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3*H*-Azepines and Related Systems. Part 5.[1] Photo-induced Ring Expansions of *o*-Azidobenzonitriles to 3-Cyano- and 7-Cyano-3*H*-azepin-2(1*H*)-ones

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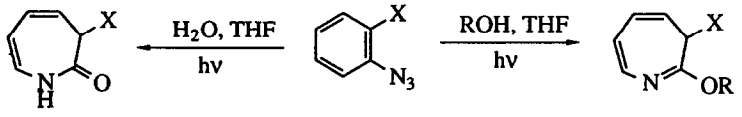
Abstract: Unlike other aryl azides bearing electron-withdrawing *ortho*-substituents, *o*-azidobenzonitriles on photolysis in aqueous-tetrahydrofuran yield mixtures of the expected 3-cyano- and the unexpected 7-cyano-3*H*-azepin-2(1*H*)-ones. In one instance ring-contraction to a 2-azabicyclo[3.2.0]hept-6-ene-3-one is noted. X-Ray crystallographic data for 7-cyano- and 4-chloro-7-cyano-3*H*-azepin-2-one, and for the azabicycloheptenone, are presented.

The photo-induced ring-expansion of an aryl azide in the presence of a nucleophile is a well-established synthetic route to 2-substituted 3*H*-azepines.[2] The method is particularly efficient for aryl azides **1** bearing an electron-withdrawing *ortho*-substituent and in a 1:1 alcohol-tetrahydrofuran solution, or in 1:1 aqueous tetrahydrofuran, practicable yields of 2-alkoxy-3*H*-azepines[3] **2** and 3*H*-azepin-2-ones[1] **3** respectively, are realised.



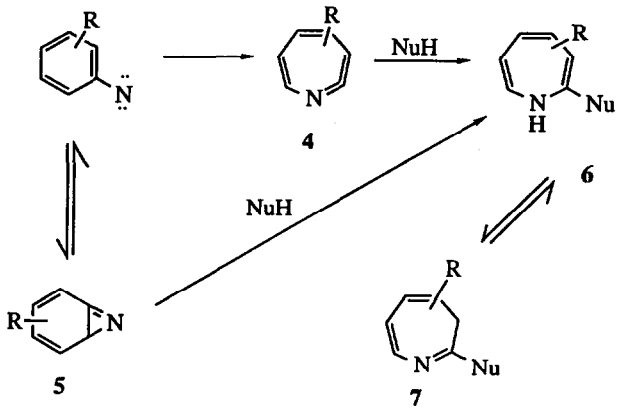
3 **1** **2**

X = CO_2Me, SO_2NH_2, CO_2H, CONHR

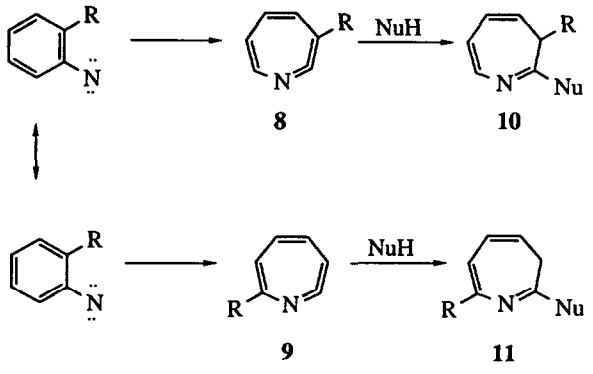
The nature of the intermediate(s) involved in these ring-expansions is still open to debate. Recent[4] kinetic evidence supports the intermediacy of both a benzazirine* **5** (as proposed originally[5]) and a didehydroazepine **4** in the photo-induced ring-expansion of 3,4-diacylaminophenyl azides, rather than a singlet nitrene-didehydroazepine system favoured by earlier workers,[6] for other aryl azides under similar conditions.

In either case, the intermediate can be trapped by a nucleophile (RNH_2, ROH or H_2O) to yield initially a 1*H*-azepine **6**,[8] which rearranges subsequently, by hydrogen shift, to the more stable 3*H*-isomer **7**.[9]

* There is convincing evidence for the participation of fused azirines in the ring-expansion of bicyclic nitrene systems.[7]



Two isomeric didehydroazepines **8** and **9** (or benzazirines) are possible from an *ortho*-substituted arylazide, but generally only one product, namely, the 3-substituted-3*H*-azepine **10**, is obtained:



However, in rare instances, the 7-substituted 3*H*-azepines, arising from trapping of the isomeric didehydroazepine **9** (or benzazirine) have been isolated. For example, irradiation of *o*-azidoacetophenone in piperidine furnished a 1:1 mixture of the 3- and 7-acetyl-2-piperidino-3*H*-azepines (**10** and **11**; R = $COCH_3$, Nu = $C_5H_{10}N$);[10] in methanol solution, 7-acetyl-2-methoxy-3*H*-azepine (identified only tentatively from its ^1H n.m.r. spectrum) was noted.†

In an earlier paper[14] we noted that *o*-azidobenzonitrile (**1**; X = CN), unlike the other *ortho*-substituted aryl azides (**1**, X = as shown) being studied, yielded a mixture (by ^1H n.m.r.) of the expected 3-cyano- and the unexpected 7-cyano-2-methoxy-3*H*-azepines (**10** and **11**; R = CN, Nu = OMe). This anomalous result prompted us to investigate further the ring-expansion of *o*-cyanoaryl azides. In this paper we report our work on the photolysis of some *o*-azidobenzonitriles in aqueous tetrahydrofuran most of which yield varying amounts of the uncommon and unexpected 7-cyano- isomer together with, in some cases, the 3-cyano-compound.

