3*H*-Azepines and Related Systems. Part 2.[1] The Photolyses of Aryl Azides Bearing Electron-withdrawing Substituents

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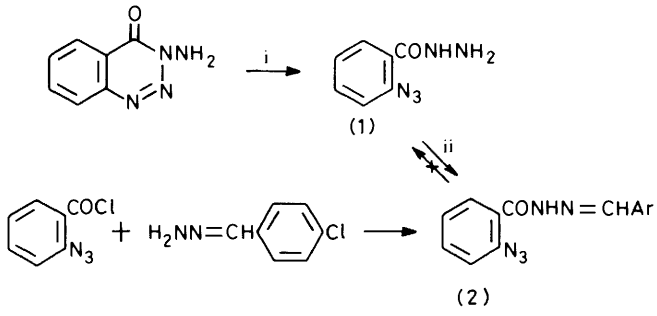
The photolyses of *ortho*-substituted aryl azides (o-$XC_6H_4N_3$ where X = $CONHNH_2$, CONHN=CHAr, NO_2, CN, CF_3, SO_2OMe, SO_2NH_2, or SO_2Ph) in methanol–tetrahydrofuran solution are described. With X = CF_3 or CONHN=CHAr, 3-substituted 2-methoxy-3*H*-azepines are products, while in other cases polymeric products, amines, or mixtures of isomeric azepines are obtained. The product from the photolysis of *o*-azidophenyl phenyl sulphoxide (X = SOPh) is identified tentatively (n.m.r. evidence) as 7-methoxy-2-phenylsulphinyl-3*H*-azepine.

In contrast, methyl *p*-azidobenzoate and *p*-cyanophenyl azide yield the corresponding 5-substituted 2-methoxy-3*H*-azepines, whereas methyl *m*-azidobenzoate yields only methyl 2-methoxy-3*H*-azepine-6-carboxylate. Irradiation of methyl *o*-azidobenzoate in aqueous tetrahydrofuran gives 1,3-dihydro-3-methoxycarbonyl-2*H*-azepin-2-one.

In previous papers from these laboratories [1] and from other workers,[2] the photo-induced ring expansions of *o*-azidobenzoates and *o*-azidobenzanilides in alcohol or alcohol–tetrahydrofuran solution to give 2-alkoxy-3*H*-azepine-3-carboxylates and -3-carboxanilides have been described. Interest in these ring expansions centred on the apparent necessity of having an electron-withdrawing carbonyl function *ortho* to the azido group in order for reaction to take place. For example, phenyl azide,† *o*-azidotoluene, and *o*-azidobenzyl alcohol fail to yield azepine when photolysed in methanol or methanol–tetrahydrofuran solution, whereas under the same conditions methyl *o*-azidobenzoate furnishes methyl 2-methoxy-3*H*-azepine-3-carboxylate in 84% yield.[1] Similarly, photolysis of *o*-azidoacetophenone in methanol yields 3-acetyl-2-methoxy-3*H*-azepine.[4] In this paper the effects on 3*H*-azepine formation of other electron-withdrawing groups *ortho* to the azide function are reported. In addition, the effect of moving the ester function to the *meta* and *para* position with respect to the azide group is noted.

Preparation of Azides.—Previously we have described the difficulties encountered in trying to prepare the hitherto unknown *o*-azidobenzohydrazide (1) by treating methyl *o*-azidobenzoate with ethanolic hydrazine hydrate.[1,5] Other attempts, involving hydrolysis of the *p*-chlorobenzylidene derivative (2; Ar = p-ClC_6H_4) were also unsuccessful. For example, hydrolysis with hydrogen chloride in ethanol, and in diethyl ether [6] gave only starting material, whereas in hot aqueous acetic acid or in 40% sodium hydroxide, a mixture of 4,4′-dichlorobenzaldehyde azine and *o*-azidobenzoic acid was produced. However, the hydrazide has now been prepared in excellent yield by azidolysis of 3-amino-1,2,3-benzotriazin-4(3*H*)-one in acetic acid, a method developed originally by Stevens *et al.*[7] for the preparation of *o*-azidobenzanilides. Its structure was confirmed by conversion into the *p*-chlorobenzylidene derivative (2) (Scheme 1, Ar = p-ClC_6H_4).

Methyl *m*- and *p*-azidobenzoate, *o*- and *p*-cyano-, *o*-nitro-, and *o*-trifluoromethyl-phenyl azides were prepared from the corresponding amines by diazotisation followed by azidation with sodium azide in buffered solution. The *o*-azido-sulphone, -sulphoxide, and -sulphonamide were prepared similarly, as was methyl *o*-azidobenzenesulphonate, although in this case azidation conditions had to be modified in order to minimise hydrolysis of the sensitive ester function.



Scheme 1. *Reagents:* i, AcOH,NaN_3; ii, p-ClC_6H_4CHO

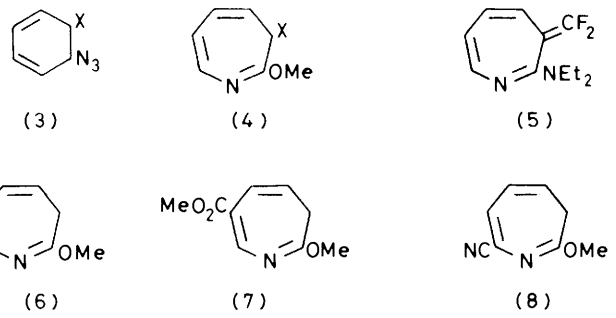
Photolyses.—All the photolyses were carried out in 1 : 1 methanol–tetrahydrofuran.[1] Photolysis of the sulphonate (3; X = SO_2OMe), the sulphonamide (3; X = SO_2NH_2), and the hydrazide (1) was disappointing in that only tarry or polymeric products were obtained. Equally unsuccessful was the photolysis of the azidosulphone (3; X = SO_2Ph) which gave only 2-aminophenyl phenyl sulphone (6%) and much tar. Predictably, *o*-nitrophenyl azide (3; X = NO_2) gave benzofuroxan, the same product as that from the thermal decomposition.[8]

