The Photo-induced Ring Expansion of Azido(methoxy)quinolines to Methoxypyridoazepines

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The yields of 9-alkylamino-5*H*-pyrido[2,3-*c*]azepines from the photo-induced ring-expansion of 8-azidoquinoline in primary amines are increased significantly by the presence of a 6-methoxy group, which also for the first time induces ring-expansion of the azide in secondary amines. Optimum conditions have been found for the ring-expansion of 8-azidoquinoline in methanol–potassium methoxide to give 9-methoxy-5*H*-pyrido[2,3-*c*]azepine, and under the same conditions 8-azido-6-methoxy- and 6-azido-8-methoxy-quinoline ring-expand in excellent yield to the corresponding dimethoxypyridoazepines.

Extensive studies [1,2] have shown that the photolysis of bicyclic aromatic azides in the presence of amines as a synthetic route to bicyclic azepines is limited by the position of the azide group and the nature of the amine. In contrast, methoxide ion causes quinolyl and isoquinolyl azides to ring-expand to bicyclic azepines in practicable yields regardless of the position of the azide group.[3]

In our search for ways to widen the synthetic scope of nitrene-mediated ring-expansions of aryl and heteroaryl azides to give mono- and bi-cyclic azepines we noted a report [4] on the beneficial effect of a *meta* methoxy group on the yield of 2-diethylamino-3*H*-azepine either from the triethyl phosphite-induced ring-expansion of *m*-nitroanisole, or from the photolysis of *m*-anisyl azide, in ethylamine solution. We now report on the yield-enhancing effect of a *meta* methoxy group on the photo-induced ring-expansion of 8-azidoquinoline to pyridoazepines in primary and secondary amine solution, and also on the influence of this group on the ring-expansion of 6- and 8-azidoquinoline in alkoxide–alcohol solution.

8-Azido-6-methoxy- and 6-azido-8-methoxy-quinoline were prepared by diazotisation of the appropriate amino(methoxy)-quinoline followed by azidation using sodium azide. 8-Amino-6-methoxyquinoline is commercially available, whereas the 6-amino-8-methoxy isomer is prepared by a Skraup reaction on 2-methoxy-4-nitroaniline followed by reduction of the resulting nitro(methoxy)quinoline.[5]

Comparison of products from the photolysis of 8-azido-6-methoxyquinoline (1) in a large excess of primary aliphatic amines with those obtained from the photolysis of 8-azidoquinoline under similar conditions reveals a remarkable increase (Table 1, a—d) in the yields of singlet-nitrene-derived products, *i.e.* azepines (2) and *ortho*-diamines (3). Of significance also is the finding that the photolysis of 8-azido-6-methoxyquinoline in secondary aliphatic amine solution results in ring-expansion (Table 1, e—j). This is contrary to our experience with α-[6,6]-fused bicyclic aromatic azides (naphthalene nomenclature) which without a methoxy substituent give amines and diamines (*cf.* Table 1, a—d).

The structures of the pyridoazepines and quinoline *ortho*-diamines were established by spectroscopic means (Table 4) and for the diamines (3; Nu = piperidino or morpholino) by diazotisation and deamination to the known 6-methoxy-8-piperidino- and 6-methoxy-8-morpholino-quinoline (3; Nu = piperidino and morpholino respectively; H in place of NH_2).

Recent debate [6] has centred on the nature of the intermediate involved in aryl azide ⟶ 3*H*-azepine ring-expansions, the two contenders being the traditionally accepted benzazirine, as in structure (4), and the more recently proposed and equally viable 1-azacycloheptatetraene or cumulene, as in (5). Studies on the low-temperature photolyses of monocyclic azides in an argon matrix,[7] and flash vacuum pyrolyses of mono- and bicyclic heteroaryl azides [6] both strongly support the azacycloheptatetraene intermediate. However, low-temperature matrix studies [8] on bicyclic aromatic azides provide convincing spectroscopic evidence for the existence of an azirine intermediate as a probable precursor of the cumulated system (5). Either intermediate is prone to nucleophilic attack by the amine (or methoxide) under our photochemical conditions and hence a mechanism to account for the ring-expansion of azido(methoxy)quinolines, analogous to that observed in the irradiation of α-naphthyl azides is an argon or nitrogen matrix,[8] can be envisaged (Scheme).