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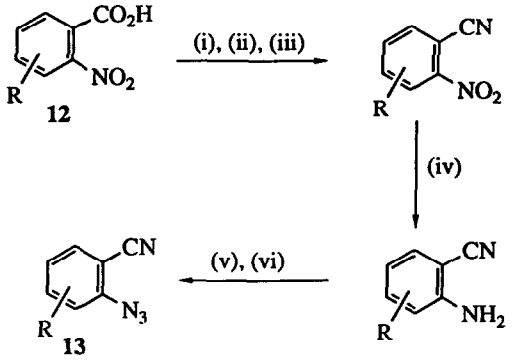
† Mixtures of 3- and 7-substituted 3*H*-azepines are also formed by photolysis of 2,2-dimethylindazole in dilute sulphuric acid,[11] and by deoxygenation of aromatic nitro-compounds with tervalent phosphorus compounds in the presence of amines[12,13]

The 4- and 5-substituted 2-azidobenzonitriles **13a,b,c** were prepared from the corresponding 2-nitrobenzoic acids as outlined in Scheme 1.



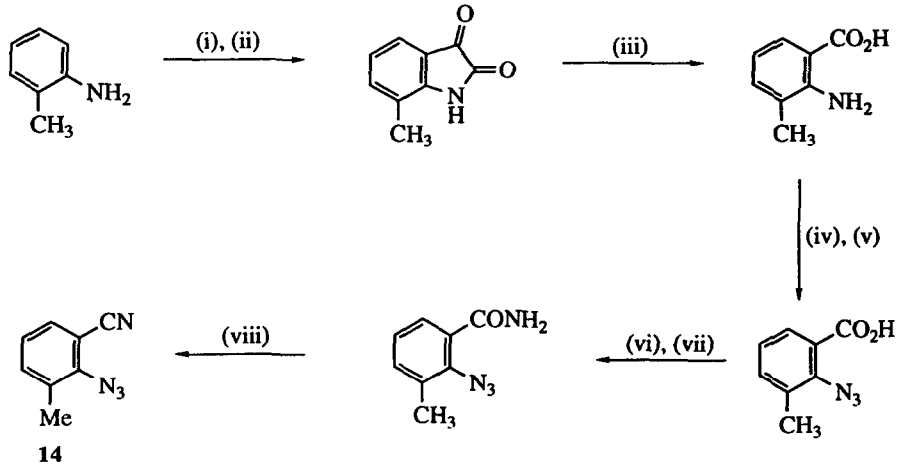
13 a) R = 4-Cl; b) R = 5-Cl; c) R = 5-Me; d) R = 5-CN.

i) $SOCl_2$, PhMe, reflux; ii) 0.88 NH_4OH; iii) $SOCl_2$, reflux; iv) $TiCl_3$, acetone, H_2O; v) $NaNO_2$, HCl, 0°C; vi) NaN_3, NaOAc, H_2O, 0-5°C.

Scheme 1

The dinitrile **13d** was prepared likewise from the nitrodicarboxylic acid (**12**; R = 5-CO_2H).

3-Methyl-2-azidobenzonitrile **14** was obtained from 7-methyl isatin as outlined in Scheme 2.



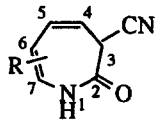
i) CCl_3CHO, NH_2OH, H_2O, EtOH; ii) 98% H_2SO_4; iii) NaOH, H_2O_2; iv) $NaNO_2$, HCl, 0°C; v) NaN_3, NaOAc, H_2O, 0-5°C; vi) $SOCl_2$, PhMe reflux; vii) 0.88 NH_4OH; viii) $SOCl_2$, reflux.

Scheme 2

We have reported previously[15] the facile cyclisation of 2-azidoanilides to 2-aryl-3-chloro-2*H*-imidazoles with thionyl chloride. In this case, however (step viii, Scheme 2), as with 2-azido-*N*-alkylbenzamides, dehydration to the nitrile, rather than cyclisation, prevails.

