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PHOTOLYTIC RING-EXPANSIONS OF 6-AZIDOQUINOLINES AND 6-AZIDODIAZINES: SOME UNEXPECTED AZEPINE RING-OPENING REACTIONS

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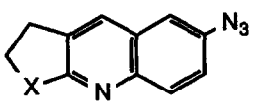
Summary : *Photolysis of 6-azidoquinazoline in MeOH-KOMe-dioxan yields 8,9-dihydro-5,7-dimethoxy-5H-pyrimido[5,4-c]azepine (5) which on acid hydrolysis ring-opens to the pyrimidine-carbaldehyde (7). The mechanism of formation of this unexpected dimethoxypyrimido-azepine is discussed and related to previous similar results involving 6-azido-2,3-dihydrofuro- and 6-azido-2,3-dihydrothieno-[2,3-b]quinolines.*

In contrast, 6-azidoquinoxaline and 6-azido-2-chloro-4-methylquinoline on photolysis under similar conditions undergo ring expansion to the expected pyrazino[2,3-c]- and pyrido[3,2-c]azepines (22a) and (17) respectively. However, photolysis of the latter azide in MeOH-dioxan yields the 3-(2-pyridyl)propenonitrile derivative (18) in a reaction analogous to that undergone by 6-azidophenazine.

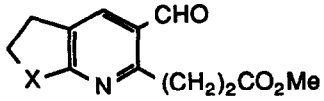
Recently,[1] we have reported an unexpected ring-opening of the azepine ring to yield pyrido-carbaldehydes (2), during the preparation of furo- and thieno-pyridoazepines by photolysis of 6-azidoquinolines (1) in methanol-dioxan-potassium methoxide solution. We now describe further work on the photolysis of 6-azidoquinolines, and of 6-azidodiazines, some of which give rise to ring-opened products rather than the expected 6,7-fused ring-systems.

At the time of our previous publication,[1] the mode of formation of the pyridine-aldehydes (2) was obscure. A clue to their origin was obtained subsequently from work on the irradiation of 6-azidoquinazoline (4). On photolysis in methanol-dioxan-potassium methoxide this azide furnished, in addition to 6-aminoquinazoline (29%), a product (16%) which, from its ^{1}H n.m.r. spectrum was clearly a pyrimido-azepine, but which unexpectedly, bore two distinct MeO-groups. Furthermore, the characteristic *cis*-alkene hydrogen resonances, anticipated for C_8-C_9 of an azepine ring, had been replaced by a complex, symmetrical AA'-BB' system at 2.6-3.4 δ; a feature which suggested the presence of an alicyclic -CH_2CH_2-unit. From these observations, coupled with mass spectral and analytical data, the product has been formulated as 8,9-dihydro-5,7-dimethoxy-5H-pyrimido[5,4-c]azepine (5). As far as we are aware the formation of partially reduced azepines of this type are unprecedented in the photolytic ring-expansions of aryl and heteroaryl azides, although incorporation of a second methoxy group accompanied by azepine-ring-contraction has been noted with naphthylazides.[2]

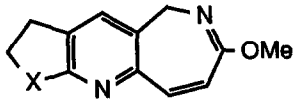
It soon became apparent that this lactim-ether (5) could by hydrolytic ring-opening *via* imine (6), as



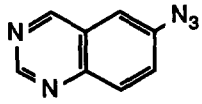
(1) a; X = O
b; X = S



(2) a; X = O
b; X = S

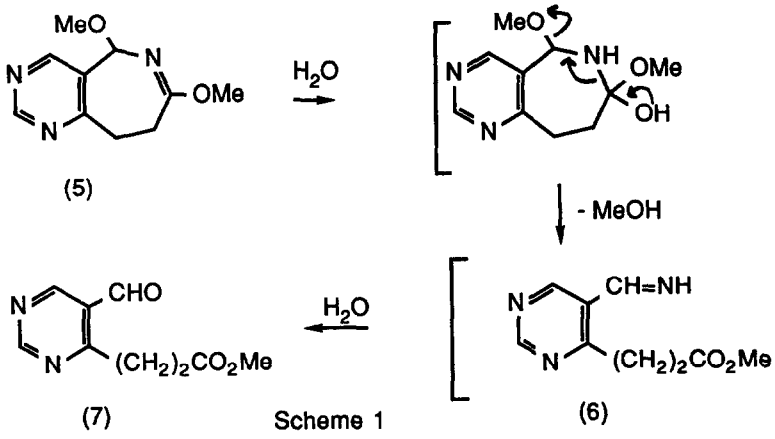


(3) a; X = O
b; X = S



(4)