It can be argued that the yield-enhancing effect of a methoxy substituent *meta* to the azide group is due to it stabilising (6) ⟷ (6a) the dipolar form (6) of the azirine intermediate (4), so as to ensure either an efficient direct interception of the

Table 1. Products from photolysis of 8-azido-6-methoxyquinoline and 8-azidoquinoline in amines

	Amine (NuH) Nu	Total yield of (2) and (3) *	% Yield of products * Azepine (2)	*ortho*-Diamine (3)	8-Amino-6-methoxy-quinoline
a	$[CH_2]_4NH$	80 (36)	15 (—)	65 (36) [b]	13 (15)
b	Et_2NH	82 (86)	28 (—)	54 (86) [c]	12 (12)
c	$[CH_2]_5NH$	82 (47)	24 (—)	58 (47) [b]	10 (29)
d	$[CH_2]_6NH$	70 (27)	15 (—)	55 (27) [b]	10 (20)
e	$C_6H_{11}NH$	92 (67)	67 (38) [a]	25 (29) [a]	4 (20)
f	Bu^nNH	85 (67)	62 (47)	23 (20) [b]	t † (12)
g	Bu^iNH	90 (68)	62 (56)	28 (12) [b]	t (17)
h	Bu^tNH	81 (79)	58 (46)	23 (32)	5 (10)
i	Pr^nNH	95 (42)	79 (42) [a]	16 (—)	t (20)
j	Pr^iNH	92 (68)	75 (43)	17 (15) [b]	t (17)

* Yields in parentheses refer to products from 8-azidoquinoline, *i.e.* (2) and (3) with H in place of OMe. † t = trace.

[a] B. Nay, E. F. V. Scriven, H. Suschitzky, and Z. U. Khan, *Synthesis*, 1977, 757. [b] F. Hollywood, B. Nay, E. F. V. Scriven, H. Suschitzky, Z. U. Khan, and R. Hull, *J. Chem. Soc., Perkin Trans. 1*, 1982, 421. [c] S. E. Carroll, B. Nay, E. F. V. Scriven, and H. Suschitzky, *Synthesis*, 1975, 710.

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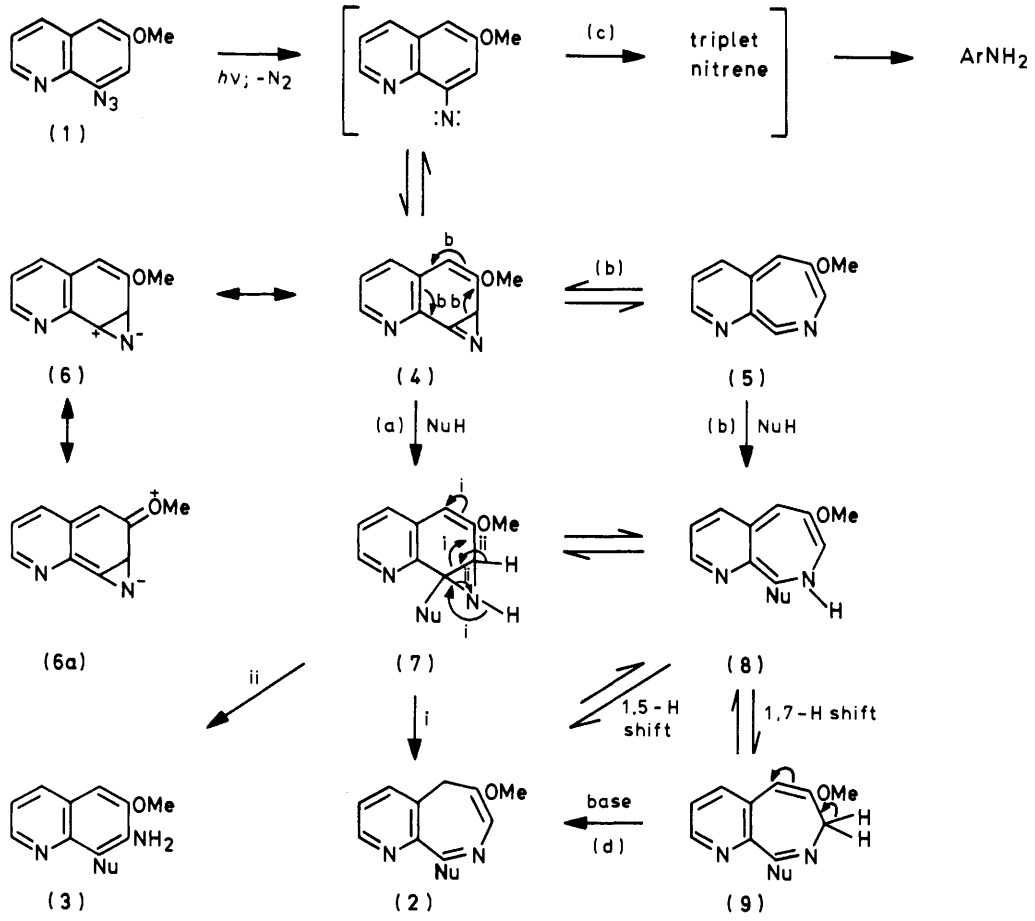


