2.**

Ring-expansion of 3-Azidoindolenines

$$R_3C\text{-}N_3 \xrightarrow[\text{or acid}]{\text{heat, light}} R_2C{=}NR$$

Chart 2

Tertiary alkyl azides are well known to undergo thermal, photochemical, or acid-catalyzed rearrangement to give anils.[2] Therefore, we have examined the behavior of 3-azidoindolenines **3** toward heat, light, and acid.

Initially, attention was directed to the differing behavior between **3a** and **3b** toward heat. Thus, refluxing **3a** in dimethylformamide for 16 hr gave 2,3-diphenylquinoxaline (**6a**) and 2,4-diphenylquinazoline (**7a**) in a ratio of 29: 1. In contrast, **3b** was transformed in this

11) A. Hassner, F.P. Boerwinkle, and A.B. Levy, *J. Am. Chem. Soc.*, **92**, 4879 (1970).
12) Y. Tamura, M.W. Chun, H. Nishida, and M. Ikeda, *Heterocycles*, **8**, 313 (1977).
13) von E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **51**, 16 (1968).
14) No reaction took place in non-acidic solvent such as acetonitrile, aqueous acetone, or dimethylformamide even under refluxing conditions.

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temperature range for 16 hr to 2-methyl-3-phenylquinoxaline (**6b**) and 4-methyl-2-phenylquinazoline (**7b**) in a ratio of 2.3: 1.[15] In both cases, the concomitant formation of a trace amount of the parent indoles **1a** and **1b** was observed. Other 3-azidoindolenines (**3c—k**) also rearranged to quinoxalines **6c—k** and quinazolines **7c—j** in variable yields and ratios along with the formation of the indoles **1c—j**.

The isomer distributions were determined by gas–liquid chromatography (GLC) analysis of the crude mixture, and the two isomeric products and indoles were separated by preparative thin–layer chromatography (TLC). Structure assignments of **6** and **7** were based mainly on the UV spectra which show diagnostic difference (see Table IV). In addition, the structures of **6a, b, j** and **7a, b, c, d** were confirmed by the direct comparisons (IR spectra and mixed mp determination) with authentic samples.

