# Ring-expansion of Azidobenzenesulphonamides and Azidobenzamides

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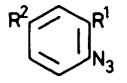
4-Azidobenzenesulphonamides and 2- and 4-azidobenzamides undergo phototransformation to 2-alkoxy-3*H*-azepines in alcohols but the yields are low. Ring-expansion of 4-azidobenzenesulphonamide and 4-azidobenzenesulphonylguanidine in aqueous tetrahydrofuran to 3*H*-azepin-2(1*H*)-ones proceeds *via* a singlet nitrene pathway; thermolysis of 4-azidobenzenesulphonamide in aqueous dioxane gave only the triplet-derived product, sulphanilamide. Efficient de-azidation of 4-azidobenzenesulphonamides and 4-azidobenzamides can be accomplished by heating the azides at 105 °C in hydrazine hydrate.

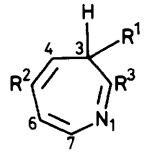
The crystallographic analysis of 5-sulphamoyl-3*H*-azepin-2(1*H*)-one shows the molecule to be non-planar with the azepine ring puckered in a boat form. The lactam configuration is confirmed with the carbonyl group having a bond length of 1.231 Å.

In an earlier paper [1] the reactions of azidoacridines were examined as part of a project to explore the biological effects of placing an azido group in crucial positions in bioactive molecules. In the present paper we report on our work on the chemistry of 4-azidobenzenesulphonamides (1a—f); these compounds are tne azido counterparts of the medicinal sulphonamides. The parent compound azidosulphanilamide (1a) has been shown to have no effect on L-1210 mouse lymphoid leukaemia cells *in vitro* in the dark ($ID_{80}$ > 1000 μg $ml^{-1}$).[2] However the azide is exceedingly cytotoxic to the cells in the light (366 nm) ($ID_{80}$ *ca.* 4.3 μg $ml^{-1}$). As pre-irradiation of the azide before exposure to L-1210 cells yielded a non-cytotoxic product it is possible that a photogenerated short-lived electrophilic species could be responsible for the inhibitory activity. Because of our wider ambition to exploit the azide ⟶ nitrene interconversion to achieve selective biological activity we were interested in the outcome of the photolysis of this azide in aqueous solution. As a prelude to the work we have examined the photolysis of 2- and 4-azidobenzamide and 4-azidobenzenesulphonamide in alcohols.



(1)

| | $R^1$ | $R^2$ |
|---|---|---|
| a | H | $SO_2NH_2$ |
| b | H | $SO_2NHC(:NH)NH_2$ |
| c | H | $SO_2NHAc$ |
| d | H | $SO_2NH$–CHN[CH]$_3$N |
| e | H | $SO_2NH$–CHNCHCHC(Me)N |
| f | H | $SO_2NH$–CHNC(Me)CHC(Me)N |
| g | $CONH_2$ | H |
| h | H | $CONH_2$ |



(2)

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | $CONH_2$ | H | OMe |
| b | $CONH_2$ | H | OEt |
| c | $CONH_2$ | H | $OPr^n$ |
| d | $CONH_2$ | H | $OBu^n$ |
| e | H | $CONH_2$ | OMe |
| f | H | $CONH_2$ | piperidino |
| g | H | $SO_2NH_2$ | OMe |

*Photolysis of* 2- *and* 4-*Azidobenzamides in Alcohols.*— Photolysis of 2-azidobenzamide (1g) and its *N*-alkyl homologues in the presence of methanol affords a series of 3-carbamoyl-2-methoxy-3*H*-azepines in moderate yield:[3] similarly 2-azidobenzoate esters photolyse in various alcohols to yield 2-alkoxy-3-alkoxycarbonyl-3*H*-azepines.[4] These transformations are considered to involve the initial generation of a singlet arylnitrene and thence proceed *via* nucleophilic addition of the alcohol to either an intermediate benzazirine [5] or, more controversially,[6] a 1-azacyclohepta-1,2,4,6-tetraene.

Although the yield of 3*H*-azepine (2a) from the photolysis of 2-azidobenzamide in methanol was reasonable (52%) [3] a less practicable outcome was achieved when photolysis was accomplished in higher aliphatic alcohols. Thus, in the present work, photolysis of 2-azidobenzamide in ethanol with a 100-W medium-pressure lamp afforded the ethoxyazepine (2b) in 27% yield and the related n-propoxy- (2c) and n-butoxy-azepines (2d) were isolated in only 23 and 19% yields, respectively.