Of more interest was *o*-trifluoromethylphenyl azide (3; X = CF_3) which on irradiation gave mainly 2-methoxy-3-trifluoromethyl-3*H*-azepine (4; X = CF_3) (49%) along with a small amount (5%) of *o*-trifluoromethylaniline. The azepine structure was established by ^1H, ^{13}C, and ^{19}F n.m.r. spectroscopy. Previously, *o*-trifluoromethylphenyl azide has been photolysed in diethylamine to give the difluoromethyleneazepine (5) (71%), ring-expansion being followed by a base-catalysed elimination of HF.[9]

In contrast to the hydrazide (1), but like the amide (3; X = $CONH_2$),[1] the acyl hydrazone (2; Ar = p-ClC_6H_4) underwent ring-expansion to the azepine (4; X = $CONHN{=}CHC_6H_4Cl$-p) in good yield.

p-Cyanophenyl azide, as expected, yielded 5-cyano-2-methoxy-3*H*-azepine (6; X = CN). Similarly, methyl *p*-azidobenzoate furnished methyl 2-methoxy-3*H*-azepine-5-carboxylate (6; X = CO_2Me). Significantly, however, in both these reactions longer photolysis times than with the analogous

† An 11% yield of 2-methoxy-3*H*-azepine is claimed from the photolysis of phenyl azide in methanol.[3] However, in our hands only aniline and tarry products were obtained.



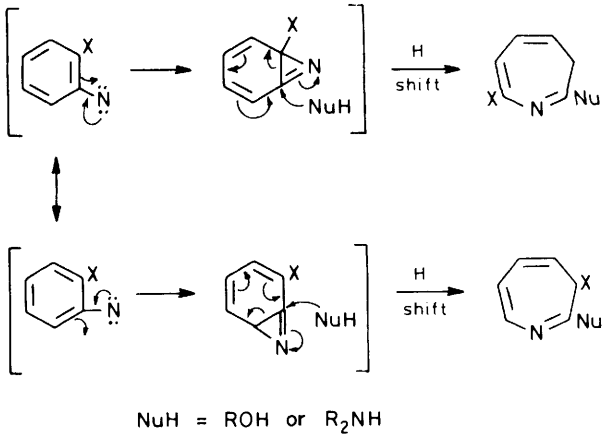
(3) (4) (5)

(6) (7) (8)

ortho azides were necessary, and much lower yields of the 3*H*-azepines resulted. The ring-expansion of methyl *m*-azidobenzoate was of special interest since not only was the electron-withdrawing group now in a non-conjugative position with respect to the developing nitrene, but, also, isomeric azepines were possible depending on whether the nitrene was incorporated at the *ortho* or *para* position to the ester group.

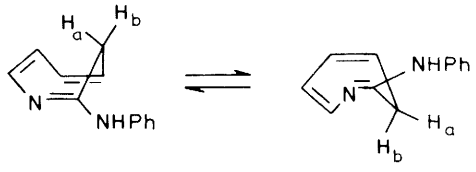
In fact, we obtained only one azepine which, on the basis of ^{1}H n.m.r. decoupling experiments, was shown to be methyl 2-methoxy-3*H*-azepine-6-carboxylate (7). This result is in accord with the findings of Atherton and Lambert,[10] who on the basis of their work on the ring-expansion of nitroarenes by trivalent phosphorus reagents in the presence of primary and secondary amines, suggested, albeit on flimsy evidence, that *meta* electron-withdrawing substituents favour the formation of 6-substituted 3*H*-azepines (*i.e.* an '*ortho*' insertion). In contrast, Cadogan and his co-workers,[11] in a similar study, isolated a mixture of 2-dimethylamino-4- and -6-methoxycarbonyl-3*H*-azepines (the latter as the major product) from the deoxygenation of methyl *m*-nitrobenzoate with triethyl phosphite in the presence of dimethylamine.

Irradiation of the cyanoazide (3; X = CN) produced an oil, that proved to be inseparable by t.l.c., but which, from the ^{1}H n.m.r. spectrum, appeared to be a mixture of two isomeric azepines, each differing significantly from the 5-cyano derivative (6; X = CN). The two singlets at δ 3.8 and 3.75 corresponded to two methoxy groups, whereas the doublets at δ 3.27 and 2.76 (the former integrating for one proton and the latter for two protons) were indicative of an aliphatic CH and CH_2 unit respectively. The presence of two isomers was confirmed by the off-resonance decoupled ^{13}C n.m.r. spectrum which contained twice the number of signals expected for a single azepine. In particular, the singlet at δ 34.0 (originally a triplet) confirmed the presence of the CH_2 unit, whereas the low-field singlet (δ 122.8) correlates with a tertiary carbon centre bearing a cyano group. In addition, the presence of signals for seven rather than eight =CH units in the ^{13}C n.m.r. spectrum led to the conclusion that the mixture consisted of the expected product, 3-cyano-2-methoxy-3*H*-azepine (4; X = CN), and its isomer, 7-cyano-2-methoxy-3*H*-azepine (8). The assignments of the peaks in the ^{1}H n.m.r. spectrum were based on decoupling experiments, and, for the 3-cyano-3*H*-azepine, on comparisons with 2-alkoxy-3*H*-azepine-3-carboxylates.[1] Proton resonances for the 7-cyano isomer (8) compared well with those reported for 7-acetyl-2-piperidino-3*H*-azepine, obtained by Berwick [4] from the photolysis of *o*-azidoacetophenone in piperidine. Examples of the formation of 7-substituted 3*H*-azepines by the ring-expansion of *ortho*-substituted aryl azides in the presence of nucleophiles are rare,[4,12] and on the basis of a benzazirine reaction intermediate (see later) must arise by attack of the nitrene at the carbon bearing the substituent group (Scheme 2). As far as we are aware, this is the first example



NuH = ROH or R_2NH

Scheme 2.