Scheme. Ar = 8-quinolyl or 6-methoxy-8-quinolyl

azirine by the nucleophile (Scheme; path a), or transformation of (4) to the azacycloheptatetraene (5), followed by addition of the nucleophile (Scheme; path b), before competing irreversible processes (*e.g.* singlet ⟶ triplet intersystem crossing: Scheme; path c) can occur. In fact, the results in Table 1 represent the highest overall yields so far recorded for azide ring-expansions of this type. The increased tendency of ring-expansion over *ortho*-diamine formation is obviously due also to the effect of the methoxy group, possibly upon the equilibria (7) ⇌ (8) ⇌ (2).

Analogous arguments have been advanced to account for the beneficial effects of a 6- or 8-methoxy group on the photo-induced ring-expansions of quinoline *N*-imides to 3*H*-1,3-benzodiazepines.[9] Apparently, with methoxy groups at other ring positions, or with electron-withdrawing groups at any position in the quinoline ring, ring-expansion does not take place.* Also of relevance is that, in azidobenzo[*b*]thiophenes [11] and related azide series,[12] only the 6-azido isomers, *i.e.* the azide positioned *meta* to the electron-donating sulphur, furnish azepines on photolysis in secondary amines.

Generally, photolysis of aryl azides in nucleophilic solvents other than amines, *e.g.* alcohols and thiols, gives only poor yields of amines.[1,2] However, excellent yields of alkoxy-3*H*-azepines are obtained if the azide has an *ortho* electron-withdrawing group (*e.g.* CONHAr [13] or CO_2R [14]), or if the photolysis is carried out in strongly basic media (*e.g.* potassium methoxide–methanol–dioxan).[15,16] Recently, we have shown [3] that under these conditions quinolyl and isoquinolyl azides yield methoxyazepines in practicable amounts. A careful investigation of the ring-expansion of 8-azidoquinoline (Table 2) demonstrates that the maximum yield of 9-methoxy-5*H*-pyrido[2,3-*c*]azepine is obtained when the photolysis is carried out in a solution of potassium methoxide (3M) in a 1 : 1 methanol–dioxan mixture using a Pyrex filter. Irradiation through a quartz filter produced 8-aminoquinoline as the sole identifiable product. The presence of 18-crown-6 had no noticeable effect on the yield of azepine. Substitution of tetrahydrofuran (THF) for dioxan as the co-solvent lowers substantially (80 ⟶ 40%) the yield of pyridoazepine.

The effect of a *meta* methoxy group on these ring-expansions is not as dramatic as that observed in amine solution, although marginally better yields of dimethoxypyridoazepines are obtained. For example, under the optimised conditions 6-azido-8-methoxyquinoline ring-expands cleanly to 7,9-dimethoxy-5*H*-pyrido[3,2-*c*]azepine (10) in 80% yield. The reaction, as measured by the rate of disappearance of the ν (N_3) band at 2 120 cm^{-1}, is complete in less than four hours and produces 6-amino-8-methoxyquinoline (15%) as the only by-product. In contrast, under the same conditions, photolysis of 8-azido-6-methoxyquinoline gives initially a mixture of the isomeric 6,9-dimethoxy-5*H*- (2; Nu = OMe) and 6,9-dimethoxy-7*H*-pyrido[2,3-*c*]azepine (9; Nu = OMe) (11% and 49% yield, respectively). With time, however, only the thermodynamically more stable [1] 5*H*-isomer (2) is obtained

* Methoxy groups also influence strongly the photoisomerisation of quinoline and isoquinoline *N*-oxides (A. Albini, E. Fusani, and L. M. Dacrema, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2738), and have a salutary effect on the yields of *o*-alkylthioquinolylamines from the photolysis of azidoquinolines.[10]

Table 2. Photolysis of 8-azidoquinoline with potassium methoxide (3M) * in various solvents

Solvent system	% Yield of 9-methoxy-5*H*-pyrido[2,3-*c*]azepine (2; H in place of OMe; Nu = OMe)
MeOH [a]	29
1 : 1 THF–MeOH [a]	54
1 : 1 THF–MeOH [b]	40
1 : 1 Dioxan–MeOH [a]	72
1 : 1 Dioxan–MeOH [b]	41
1 : 1 Dioxan–MeOH [c]	68
1 : 3 TMEDA–MeOH [a,d]	48
1 : 1 Dioxan–MeOH [e]	none

* In methanol, in the absence of KOMe, the methoxyazepine was obtained in 15% yield, along with 8-aminoquinoline (44%).