The electron-impact initiated mass spectra of the 2-alkoxy-azepines (2b—d) show molecular ions of low abundance and the dominant fragmentation involves loss of a carbamoyl radical to give azatropylium ions (3) which are the base peaks in the ethoxy and propoxy derivatives. Subsequent ejection of an alkene to afford the common ion at *m/z* 108 is followed by successive losses of carbon monoxide and hydrogen cyanide (Scheme 1). The mass spectrum of the methoxyazepine (2a) differs, presumably because the stage corresponding to alkene loss would require an unfavourable elimination of methylene: instead there is a direct loss of carbon monoxide from the azatropylium ion at *m/z* 122.

Photolysis of 4-azidobenzamide (1 h) in methanol afforded a small yield of the 3*H*-azepine (2e); this was characterised by its $^1H$ n.m.r. spectrum in [$^2H_6$]DMSO which showed absorptions at δ 2.64 (d, 2 H, 3-H, *J* 6.6 Hz), 3.53 (s, 3 H, OMe),

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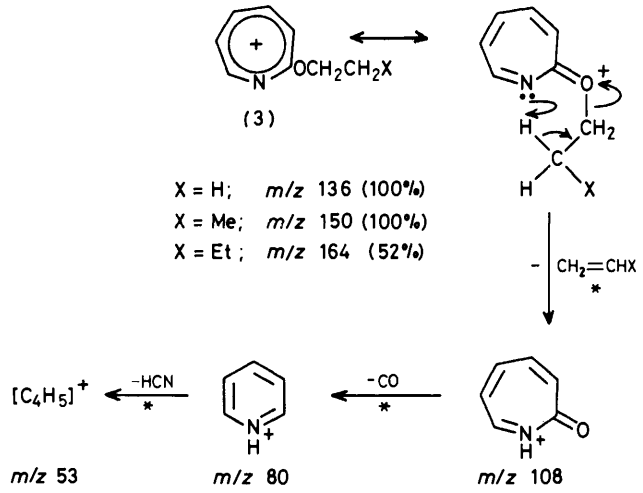



**Scheme 1.** * Denotes metastable-supported fragmentation

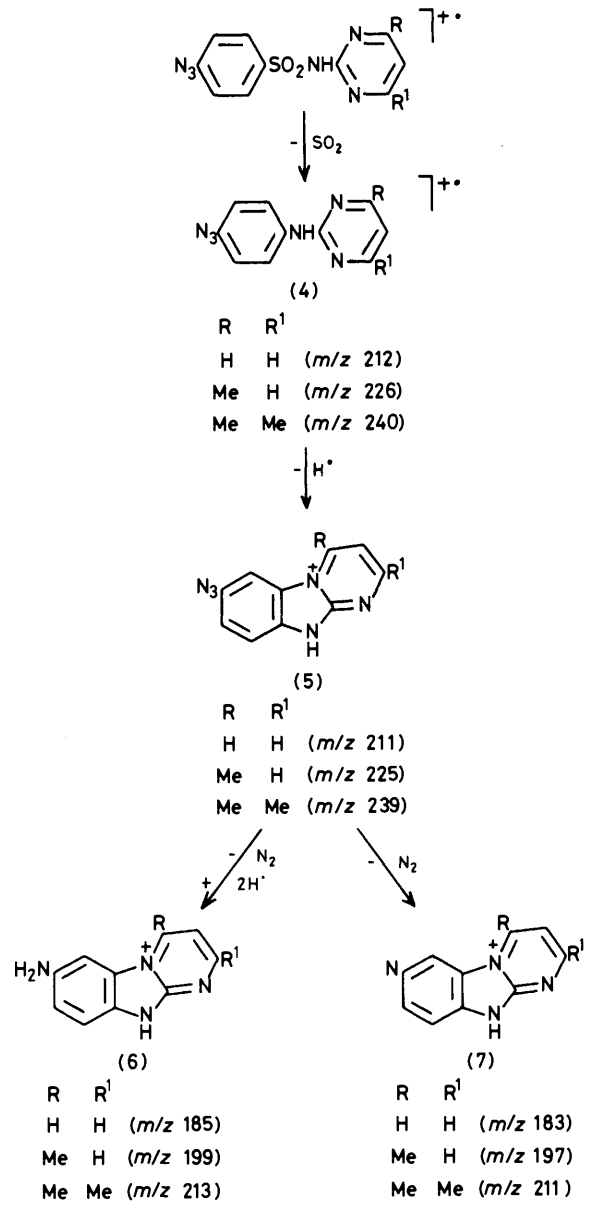
6.04 (t, 1 H, 4-H, *J* 6.6 Hz), 6.38 (d, 1 H, 6-H, *J* 8 Hz), and 6.98 (d, 1 H, 7-H, *J* 8 Hz). The enamino ether nature of the methoxy group of (2e) was indicated by its facile replacement in boiling piperidine to yield the cyclic amidine (2f).