(9) (10)

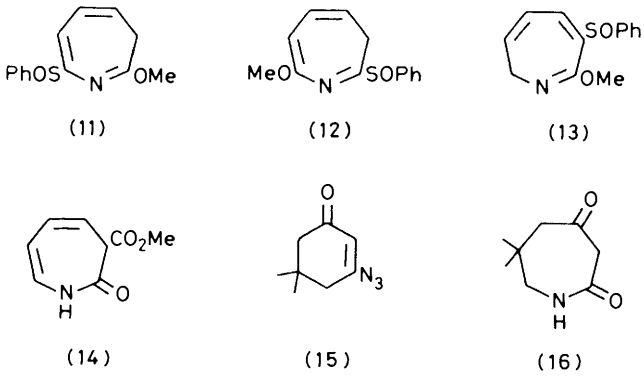
with an alcohol as the nucleophile, although 7-acetyl-2-methoxy-3*H*-azepine was identified tentatively (from ^{1}H n.m.r. evidence) * as a product from the photolysis of *o*-azidoacetophenone in methanol.[4] Curiously, no azepines were formed during the deoxygenation of *o*-nitrobenzonitrile with triethyl phosphite in the presence of diethylamine.[11]

The structure of the unstable oil obtained in low yield (20%) from the photolysis of the *o*-azidophenyl phenyl sulphoxide (3; X = SOPh) has not been assigned unequivocally. Spectral data suggested a methoxysulphinylazepine, although acceptable carbon analysis figures could not be obtained. The ^{1}H and ^{13}C n.m.r. spectra, although indicating a single isomer, were incompatible with the expected 2-methoxy-3-phenylsulphinyl-3*H*-azepine (4; X = SOPh), the most obvious difference being the presence of a CH_2 unit which in the ^{1}H n.m.r. spectrum appeared as a well-defined ABX system, indicative of geminal coupling (*J* 13 Hz) and additional coupling to an adjacent proton.

Geminal couplings can arise as a result of slow ring-flipping of the azepine ring between the two tub conformers [*e.g.* (9) and (10)], and have been observed previously with 3*H*-azepines unsubstituted at the 3-position, although only at low temperatures.[13,14] However, it is difficult to see why the 7-phenylsulphinyl group in the 3*H*-azepine (11) should promote such behaviour, particularly as the corresponding 3-methylene groups in the 7-cyano derivative (8) and in 7-acetyl-2-methoxy- and 7-acetyl-2-piperidino-3*H*-azepine [4] appear as simple doublets.

A more likely structure is the isomeric 7-methoxy-2-phenylsulphinyl-3*H*-azepine (12). This isomer has the asymmetric phenylsulphinyl group, which is known [15] to impart non-equivalence to β-protons and β-*gem* dimethyl groups, in close proximity to the methylene unit as demanded by the magnitude (13 Hz) of the geminal coupling constant.[16]

* The proton resonances cited are also in accord with those shown by 7-cyano-2-methoxy-3*H*-azepine.



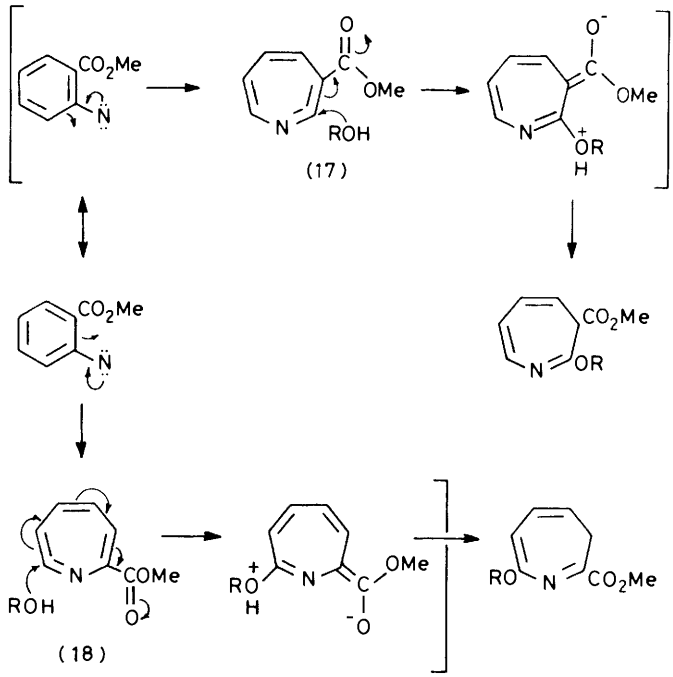
[1,5]-H Shifts of the type (11) ⇌ (12) are rare in the 3*H*-azepine series.[17,18]

The alternative structure (13) is most unlikely both on spectroscopic grounds and by the fact that 2*H*-azepines are the least stable of the three possible azepine structures bearing the tautomeric hydrogen on carbon.[19]

Ring-expansions in the presence of other simple nucleophiles were only partially successful. Photolysis of methyl *o*-azidobenzoate in tetrahydrofuran saturated with ammonia or hydrogen sulphide produced methyl anthranilate (54 and 37% respectively) as the sole identifiable product. However, photolysis of the azidoester in aqueous tetrahydrofuran furnished 1,3-dihydro-3-methoxycarbonyl-2*H*-azepin-2-one (14) in 59% yield. This reaction has some synthetic merit as the azepinone is not readily available by hydrolysis of the 2-methoxy derivative (4; X = CO_2Me). In fact, efforts to hydrolyse this methoxyester under a variety of conditions (2M-sodium hydroxide or hydrochloric acid) led to the destruction of the azepine ring and the formation of uncharacterised water-soluble products.