[a] With a 125-W medium-pressure mercury street lamp; Pyrex filter. [b] With an 85-W medium-pressure lamp. [c] In the presence of 18-crown-6 ether (0.2 g). [d] TMEDA = Tetramethylethylenediamine. [e] In a quartz apparatus the only product identified was 8-aminoquinoline.

from the photosylate. Subsequently, it has been found that isomerisation (9) ⟶ (2) can be achieved in boiling ethanol. Isomerisation may involve sequential 1,7- and 1,5-H shifts as indicated in the Scheme (9) ⇌ (8) ⇌ (2), or alternatively may be due to a base-catalysed allylic rearrangement of the cross-conjugated 7*H*-isomer to the more stable fully conjugated 5*H*-derivative (Scheme; path d). In fact, we have noted [17] analogous base-catalysed isomerisations of a variety of other 7*H*-pyridoazepines.

Attempts to prepare hydroxypyridoazepines by irradiation of 6-azido-8-hydroxyquinoline in a KOH–MeOH–dioxan mixture were disappointing. Azide decomposition was complete in four hours, but only a foul-smelling, unidentifiable oily mixture was obtained. Interestingly, attempts to demethylate the dimethoxypyridoazepine (2; Nu = OMe) using 48% hydrobromic acid gave similar mixtures.

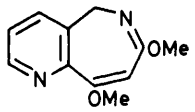
In view of the success of the *meta* methoxy group in promoting azepine formation, it is not surprising that azidoquinolines bearing a *meta* electron-withdrawing group fail to ring-expand. For example, irradiation of 8-azido-6-nitroquinoline under the standard conditions (KOMe–MeOH–dioxan) gave only 8-amino-6-nitroquinoline (36%) and much tar. In fact, a ^{1}H n.m.r. spectrum of the crude photolysate showed no trace of the characteristic azepine proton resonances.

Experimental

I.r. and mass spectra were measured on a Perkin-Elmer 257 and an AEI MS12 or MS9 spectrometer, respectively. ^{1}H and ^{13}C n.m.r. spectra were recorded on a Perkin-Elmer R32 90 MHz and a Varian Associates CFT20 spectrometer, and were calibrated with reference to tetramethylsilane and deuteriochloroform, respectively, as internal standards.

Dioxan (1 l) was purified by being heated under reflux with concentrated hydrochloric acid (15 ml) and water (100 ml) for 6 h. The cold mixture was then kept overnight over potassium hydroxide pellets (100 g). The decanted solvent was heated under reflux with sodium shavings for 3 h, and finally distilled off from the sodium under dry nitrogen. THF was purified by being heated under reflux with benzophenone over sodium wire until the solution became blue. Pure, dry THF was obtained by distillation.

8-Azido-6-methoxyquinoline (1) was prepared from the corresponding amine, available from the Aldrich Chemical Company, by diazotisation followed by azidation with sodium azide in the presence of sodium acetate buffer as described previously.[10] The azide was purified by column chromatography (Al_2O_3; Et_2O) and was obtained as a cream solid (75%), m.p. 84 °C (lit.,[18] 83 °C), ν (N_3) 2 130 cm^{-1}.


(10)

6-Azido-8-methoxyquinoline.—A Skraup reaction on 2-methoxy-4-nitroaniline provided 8-methoxy-6-nitroquinoline (80%) as yellow needles, m.p. 143 °C (lit.,[5] 145 °C) which, on reduction with 5% Pd–C and hydrazine hydrate, gave 6-amino-8-methoxyquinoline (70%), m.p. 168 °C (lit.,[5] 168 °C). Diazotisation of the amine followed by azidation, as previously, yielded *6-azido-8-methoxyquinoline* (75%), m.p. 78 °C (Found: C, 59.85; H, 4.15; N, 28.0. $C_{10}H_8N_4O$ requires C, 59.99; H, 4.03; N, 27.99%); $\nu_{max.}$ (Nujol) 2 100 cm^{-1} (N_3); δ($CDCl_3$) 8.7 (1 H, dd, 2-H), 7.9 (1 H, dd, 4-H), 7.0 (1 H, dd, 3-H), 6.45 (2 H, s, 5-H and 7-H), and 4.0 (3 H, s, OCH_3).