*Properties of 4-Azidobenzenesulphonamides.*—The 4-azidobenzenesulphonamides (1a—f) were prepared in high yield from their medicinal 4-aminobenzenesulphonamide precursors by the conventional diazotisation–azidation process. A characteristic feature of the i.r. spectra of these derivatives is the multiplicity of the azide absorption in the 2 100—2 150 $cm^{-1}$ region attributable to Fermi resonance:[7] thus the spectrum of azidosulphanilamide (1a) exhibits strong absorptions at 2 100, 2 121, and 2 140 $cm^{-1}$ and comparable triplets of peaks are observed in the spectra of all the other azidobenzenesulphonamides with the exception of that of azidosulphacetamide (1c) which shows only a doublet at 2 100 (weak) and 2 135 (strong) $cm^{-1}$.

The mass spectra of azidosulphanilamide (1a) and azidosulphaguanidine (1b) show prominent molecular ions and significant ($M - 26$) peaks ($M^{+\cdot} - N_2 + 2\ H^{\cdot}$); thereafter the spectra closely parallel those reported for sulphanilamide and sulphaguanidine respectively.[8] Formation of nitrene fragments (or ring-expanded ions) by loss of nitrogen from the molecular ions is a less-favoured pathway. The spectra of the pyrimidine derivatives (1d—f) show no molecular ions and are characterised by the initial loss of sulphur dioxide and the major ions produced correspond to the radical ion (4) and the pyrimidobenzimidazolium ions (5)—(7) (Scheme 2).

Photolysis of azidosulphanilamide in methanol afforded a meagre yield of the 3*H*-azepine (2g) which was characterised by its $^1H$ n.m.r. spectrum, which closely resembled the spectrum of the carboxamide analogue (2e). The formation of a ring-expanded product in the photolysis of azidosulphanilamide undoubtedly involves the intermediacy of a singlet nitrene species: possible triplet-derived products [*e.g.* 4-aminobenzenesulphonamide (sulphanilamide) (8a), azobenzene-4,4′-disulphonamide (8b), or hydrazobenzene-4,4′-disulphonamide (8c)] were not detected (t.l.c.) amongst the photolysis products. The only product identified in the mixture formed on photolysis of the azidosulphadimidine (1f) in methanol was 2-amino-4,6-dimethylpyrimidine (15%) resulting (presumably) from photo-methanolysis of the S–N bond. Photolysis of the azide (1f), in part, parallels the pyrolytic behaviour[9] of sulphadimidine at 770 °C.

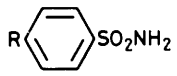
Satisfactory yields of the azepinones (9a) and (9b) were




**Scheme 2.**

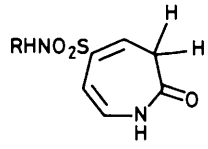
obtained when azidosulphanilamide (1a) and azidosulphaguanidine (1b) were photolysed in 30% aqueous tetrahydrofuran. Again, no sulphanilamide, azobenzene-4,4′-disulphonamide, or hydrazobenzene-4,4′-disulphonamide was detected in the photolysates.

Important spectroscopic information to corroborate the assignment of a 3*H*-azepinone structure for products (9a) and (9b) was forthcoming. The presence of strong absorptions at 1 665 and 1 670 $cm^{-1}$ respectively in their i.r. spectra confirmed the predominance of the lactam tautomers in the solid state. The 220 MHz $^1H$ n.m.r. spectrum of (9a) in [$^2H_6$]DMSO showed the presence of three olefinic protons. In the case of the azepinone (9b) there was an additional feature diagnostic of the lactam configuration. The proton at 7-H absorbed as a double doublet being coupled both to 6-H (*J* 9 Hz) and N-1 (*J ca.* 4 Hz). In $D_2O$ the doublet at δ 9.93 (N-1) disappeared and the double doublet collapsed to the expected doublet signal.