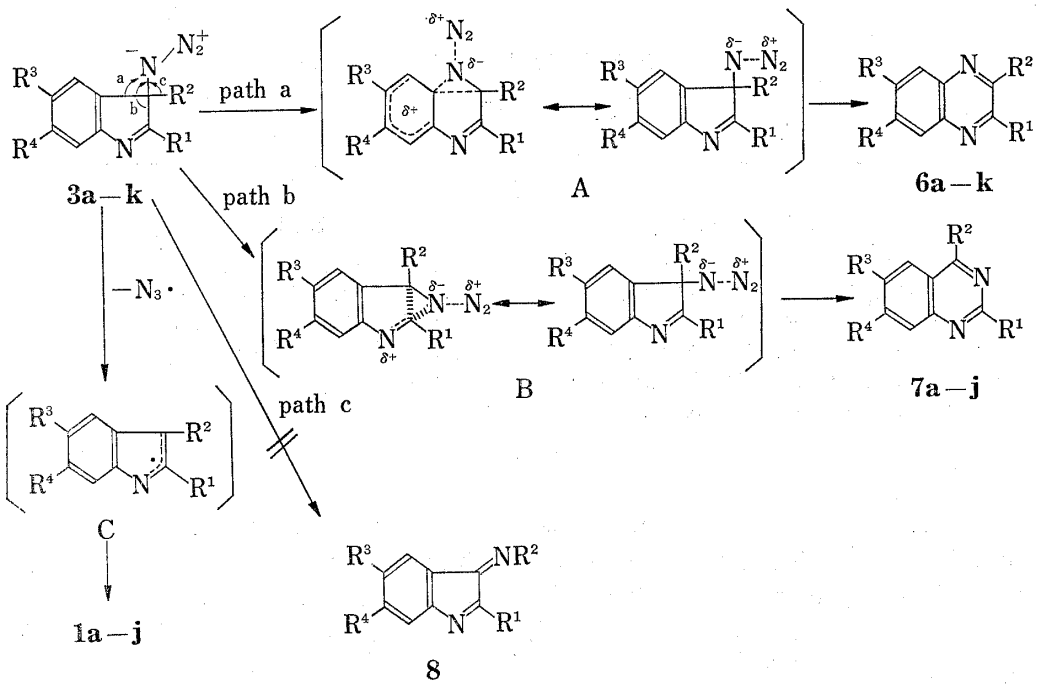

Chart 3

Table I. Product Distribution in Thermolysis of 3-Azidoindolenines

3	R^1	R^2	R^3	R^4	Quinoxaline **6**	Quinazoline **7**	Indole **1**	Ratio (6/7)
a	Ph	Ph	H	H	95[a] (82)[b]	3[a] (0.4)[b]	2[a] (trace)[b]	29
b	Ph	Me	H	H	64 (47)	29 (26)	7 (trace)	2.3
c	Ph	Et	H	H	67 (47)	29 (31)	4 (trace)	2.3
d	Ph	*n*-Pr	H	H	76 (47)	15 (17)	9 (trace)	5.1
e	Ph	Me	Me	H	60 (46)	36 (26)	4 (trace)	1.7
f	Ph	Me	Cl	H	46 (20)	47 (30)	7 (trace)	1.0
g	Ph	Me	NO_2	H	15 (10)	0.7[c] (0)	84.3 (55)	22
h	Ph	Me	H	Me	78 (34)	15 (19)	7 (trace)	5.3
i	Ph	Me	H	Br	65 (39)	30 (25)	5 (trace)	2.2
j	CO_2Et	Me	H	H	62 (28)	7[c] (0)	31 (19)	8.6
k	CO_2Me	CO_2Me	H	H	*ca.* 100 (47)	*ca.* 0 (0)	*ca.* 0 (0)	only **6**

a) Product ratio determined by GLC analysis.
b) Isolated yield (%) in parentheses.
c) The structure was not confirmed.

15) In a preliminary communication,[9] we described that **3a** and **3b** rearrange exclusively **6a** and **7b**, respectively. However, careful examination revealed that this is actually incorrect.

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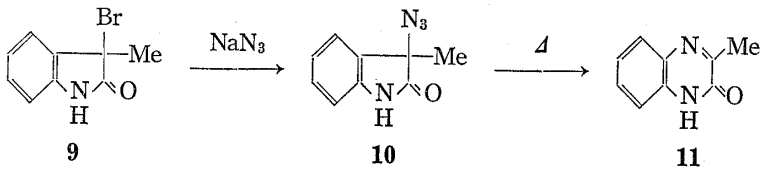
The results summarized in Table I indicate a general preference for phenyl over C=N group migration and significant effects by substituents of the 3-azidoindolenines on the migratory aptitude.

One possible rationalization for the observed migratory aptitude involves the assumption that the loss of nitrogen is assisted "with some degree" by the migrating group and the transition states would be represented by resonance structures A and B.[16] In view of the intrinsic migration aptitude of the phenyl ring and the development of a positive charge on the more electronegative nitrogen atom of the C=N group in the transition state B (although this positive charge may get stabilization by conjugation with the phenyl ring), path a would be favored over path b. As expected, the electron-donating R^4 (6-methyl) enhanced the phenyl migration (compared with **3b**), while the electron-donating R^3 (5-methyl) slightly facilitated the C=N migration. The situation with halogens (on either 5- or 6-position) is complicated by the fact that they have both electron-withdrawing effect at the *meta*-position by induction and electron-donating effect at the *para*-position by conjugation. The observed migratory aptitudes may be a result of a combination of these two opposing effects. The electron-withdrawing R^1 (2-alkoxycarbonyl) increased the ratio of Ph/C=N migration probably by retardation of the participation of the C=N group. The increasing proportion of the phenyl migration with the increasing bulk of R^2 substituents may be accounted for by steric factor; the participation of the C=N group would be expected to be lowered as a result of non-bonded interaction between R^1 and R^2 in the transition state B.

Apparently the driving force for this rearrangement is derived from the relief of strain in the five-membered ring and the formation of a new aromatic ring. This would account for the fact that the product **8** derived from the migration of 3-substituent (path c) was not detected in the reaction mixture.