illustrated in Scheme 1, be a viable precursor of aldehyde (7), the pyrimidine analogue of the previously obtained aldehydes (2a,b). In fact, gentle acid hydrolysis, (pH 5) prior to work-up, of the photolysate from (4) yielded not pyrimido-azepine (5) but aldehyde (7).

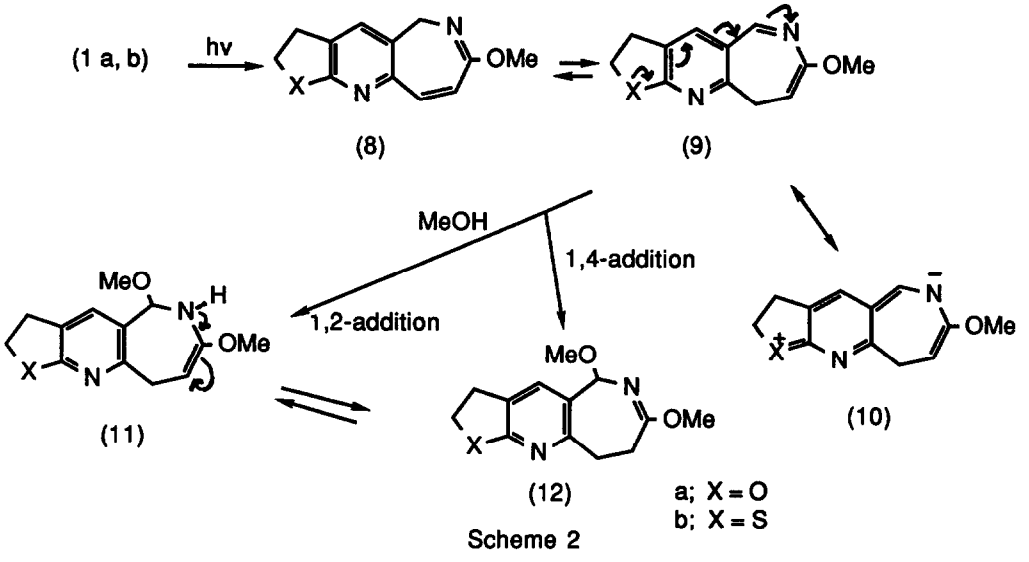


Scheme 1

A check on the work-up procedure employed previously for the photolysis of azidoquinolines (1a,b) revealed that the photolysate had been acidified, albeit briefly, prior to isolation of the products. It was probable, therefore, that aldehydes (2a,b) arose by hydrolysis of initially formed dihydro-dimethoxypyridoazepines (11a,b). Accordingly, the photolysis of azidoquinoline (1a) was repeated and the work-up carried out whilst maintaining the photolysate at pH > 7 at all times. A new product, (12a) was obtained whose ^{1}H n.m.r. spectrum resembled closely that of the pyrimido-derivative (5), and which showed clearly the presence of two non-equivalent MeO groups and a $-CH_2-CH_2-$ unit, the latter as a complex set of resonances at 2.5-3.3 δ. Hydrolysis of this dihydropyridoazepine with concentrated hydrochloric acid in methanol at 0°C was complete in 10 minutes, and after basification, extraction with dichloromethane and purification by column chromatography (Al_2O_3), yielded 6-[(2-methoxycarbonyl)ethyl]-2,3-dihydrofuro[2,3-b]pyridine-5-carbaldehyde (2a; 63%).