(8)

a; R = $NH_2$
b; R = 4-sulphamoylphenylazo
c; R = 4-sulphamoylphenylhydrazino



(9)

a; R = H
b; R = C(:NH)$NH_2$

The exclusive presence of the lactam arrangement in (9a) was confirmed by a crystallographic analysis (see later).

Efforts to effect a more efficient ring-expansion of azidosulphanilamide (1a) by thermolytic methods were unrewarding. Degradation of the azide in sealed glass ampoules in 30% aqueous dioxane at 130 or 165 °C for 3 h produced no azepinone (9a): only starting material and the triplet-derived product sulphanilamide (8a) were detected (t.l.c.). In neither case were the other possible triplet-derived products (8b) and (8c) present amongst the thermolysis products. Azidosulphanilamide rapidly decomposed in boiling cyclohexanol (160 °C) or ethylene glycol (195 °C) to yield dark solutions from which only shiny-black polymeric materials were recovered.

When 4-azidobenzenesulphonamide was heated with phenylhydrazine no reaction occurred. However, with hydrazine hydrate in boiling ethanol the azide yielded benzenesulphonamide (45%). The same product (85%) was formed from the azide in hydrazine hydrate alone at 105 °C, the vigorous reaction being complete in 5 min. Benzenesulphonamide was formed in high yield from azidosulphacetamide (1c) and hot hydrazine hydrate, reductive de-azidation being accompanied by deacetylation in this case. Azidosulphaguanidine and 4-azidobenzamide also underwent de-azidation in hydrazine hydrate at 105 °C to yield benzenesulphonylguanidine and benzamide respectively. This useful degradation has been observed by others [10] and appears to be a general reaction except when the azido group is attached at α- or γ-positions with respect to nitrogen in π-deficient heterocycles.[11]

*Crystal Structure of 5-Sulphamoyl-3H-azepin-2(1H)-one* (9a).—The numbering scheme used in the crystallographic determination is shown in Figure 1. The crystal was grown from water and had dimensions 1.08 × 0.80 × 0.32 mm. The data were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-$K_\alpha$ radiation, λ = 0.71069 Å.

*Crystal data.* $C_6H_8N_2O_3S$, $M$ = 188.2, monoclinic, $a$ = 11.243(6), $b$ = 8.124(3), $c$ = 8.795(6) Å, β = 100.78(5)°, $V$ = 789.1(8) Å$^3$, $Z$ = 4, $D_m$ = 1.59(1) g cm$^{-3}$, $D_x$ = 1.58 g cm$^{-3}$, $F(000)$ = 392, μ(Mo-$K_\alpha$) = 3.2 cm$^{-1}$, space group $P2_1/a$.

The 1 389 unique intensity data were collected by the ω − 2θ scan technique, and of these 1 287 reflections were deemed observed with $F_o > 3\sigma$. Using MULTAN,[12] an $E$-map was produced in which all non-hydrogen atoms were located. After refinement with isotropic temperature factors, a difference Fourier synthesis located four of the hydrogen atoms. The remaining hydrogens were entered in calculated positions since they were all bonded to ring carbon atoms of well defined geometry. Each hydrogen atom was assigned the isotropic temperature factor of its attached atom. Further refinement of co-ordinates and anisotropic thermal parameters for non-hydrogen atoms, and co-ordinates and isotropic temperature factors for hydrogens, was carried out with SHELX [13] with those hydrogens in calculated positions being constrained to ' ride ' on the corresponding carbon atom. This reduced the unweighted discrepancy index to $R$ = 0.035 for the observed data. In the latter stages of refinement, reflections were weighted according to $w = K/\sigma^2(F_o)$. Refinement was terminated when no positional parameter shifted by more than 0.13σ. At convergence the weighted discrepancy index was $R_g = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.050$. Finally a difference electron density map was calculated which showed no feature greater than 0.33 e Å$^{-3}$. Observed and calculated structure factors, and atom thermal parameters are given in a Supplementary Publication * (SUP No. 23695, 26 pages).