Attempts to extend the ring-expansion process to a bicyclic system were unsuccessful. Methyl 2-azido-3-naphthoate in methanol–tetrahydrofuran gave mainly tars together with trace amounts of unidentifiable oils.

In a previous paper [1] it was suggested that the success of the ring-expansion of *o*-substituted phenyl azides was due to stabilisation of the developing nitrene by the oxygens of the adjacent carbonyl group, and the increased electrophilicity of the singlet nitrene. The current results, however, make it clear that other electron-withdrawing substituents, *e.g.* CN and CF_3, not possessing a stabilising oxygen or lone-pair bearing function, are also capable of promoting azepine formation. In addition, the location of the substituent at the *para*, and more significantly (in the case of CO_2Et) at the *meta* position, also results in azepine formation, although yields are lower and photolysis times markedly increased. An alternative, and equally plausible, explanation of these ring expansions is by stabilisation of a heterocumulene intermediate (17) of the type proposed * by Chapman [21] for the decomposition of aryl azides in a solid matrix at 10 K and by Wentrup [22] for heteroaryl azides under flash pyrolysis conditions. In fact, the heterocumulene (18) offers a more attractive explanation for the formation of 2,7-disubstituted 3*H*-azepines (Scheme 3) † than the benzazirine mechanism, as this latter process necessitates nitrene insertion at the carbon centre bearing the electron-withdrawing group, an unlikely event.



Scheme 3.

Experimental

I.r. spectra were recorded as Nujol mulls or liquid films on a Perkin-Elmer 297 or 257 grating infrared spectrophotometer. ^1H and ^{13}C N.m.r. spectra were measured, unless otherwise stated, for $CDCl_3$ solutions ($SiMe_4$ as internal standard) on a Perkin-Elmer R32 90 MHz and a Varian Associates CFT 20 spectrometer, respectively. Mass spectra were obtained on an A.E.I. MS12 mass spectrometer, and u.v. spectra as ethanol solutions on a Unicam SP 800A spectrophotometer. The tetrahydrofuran (THF) used in the photolyses was dried ($MgSO_4$ and then sodium wire), and finally distilled under nitrogen from sodium and benzophenone. All m.p.s are uncorrected and distillation of all liquid samples was performed using a Kugelrohr. T.l.c. was on Alumina G (type E), whereas column chromatography was carried out on Alumina (type H).

Preparation of Azides.—In all cases, other than those described separately, the azides (Table) were prepared by diazotisation of the corresponding amine in hydrochloric acid solution at 0—5 °C, followed by azidation of the resulting diazonium chloride with sodium azide in buffered (NaOAc) solution.

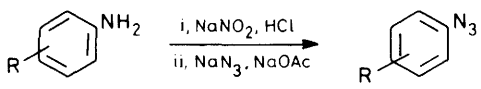
3-Azido-2-naphthoic Acid.—3-Azido-2-naphthoic acid, white needles from benzene–light petroleum (b.p. 80—100 °C), m.p. 183 °C (decomp.) (lit.,[24] m.p. 170 °C) (Found: C, 61.7; H, 3.5; N, 20.0. Calc. for $C_{11}H_7N_3O_2$: C, 62.0; H, 3.3; N, 19.7%), was prepared from 3-amino-2-naphthoic acid by the inverse diazotisation procedure and then azidation, as described [1] for 2-azido-3-chlorobenzoic acid.

Methyl 3-Azido-2-naphthoate.—A mixture of 3-azido-2-naphthoic acid (2.8 g), dry benzene (50 ml), and thionyl chloride (10 ml) were heated under reflux for 45 min. The excess of thionyl chloride was removed by co-distillation with benzene (2 × 20 ml) under reduced pressure. The residual oil, $\nu_{max.}$ 2 145 (N_3), 1 750 cm^{-1} (C=O), was dissolved in methanol and the solution stirred overnight. Removal of the

* A heterocumulene intermediate had been proposed earlier by Sato [20] in order to explain the ring-expansion of the azido-cyclohexenone (15) to the 1*H*-azepine-2,4-dione (16).

† We thank a referee for suggestions concerning this mechanism.

Table. Preparation of substituted aryl azides



	Amine		Azide		
R	M.p. (°C)	Lit. m.p. (°C)	M.p. (°C)	Lit. m.p. (°C)	Yield (%)
o-CO_2Me	*a*		Oil	Oil [23]	96
m-CO_2Me	38	38 [23]	Oil	Oil [23]	96
p-CO_2Me	*a*		38	39 [23]	92
o-CN	*a*		54	58 [23]	79
p-CN	*a*		67	70 [23]	89
o-NO_2	*a*		53	53 [26]	92
o-CF_3	*a*		29 [b]	Ref. 27	81
o-SO_2NH_2	156	157 [28]	183 (decomp.) [c]		61
o-SO_2Ph	118	122 [29]	160 (decomp.)	165 [30]	94
o-SOPh	Oil	Oil [30]	117 (decomp.) [d]	102 (decomp.) [30]	89

[a] Commercially available; other amines prepared as in reference cited. [b] Described in ref. 27 as an oil. [c] Crystallised from ethyl acetate as white needles (Found: C, 36.3; H, 3.1; N, 28.5. $C_6H_6N_4O_2S$ requires C, 36.35; H, 3.05; N, 28.25%); $\nu_{max.}$ 3 360 and 3 260 (NH_2), 2 140 cm^{-1} (N_3). [d] Crystallised from cold chloroform as white needles on careful addition of light petroleum (b.p. 60—80 °C) (Found: C, 58.7; H, 3.8; N, 17.6. Calc. for $C_{12}H_9N_3OS$: C, 59.2; H, 3.7; N, 17.3%); $\nu_{max.}$ 2 140 and 2 105 (N_3), 1 040 cm^{-1} (SO).

methanol produced an oily residue which was purified by column chromatography (Al_2O_3, benzene as eluant) to give methyl 3-azido-2-naphthoate (2.5 g, 84%), m.p. 60 °C (lit.,[31] 58 °C); $\nu_{max.}$ 2 140 (N_3), 1 730 cm^{-1} (C=O).