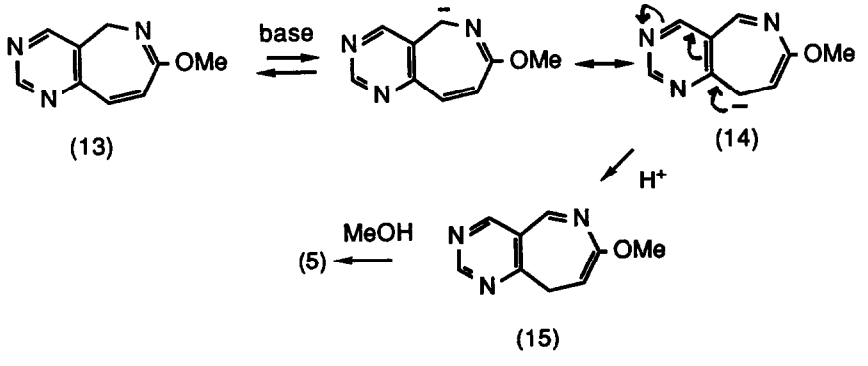
The reasons for these anomalous ring-openings are not clear, particularly since several 6-

azidoquinolines have been photolysed previously[3] in these laboratories to yield pyridoazepines without dihydroazepine, or ring-opened, by-products. A possible explanation for the odd behaviour of the furo- (1a) and thieno- (1b) systems is that the pyrido-azepines are formed initially as the 9H- (9a,b) rather than the more usual 5H-isomers (8a,b). Loss of the stabilising imino-ether resonance in structures (8a,b) is compensated for by a gain of enol-ether resonance in isomers (9a,b) and, more importantly, by mesomeric conjugation (9 ↔ 10) with the lone-pair of the hetero-atom (X). Direct 1,4- [or 1,2-addition followed by an enamine-imine tautomerism (11⇌12)] of methanol to the azepine 2-azadiene system can then yield the 8,9-dihydro-derivatives (12a,b) as indicated in Scheme 2.

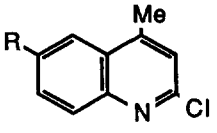


Scheme 2

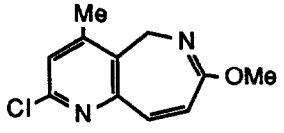
In the case of the pyrimido-azepine, the 9H-isomer (15) could well arise by a base-induced anionotropic shift in the initially formed 5H-isomer (13) to the thermodynamically more stable anion (14), and hence by 1,4- or 1,2-addition of methanol, the dimethoxy-derivative (5). Base-induced isomerisations of 5H-pyrido-azepines have been noted previously.[4]



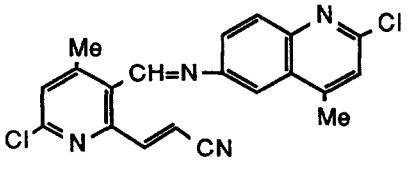
Photolysis of 6-azido-2-chloro-4-methylquinoline (16a) in potassium methoxide-methanol-dioxan was uneventful and gave the chloromethoxypyrido-azepine (17), although in only moderate (30%) yield.* In contrast, however, photolysis of azide (16a) in methanol-dioxan in the absence of potassium methoxide gave not the pyrido-azepine as anticipated from previous work,[5] but the 6-amino-derivative (16b) (5%) and a difficult to separate mixture of the azo-compound (16c; 3%) and a new product (9%) which, from its i.r. spectrum was clearly a nitrile. The p.m.r. spectrum of this last product was definitely not that of a pyridoazepine and was confusing in that it revealed the presence of 5-aromatic protons, two singlet methyls, and no MeO- groups. In addition, a typical AX splitting pattern (doublets at δ 8.29 and δ 6.82, J 16 Hz) was indicative of *trans*-alkene protons. From the mass spectrum it was obvious that the molecule contained 2-chlorine atoms and had the same molecular weight as the azo-compound (16c). On the basis of the spectroscopic evidence structure (18) is proposed for this minor-product. Interestingly, Italian workers[6] have isolated low yields of cyano-aldehydes (19a) and cyano-esters (19b) from the photolysis of 6-azidophenazine in benzene. Reaction of initially formed nitrene with oxygen present in the system is thought to be the source of these ring-opened products. It is reasonable to assume that nitrile (18) could arise by a similar route, the initially formed pyridine-aldehyde (20) undergoing condensation with triplet nitrene derived amine (16b).