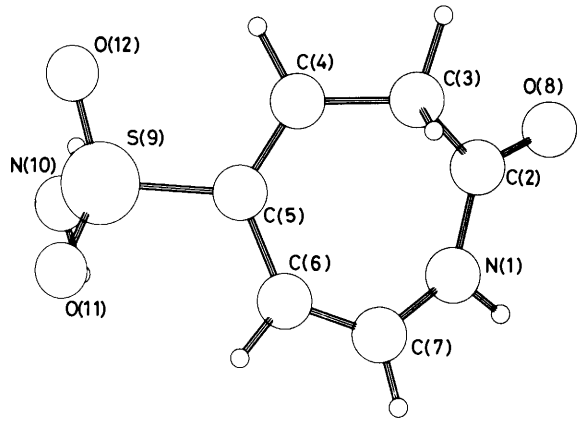



**Figure 1.** Molecular structure and numbering scheme for 5-sulphamoyl-3*H*-azepin-2(1*H*)-one (9a)

Atomic co-ordinates are given in Table 1. The seven-membered ring and lactam configuration are confirmed, the latter having a C=O bond length of 1.231(2) Å (Table 2) and the hydrogen attached to N-1 having been located in a difference Fourier synthesis.

As with sulphanilamide,[14] the sulphamoyl group is approximately tetrahedral (Table 3) with the largest difference from the ideal tetrahedron occurring in the O(11)–S(9)–O(12) bond angle [119.1(1)°] compared with sulphanilamide [118.2(1)°]. The two S–O bonds in (9a) are almost identical in length, 1.434(2) Å and 1.431(2) Å, albeit that only O(12) is hydrogen bonded, suggesting π bond orders of *ca.* 0.66.[15] The S(9)–N(10) and S(9)–C(5) bond lengths of 1.610(2) Å and 1.781(2) Å respectively, show some double bond character compared to observed single bond distances; [16,17] however, the π bond order of the S–C bond in (9a) appears to be somewhat less than in sulphanilamide where the S–C distance is 1.750(18) Å. The amide portion of the azepinone system shows considerable delocalization of electrons but the other double bonds are largely isolated.

The torsion angles (Table 4; see also Figure 2) show the molecule to be substantially non-planar with the seven-membered ring puckering into a boat form. The sulphamoyl group aligns with the two oxygens O(11) and O(12) closest to

* For details of the Supplementary Publications Scheme see Instructions to Authors (1983) in *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

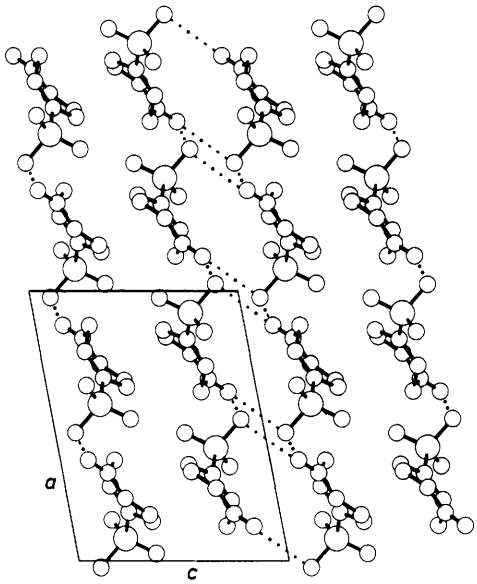



**Figure 2.** Molecular packing and hydrogen bonding for 5-sulphamoyl-3*H*-azepin-2(1*H*)-one (9a). The N(1)–H(15) · · · O(12) hydrogen bond is not shown

**Table 1.** Final atomic co-ordinates (× $10^4$) for 5-sulphamoyl-3*H*-azepin-2(1*H*)-one (9a) with e.s.d.s in parentheses

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| N(1) | 7 302(1) | −3 152(2) | 2 789(2) |
| C(2) | 8 252(2) | −2 611(2) | 2 180(2) |
| C(3) | 8 716(2) | −902(2) | 2 619(3) |
| C(4) | 7 770(2) | 397(2) | 2 178(2) |
| C(5) | 6 788(2) | 470(2) | 2 836(2) |
| C(6) | 6 449(2) | −756(2) | 3 878(2) |
| C(7) | 6 692(2) | −2 352(2) | 3 817(3) |
| O(8) | 8 725(1) | −3 525(2) | 1 348(2) |
| S(9) | 5 817.4(4) | 2 212.0(6) | 2 442.9(6) |
| N(10) | 4 750(1) | 1 823(2) | 993(2) |
| O(11) | 5 265(1) | 2 442(2) | 3 771(2) |
| O(12) | 6 504(1) | 3 528(2) | 1 956(2) |
| H(13) | 5 994 | −348 | 4 789 |
| H(14) | 6 390(18) | −3 040(25) | 4 490(25) |
| H(15) | 7 140(24) | −4 270(27) | 2 580(32) |
| H(16) | 9 039 | −856 | 3 854 |
| H(17) | 9 453 | −633 | 2 027 |
| H(18) | 7 863 | 1 272 | 1 283 |
| H(19) | 4 330(20) | 940(27) | 1 310(29) |
| H(20) | 5 000(25) | 1 760(29) | 30(26) |