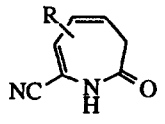
Photolysis of 2-Azidobenzonitriles

Irradiation (10 h.) of 2-azidobenzonitrile in 1:1 tetrahydrofuran-water solution furnished a separable mixture of azepinones along with unreacted azide and trace amounts of *o*-aminobenzonitrile. The major product (30%), on the basis of its ^{1}H n.m.r. spectrum, was assigned as 3-cyano-3*H*-azepin-2(1*H*)-one **15a**



15

a) R = H
b) R = 5-Me
c) R = 6-Cl



16

a) R = H
b) R = 5-Me
c) R = 4-Cl
d) R = 5-CN

The minor product (16%), again on the basis of its ^{1}H n.m.r. spectrum was designated as the isomeric 7-cyano-3*H*-azepin-2(1*H*)-one **16a**. The methylene unit at C-3 appears as a high field doublet (δ 2.99) coupled (J 6.8 Hz) to the triplet alkene proton (δ 5.93) at C-4. Unequivocal evidence for the 7-cyano-2-azepinone structure was obtained by X-ray analysis (Fig. 1).

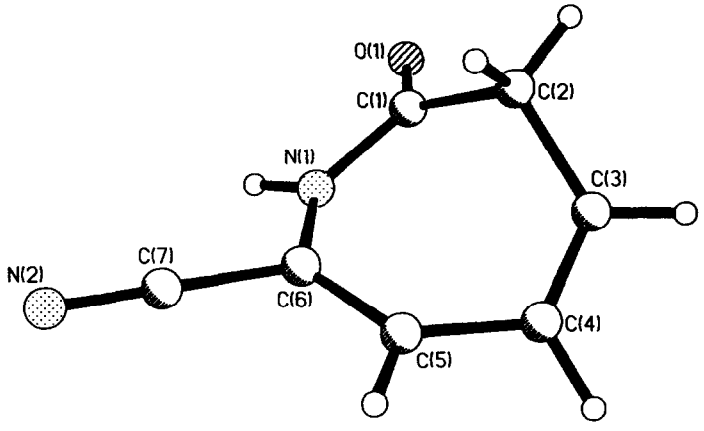


Figure 1. Molecular structure of 7-cyano-3*H*-azepin-2(1*H*)-one (16a)

Prolonged irradiation (21 h) of 2-azidobenzonitrile in aqueous-THF resulted in a decrease in yield of the 3-cyano isomer (to 10%) and an increase in yield (to 21%) of the 7-cyano derivative. However, the possibility of photoisomerisation of the 3-cyano- compound to the 7-cyano- was discounted when it was found that irradiation of pure 3-cyano-3*H*-azepin-2(1*H*)-one in aqueous-THF produced no 7-cyano-isomer (by t.l.c.), only tarry products.

Photolysis of 2-azido-5-methyl **13c** and 2-azido-4-chloro-benzonitrile **13a** proceeded in a similar manner to give mixtures of the 3-cyano- **15b, 15c** and 7-cyano-2-azepinones **16b, 16c** in 30% and 14%, and 25% and 14% yields, respectively.

Whereas, the structures of the isomeric methyl azepinones could be assigned unambiguously on the basis of their ^{1}H n.m.r. spectra, the p.m.r. spectrum of the 7-cyano-chloroazepinone was not immediately understandable. In addition to the singlet expected for the 3-CH_2-unit, there was only a 2 proton singlet resonance signal (δ 6.2) for the alkene protons at C-5 and C-6 rather than the anticipated two sets of doublets. However, this is a coincidental overlap of the two signals, since an X-ray analysis (Fig. 2) of the product confirmed its structure as the 7-cyano-3*H*-azepin-2-one **16c**.

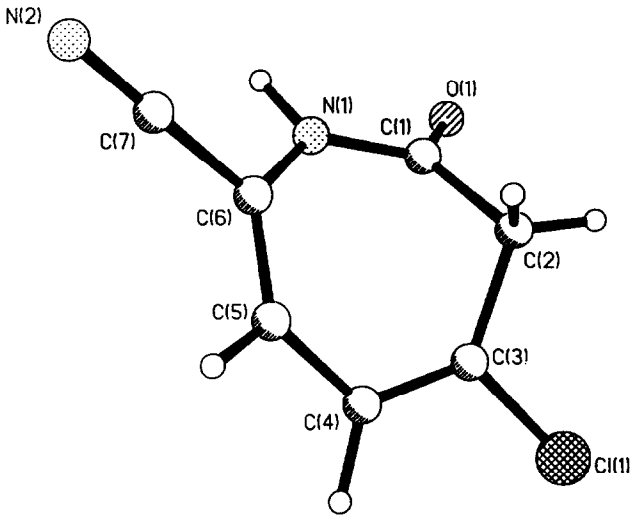
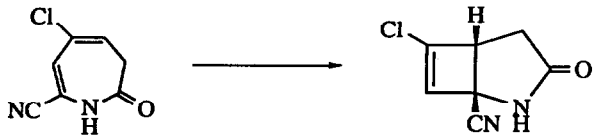


Figure 2. Molecular structure of 4-chloro-7-cyano-3*H*-azepin-2(1*H*)-one (16c)

Irradiation of 2-azido-5-chlorobenzonitrile furnished a different mixture of products. Chromatographic separation of the two major products yielded 7-cyano-5-chloro-3*H*-azepinone **17** (10%) and a minor (8%) isomeric product which, from its ^{1}H n.m.r. spectrum was not the 3-cyano-5-chloro-isomer. In particular, the characteristic doublet 3-methine signal was absent and there was only a single uncoupled alkene proton resonance. An X-ray structure determination (Fig. 3) revealed that the product is in fact the bicycle **18** formed by a 4π-electrocyclic, disrotatory ring closure of the 7-cyano-azepin-2(1*H*)-one.