The occurrence of **1a—j** may be rationalized on the basis of the formation of radical intermediate C, which would abstract hydrogen from solvent.[18] This process became particularly important in the case of **3g**. Apparently the loss of N_3 radical can compete successfully with the migration of phenyl or C=N group, perhaps because the strong electron-withdrawing nitro group at the 5-position may retard the participation of both phenyl (by induction) and C=N (more strongly by conjugation) group in the loss of nitrogen.

For comparison, we have also investigated the thermal rearrangement of 3-azido-3-methyloxindole (**10**) which was easily prepared from the reaction of 3-bromo-3-methyloxindole (**9**) with sodium azide. Refluxing **10** in xylene gave 3-methyl-2(1H)-quinoxalinone (**11**) in quantitative yield. This result is in accordance with the observation of Boyer and Straw[19] that the acyl group never migrates in thermolysis of α-azidocarbonyl compounds.[20]



9 **10** **11**

Chart 4

16) This hypothesis is based on the extensive studies by Saunders and Ware[17] on the thermal rearrangement of triarylmethyl azides. However, it should be emphasized that the discrete nitrene mechanism has not been ruled out.

17) W.H. Saunders, Jr. and J.C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

18) R.A. Abramovitch and E.P. Kyba, *Chem. Commun.*, **1969**, 265.

19) *a*) J.H. Boyer and D. Straw, *J. Am. Chem. Soc.*, **74**, 4506 (1952); *b*) J.H. Boyer and D. Straw, *J. Am. Chem. Soc.*, **75**, 1642 (1953); *c*) J.H. Boyer and D. Straw, *J. Am. Chem. Soc.*, **75**, 2683 (1953).

20) However, rare examples of acyl migration in the decomposition of alkyl azides have recently been reported.[6,7]

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The ring-expansion of **3a** to **6a** was found to occur by treatment with conc.H_2SO_4 in chloroform at room temperature but in much lower yield (26%). The remainder of the crude product was black resinous material.

Finally, it was of interest to see if the 3-azidoindolenines might undergo photosensitized ring-expansion.[21] In fact, irradiation of a benzene solution of **3a, b** with a 100 W low-pressure lamp in a quartz tube for a period of 45 hr afforded **1a, b** in 63 and 50% yields, respectively.

Experimental[22]

General Procedure for 3-Chloroindolenines 4——Essentially the procedure of Godtfredsen and Vangedal[23] was employed for preparation of 3-chloroindolenines. To an ice-cooled solution of an indole **1** (1 mmol) and triethylamine (0.3 ml) in methylene chloride (10 ml) was added dropwise *tert*-butyl hypochlorite (0.3 ml) with stirring. After the reaction mixture was stirred at 0° for 30 min, the mixture was washed with 10% HCl and H_2O, dried ($MgSO_4$), and the solvent was removed *in vacuo* to give a crude product **4.**

3-Chloro-2,3-diphenylindolenine (**4a**) was obtained from **1a** in quantitative yield, mp 127—128° (from ligroin). IR ν_{max}^{KCl} cm^{-1}: 1530 (C=N). UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε) 225 (4.22) and 328 (3.88). *Anal.* Calcd. for $C_{20}H_{14}ClN$: C, 79.07; H, 4.65; N, 4.61. Found: C, 79.18; H, 4.70; N, 4.60.

3-Chloro-3-methyl-2-phenylindolenine (**4b**) was obtained from **1b** in quantitative yield as an oil and purified by passing a short column on silica gel with *n*-hexane–ether. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1530 (C=N). UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε): 248 (4.43) and 324 (4.04). NMR ($CDCl_3$) δ: 8.5—8.3 (m, 2H, arom. protons), 7.8—7.2 (m, 7H, arom. protons), and 2.00 (s, 3H, CH_3).

2-Ethoxycarbonyl-3-chloro-3-methylindolenine (**4j**) could not be isolated because of its sensitivity and the solution in methylene chloride was used directly for the next reaction.