N-(o-*Azidobenzoyl*)-p-*chlorobenzaldehyde Hydrazone* (2; Ar = *p*-ClC_6H_4).—Freshly prepared *o*-azidobenzoyl chloride[1] (9.75 g, 0.05 mol) was added dropwise with stirring to a solution of *p*-chlorobenzaldehyde hydrazone [32] (7.7 g, 0.05 mol) in pyridine (30 ml). After 1 h, the reaction mixture was poured into cold water (50 ml), then filtered to give the N-(o-*azidobenzoyl*)-p-*chlorobenzaldehyde hydrazone* (2; Ar = *p*-ClC_6H_4) (85%), which crystallised from benzene as pale yellow needles, m.p. 168 °C (170 °C decomp.) (Found: C, 56.2; H, 3.4; N, 23.5. $C_{14}H_{10}ClN_5O$ requires C, 56.1; H, 3.3; N, 23.3%).

The hydrazone was also obtained by condensing 2-azidobenzohydrazide with *p*-chlorobenzaldehyde in ethanol solution.

Hydrolysis of the Hydrazone (2; Ar = *p*-ClC_6H_4).—A suspension of the azidohydrazone (1 g) in a mixture of acetic acid and water (20 ml, 9 : 1 v/v) was heated on a steam-bath for 6 h. The reaction mixture was filtered to give a brown residue which, on purification by column chromatography (Al_2O_3; $CHCl_3$ then EtOH as eluants) gave 4,4'-*dichlorobenzaldehyde azine* (55%), m.p. 212 °C (Found: C, 60.6; H, 3.7; N, 10.05. $C_{14}H_{10}Cl_2N_2$ requires C, 60.7; H, 3.6; N, 10.1%); δ_H 8.7 (2 H, s, CH), 7.9—8.0 (4 H, d, ArH), and 7.55—8.05 (4 H, d, ArH); and *o*-azidobenzoic acid (27%).

2-*Azidobenzohydrazide* (1).—A solution of 3-amino-1,2,3-benzotriazin-4(3*H*)-one [33] (5 g) in concentrated hydrochloric acid (50 ml) was added, with stirring, to a solution of sodium azide (15 g) in water (50 ml). **CAUTION:** this operation must be carried out in an efficient fume-hood as copious amounts of HN_3, a toxic gas, are evolved. The immediate evolution of nitrogen was accompanied by the precipitation of a white product. The reaction mixture was allowed to stand overnight at room temperature, then neutralised carefully by addition of concentrated potassium hydroxide while maintaining the temperature of the mixture at 0—10 °C. The solid product was removed by filtration, air dried in the dark, and then stirred with chloroform (100 ml) for 5 min. The chloroform solution was filtered and the filtrate passed down a short (30 cm) chromatography column (Al_2O_3). Further elution of the column with chloroform gave 2-*azidobenzohydrazide* (1) (3.6 g, 60%) as a white solid, m.p. 96 °C (Found: C, 47.3; H, 3.95; N, 39.6. $C_7H_7N_5O$ requires C, 47.45; H, 4.0; N, 39.5%); $\nu_{max.}$ (Nujol) 3 300br (NH), 2 130, 2 080 (N_3), and 1 620br cm^{-1} (C=O).

Methyl 2-Aminobenzenesulphonate Hydrochloride.—Hydrogen chloride was passed for 2 h through an efficiently stirred mixture of methyl 2-nitrobenzenesulphonate [34] (6 g, 0.028 mol), powdered stannous chloride (19 g, 0.8 mol), and glacial acetic acid (40 ml) contained in a 1-l, three-necked flask, fitted with a mechanical stirrer, gas inlet, and a thermometer. At the end of this time, the mixture was allowed to stand at 0 °C (ice-bath) for 2 h before diethyl ether (250 ml) was added. The stirred two-phase mixture was carefully neutralised (pH 7) by dropwise addition of cold 20% sodium hydroxide while maintaining the reaction mixture at 10—15 °C. The ether layer was separated, and the aqueous phase extracted with diethyl ether (2 × 50 ml). The combined ether layers were then washed with cold water (2 × 50 ml) and dried ($MgSO_4$). Evaporation of the ether gave methyl 2-aminobenzenesulphonate as an unstable yellow oil (4.38 g, 85%), $\nu_{max.}$ (liquid film) 3 490, 3 390 (NH_2), 1 350, and 1 180 cm^{-1} (SO_2), which was converted as quickly as possible into its stable hydrochloride by passing hydrogen chloride for 15 min through a solution of the amine in dry diethyl ether (100 ml). Methyl 2-aminobenzenesulphonate hydrochloride (3.6 g, 69%) precipitated from the ether solution as a white powder which decomposed without melting at >320 °C.

Methyl 2-Azidobenzenesulphonate.—A solution of methyl 2-aminobenzenesulphonate hydrochloride (2.24 g, 0.01 mol) in 4M-hydrochloric acid (20 ml) maintained at −5 °C, was diazotised by careful dropwise addition of a cold (−5 °C) solution of sodium nitrite (0.75 g, 0.011 mol) in water (10 ml). After completion of nitrite addition, the diazonium solution was added dropwise to a cold (−5 °C) freshly prepared solution of sodium azide (10 g) in water (30 ml) maintained at 0 °C. (**CAUTION:** see warning concerning HN_3 in the preparation of *o*-azidobenzohydrazide.) The solution was extracted with diethyl ether (3 × 50 ml), the combined extracts dried ($MgSO_4$) and then evaporated to give *methyl 2-azidobenzenesulphonate* as a yellow oil (0.6 g, 32%), $\nu_{max.}$ (liquid film) 2 120 (N_3), 1 360 and 1 180 cm^{-1} (SO_2); *m/z* 213 (M^+), 185 [$(M - N_2)^+$, 100%].