17 **18**

Similar ring contractions have been noted previously for 3*H*-azepin-2(1*H*)-ones,[16-18] and for 3*H*-azepines.[19]

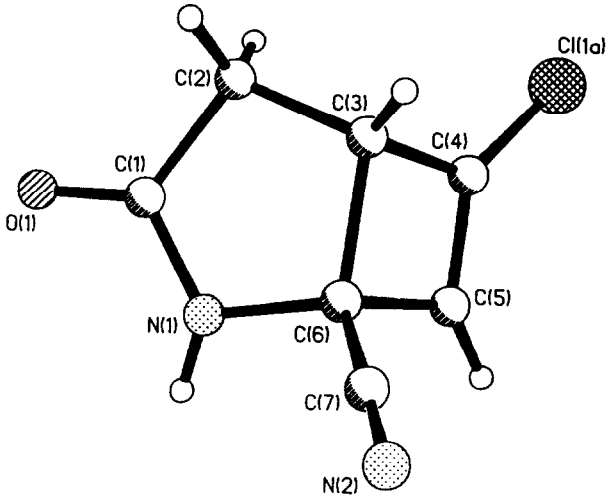


Figure 3. Molecular structure of 6-chloro-1-cyano-2-azabicyclo[3.2.0]hept-6-ene-3-one

The dicyanoaryl azide **13d** also failed to yield a 3-cyano-3*H*-azepin-2(1*H*)-one. In this case an approximately 50:50 mixture (by ^{1}H n.m.r. spectroscopy) of 5,7-dicyano-3*H*-azepin-2(1*H*)-one (**16d**; R = 5-CN) and 2,4-dicyanoaniline was obtained.

Irradiation of 2-azido-3-methylbenzonitrile, in which both *ortho* positions to the azide group are blocked by substituents, furnished 2,2'-dicyano-6,6'-dimethylazobenzene (10%) as the sole identifiable product. The inhibition of the photo-induced ring-expansion of 2,6-disubstituted phenyl azides to azepines has been noted previously.[20]

We offer no explanation for this anomalous behaviour of *o*-azidobenzonitriles. From a recent communication[4] on the benzazirine *vs.* didehydroazepine controversy, it appears that subtle steric and electronic effects are instrumental in determining the nature of the intermediate involved in these ring-expansions. However, it is not obvious to us why the nitrile group should differ so markedly from other similar electron-withdrawing groups (e.g. CO_2Et) in its effect on 3*H*-azepine formation.

Attempts to bring about ring-expansion of *o*-azidobenzonitrile in the presence of other nucleophilic anions was unsuccessful. For example, irradiation of the azidonitrile in aqueous-THF containing potassium fluoride, bromide, or chloride, and in the presence of 18-crown-6 failed, as did photolyses in the presence of potassium phthalimide and sodium *p*-toluenesulphinate. Unchanged azidonitrile and/or intractable tars resulted.

EXPERIMENTAL

Reduction of o-nitrobenzonitriles to 2-aminobenzonitriles - General method. A solution of the *o*-nitrobenzonitrile (5 mmol) in Analar acetone at room temperature, and under a nitrogen atmosphere, was treated dropwise with 15% titanous chloride solution (8 equivs.) over a period of 30 min. After completion of addition, the mixture was stirred for 30 min. then basified by careful addition of 15% sodium hydroxide, and the mixture filtered. The residue was extracted with ethyl acetate (3 x 20 ml), the extracts combined, and the solvent removed to yield the *o*-aminobenzonitrile.

Preparation of o-azidonitriles - General method. A solution of the *o*-aminobenzonitrile (25 mmol) in 5M hydrochloric acid (120 ml) was cooled to 0-5°C and diazotised by slow addition of a solution of sodium nitrite (28 mmol) in water (15 ml). The resulting diazonium chloride solution was stirred at 0-5°C for 10 min., then filtered and added slowly (5-10 min.) to a solution of sodium azide (25 mmol) and sodium acetate (0.25 mol) in water (50 ml).

[CAUTION - all operations involving NaN_3 must be carried out in an efficient fume-hood. The large excess of sodium acetate acts as a buffer and minimises the formation of toxic hydrazoic acid during azide production.]

The resulting solution is stirred at 0-5°C for 0.5 h, then filtered to yield the *o*-azidonitrile as a white solid. The azide was washed with water (3 x 100 ml) and dried at the pump. Purification was by flash chromatography on silica.

All azides so prepared were kept in the dark, and in a refrigerator (0-5°C) until ready for use.

[CAUTION - all azides are potentially explosive, and should, therefore, never be heated as the solid or neat liquid. All decompositions described in this paper were carried out in dilute (1-2%) solution.]