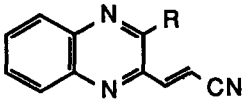
(16) a: R = N_3
b; R = NH_2
c; R = (2-Cl-4-Me-6-quinolyl)-N=N-



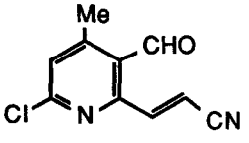
(17)



(18)



(19) a; R = CHO
b; R = CO_2Et



(20)

In contrast, to the complex mode of photodecomposition undergone by 6-azidophenazines,[6] we find that 6-azidoquinoxaline (21) on photolysis in methanol-potassium methoxide-dioxan is relatively simple and furnishes 6-aminoquinoxaline (12%) together with the pyrazino-azepine (22a) (55%). As found for methoxypyridoazepines,[4] the methoxy-group is nucleophilically labile and with, for example 3-(dimethyl-amino)propylamine, yields the amidine (22b).

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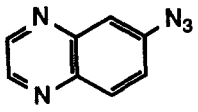
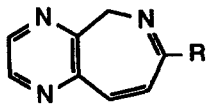
*Curiously, unlike other azido-2-chloroquinolines,[1] no products arising from methoxydechlorination at the 2 position of the quinoline ring were isolated.



(21)



(22) a; R = OMe
b; R = $NH(CH_2)_3NMe_2$

Experimental

I.r. and low resolution mass spectra were measured on a Perkin-Elmer 257 and a Kratos MS30 spectrometer, respectively. High resolution mass spectra were measured at Glaxo Group Research on a VG Analytical Ltd. VG7070E interfaced to a multispec 11 data system.

^1H N.m.r. spectra were calibrated with reference to TMS as internal standard in $CDCl_3$ unless otherwise stated, and recorded on a Varian Associates EM360 (60 MHz); a Perkin Elmer R32 (90 MHz), or a Bruker WM250 (250 MHz) instrument.

T.l.c. was conducted on Camlab Polygram silica G/UV_{254} or alumina N/UV_{254} plates. Flash column chromatography was carried out on silica gel 60 (Merck 9385), medium pressure column chromatography on silica gel 60H (Merck 7736) and alumina column chromatography on neutral aluminium oxide Type H, (B.D.H. Ltd.).

1,4-Dioxan and methanol were dried prior to use as photolysis solvents by distillation under N_2 from sodium-benzophenone, and magnesium-magnesium methoxide, respectively, and then stored over A4 molecular sieve.

6-Azidoquinazoline (4) - Reduction of 6-nitroquinazoline, (2 g; 0.0114 mol) m.p. 174°C (lit.,[8] 175°C) with 15% aqueous titanous chloride (6.2 equivalents) in acetone solution (20 ml/g) under a nitrogen atmosphere at room temperature for 1 h., and work-up as described[9] gave 6-aminoquinazoline (1.38 g; 83%) as a yellow solid, ν_{max} (Nujol) 3350, 3190 (NH_2) cm^{-1}. δ_H (250 MHz; d-4 MeOH), 9.14 (1H, s, 2-H), 8.86 (1H, s, 4-H), 7.73 (1H, d, 8-H), 7.47 (1H, dd, 7-H), 7.0 (1H, d, 5-H), which was used without further purification.

Diazotisation of the amine (1.38 g; 0.095 mol) using sodium nitrite in 4M hydrochloric acid at 0-5°C followed by azidation of the resulting diazonium chloride with sodium azide buffered by aqueous sodium acetate was as described previously[10] [CAUTION - all operations using sodium azide must be carried out in an efficient fume-cupboard. All azides are potentially explosive and should not be heated as the neat solid or neat liquid. All azide decompositions described in this paper were carried out in solution!].

6-Azidoquinazoline was obtained (1.59 g; 96%) as a pale yellow solid which was purified by flash chromatography [eluant EtOAc-hexane (4:1)] and which crystallised from hexane-EtOAc as pale-yellow needles, m.p. 117°C. [Found: C, 55.96; H, 2.81; N, 40.95 $C_8H_5N_5$ requires C, 56.14; H, 2.94; N, 40.9%]. ν_{max} (nujol) 2120 (N_3) cm^{-1}; δ_H (250 MHz) 9.38 (1H, s, 2-H), 9.32 (1H, s, 4-H), 8.08 (1H, d, 8-H), 7.62 (1H, dd, 7-H), 7.55 (1H, d, 5-H).