2,3-Dimethoxycarbonyl-3-chloroindolenine (**4k**) was obtained from **1k** in quantitative yield as pale yellow crystals, mp 102—103° (from *n*-hexane). IR ν_{max}^{KCl} cm^{-1}: 1762 (C=O), 1720 (C=O), and 1560 (C=N). UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε): 240 (3.92) and 300 (3.49). NMR ($CDCl_3$) δ: 7.9—7.0 (m, 4H, arom. protons), 3.97 (s, 3H, OCH_3), and 3.69 (s, 3H, OCH_3). *Anal.* Calcd. for $C_{12}H_{10}ClNO_4$: C, 53.84; H, 3.77; N, 5.23. Found: C, 53.89; H, 3.84; N, 5.33.

3-Bromo-2,3-diphenylindolenine (5a)——To a stirred solution of **1a** (300 mg) in dry methylene chloride (15 ml), N-bromosuccinimide[24] (168 mg) was added at room temperature for 10 min and the reaction mixture was stirred for 30 min. The solvent was removed and the residual solid was chromatographed on silica gel with chloroform to give yellow crystals of **5a** (329 mg), mp 131—132° (from ligroin). IR ν_{max}^{KCl} cm^{-1}: 1530 (C=N). UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε): 260 (4.03) and 318 (3.70). *Anal.* Calcd. for $C_{20}H_{14}BrN$: C, 68.98; H, 4.05; N, 4.02. Found: C, 69.18; H, 4.00; N, 4.02.

Using a similar procedure, **1b** gave unstable **5b.** The solution of **5b** in methylene chloride was directly used for the next reaction.

General Procedure for 3-Azidoindolenines 3——Method A: A solution of the indole **1** (5 mmol) in dry acetonitrile (10 ml) was added dropwise to a stirred solution of IN_3[10] [prepared *in situ* from ICl (10 mmol) and NaN_3 (15 mmol) at 0°] in dry acetonitrile (10 ml) at −10—0°. After the reaction mixture was stirred at the same temperature for 3 hr and then at room temperature for 2 hr, the mixture was diluted with H_2O and extracted with ether. The extract was washed with 5% $Na_2S_2O_2$ solution and H_2O, dried ($MgSO_4$), and concentrated *in vacuo* to give a crude product, which was purified either by recrystallization (for **3a, f, g,** and **k**) or by silica gel column chromatography with *n*-hexane–ether (for **3b—e** and **h—j**).

Similar conversion was also accomplished by using bromine azide. A solution of bromine azide[11] [prepared *in situ* from Br_2 (11.36 mmol) and NaN_3 (113.6 mmol) at 0°] in methylene chloride (24 ml) was added dropwise to a stirred solution of **1a, b** (5 mmol) in methylene chloride (20 ml) at 0°. After the reaction mixture was stirred at the same temperature for 1 hr and then at room temperature for 1 hr, the mixture was

21) *a*) A. Reiser and H.M. Wagner, "The Chemistry of Azido Group," ed. by S. Patai, Intersciences Publishers, London, 1971, p. 441; *b*) R.A. Abramovitch and E.P. Kyba, *J. Am. Chem. Soc.*, **93**, 1537 (1971); *c*) F.C. Montgomery and W.H. Saunders, Jr., *J. Org. Chem.*, **41**, 2368 (1976), and references cited therein.

22) All melting points are uncorrected. The NMR spectra were recorded with a Hitachi R-20A (60 MHz) spectrometer with tetramethylsilane as internal standard, IR spectra with a Hitachi EPI-G2 spectrophotometer, UV spectra with a Hitachi 124 spectrophotometer, and high resolution mass spectra with a JEOL-JMS-01SG instrument with a direct inlet system at 75 eV. Preparative TLC was carried out on Merck Silica gel GF_{254}. GLC was performed on a Shimadzu GC-4B gas chromatograph [nitrogen as carrier gas; 2 m×4 mm column packed with 5% SE-30 at 280°].

23) W.O. Godtfredsen and S. Vangedal, *Acta Chem. Scand.*, **10**, 1414 (1956).

24) T. Hino, M. Endo, M. Tonozuka, and M. Nakagawa, *Heterocycles*, **2**, 565 (1974).