the least squares plane * through the seven-membered ring, the deviations being −0.250(2) Å and −0.787(2) Å respectively with the nitrogen pointing out of the plane with a deviation of −2.473(2) Å. The sum of the two SNH bond angles and the HNH angle at N(10) is 338(6)°, suggesting hybridisation that is intermediate between $sp^2$ and $sp^3$ for this nitrogen atom.

The molecular packing occurs as infinite chains of molecules linked by N(10)–H(19) · · · O(8) hydrogen bonds [2.956(3) Å] running parallel to the *a* axis, pairs of chains being firmly linked in the direction of *c* by N(10)–H(20) · · · O(8) interactions [2.929(3) Å]. Further hydrogen bonding of the type N(1)–H(15) · · · O(12) [2.893(3) Å] occurs between molecules parallel to the *b* axis, the whole structure thus comprising pairs of layers linked by intermolecular hydrogen bonds (Figure 2 and Table 5).

* The equation of the plane is $0.615x + 0.086y + 0.784z + 5.730 = 0$ where *x*, *y*, and *z* are orthogonal co-ordinates in Å along *a**, *b*, and *c*.

**Table 2.** Interatomic distances (Å) for 5-sulphamoyl-3*H*-azepin-2(1*H*)-one (9a) with e.s.d.s in parentheses

| Bond | Interatomic distance (Å) | Bond | Interatomic distance (Å) |
|---|---|---|---|
| N(1)–C(2) | 1.355(2) | S(9)–O(11) | 1.434(2) |
| C(2)–C(3) | 1.508(3) | S(9)–O(12) | 1.431(2) |
| C(3)–C(4) | 1.497(3) | N(1)–H(15) | .94(2) |
| C(4)–C(5) | 1.340(3) | C(3)–H(16) | 1.08 |
| C(5)–C(6) | 1.452(3) | C(3)–H(17) | 1.08 |
| C(6)–C(7) | 1.328(3) | C(4)–H(18) | 1.08 |
| C(7)–N(1) | 1.394(3) | C(6)–H(13) | 1.08 |
| C(2)–O(8) | 1.231(2) | C(7)–H(14) | .92(2) |
| S(9)–C(5) | 1.781(2) | N(10)–H(19) | .93(2) |
| S(9)–N(10) | 1.610(2) | N(10)–H(20) | .95(2) |

**Table 3.** Interatomic angles (°) for C, N, O, and S atoms of 5-sulphamoyl-3*H*-azepin-2(1*H*)-one (9a), with e.s.d.s in parentheses

| Atoms | Bond angle (°) | Atoms | Bond angle (°) |
|---|---|---|---|
| N(1)–C(2)–C(3) | 117.3(2) | O(11)–S(9)–O(12) | 119.1(1) |
| N(1)–C(2)–O(8) | 120.0(2) | O(11)–S(9)–C(5) | 106.8(1) |
| O(8)–C(2)–C(3) | 122.7(2) | O(12)–S(9)–C(5) | 107.8(1) |
| C(2)–C(3)–C(4) | 112.8(2) | N(10)–S(9)–O(11) | 107.4(1) |
| C(3)–C(4)–C(5) | 121.5(2) | N(10)–S(9)–O(12) | 105.9(1) |
| C(4)–C(5)–C(6) | 125.2(2) | N(10)–S(9)–C(5) | 109.7(1) |
| C(4)–C(5)–S(9) | 118.4(2) | | |
| S(9)–C(5)–C(6) | 116.3(1) | | |
| C(5)–C(6)–C(7) | 124.3(2) | | |
| C(6)–C(7)–N(1) | 127.7(2) | | |
| C(7)–N(1)–C(2) | 128.7(2) | | |

## Experimental

*Preparation of the Azides.*—Solutions of the appropriate arylamines were dissolved in 2M-hydrochloric acid, diazotised at 0 °C with a solution of sodium nitrite (1.1 mol equiv.) in a minimum of water, and then treated with solid sodium azide (2 mol equiv.). When reaction was complete the precipitated azides were collected, washed with water, and crystallised from aqueous ethanol.