2-Azidobenzonitrile, from 2-aminobenzonitrile (ALDRICH) was obtained (79%) as yellow needles from light petrol, m.p. 54°C (lit.[21], 58°C).

2-Azido-5-chlorobenzonitrile **13b**. Reduction of 5-chloro-2-nitrobenzonitrile (m.p. 88-9°C; lit.[22] m.p. 94°C), obtained by treatment of 5-chloro-2-nitrobenzamide (m.p. 155°C; lit.[23] 154°C) with thionyl chloride, yielded 2-amino-5-chlorobenzonitrile as a yellow solid m.p. 96°C (lit.[24], 98°C). Diazotisation followed by azidation (see General method) gave *2-azido-5-chlorobenzonitrile*, which after chromatography [SiO_2: light petrol-diethyl ether (8.5:1.5) as eluant], formed pale yellow crystals, m.p. 85°C; ν_{max} (nujol) 2230 (CN), 2130 (N_3) cm^{-1}; δ_H ($CDCl_3$) 7.3 (1H, d, 3H), 7.65 (1H, d, 6-H), 7.68 (1H, m, 4-H); m/z (EI) 178 (M^+).

2-Azido-4-chlorobenzonitrile **13a**. Reduction of 4-chloro-2-nitrobenzonitrile (m.p. 98-99°: Lit.[25] 97°C) obtained by treating 4-chloro-2-nitrobenzamide (m.p. 172-3°C: lit.[26], m.p. 172°C) with thionyl chloride, gave 2-amino-4-chlorobenzonitrile (50%) as a yellow solid which crystallised from light petrol-ethyl acetate as white needles, m.p. 158-9°C (lit.[27] 162°C). Diazotisation followed by azidation gave *2-azido-4-*

chlorobenzonitrile (64%) as a white solid, m.p. 112-3°C; ν_{max} (nujol) 2235 (CN), 2130 (N_3) cm^{-1}; δ_H ($CDCl_3$) 7.2 (1H, d, 5-H), 7.25 (1H, s, 3-H), 7.55 (1H, d, 6-H); m/z (EI) 178 (M^+).

2-Azido-5-methylbenzonitrile **13c**. Reduction of 5-methyl-2-nitrobenzonitrile (m.p. 89-90.5°C; Lit.,[29] 93-4°C) obtained by treating 5-methyl-2-nitrobenzamide (m.p. 169-70°C; Lit.[28] m.p. 176-7°C) with thionyl chloride gave 2-amino-5-methylbenzonitrile (92%) as a yellow solid m.p. 60°C (Lit.[28] 63°C). Diazotisation followed by azidation gave *2-azido-5-methylbenzonitrile* as a white solid (52%) m.p. 61-2°C; ν_{max} 2227 (CN) 2129 (N_3) cm^{-1}: δ_H ($CDCl_3$) 2.4 (3H, s, Me), 7.3 (1H, d, 3-H), 7.5 (2H, m, 4-H and 6-H).

2,4-Dicyanophenylazide **13d**. Reduction of 2,4-dicyanonitrobenzene (m.p. 224°C: Lit.[29], 224°C), obtained by treating the diamide of 4-nitrobenzene-1,3-dicarboxylic acid [m.p. 280-90°C (decomp.); ν_{max} 3445, 3292, 3144 ($CONH_2$), 1668 (broad) (CO); δ_H (d^6-DMSO) 7.9 (2H, s, $CONH_2$), 8.35 (5H, m, 3-H, 5-H, 6-H and $CONH_2$). m/z (EI) 209 (M^+)] with thionyl chloride, furnished 2,4-dicyanoaniline (85%) as white crystals, m.p. 218°C (decomp.) Lit.[30] m.p. 213-4°C).

Diazotisation of the amine followed by azidation yielded *2,4-dicyanophenyl azide* (52%), which crystallised from light petrol-ethyl acetate as yellow crystals m.p. 172°C (decomp.): ν_{max} 2223 (CN), 2133, 2093 (N_3) cm^{-1}. δ_H ($CDCl_3$) 7.45 (1H, s, 6-H), 7.95 (1H, d, 5-H), 8.0 (1H, s, 3-H); m/z (EI)169 (M^+).

2-Azido-3-methylbenzonitrile **14**. 3-Methylanthranilic acid (90%) m.p. 172-4°C (Lit.[31], 172°C) obtained by oxidative ring-opening of 7-methylisatin (m.p. 220°C; Lit.[32] m.p. 267°C), was converted into *2-azido-3-methylbenzoic acid* by diazotisation and azidation (General method). M.p. 155°C (decomp.); ν_{max} (nujol) 2156 (N_3): 1694 (CO) cm^{-1}; δ_H (d^6-DMSO) 2.35 (3H, s, Me), 7.25 (1H,m, 5-H), 7.45 (1H, dd, 4-H), 7.8 (1H, dd, 6-H), 9.55 (1H, bs, H); m/z (EI) 177 (M^+). *2-Azido-3-methylbenzamide*, (obtained from the acid chloride with 0.88 ammonia solution) crystallised from light petrol-ethyl acetate as white crystals, m.p. 147°C (decomp.): ν_{max} (nujol) 3367, 3185 ($CONH_2$), 2112 (N_3), 1645 (CO); δ_H (d^6-DMSO) 2.2 (3H, s, Me), 7.1 (2H, m, 4-H and 5-H), 7.5 (1H, d, 6-H), 8.0 (2H, bs, $CONH_2$); m/z 176 (M^+).