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washed with H_2O, 5% $Na_2S_2O_3$ solution, and H_2O, dried ($MgSO_4$), and concentrated to give a crude product, which was purified in a similar manner as described above to give **3a, b.**

The results are summarized in Tables II and III.

Method B (*via* 3-Haloindolenines): A solution of 3-chloroindolenine **4** or 3-bromoindolenine **5** (0.63 mmol) in acetic acid (5 ml) [in the case of **4j** and **5b**, a methylene chloride solution of **4j** and **5b** prepared *in situ* from **1j** (128 mg) and **1b** (130 mg) was used] was added dropwise to a stirred solution of NaN_3 (1.89 mmol) in acetic acid (5 ml) at room temperature for 2 hr.[12] The reaction mixture was diluted with H_2O and extracted with ether, washed with 5% Na_2CO_3 solution and H_2O, dried ($MgSO_4$), and concentrated to give a crude product, which was purified by the same procedure as described for method A. The results are summarized in Tables II and III.

TABLE II. Preparation of 3-Azidoindolenines **3**

3	mp (°C) (Recryst'd from)	Yield (%)		Formula	Analysis (%)					
					Calcd.			Found		
		Method A	Method B		C	H	N	C	H	N
a	106—107 (MeOH)	100 (99)[a]	100 (100)[b]	$C_{20}H_{14}N_4$	77.40	4.55	18.06	77.23	4.57	18.00
b	Oil	100 (98)[a]	100 (100)[b]	—						
c	Oil	100	—	—						
d	Oil	100	—	—						
e	Oil	100	—	—						
f	70—71 (MeOH)	100	—	$C_{15}H_{11}ClN_4$	63.72	3.92	19.82	63.75	3.96	19.77
g	146—147 (C_6H_6–*n*-hexane)	86	—	$C_{15}H_{11}N_5O_2$	61.43	3.78	23.88	61.59	3.83	23.56
h	48—51	100	—	—						
i	Oil	100	—	—						
j	46—48	85	100	—						
k	90—91 (*n*-hexane)	n.r.	74	$C_{12}H_{10}N_4O_4$	52.55	3.68	20.43	52.62	3.74	20.17

a) by BrN_3.
b) *via* 3-bromoindolenines.

TABLE III. Physical Data of 3-Azidoindolenines **3**

3	IR $\nu_{max}^{CHCl_3}$ cm^{-1}	UV λ_{max}^{EtOH} nm (log ε)	NMR ($CDCl_3$) δ
a	2070	220(4.19), 249(4.13), 318(4.05)	
b	2080	227(4.09), 233(4.11), 241(4.12), 248(4.10) 314(4.05)	1.60 (s, 3H, 3-CH_3)
c	2090	227(4.19), 233(4.22), 242(4.24), 247(4.23) 314(4.16)	1.95—2.35 (m, 2H, 3-$\underline{CH_2}CH_3$) 0.48 (t, 3H, J=7 Hz, 3-$CH_2\underline{CH_3}$)
d	2080	227(4.13), 233(4.16), 241(4.18), 248(4.16) 314(4.07)	1.7—2.4 (m, 2H, 3-$\underline{CH_2}CH_2CH_3$) 0.7—1.2 (m, 5H, 3-$CH_2\underline{CH_2CH_3}$)
e	2090	228(4.20), 237(4.25), 246(4.31), 252(4.32) 288(4.03), 297(4.11), 327(4.23)	1.64 (s, 3H, 3-CH_3) 2.41 (s, 3H, 5-CH_3)
f	2080	224(4.21), 231(4.19), 277(4.04), 287(4.09) 297(4.13), 306(4.15)	1.60 (s, 3H, 3-CH_3)
g	2090, 1515 1340	232(4.12), 335(4.25)	1.72 (s, 3H, 3-CH_3)
h	2080	228(3.99), 234(4.03), 248(4.16), 315(3.99)	2.43 (s, 3H, 6-CH_3) 1.64 (s, 3H, 3-CH_3)
i	2090	226(3.98), 233(4.01), 248(4.21), 254(4.22) 306(4.01), 316(4.00)	1.59 (s, 3H, 3-CH_3)
j	2090, 1735	233(4.08), 297(3.82)	4.50 (q, 2H, J=7 Hz, $O\underline{CH_2}CH_3$), 1.83 (s, 3H, 3-CH_3), 1.47 (t, 3H, J=7 Hz, $OCH_2\underline{CH_3}$)
k	2110, 1755 1725	236(4.09), 239(4.09), 305(3.78)	3.99 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3)