8,9-Dihydro-5,7-dimethoxy-5H-pyrimido[5,4-c]azepine (5) - A solution of 6-azidoquinazoline (0.677 g; 0.00396 mol) in dry dioxan (40 ml) and 3M KOMe in methanol contained in a Pyrex photolysis cell was degassed with dry nitrogen gas for 10 min. and then irradiated using a 125W medium pressure mercury vapour

lamps; with a continuous flow of nitrogen. After reaction was complete, (4 h) (followed by t.l.c.) the photolysate was brought to pH 8 by careful dropwise addition, with cooling, of methanol- concentrated hydrochloric acid (1:1; v/v). The precipitated KCl was filtered off, the residue washed with methanol, and the combined filtrate and washings evaporated to dryness under vacuum. Purification by flash chromatography (eluant EtOAc) gave 8,9-dihydro-5,7-dimethoxy-5H-pyrimido[5,4-c]azepine (0.13 g, 16%) as an unstable colourless solid, m.p. 55-60°C (decomp.): δ_H (250 MHz) 9.03 (1H, s, 2-H), 8.90 (1H, s, 4-H), 5.85 (1H, s, 5-H), 3.7 (3H, s, OMe), 3.62 (3H, s, OMe), 3.4-2.6 (4H, AA'BB' complex m, CH_2CH_2).

Methyl 3-[4-(5-Formylpyrimidyl)propanoate (7) - The photolysis of azide (4), (0.45 g; 0.00263 mol) was repeated and after 4 h. the irradiation was stopped and the photolysate acidified to pH 5 by dropwise addition of MeOH-conc. hydrochloric acid (1:1; v/v). Subsequent work-up as in the previous experiment and purification of the product by flash chromatography (EtOAc as eluant) gave methyl 3-[4-(5-formylpyrimidyl)]-propanoate as a pale orange oil (0.25 g; 49%); ν_{max} (liquid film) 1740 (CO_2Me), 1700 (CHO) cm^{-1}; δ_H (90 MHz) 10.4 (1H, s, CHO), 9.25 (1H, s, 2-H), 9.1 (1H, s, 4-H), 3.7 (3H, s, OMe), 3.55 (2H, t, $ArCH_2$), 2.95 (2H, t, CH_2CO).

Photolysis of 6-Azido-2,3-dihydrofuro[2,3-b]quinoline (1a) - A solution of 6-azido-2,3-dihydrofuro-[2,3-b]quinoline (0.5 g; 0.023 mol) in dioxan-KOMe-MeOH was irradiated (4 h) as described in the previous experiments. The pH of the photolysate was adjusted to pH 10 by addition of MeOH- conc. HCl (1:1; v/v). Work-up as before and purification of the residue by column chromatography (Al_2O_3) using $CHCl_3$ as eluant gave 5,7-dimethoxy-3,5,8,9-tetrahydro-2H-furo[3',2';5,6]pyrido[2,3-c]azepine (12a) (0.28 g; 48%), which recrystallised from diethyl ether as white needles, m.p. 127-9°C. (Found: C, 62.65; H, 6.3; N, 10.8. $C_{13}H_{16}N_2O_3$ requires C, 62.9; H, 6.5; N, 11.3%); δ_H (300 MHz), 7.69 (1H, s, 4-H), 5.72 (1H, s, 5-H), 4.57 (2H, t, CH_2O), 3.57 (3H, s, OMe), 3.55 (3H, s, OMe), 3.17 (2H, t, $ArCH_2$), 3.17-2.41 (4H, m, 8-CH_2 and 9-CH_2).