6-Azido-8-hydroxyquinoline.—A mixture of 8-methoxy-6-nitroquinoline (4.5 g), 48% hydrobromic acid (20 ml), and trifluoroacetic acid (10 ml) was heated under reflux for 3 h. The mixture was cooled, filtered, and the residue dissolved in water. Neutralisation of the aqueous solution with sodium carbonate gave 8-hydroxy-6-nitroquinoline (2.4 g, 68%), m.p. 203 °C (lit.,[19] 204 °C). Reduction of the hydroxy nitro compound (2.4 g) as described for the methoxy nitro compound gave 6-amino-8-hydroxyquinoline (1.35 g, 60%), m.p. 134 °C (lit.,[20] 132.5 °C). Diazotisation and azidation as previously gave *6-azido-8-hydroxyquinoline*, m.p. 138 °C (decomp.); $\nu_{max.}$ (Nujol) 3 125—3 350 (OH) and 2 100 cm^{-1} (N_3); δ($CDCl_3$) 8.7 (1 H, dd, 2-H), 8.05 (1 H, dd, 4-H), 7.4 (1 H, dd, 3-H), and 6.9 (2 H, d, 5-H and 7-H) (Found: M^+, 186.174. $C_9H_6N_4O$ requires M^+, 186.174); a satisfactory elemental analysis was not obtained.

8-Azido-6-nitroquinoline.—6,8-Dinitroquinoline, m.p. 153 °C (lit.,[21] 153 °C), obtained by a Skraup reaction (66% yield) on 2,4-dinitroaniline, was selectively reduced with ammonium polysulphide as directed [21,22] to give 8-amino-6-nitroquinoline (64%), m.p. 179 °C (lit.,[21,22] 180 °C). Diazotisation and azidation of the nitroamine, as before, gave *8-azido-6-nitroquinoline*, m.p. 142 °C; $\nu_{max.}$ (Nujol) 2 100 (N_3) and 1 505 cm^{-1} (NO_2); δ($CDCl_3$) 8.85 (1 H, dd, 2-H), 8.1 (2 H, m, 4-H and 5- or 7-H), 7.70 (1 H, d, 7- or 5-H), and 7.35 (1 H, dd, 3-H) (Found: M^+, 215.143. $C_9H_5N_5O_2$ requires M, 215.143); satisfactory elemental analysis was not obtained).

Photolysis of 8-Azido-6-methoxyquinoline in Amines.—General procedure. A solution of the azide (0.8 g), the amine (60 ml), and TMEDA (20 ml) was purged with nitrogen for 10 min prior to photolysis. The stirred solution was irradiated at room temperature under nitrogen in a quartz apparatus for 5—10 h with a water-cooled immersion well containing a medium-pressure mercury arc. Each reaction was monitored by observing the disappearance of the azide absorption in the i.r. at 2 100—2 120 cm^{-1}. After the azide peak had disappeared the amine was distilled off under reduced pressure, and the residue was chromatographed on alumina (type H) to yield the products (Table 1). Physical and spectroscopic data for the products are listed in Tables 3 and 4.

Table 3. Physical and i.r. spectroscopic data for azepines and *ortho*-diamines

Azepine	M.p. (°C) (B.p. [°C/mmHg])	Molecular formula	Elemental analysis Required (Found) C	H	N	$\nu_{max.}$ (cm^{-1}) in Nujol ν_{NH}	$\nu_{C=N}$	ν_{NH_2}
(2a)	107	$C_{14}H_{17}N_3O$	69.1 (69.1	7.0 7.05	17.3 17.3)		1 590	—
(2b)	(172/0.2)	$C_{14}H_{19}N_3O$	68.5 (68.45	7.8 8.0	17.1 17.3)	—	1 585	—
(2c)	(179/0.2)	$C_{15}H_{19}N_3O$	70.0 (70.2	7.4 7.25	16.3 16.4)	—	1 595	—
(2d)	87	$C_{16}H_{21}N_3O$	70.8 (70.9	7.8 7.9	15.5 15.4)	—	1 595	—
(2e)	67	$C_{16}H_{21}N_3O$	70.8 (70.8	7.8 7.8	15.5 15.4)	3 400	1 600	—
(2f)	(150/0.2)	$C_{14}H_{19}N_3O$	68.5 (68.65	7.8 7.95	17.1 17.4)	3 400	1 600	—
(2g)	(168/0.2)	$C_{14}H_{19}N_3O$	68.5 (68.5	7.8 7.7	17.1 17.4)	3 400	1 605	—
(2h)	109	$C_{14}H_{19}N_3O$	68.5 (68.5	7.8 7.8	17.1 17.15)	3 400	1 600	—
(2i)	59	$C_{13}H_{17}N_3O$	67.5 (67.55	7.4 7.4	18.2 18.1)	3 400	1 605	—
(2j)	88	$C_{13}H_{17}N_3O$	67.5 (67.45	7.4 7.4	18.2 17.95)	3 260	1 595	—
(3a)	82	$C_{14}H_{17}N_3O$	69.1 (69.2	7.0 7.0	17.3 17.3)	—	—	3 480, 3 360
(3b)	42	$C_{14}H_{19}N_3O$	68.5 (68.5	7.8 7.8	17.1 17.1)	—	—	3 480, 3 360
(3c)	103	$C_{15}H_{19}N_3O$	70.0 (70.15	7.4 7.5	16.3 16.5)	—	—	3 480, 3 360
(3d)	95.6	$C_{16}H_{21}N_3O$	70.8 (70.85	7.8 7.9	15.5 15.5)	—	—	3 480, 3 360
(3e)	135	$C_{16}H_{21}N_3O$	70.8 (70.8	7.8 7.9	15.5 15.4)	3 260	—	3 440, 3 340
(3f)	(164/0.2)	$C_{14}H_{19}N_3O$	68.5 (68.8	7.8 7.6	17.1 17.1)	3 200	—	3 450, 3 350
(3g)	(160/0.2)	$C_{14}H_{19}N_3O$	68.5 (68.7	7.8 7.8	17.1 17.4)	3 200	—	3 450, 3 350
(3h)	83	$C_{14}H_{19}N_3O$	68.5 (68.6	7.8 7.75	17.1 17.4)	3 320	—	3 420, 3 350
(3i)	(150/0.2)	$C_{13}H_{17}N_3O$	67.5 (67.4	7.4 7.15	18.2 18.2)	3 200	—	3 450, 3 350
(3j)	(179/0.2)	$C_{13}H_{17}N_3O$	67.5 (67.6	7.4 7.4	18.2 18.35)	3 200	—	3 400, 3 300