Dehydration of the amide, with boiling thionyl chloride gave *2-azido-3-methylbenzonitrile*, as a dark brown residue, which, after chromatography on alumina (light petrol-ethyl acetate as eluant), was obtained as a pale yellow oil (96%) which solidified in the refrigerator: ν_{max} 2227 (CN), 2138, 2108 (N_3) cm^{-1}: δ_H ($CDCl_3$) 2.3 (3H, s, Me), 7.2 (2H, m, 4-H and 5-H), 7.6 (1H, d, 6-H); m/z (EI), 158 (M^+).

Photolysis of 2-Azidobenzonitriles in Aqueous-Tetrahydrofuran. - General method: A solution of the 2-azidonitrile (14 mmol) in THF (115 ml) and water (115 ml) was irradiated under nitrogen using a 400 Watt medium pressure u.v. lamp (Pyrex-filter). The irradiation was continued until most of the azide had disappeared, as indicated by examination of the photolysate by t.l.c. Removal of the solvent under reduced pressure yielded a dark oily residue which was separated and purified by flash chromatography on a silica.

2-Azidobenzonitrile, (2 g, 14 mmol), - (photolysed for 18 h.), gave after flash chromatography [light petrol-ethyl acetate (6:4 v/v) as eluant] *7-cyano-3H-azepin-2(1H)-one* **16a** as a white solid (0.4 g; 21%) which crystallised from light petrol-ethyl acetate as white needles, m.p. 143°C; (Found: C, 62.5; H, 4.4; N, 20.6 $C_7H_6N_2O$ requires C, 62.7; H, 4.5; N, 20.9%) ν_{max} (nujol) 3175 (NH), 2210 (CN), 1600 (CO) cm^{-1}; δ_H ($CDCl_3$) 2.99 (2H, d, 3-CH_2, $J_{3,4}$ 6.8 Hz); 5.95 (1H, m, 4-H, $J_{4,5}$ 9.5 Hz, $J_{3,4}$ 6.8 Hz); 6.26 (1H, dd, 5-H, $J_{5,6}$

5.5 Hz, $J_{4,5}$ 9.5 Hz); 6.57 (1H, d, 6-H, $J_{5,6}$ 5.5 Hz); 8.68 (1H, bs, 1H, removed on addition of D_2O): m/z (EI) 134 (M^+):

Further elution with the same solvent mixture gave a brown solid which on trituration with dichloromethane and crystallisation from light petrol-ethyl acetate gave *3-cyano-3H-azepin-2(1H)-one* **15a** as pale yellow crystals (0.1 g, 5%), m.p. 148-9°C [Found: C, 62.47; H, 4.7; N, 20.6. $C_7H_6N_2O$ requires C, 62.7; H, 4.5; N, 20.9%); ν_{max} (nujol) 3179 (NH), 2250 (CN), 1660 (CO) cm^{-1}; δ_H (d^6-DMSO) 3.47 (1H, d, 3-CH, $J_{3,4}$ 5.8 Hz); 5.35 (1H, dd, 4-H, $J_{4,5}$ 9.2 Hz, $J_{3,4}$ 5.8 Hz), 5.65 (1H, dd, 6-H, $J_{5,6}$ 5.4 Hz, $J_{6,7}$ 8.9 Hz), 6.1 (2H, m, 7-H and 5-H), 9.82 (1H, bs, NH; removed on addition of D_2O), m/z (EI) 134 (M^+).

2-Azido-5-chlorobenzonitrile (2 g; 11 mmol), (photolysed for 12 h), gave after chromatography an alumina [light petrol-ethyl acetate (2:8 v/v)] as eluant, 2-amino-5-chlorobenzonitrile (< 5%), followed by an off-white solid mixture which was further purified by flash chromatography on silica [light petrol-ethyl acetate (7:3 v/v)] as eluant. *5-Chloro-7-cyano-3H-azepin-2(1H)-one* **17** was obtained as a white solid (0.3 g; 16%), which crystallised from light petrol-ethyl acetate as white crystals, m.p. 170°C [Found: C, 50.1; H, 3.0; N, 16.6: $C_7H_5ClN_2O$ requires C, 49.9; H, 3.0; N, 16.6%); ν_{max} (nujol) 3200 (NH), 2232 (CN), 1703 (CO) cm^{-1}; δ_H ($CDCl_3$) 2.73 (2H, d, 3-CH_2, $J_{3,4}$ 7.3 Hz) 5.78 (1H, t, 4-H, $J_{3,4}$ 7.6); 6.2 (1H, s, 6-H), m/z (EI) 170 (M + 2), 168 (M^+).