6-[(2-Methoxycarbonyl)ethyl]-2,3-dihydrofuro[2,3-b]pyridine-5-carbaldehyde (2a). To a magnetically stirred solution of dimethoxy-pyrido-azepine (12a) (1.24 g; 0.005 mol) in methanol (30 ml) at 0°C was added concentrated hydrochloric acid (3 ml). The reaction mixture was stirred at 0°C for 10 min. then basified by addition of 0.880 ammonia solution. The solvent was removed under reduced pressure, the residue dissolved in dichloromethane and the solution dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave an oil which was purified by column chromatography (Al_2O_3) using $CHCl_3$ as eluant. 6-[(2-Methoxycarbonyl)-ethyl]2,3-dihydrofuro[2,3-b]pyridine-5-carbaldehyde was obtained (0.74 g; 63.2%) as a crystalline solid, m.p. 67°C (lit.,[1] 67°C), identical in all respects to the product reported previously.[1]

6-Azido-2-chloro-4-methylquinoline (16a) 4-Methyl-6-nitro-2-quinolone (m.p. 330-5°C; lit.[11] 340°C), prepared by nitration of 4-methyl-2-quinolone, was converted into 2-chloro-4-methyl-6-nitroquinoline, (70%) m.p. 211°C, using phosphorous oxychloride at 100°C.[12] Reduction of the chloronitro-compound (1.5 g) with titanous chloride as described for 6-nitroquinazoline gave 6-amino-2-chloro-4-methylquinoline (1.22; 94%) as a pale-green solid, [m.p. 148°C (lit.[13] m.p. 152°C); ν_{max} 3455, 3315 (NH_2) cm^{-1}] which was converted directly, *via* the diazonium chloride,[10] and without further purification, to 6-azido-2-chloro-4-methylquinoline (16a), buff needles from hexane (1.28 g, 92%), m.p. 147°C (decomp.); (Found: C, 55.1; H, 3.2; N, 25.55. $C_{10}H_7N_4Cl$ requires C, 54.9; H, 3.2; N, 25.6%) ν_{max} 2110 cm^{-1} (N_3); δ_H (250 MHz) 8.0 (1H, d, 8-H), 7.48 (1H, d, 5-H), 7.4 (1H, dd, 7-H), 7.25 (1H, s, 3-H), 2.64 (3H,

s, Me).

Photolysis of 6-Azido-2-chloro-4-methylquinoline - a) In MeOH-KOMe-dioxan. The azide (0.92 g, 0.0042 mol) was photolysed (5.5. h) as described for 6-azidoquinazoline. Purification of the product by flash chromatography (SiO_2; hexane:EtOAc 1:1 as eluant) gave 2-chloro-7-methoxy-5H-pyrido[3,2-c]azepine (17) (0.3 g; 32%) as a pale yellow solid which after repeated (x 3) crystallisations from hexane, was obtained as tiny white plates, m.p. 106-8°C. (Found: C, 59.1; H, 5.0; N, 12.3. $C_{11}H_{11}ClN_2O$ requires C, 59.3; H, 5.0; N, 12.6%); δ_H (90 MHz) 7.3 (1H, d, 9-H, $J_{8,9}$ 12 Hz), 7.17 (1H, s, 3-H), 6.55 (1H, d, 8-H, $J_{8,9}$ 12 Hz), 4.2 (2H, s, 5-CH_2), 3.65 (3H, s, OMe), 2.5 (3H, s, Me); m/z 224, $(M + 2)^+$ 222 (M^+, 53%).

b) In MeOH-dioxan A solution of the azide (0.67 g; 0.00306 mole) in methanol (40 ml) and dioxan (40 ml) was irradiated for 5 h. according to the procedure already outlined. Purification of the residue, after normal work-up by flash chromatography (hexane-EtOAc; 1:1) yielded initially a yellow solid whose high resolution mass spectrum (C.I.; NH_3) indicated m/z 380.0595 (M^+) $C_{20}H_{14}{}^{35}Cl_2N_4$ requires 380.0596.

Crystallisation of the product from MeOH-$CHCl_3$ preferentially deposited the 6-azo-2-chloro-4-methylquinoline (16c) (0.035; 3%) as red needles, m.p. 154°C; δ_H (250 MHz) 8.65 (1H, d, 5-H), 8.38 (1H, dd, 7-H), 8.14 (1H, d, 8-H), 7.38 (1H, s, 3-H), 2.85 (3H, s, Me).