Deamination of 7-Amino-6-methoxy-8-piperidinoquinoline (3; Nu = piperidino).—An aqueous solution of sodium nitrite (0.4 g) was added dropwise to a solution of 7-amino-6-methoxy-8-piperidinoquinoline in 4M hydrochloric acid (5 ml) maintained at 0—5 °C. The resulting diazonium solution was added to 50% hypophosphorous acid (10 ml) and the red solution was stirred at room temperature until nitrogen evolution ceased (*ca.* 3 h). The solution was then basified with 4M sodium hydroxide solution (25 ml) and extracted with chloroform (3 × 40 ml). The extracts were combined, washed with water, and dried over $MgSO_4$. Removal of the chloroform, followed by distillation of the residue, gave 6-methoxy-8-piperidinoquinoline (0.65 g, 83%), m.p. 79 °C (lit.,[23] 80 °C); * δ($CDCl_3$) 8.7 (1 H, dd, 2-H), 7.25 (1 H, dd, 3-H), 7.95 (1 H, dd, 4-H), 6.8 (1 H, d, 5-H), 6.65 (1 H, d, 7-H) [$J_{2,3}$ 5, $J_{3,4}$ 8, $J_{2,4}$ 2, and $J_{5,7}$ 3 Hz], 3.87 (3 H, s, OCH_3), 3.3 (4 H, t, CH_2NCH_2), and 1.8 (6 H, m, $CH_2CH_2CH_2$).

7-Amino-6-methoxy-8-morpholinoquinoline (3; Nu = morpholino) (0.4 g) was deaminated as described above to give 6-methoxy-8-morpholinoquinoline (0.27 g, 72%), m.p. 93 °C (lit.,[24] 122 °C); δ($CDCl_3$) 8.7 (1 H, dd, 2-H), 7.3 (1 H, dd, 3-H), 8.0 (1 H, dd, 4-H), 6.77 (1 H, d, 5-H), 6.69 (1 H, d, 7-H), 4.02 (4 H, t, CH_2OCH_2), 3.9 (3 H, s, OCH_3), and 3.4 (4 H, t, CH_2NCH_2); *m/z* (M^+) 244.

Photolysis of Azidoquinolines in Potassium Methoxide–Methanol–Dioxan.—General procedure under optimum conditions. A solution of 8-azidoquinoline in a mixture of potassium methoxide (3M) in methanol and dioxan (1 : 1 v/v) was irradiated at room temperature under nitrogen with a water-cooled immersion well containing a 125-W medium-pressure mercury lamp until the azide absorption at 2 120 cm^{-1} had disappeared. The photolysate was left at room temperature for 24 h and was then neutralised with 4M hydrochloric acid in methanol. Removal of the solvent (rotary evaporator) gave a residue of 9-methoxy-5*H*-pyrido[2,3-*c*]azepine which was purified by column chromatography (Al_2O_3 type H; toluene as eluant) followed by crystallisation from light petroleum (b.p. 40—60 °C), m.p. 99 °C (lit.,[3] 99 °C); δ_C($CDCl_3$) 160.81 (s, C-9), 147.37 (d, C-2), 138.34 (s, C-9a), 134.71, and 134.34 (d,d, and s, together C-4, C-7, and C-4a), 125.89 (d, C-3), 112.71 (d, C-6), 53.39 (q, CH_3), and 29.4 p.p.m. (t, CH_2).