Further elution gave *6-chloro-1-cyano-2-azabicyclic[3.2.0]hept-6-ene-3-one* **18** as a white solid (0.15 g; 8%), which crystallised from light petrol-ethyl acetate as colourless crystals m.p. 207°C [Found: C, 49.9; H, 2.9; N, 16.3; $C_7H_5ClN_2O$ requires C, 49.9; H, 3.0; N, 16.6%); ν_{max} (nujol) 3200 (NH), 2232 (CN), 1703 (CO) cm^{-1}; δ_H (d^6-DMSO) 1.9 (1H, dd, 4-H', $J_{4',5}$ 3 Hz, $J_{4,4'}$ 18 Hz); 2.15 (1H, dd, 4-H, $J_{4,5}$ 10 Hz, $J_{4,4'}$ 18 Hz), 3.6 (1H, dd, 5-H, $J_{4,5}$ 10 Hz, $J_{4',5}$ 3 Hz); 5.93 (1H, s, 7-H); 8.5 (1H, s, NH, removed on addition of D_2O), m/z (EI) 170 $(M + 2)^+$, 168 (M^+).

2-Azido-4-chlorobenzonitrile (1.5 g, 8.5 mmol), (photolysed for 7 h.), gave after flash chromatography on SiO_2 [light petrol-ethyl acetate (8:2) as eluant] 2-amino-4-chlorobenzonitrile (< 5%). Further elution with light petrol-ethyl acetate (7:3) furnished *4-chloro-7-cyano-3H-azepin-2(1H)-one* **16c** as a white solid (0.2 g, 14%) which crystallised from light petrol-ethyl acetate as white needles, m.p. 189-90°C [Found: C, 49.6; H, 2.7; N, 16.5. $C_7H_5ClN_2O$ requires C, 49.9; H, 3.0; N, 16.6%]; ν_{max} (nujol) 3242 (NH); 2260 (CN), 1705 (CO) cm^{-1}; δ_H (d^6-DMSO) 3.0 (2H, s, 3-CH_2); 6.17 (2H, s, 6-H and 5-H) 10.44 (1H, bs, NH, removed on addition of D_2O); m/z EI 170 $(M + 2)^+$, 168 (M^+).

Further elution with light petrol-ethyl acetate produced an impure yellow solid which was rechromatographed on [silica light petrol-ethyl acetate (6:4 v/v) as eluant], to give *6-chloro-3-cyano-3H-azepin-2(1H)-one* **15c** as white crystals (0.35 g; 25%), m.p. 156°C. [Found: C, 49.7; H, 2.9; N, 16.4. $C_7H_5ClN_2O$ requires C, 49.9; H, 3.0; N, 16.6%]; ν_{max} (nujol) 3242 (NH), 2260 (CN), 1705 (CO) cm^{-1}; δ_H ($CDCl_3$)

3.65 (1H, dd, 3-CH, $J_{3,4}$ 6 Hz, $J_{3,5}$ 1.5 Hz); 5.52 (1H, dd, 4-H, $J_{4,5}$ 9.4 Hz, $J_{3,4}$ 6 Hz); 6.18 (1H, dd, 5-H; $J_{4,5}$ 9.4 Hz, $J_{3,5}$ 1.5 Hz); 6.37 (1H, d, 7-H, $J_{1,7}$ 5.25 Hz; on addition of D_2O the signal became a singlet at δ 6.37); 10.2 (1H, bs, NH-removed on addition of D_2O). Double irradiation of 3H at δ 3.65 produced 6.18 (d, 5-H; $J_{4,5}$ 9.4 Hz); 5.52 (d, 4-H, $J_{4,5}$ 9.4 Hz); m/z 170 $(M + 2)^+$ 168 (M^+).

2-Azido-5-methylbenzonitrile (1.2 g; 7.6 mmol) (photolysed for 2 h), on flash chromatography on silica [light petrol-ethyl acetate (7:3 v/v) as eluant] gave, successively, unchanged azide (< 5%), 2-amino-5-methylbenzonitrile (< 10%), and a brown oil, which when triturated with light petrol furnished *7-cyano-5-*

methyl-3H-azepin-2(1H)-one **16b** as a dark brown solid (0.16 g; 14%) which crystallised from light petrol-ethyl acetate as tan crystals, m.p. 136-7°C [Found: C, 64.9; H, 5.3; N, 18.8: $C_8H_8N_2O$ requires C, 64.8; H, 5.4; N, 18.9%] ν_{max} (nujol) 3181 (NH), 2221 (CN), 1674 (CO) cm^{-1}; δ_H ($CDCl_3$) 1.9 (3H, s, 5-Me), 2.87 (2H, d, 3-CH_2, $J_{3,4}$ 7 Hz), 5.66 (1H, t, 4-H, $J_{3,4}$ 7 Hz) 6.46 (1H, s, 6-H), 8.61 (1H, s, NH-removed on addition of D_2O); m/z (EI) 148 (M^+):