Yields of azide are reduced drastically (often to zero) if, as is usual, the diazonium solution is added to buffered (sodium acetate) sodium azide solution. Even with the procedure outlined above, the preparation sometimes failed or gave inferior yields to that quoted.

Photolysis of Aryl Azides.—The general procedure was as outlined in a previous paper [1] for the photolysis of *o*-azidoesters. Irradiation times for each azide are given at the begin-

ning of the individual section, and photolyses were carried out in a mixture of methanol (130 ml) and dry THF (130 ml) unless stated otherwise.

(*a*) *Methyl 3-azidobenzoate*. The aryl azide (2 g) was photolysed for 35 h. Chromatographic separation on alumina, light petroleum (b.p. 40—60 °C)–ethyl acetate as eluant, gave the azidoester (0.15 g, 7%) and *methyl 2-methoxy-3H-azepine-6-carboxylate* (7) as a pale yellow oil (0.7 g, 34%), b.p. 88—93 °C/0.5 Torr) (Found: C, 60.05; H, 6.3; N, 7.8. $C_9H_{11}NO_3$ requires C, 59.65; H, 6.1; N, 7.7%); $\nu_{max.}$ (liquid film) 1 710 (C=O) and 1 610 cm^{-1} (C=N); δ_H (CCl_4) 7.95 (1 H, s, 7-H), 6.70 (1 H, d, $J_{4,5}$ 9 Hz, 5-H), 5.34 (1 H, dt, $J_{3,4}$ 7 Hz, 4-H), 3.76 (3 H, s, OMe), 3.72 (3 H, s, OMe), and 2.62 (2 H, d, 3-H). Double irradiation of 5-H gave δ 7.95 (s, 7-H) and 5.32 (t, 4-H, $J_{3,4}$ 7 Hz). Double irradiation of 3-H gave δ 7.72 (dd, 5-H, $J_{4,5}$ 9 Hz, $J_{4,7}$ 2 Hz) and 5.34 (d, 4-H); δ_C (CCl_4) 33.7 (t, C-3), 51.0 (q, CO_2CH_3), 55.0 (q, OCH_3), 115.8 (d, C-4), 117.8 (d, C-6), 127.0 (s, C-5), 144.5 (d, C-7), 152.4 (s, C-2), and 166.7 p.p.m. (s, C=O); $\lambda_{max.}$ (log ε) 279 (3.94); *m/z* 181 (M^+).

(*b*) *Methyl 4-azidobenzoate*. The aryl azide was photolysed for 22 h. Chromatographic separation on alumina, light petroleum (b.p. 40—60 °C)–ethyl acetate as eluant, gave the azidoester (0.2 g, 10%), followed by *methyl 2-methoxy-3H-azepine-5-carboxylate* (6; X = CO_2Me) (0.9 g, 44%), as a pale yellow oil, b.p. 77—87 °C C/0.5 Torr (Found: C, 60.0; H, 6.25; N, 7.7. $C_9H_{11}NO_3$ requires C, 59.65; H, 6.1; N, 7.7%); $\nu_{max.}$ (liquid film) 1 720 (C=O) and 1 625 cm^{-1} (C=N); δ_H (CCl_4) 6.98 (1 H, d, $J_{6,7}$ 8 Hz, 7-H), 6.5—6.1 (2 H, m, 6- and 4-H), 3.71 (3 H, s, OMe), 3.68 (3 H, s, OMe), 2.68 (2 H, d, $J_{3,4}$ 7 Hz, 3-CH_2). Double irradiation of 7-H gave δ 6.40 (s, 6-H) and 6.25 (t, $J_{3,4}$ 7 Hz, 4-H). Double irradiation of 3-H gave δ 6.40 (d, $J_{6,7}$ 7 Hz, 6-H) and 6.26 (s, 4-H); δ_C (CCl_4) 33.3 (t, C-3), 51.6 (q, CO_2CH_3), 54.8 (q, OCH_3), 112.2 (d, C-4), 124.5 (s, C-6), 131.7 (d, C-5), 139.0 (d, C-7), 151.1 (s, C-2), and 165.9 (s, C=O); $\lambda_{max.}$ (log ε) 240sh (3.65), 275sh (3.46), and 279sh (3.44); *m/z* 181 (M^+).

Further elution with ethyl acetate and then methanol gave only a red tar (0.05 g, 2%).

(*c*) *2-Azidobenzonitrile*. The arylazide (2 g) was photolysed for 17 h. Chromatographic separation on alumina, benzene as eluant, gave an oil (0.9 g, 44%), b.p. 80—84 °C/0.15 Torr (Found: C, 64.6; H, 5.45; N, 18.9. $C_8H_8N_2O$ requires C, 64.85; H, 5.45; N, 18.9%); $\lambda_{max.}$ (log ε) 269 nm (3.76); $\nu_{max.}$ (liquid film) 2 250 (C≡N), 1 620 cm^{-1} (C=N); the ^1H n.m.r. spectrum indicated a mixture of *3-cyano-2-methoxy-3H-azepine* (4; X = CN); δ_H ($CDCl_3$) 7.05 (1 H, d, $J_{6,7}$ 8 Hz, 7-H), 6.5—6.2 (1 H, m, 5-H), 6.12 (1 H, dd, $J_{6,7}$ 8 Hz, $J_{5,6}$ 6 Hz, 6-H), 5.36 (1 H, dd, $J_{4,5}$ 8.5 Hz, $J_{3,4}$ 6 Hz, 4-H), 3.27 (1 H, d, $J_{3,4}$ 6 Hz, 3-H), and 7-*cyano-2-methoxy-3H-azepine* (8); δ_H ($CDCl_3$) 6.68 (1 H, d, $J_{5,6}$ 6 Hz, 6-H), 6.35 (1 H, dd, $J_{4,5}$ 9 Hz, $J_{5,6}$ 6 Hz, 5-H), 5.65 (1 H, dt, $J_{4,5}$ 9 Hz, $J_{3,4}$ 7 Hz, 4-H), and 2.76 (2 H, d, $J_{3,4}$ 7 Hz, 3-CH_2). Other absorptions were at δ 3.80 (3 H, s, OMe) and 3.75 (3 H, s, OMe). Integration of the 3-H and 3-CH_2 resonances indicated an isomer ratio of *ca.* 1 : 1.