Evaporation of the liquors from the above crystallisation yielded the α,β-unsaturated nitrile derivative (18) as a pale yellow solid m.p. > 250°C (blackens at 185-95°C) (0.1 g; 9%); δ_H (250 MHz) 8.93 (1H, s, C<u>H</u>=N), 8.29 (1H, d, C<u>H</u>=CHCN, J 16 Hz), 8.11 (1H, d, quinolyl 8-H), 7.75 (1H, d, quinolyl 5-H), 7.66 (1H, dd, quinolyl 7-H), 7.33 (2H, s + s, pyridyl and quinolyl 3-H's), 6.82 (1H, d, CH=C<u>H</u>CN, J 16 Hz), 2.76 (3H, s) and 2.61 (3H, s - quinolyl and pyridyl Me's).

Further elution of the column gave 6-amino-2-chloro-4-methylquinoline (0.029 g; 5%).

6-Azidoquinoxaline (21) - 6-Nitroquinoxaline m.p. 175°C (lit.[14] 177°C), (1.70 g; 0.0097 mole), prepared from 4-nitro-o-phenylenediamine and 2,3-dihydroxydioxan[15] (2.05 g; 0.0171 mol) in ethanol, was reduced, as in previous examples using titanous chloride, to 6-aminoquinoxaline (1 g; 71%) which after flash chromatography (eluant EtOAc-EtOH 95:5) and crystallisation from ethyl acetate, was obtained as yellow needles, m.p. 157°C (lit.[16] m.p. 157°C); ν_{max} 3400, 3320, 3290 cm^{-1} (NH_2). δ_H 250 MHz, 8.67 and 8.56 (2H, d + d, 2-H and 3-H), 7.88 (1H, d, 8-H), 7.2 (1H, dd, 7-H), 7.15 (1H, d, 5-H), 4.25 (2H, bs, NH_2).

Diazotisation of the amine (0.99 g; 0.0068 mol) followed by azidation with NaN_3 in aqueous sodium acetate as previously,[10] gave 6-azidoquinoxaline, (0.652 g, 56%) as a pale brown solid which was purified by flash chromatography. M.p. 103-104°C; ν_{max} 2100 cm^{-1} (N_3); δ_H (250 MHz) 8.84 and 8.80 (2H, d + d, 2-H and 3-H), 8.1 (1H, d, 8-H), 7.75 (1H, d, 5-H), 7.45 (1H, dd, 7-H).

7-Methoxy-5H-pyrazino[2,3-c]azepine (22a) - Irradiation (3.5 h) of 6-azidoquinoxaline (0.62 g; 0.00362 mol) in MeOH-KOMe-dioxan and work-up as in previous examples, gave a solid mixture which was separated by flash chromatography (EtOAc as eluant) to give initially 7-methoxy-5H-pyrazino[2,3-c]azepine (0.34 g; 55%) which crystallised from hexane; as pale-yellow plates, m.p. 81-2°C (Found: C, 61.8; H, 5.2; N, 24.1. $C_9H_9N_3O$ requires C, 61.7; H, 5.2; N, 24.0%); δ_H (250 MHz), 8.52 (2H, ABq, 2-H and 3-H), 7.32 (1H, d, 9-H), 6.63 (1H, d, 8-H), 4.5 (2H, s, CH_2), 3.7 (3H, s, OMe).

Further elution gave 6-aminoquinoxaline (0.063 g; 12%).

7-[(3-Dimethylamino)propylamino]-5H-pyrazino[2,3-c]azepine (22b) - A solution of the methoxy-pyrazino-azepine (22a) (0.293 g; 0.00167 mol) in 3-(dimethylamino)-n-propylamine (10 ml) and glacial acetic acid (0.2 ml) was heated under nitrogen at 110-135°C for 6 h. The solution was evaporated to dryness and the dark oily residue purified by column chromatography (Al_2O_3; EtOAc-EtOH-Et_3N - 75:23:2 as eluant) to give 7-[(3-dimethylamino)propylamino]-5-pyrazino[2,3-c]azepine (0.14 g; 34%) as a light brown oil. δ_H (250 MHz) 8.51 (2H, AB q, 2-H and 3-H), 7.28 (1H, d, 9-H), 6.65 (1H, d, 8-H), 4.47 (2H, s, CH_2), 3.23 (2H, t, CH_2NH), 2.38 (2H, t, CH_2NMe_2), 2.25 (6H, s, NMe_2), 1.75 (2H, quintet, C-CH_2-C).

Maleate salt, m.p. 185-90°C.

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