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Table IV. Physical Data of Quinoxalines **6** and Quinazolines **7**

6	mp (°C) (Recryst'd from)	UV λ_{max}^{EtOH} nm (log ε)	**7**	mp (°C) (Recryst'd from)	UV λ_{max}^{EtOH} nm (log ε)
a	123—124 (lit.[a] 124)	244(4.60) 264(4.33) 342(4.08)	**a**	120 (lit.[b] 119)	265(4.49) 307(3.71) 332(3.57)
b	54—57 (lit.[c] 57—58)	240(4.22) 324(3.77)	**b**	88—89 (lit.[b] 90)	253(4.38) 261(4.43) 284(3.93) 320(3.43) 336(3.21)
c	46—48 (lit.[d] 47—47.5)	238(4.41) 322(3.89)	**c**	44—46 (lit.[b] 45)	262(4.45) 269(4.51) 294(4.02) 328(3.54) 343(3.38)
d	Oil[e]	239(4.88) 324(4.36)	**d**	79[f] (*n*-hexane)	254(4.04) 262(4.09) 287(3.57) 320(3.08) 333(2.93)
e	69—72[g]	244(4.40) 329(3.92)	**e**	94—95[h] (EtOH)	254(4.40) 262(4.44) 288(3.98) 326(3.56) 341(3.39)
f	104—106[i] (ligroin)	244(4.44) 326(3.99)	**f**	141—143[j] (ligroin)	253(4.41) 262(4.40) 288(4.14) 301(4.04) 328(3.53) 344(3.38)
g	128—131[k] (*n*-hexane)	255(4.28) 318(4.11)			
h	70—70.5[l] (ligroin)	243(4.27) 328(3.77)	**h**	Oil	247(4.41) 258(4.47) 288(3.90) 305(3.93) 318(3.92)
i	102—104[m] (ligroin)	243(4.49) 331(3.95)	**i**	106—108[n] (ligroin)	260(4.45) 265(4.47) 290(4.00) 303(3.94) 322(3.87) 334(3.72)
j	73—74 (lit.[o] 73)	240(4.46) 316(3.71)			
k	132—133 (lit.[o] 130)	246(4.57) 317(3.69)			

a) R.W. Bost and E.E. Towell, *J. Am. Chem. Soc.*, **70**, 903 (1948).
b) H. Meerwein, P. Laasch, R. Mersch, and J. Nentwig, *Chem. Ber.*, **89**, 224 (1956).
c) K.V. Auwers, *Ber.*, **50**, 1177 (1917).
d) Y.-L. Pascal, *Ann. Chim.* (France), **3**, 67 (1968).
e) Characterized as its picrate, mp 120.5—121° (from EtOH) (*Anal.* Calcd. for $C_{23}H_{19}N_5O_7$; C, 57.86; H, 4.01; N, 14.67. Found: C, 57.85; H, 4.04; N, 14.68).
f) *Anal.* Calcd. for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.03; H, 6.48; N, 11.45.
g) Characterized as its picrate, mp 155—156° (from EtOH) (*Anal.* Calcd. for $C_{22}H_{17}N_5O_7$; C, 57.02; H, 3.70; N, 15.11. Found: C, 56.71; H, 3.74; N, 15.13).
h) *Anal.* Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.85; H, 6.06; N, 12.03.
i) *Anal.* Calcd. for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00. Found: C, 70.71; H, 4.38; N, 10.68.
j) *Anal.* Calcd. for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00. Found: C, 70.87; H, 4.40; N, 10.86.
k) Mass Calcd. for $C_{15}H_{11}N_3O_2$: 265.0851. Found: 265.0811.
l) *Anal.* Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.82; H, 6.02; N, 11.98.
m) *Anal.* Calcd. for $C_{15}H_{11}BrN_2$: C, 60.22; H, 3.71; N, 9.36. Found: C, 60.16; H, 3.71; N, 9.23.
n) *Anal.* Calcd. for $C_{15}H_{11}BrN_2$: C, 60.22; H, 3.71; N, 9.36. Found: C, 60.20; H, 3.78; N, 9.04.
o) R.A. Baxter and F.S. Spring, *J. Chem. Soc.*, **1945**, 229.