No change in the ^1H n.m.r. spectrum was observed between −85 and 35 °C in $CDCl_3$ solution, nor in $(CD_3)_2SO$ between 0 and 120 °C.

3-Cyano isomer: δ_C (liquid) 35.8 p.p.m. (d, C-3); 7-cyano isomer: 34.0 p.p.m. (t, 3-C). Other absorptions: δ 55.9 (q, OCH_3), 56.1 (q, OCH_3), 141.1 (d), 114.9 (d), 115.8 (s, CN), 118.7 (s, CN), 122.8 (s, C-7 in 7-cyano isomer), 123.6 (d), 125.9 (d), 127.1 (d), 128.9 (d), 138.1 (d), 143.6 (s), and 154.7 p.p.m. (s).

(*d*) *4-Azidobenzonitrile*. The arylazide (2 g) was photolysed for 20 h. Chromatographic separation on alumina, light petroleum (b.p. 40—60 °C)–ethyl acetate (9 : 1) as eluant, gave the azidonitrile (0.3 g, 15%), followed by *5-cyano-2-methoxy-3H-azepine* (6; X = CN) (0.7 g, 34%) as white crystals, m.p. 56 °C. An analysis sample was prepared by vacuum sublimation (85 °C/3 Torr) (Found: C, 64.6; H, 5.45; N, 18.6. $C_8H_8N_2O$ requires C, 64.8; H, 5.45; N, 18.9%); $\nu_{max.}$ (Nujol) 2 210 (C≡N) and 1 620 cm^{-1} (C=O); δ_H (CCl_4) 7.05 (1 H, d, $J_{6,7}$ 8 Hz, 7-H), 6.1—5.8 (2 H, m, 6- and 4-H), 3.72 (3 H, s, OMe), and 2.76 (2 H, d, $J_{3,4}$ 7 Hz, 3-H); δ_C (CCl_4) 34.0 (t, C-3), 55.2 (q, OCH_3), 111.6 (d, C-4), 114.0 (s, C-5), 117.2 (s, CN), 128.2 (d, C-6), 140.6 (d, C-7) and 150.7 p.p.m. (s, C-2); $\lambda_{max.}$ (log ε) 241 (3.52) and 278 nm (3.55); *m/z* 148 (M^+). Further elution with ethyl acetate gave an intractable tar (0.3 g, 15%).

(*e*) *2-Azido(trifluoromethyl)benzene*. The arylazide (2 g) was photolysed for 15 h. Careful evaporation of the solvent on a rotary evaporator at 35 °C gave the impure product as a volatile yellow oil. Chromatographic separation on alumina, light petroleum (b.p. 40—60 °C) as eluant, gave the azide (0.06 g, 3%) followed by *2-methoxy-3-trifluoromethyl-3H-azepine* (4; X = CF_3) (1 g, 49%) as a colourless oil, b.p. 80 °C/0.6 Torr (Found: C, 50.5; H, 4.25; N, 7.45. $C_8H_8F_3NO$ requires C, 50.3; H, 4.2; N, 7.3%); δ_H (CCl_4) 6.97 (1 H, d, $J_{6,7}$ 8 Hz, 7-H), 6.6—6.2 (1 H, m, 5-H), 6.0 (1 H, dd, $J_{5,6}$ 5.5 Hz, 6-H), 5.25 (1 H, dd, $J_{4,5}$ 9 Hz, $J_{3,4}$ 6 Hz, 4-H), 3.77 (3 H, s, OMe), and 2.65—2.25 (1 H, m, 3-H); δ_F ($CDCl_3$; CF_3CO_2H as external reference) 11.07 (d, $J_{H,F}$ 12 Hz); δ_C ($CDCl_3$) 48.8 (dq, $^2J_{C,F}$ 148 Hz, C-3), 55.4 (q, OCH_3), 112.8 (dd, $^3J_{C,F}$ 18 Hz, C-4), 115.0 (d, C-6), 123.8 (q, CF_3, $J_{C,F}$ 670 Hz), 128.4 (d, C-5), 137.7 (d, C-7), and 144.9 p.p.m. (s, C-2).

Further elution with diethyl ether, then successively with $CHCl_3$, EtOAc, and finally methanol, gave only small amounts of tar.

(*f*) *Methyl 2-azidobenzenesulphonate*. The arylazide (2 g) was photolysed for 12 h; only tars and uncharacterisable oils were obtained.

(*g*) *2-Azidobenzenesulphonamide*. The aryl azide (2 g) was photolysed for 78 h. A brown solid, m.p. >360 °C was the sole product, and defied all attempts at purification and characterisation.

(*h*) *2-Azidophenyl phenyl sulphone*. The aryl azide (1 g) was photolysed for 24 h. Chromatographic separation on alumina, diethyl ether as eluant, gave bis(2-aminophenyl) sulphone (0.05 g, 6%), m.p. 116 °C as the only identifiable product, along with a brown oil (0.35 g, 35%) and a brown polymeric solid (0.15 g, 15%).