Further elution yielded *3-cyano-5-methyl-3H-azepin-2(1H)-one* **15b** as a brown solid (0.34 g; 30%), which crystallised from light petrol-ethyl acetate as pale-yellow needles, m.p. 105°C. [Found: C, 64.5; H, 5.6; N, 18.7: $C_8H_8N_2O$ requires C, 64.8; H, 5.4; N, 18.9%]; ν_{max} (nujol) 3205 (NH), 2253 (CN), 1674 (CO) cm^{-1}; δ_H ($CDCl_3$) 1.9 (3H, s, 5-Me); 3.68 (1H, d, 3-CH; $J_{3,4}$, 5.5 Hz), 5.35 (1H, d, 4-H; $J_{3,4}$ 5.7 Hz); 5.82 (1H, d, 6-H, $J_{6,7}$ 9 Hz); 6.25 (1H, dd, 7-H, $J_{6,7}$ 9 Hz, $J_{1,7}$ 4.8 Hz, which on addition of D_2O collapsed to a doublet at 6.25); 8.72 (1H, bs, NH-removed on addition of D_2O); m/z (EI) 148 (M^+).

2,4-Dicyanophenyl azide (0.5 g; 3 mmol), (photolysed for 4 h), gave after flash chromatography on silica (dichloromethane as eluant) a yellow, unseparated mixture of 2,4-dicyanoaniline and *5,7-dicyano-3H-azepin-2(1H)*-one **16d** (0.33 g; 54%), m.p. 155-7°C; ν_{max} 3375, 3275 (NH_2), 3200 (NH), 2216 (CN), 1699 (CO) cm^{-1} δ_H (d^6-DMSO) 2.75 (2H, d, 3-CH_2; $J_{3,4}$ 7.4 Hz), 6.0 (2H, s, NH_2); 6.2 (1H, s, 6-H), 6.35 (1H, t, 4-H, $J_{3,4}$ 7.4 Hz), 6.5 (1H, d, Ar 6-H), 7.08 (1H, dd, Ar 5-H), 7.27 (1H, dd, Ar 3-H), 10.77 (1H, bs, NH); m/z (EI) m/z 159 (M^+), 143 (M^+) $ArNH_2$.

2-Azido-3-methylbenzonitrile (1.6 g; 10 mmol) photolysed for 16 h., gave after flash chromatography on silica, [light petrol-ethyl acetate (7:3 v/v) as eluant] 2,2'-dicyano-6,6'-dimethylazobenzene as red prisms (0.35 g; 13%) m.p. 189°C; ν_{max} (nujol) 2217 (CN) cm^{-1}. δ_H ($CDCl_3$) 2.85 (6H, s, 2 x Me); 7.44 (2H, t, 4-H and 4'-H); 7.62 (2H, d, 5-H and 5-H'), 7.64 (2H, d, 3-H and 3'-H); m/z (EI) 260 (M^+).

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Summary of X-Ray Crystallographic Data

Compound	18	16c	16a
Formula	$C_7H_5ClN_2O$	$C_7H_5ClN_2O$	$C_7H_6N_2O$
Formula Weight	168.6	168.6	134.1
Crystal Size (mm)	0.5 x 0.3 x 0.3	0.3 x 0.2 x 0.2	0.3 x 0.2 x 0.1
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a(A)	6.870(3)	8.566(3)	8.586(1)
b(A)	8.445(4)	7.445(1)	7.044(1)
c(A)	13.245(5)	11.937(3)	11.682(1)
β°	104.69(4)	91.74(3)	105.94(1)
Volume(A^3)	743	760.9(3)	679.3(2)
Z	4	4	4
μ(MoKα) mm^{-1}	0.447	0.436	0.086
D_c(Mg m^{-3})	1.506	1.472	1.311
F(000)	344	344	280
Temperature (K)	201	293	293
Index ranges h	$-4 \rightarrow 8$	$0 \rightarrow 10$	$-10 \rightarrow 10$
k	$-1 \rightarrow 10$	$0 \rightarrow 8$	$-8 \rightarrow 8$
l	$-17 \rightarrow 17$	$-14 \rightarrow 14$	$-13 \rightarrow 13$
Total no. of reflections	3061	1574	4803
Independent reflections	1701	1354	1202
R_{int}	0.03	0.02	0.02
F> nσ(F)	4	4	4
Observed reflections	1516	962	998
$w^{-1}=\sigma^2(F)+gF^2$, g	0.0001	0.0014	0.0003
No. of parameters	100	100	91
R(observed data, all data)	0.037, 0.050	0.042, 0.054	0.037,0.043
wR(observed data, all data)	0.042, 0.052	0.065, 0.062	0.047,0.046
Goodness of Fit	2.27	1.04	1.62
Largest shift:esd	0.001	0.001	0.001
Data:parameter ratio	15.2:1	9.6:1	11.0:1
Δρ max(cA^{-3})	+0.27	+0.17	+0.17
Δρ min(A^{-3})	-0.42	-0.25	-0.21

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