* Cited as m.p. 58 °C in ref. 24.

Table 4. ^{1}H N.m.r. spectroscopic data for azepines and *ortho*-diamines

Azepine	2-H dd, *J* 5 Hz	3-H dd, *J* 8 Hz	4-H dd, *J* 2 Hz	5-CH_2 s	6-OMe s	7-H s	NH brd	Nu	
(2a)	1.45	2.72	2.45	6.90	6.50	3.90	—	C_4H_8N	6.20 t, 8.10 m
(2b)	1.45	2.72	2.47	6.94	6.50	3.95	—	Et_2N	6.65 q, 8.90 t
(2c)	1.45	2.62	2.35	6.95	6.50	4.00	—	$C_5H_{10}N$	6.60 brs, 8.40 brs
(2d)	1.45	2.72	2.45	6.93	6.50	3.95	—	$C_6H_{12}N$	6.40 t, 8.40 brs
(2e)	1.50	2.70	2.47	6.80	6.48	3.92	4.35	C_6H_{11}	6.05 brm, 7.8—8.7 m
(2f)	1.50	2.68	2.45	6.78	6.46	3.90	4.30	Bu^n	6.60 t, 8.40 m, 9.02 t
(2g)	1.50	2.70	2.47	6.80	6.50	3.90	4.20	Bu^i	6.70 t, 8.00 m, 9.00 d
(2h)	1.50	2.70	2.50	6.80	6.45	3.90	4.42	Bu^t	8.45 s
(2i)	1.50	2.67	2.45	6.78	6.45	3.90	4.20	Pr^n	6.60 t, 8.30 m, 9.00 t
(2j)	1.50	2.70	2.46	6.78	6.45	3.90	4.40	Pr^i	5.75 m, 8.70 d
ortho-Diamine				5-H s		7-NH_2 brs			
(3a)	1.40	2.98	2.15	3.20	6.10	5.15	—	C_4H_8N	6.53 t, 7.93 m
(3b)	1.40	3.00	2.20	3.22	6.15	5.06	—	Et_2N	6.38 q, 6.65 q, 9.02 t
(3c)	1.36	2.98	2.15	3.22	6.10	5.10	—	$C_5H_{10}N$	7.10brd, 8.30brs
(3d)	1.35	2.97	1.35	3.22	6.10	5.12	—	$C_6H_{12}N$	6.38brs, 6.92brs, 8.20brs
(3e)	1.40	2.92	2.15	3.32	6.10	5.80	4.90	C_6H_{11}	6.75brs, 8.2—8.8 m
(3f)	1.36	2.92	2.15	3.32	6.10	5.70	4.90	Bu^n	6.70 t, 8.45 m, 9.1 t
(3g)	1.40	2.90	2.12	3.30	6.10	5.80	5.00	Bu^i	7.10 d, 8.10 m, 8.96 d
(3h)	1.37	2.90	2.10	3.21	6.06	5.45	5.45	Bu^t	8.72 s
(3i)	1.40	2.90	2.15	3.30	6.10	5.72	4.90	Pr^n	6.90 t, 8.35 m, 9.00 t
(3j)	1.40	2.92	2.15	3.30	6.10	5.75	5.05	Pr^i	6.40 s, 8.85 d

The yields of pyridoazepine obtained under other photolytic conditions are given in Table 2.

Photolysis of 6-*azido*-8-*methoxyquinoline*. 6-Azido-8-methoxyquinoline (1 g) was irradiated under the conditions described in the general procedure for 8-azidoquinoline. Chromatography of the crude product on alumina with toluene–ethyl acetate (4 : 1 v/v) as eluant gave 7,9-*dimethoxy*-5H-*pyrido*[3,2-c]*azepine* (10) (0.8 g, 80%), m.p. 120 °C (Found: C, 64.65; H, 6.05; N, 13.7. $C_{11}H_{12}N_2O_2$ requires C, 64.69; H, 5.92; N, 13.72%); δ($CDCl_3$) 8.69 (1 H, dd, 2-H), 7.6 (2 H, m, 3- and 4-H), 5.7 (1 H, s, 8-H), 4.17 (2 H, s, 5-H_2), 3.9 (3 H, s, 9-OCH_3), and 3.7 (3 H, s, 7-OCH_3); δ_C($CDCl_3$) 163.32 (s, C-7), 161.74 (s, C-9), 149.77 (s, C-9a), 147.72 (d, C-2 ?) 135.01 (d, C-4 ?), 133.91 (s, C-4a), 124.03 (d, C-3 ?), 98.08 (d, C-7), 55.17 and 52.52 (each q, together 7- and 9-OCH_3), and 49.85 p.p.m. (t, C-5); *m*/*z* (M^+) 204.