(*i*) *2-Azidophenyl phenyl sulphoxide*. The aryl azide (2 g) was photolysed for 30 h. Chromatographic separation on alumina, diethyl ether–ethyl acetate as eluant gave a methoxysulphinyl-3*H*-azepine (0.2 g, 20%) as a colourless oil, b.p. 100 °C/0.8 Torr, which darkened on standing [Found: C, 61.8 (62.0); H, 5.4 (5.5); N, 5.6 (5.2). $C_{13}H_{13}NO_2S$ requires C, 63.1; H, 5.3; N, 5.65%]; $\nu_{max.}$ (liquid film) 1 610 (C=N) and 1 050 cm^{-1} (SO); δ_H (CCl_4) 8.0—7.0 (5 H, br m, ArH), 6.81 (1 H, d, $J_{5,6?}$ 6 Hz, 6-H?), 6.40 (1 H, dd, $J_{5,6?}$ 6 Hz, $J_{4,5}$ 9 Hz, 5-H?), 5.32 (1 H, dt, $J_{4,5?}$ 9 Hz, $J_{3,4}$ 7 Hz, $J_{3',4}$ 7 Hz, 4-H), 3.71 (3 H, s, OMe), 3.1—2.6 (1 H, dd, J_{gem} 13 Hz, $J_{3,4}$ 7 Hz, 3-H?), 2.5—2.0 (1 H, dd, J_{gem} 13 Hz, $J_{3,4}$ 7 Hz, 3'-H). Double irradiation of 6-H gave δ 6.4 (d, 5-H); double irradiation of 5-H gave δ 6.81 (s, 6-H) and 5.32 (m, 4-H); double irradiation of 4-H gave δ 6.4 (bs, 5-H) and an AB pattern for 3-H centred at δ 2.8 (d, J_{gem} 13 Hz, 3-H) and 2.2 (d, J_{gem} 13 Hz, 3'-H); double irradiation of 3-H or 3'-H gave δ 5.32 (m, 4-H) and 2.2 or 2.8 (m, 3'- or 3-H); δ_C (CCl_4–$CDCl_3$) 33.5 (t C-3), 55.4 (q, OCH_3), 111.6 (d, C-6?), 117.7 (d, C-5?), 125.2 (d, C-2' and -6'), 127.3 (d, C-4?), 127.6 (s, C-2?), 128.7 (d, C-3' and -5'), 130.7 (d, C-4'), 145.0 (s, C-1'?), and 153.5 p.p.m. (s, C-7?); $\lambda_{max.}$ (log ε) 263 nm (3.91); *m/z* 247 (*M*). Further elution with methanol gave an intractable brown tar (0.5 g, 50%).

(*j*) *2-Azidobenzohydrazide*. The aryl azide (1 g) was photo-

lysed for 24 h. Chromatographic separation on alumina gave only intractable materials.

(*k*) N-(o-*Azidobenzoyl*)-p-*chlorobenzaldehyde hydrazone*. The aryl azide (2 g) was photolysed for 33 h. Chromatographic separation on alumina, light petroleum (b.p. 40—60 °C) as eluant, gave unchanged azide (0.05 g, 2.5%). Further elution with chloroform gave firstly 4,4′-dichlorobenzaldehyde azine, m.p. 100 °C, then the p-*chlorobenzylidene derivative* of 2-methoxy-3*H*-azepine-3-carboxylic acid hydrazide (4; X = $CONHN{=}CHC_6H_4Cl$-*p*) (1.4 g, 68%) as a brown solid which crystallised from methanol as white prisms, m.p. 226 °C (Found: C, 59.15; H, 4.6; N, 13.6. $C_{15}H_{13}ClN_3O_2$ requires C, 59.3; H, 4.65; N, 13.8%).

Photolysis of Methyl o-*Azidobenzoate in the Presence of Other Nucleophiles*.—A solution of methyl *o*-azidobenzoate (2 g) in a saturated solution of ammonia in THF (150 ml) was photolysed (14 h) as described in the general method. Evaporation of the reaction mixture gave an oily residue which on purification (alumina column, ethyl acetate as eluant) gave the *o*-azidoester (1%) and methyl anthranilate (0.9 g, 52%) as the only identifiable products.

Similarly photolysis (16 h) of the azidoester (2 g) in a saturated solution of H_2S in THF gave only methyl anthranilate (0.64 g, 37%).

1,3-*Dihydro*-3-*methoxycarbonyl*-2H-*azepin*-2-*one*.—A solution of methyl *o*-azidobenzoate (2 g) in water (115 ml) and THF (115 ml) was irradiated for 8 h. Work-up as in the previous experiment (alumina column, ethyl acetate as eluant) gave the product as a yellow oil which solidified on trituration with diethyl ether. 1,3-*Dihydro*-3-*methoxycarbonyl*-2H-*azepin*-2-*one* (1.25 g, 59%) crystallised from light petroleum–ethyl acetate as pale yellow prisms, m.p. 113 °C (Found: C, 57.2; H, 5.5; N, 8.3. $C_8H_9NO_3$ requires C, 57.5; H, 5.4; N, 8.4%); $\nu_{max.}$ (Nujol) 3 200 (NH), 1 735 (ester CO), and 1 660 cm^{-1} (amide CO); δ_H 9.1 (1 H, bs, NH), 6.6—5.6 (4 H, m, =CH), 3.89 (3 H, s, OCH_3), and 3.52 (1 H, d, $J_{3,4}$ 5 Hz, 3-H); δ_C [$(CD_3)_2SO$] 52.0 and 52.7 (CH_3 and CH_2), 112.7, 119.5, 126.7, and 126.7 (d's, 4 × CH), 162.7 (s, CO_2Me), and 168.6 p.p.m. (s, NCO^-); $\lambda_{max.}$ (log ε) 256 (3.74); *m/z* 167 (M^+).

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