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Reduction of 3a, b——(A) By Catalytic Hydrogenation: Compound **3a** (300 mg) was hydrogenated in ethanol (10 ml) over 5% Pd–C (40 mg) at atmospheric pressure and room temperature for 3 hr. The mixture was filtered and the filtrate was concentrated. The residue was purified by recrystallization from ligroin to give **1a** (187 mg, 72%), mp 122—124°.

Similar treatment of **3b** gave **1b** in 96% yield.

(B) By $LiAlH_4$: A solution of **3a** (300 mg) in dry ether (5 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (40 mg) in dry ether (5 ml) and the mixture was refluxed for 1.5 hr. The excess $LiAlH_4$ was decomposed by adding ethyl acetate and H_2O, and the mixture was extracted with ether. The extract was washed with H_2O and dried ($MgSO_4$), and concentrated to give **1a** (239 mg, 92%).

Similarly, **3b** gave **1b** in 84% yield.

Thermolysis of 3——A solution of **3** (2 mmol) in dimethylformamide (10 ml) was heated under reflux for 16 hr. The reaction mixture was poured into H_2O and extracted with ether, and the extract was washed with H_2O, dried ($MgSO_4$), and concentrated. The residue was separated by preparative TLC on silica gel with *n*-hexane–ether (4: 1) to give the quinoxaline **6**, the quinazoline **7**, and the indole **1**. The results are summarized in Tables I and IV.

3-Azido-3-methyloxindole (10)——A solution of 3-bromo-3-methyloxindole (**9**) (500 mg) and NaN_3 (150 mg) in *tert*-butanol (20 ml) and H_2O (5 ml) was stirred at room temperature for 20 hr and the solvent was removed *in vacuo* and the residual solid was recrystallized from *n*-hexane to give **10** (360 mg, 87%), mp 94—95°. IR ν_{max}^{KCl} cm^{-1}: 3170 (NH), 2070 (N_3), and 1700 (C=O). UV λ_{max}^{EtOH} nm (log ε): 253 (3.84) and 290 (3.21). NMR ($CDCl_3$) δ: 9.48 (b, 1H, NH), 7.4—6.9 (m, 4H, arom. protons), and 1.69 (s, 3H, CH_3). *Anal.* Calcd. $C_9H_8N_4O$: C, 57.44; H, 4.29; N, 29.77. Found: C, 57.54; H, 4.30; N, 29.58.

3-Methyl-2(1H)-quinoxalinone (11)——A solution of **10** (200 mg) in xylene (10 ml) was heated under reflux for 8 hr. The mixture was concentrated *in vacuo* to give **11** as colorless needles (177 mg, quantitative), mp 244° (lit.[25] 245°).

Reaction of 3a with conc. H_2SO_4——A solution of **3a** (200 mg) and conc. H_2SO_4 (1 ml) in chloroform (10 ml) was stirred at room temperature for 3 hr. The reaction mixture was neutralized with 10% Na_2CO_3 solution. The organic layer was washed with H_2O and dried ($MgSO_4$), and concentrated. The residue was submitted to preparative TLC on silica gel with *n*-hexane–ether (4: 1) to give **6a** (47 mg, 26%) and an unidentified product (trace).

Photolysis of 3a, b——A solution of **3a** (100 mg) in dry benzene (25 ml) was irradiated (100 W, low-pressure mercury lamp) in a quartz tube for 45 hr under nitrogen. The solvent was evaporated *in vacuo*, and the residue was purified by silica gel column chromatography with *n*-hexane–ether to give **1a** (42 mg, 50%), mp 124—125° (from ligroin).

Similarly, irradiation of **3b** (100 mg) gave **1b** (55 mg, 63%), mp 90—91° (from ligroin).

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25) O. Hinsberg, *Ann.*, **292**, 245 (1896).

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