Further elution with toluene–ethyl acetate (3 : 2 v/v) gave 6-amino-8-methoxyquinoline (0.1 g, 15%).

Photolysis of 8-*azido*-6-*methoxyquinoline*. (*a*) Irradiation of the azidomethoxyquinoline (0.8 g) and work-up as described in the previous experiment gave 6,9-*dimethoxy*-5H-*pyrido*-[2,3-c]*azepine* (0.64 g, 76%) as an oil, b.p. 123 °C/0.2 mmHg (Found: C, 64.55; H, 5.8; N, 13.65. $C_{11}H_{12}N_2O_2$ requires C, 64.69; H, 5.9; N, 13.71%); δ($CDCl_3$) 8.64 (1 H, dd, 2-H), 7.36 (1 H, dd, 3-H), 7.55 (1 H, dd, 4-H), 6.06 (1 H, s, 7-H), 4.0 (3 H, s, 9-OCH_3), 3.55 (3 H, s, 6-OCH_3), and 3.2 (2 H, s, CH_2); δ_C($CDCl_3$) 156.72 (s, C-9), 147.08 (d, C-2), 145.98 (s) and 144.87 (s) (together C-6 and C-9a), 134.13 (s + d, C-4 and C-4a), 125.01 (d, C-3), 106.67 (d, C-7), 54.81 and 52.82 (each q, together 6- and 9-OCH_3), and 34.19 p.p.m. (t, CH_2).

(*b*) The irradiation was carried out as in (*a*), but the reaction mixture was neutralised immediately rather than after being kept overnight. Chromatographic separation of the oily mixture on Al_2O_3 with toluene as eluant gave 6,9-dimethoxy-5*H*-pyrido[2,3-*c*]azepine (0.09 g, 11%). Further elution with toluene–ethyl acetate (4 : 1 v/v) gave 6,9-*dimethoxy*-7H-*pyrido*[2,3-c]*azepine* (0.4 g, 49%), b.p. 150 °C/0.2 mmHg (Found: C, 65.0; H, 6.15; N, 13.45. $C_{11}H_{12}N_2O_2$ requires C, 64.69; H, 5.92; N, 13.71%); δ($CDCl_3$) 8.55 (1 H, dd, 2-H), 7.3 (1 H, dd, 3-H), 7.55 (1 H, dd, 4-H), 5.6 (1 H, s, 5-H), 3.9 (3 H, s, 9-OCH_3), 3.8 (2 H, s, 5-H_2), and 3.7 (3 H, s, 6-OCH_3); δ_C($CDCl_3$) 162.71 and 162.34 (each s, together C-6 and C-9), 145.85 (s, C-9a), 145.12 (d, C-2), 135.73 (d, C-4), 134.26 (s, C-4a), 123.89 (d, C-3), 95.81 (d, C-5), 55.17 and 53.94 (each q, together 6- and 9-OCH_3), and 48.1 p.p.m. (t, CH_2).

Photolysis of 6-*azido*-8-*hydroxyquinoline*. The azidohydroxyquinoline (0.88 g) was photolysed under the conditions described in the general method. After the photolysate had been kept overnight work-up as described previously gave an oily mixture (t.l.c.) of products which, on chromatographic separation (light petroleum or ethyl acetate), gave only tarry material and a foul-smelling semi-solid substance which rapidly decomposed.

Photolysis of 8-*azido*-6-*nitroquinoline*. The azidonitroquinoline (0.4 g) was photolysed as above. Work-up in the standard manner gave a brown solid residue which, on chromatography (Al_2O_3) with light petroleum (b.p. 60—80 °C)–ethyl acetate (1 : 1 v/v) as eluant, gave unchanged azide (10% recovery). Further elution with ethyl acetate–light petroleum (b.p. 60—80 °C) (8 : 1 v/v) gave 8-amino-6-nitroquinoline (0.12 g, 36%), identical with an authentic sample. Further elution with ethyl acetate–methanol (1 : 1 v/v) gave only intractable tars.

Acknowledgements

We thank the S.E.R.C. and Glaxo Group Research (Ware) for a CASE award (D. I. P.), the University of Salford for a College Demonstratorship (Z. U. K.), and Dr. David Scopes and Dr. Roger Newton (Glaxo Group Research) for their keen interest.

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Received 3rd *March* 1983; *Paper* 3/342