The following azides were prepared: 4-azidobenzenesulphonamide (azidosulphanilamide) (1a) (83%), m.p. 113—114 °C (decomp.) (lit.,[18] m.p. 119 °C), $\nu_{max.}$ (KBr) 3 340 and 3 250 (NH), 2 140, 2 123 and 2 100 $cm^{-1}$ ($N_3$); *4-azidobenzenesulphonylguanidine* (*azidosulphaguanidine*) (1b) (78%), m.p. 171—172 °C (decomp.) (Found: C, 35.1; H, 3.4; N, 35.4. $C_7H_8N_6O_2S$ requires C, 35.0; H, 3.4; N, 35.0%), $\nu_{max.}$ (KBr) 3 490, 3 440, 3 350 and 3 220 (NH), 2 125, 2 110 and 2 095 $cm^{-1}$ ($N_3$); *N-acetyl-4-azidobenzenesulphonamide* (1c) (*azidosulphacetamide*) (85%), m.p. 115—118 °C (decomp.) (Found: C, 46.4; H, 4.0; N, 26.5. $C_8H_8N_4SO_3$ requires C, 46.2; H, 3.9; N, 26.9%), $\nu_{max.}$ (KBr) 3 300 (NH), 2 135 and 2 100 ($N_3$), and 1 725 $cm^{-1}$ (CO); *2-(4-azidobenzenesulphonamido)pyrimidine* (1d) (*azidosulphadiazine*) (90%), m.p. 215—216 °C (Found: C, 43.8; H, 3.0; N, 30.1. $C_{10}H_8N_6O_2S$ requires C, 43.5; H, 2.9; N, 30.4%), $\nu_{max.}$ (KBr) 3 240—2 700br (bonded NH), 2 142 and 2 100 $cm^{-1}$ ($N_3$); *2-(4-azidobenzenesulphonamido)-4-methylpyrimidine* (1e) (*azidosulphamerazine*) (86%), m.p. 191—

**Table 4.** Torsion angles (°) for bonds involving non-hydrogen atoms

| | | | | | |
|---|---|---|---|---|---|
| * N(1)–C(2)–C(3)–C(4) | −59.1 | * C(5)–C(6)–C(7)–N(1) | 0.3 | * C(7)–N(1)–C(2)–C(3) | −1.6 |
| * C(2)–C(3)–C(4)–C(5) | 65.6 | * C(6)–C(7)–N(1)–C(2) | 36.0 | C(7)–N(1)–C(2)–O(8) | 176.0 |
| * C(4)–C(5)–C(6)–C(7) | −31.0 | C(6)–C(5)–S(9)–N(10) | −88.0 | O(8)–C(2)–C(3)–C(4) | 123.4 |
| C(4)–C(5)–S(9)–N(10) | 92.8 | C(6)–C(5)–S(9)–O(11) | 28.0 | S(9)–C(5)–C(4)–C(3) | 171.5 |
| C(4)–C(5)–S(9)–O(11) | −151.1 | C(6)–C(5)–S(9)–O(12) | 157.1 | S(9)–C(5)–C(6)–C(7) | 150.0 |
| C(4)–C(5)–S(9)–O(12) | −22.0 | * C(6)–C(5)–C(4)–C(3) | −7.5 | | |

* Torsion angles involving only ring atoms.

**Table 5.** Hydrogen bond contact distances and angles

| Hydrogen bond * | Angle at H (°) | N ··· O Distance (Å) |
|---|---|---|
| $N(1)_{II}$–H(15) ··· $O(12)_I$ | 170 | 2.893(3) |
| $N(10)_{III}$–H(19) ··· $O(8)_I$ | 156 | 2.956(3) |
| $N(10)_I$–H(20) ··· $O(8)_{IV}$ | 153 | 2.929(3) |

* I, II, III, IV refer to the equivalent position $x, y, z$; $x, 1 + y, z$; $0.5 + x, -0.5 - y, z$; and $1.5 - x, 0.5 + y, -z$, respectively.

192 °C (Found: C, 45.5; H, 3.5; N, 29.2. $C_{11}H_{10}N_6O_2S$ requires C, 45.5; H, 3.5; N, 29.0%), $\nu_{max.}$ (KBr) 3 100—2 650br (bonded NH), 2 140, 2 130 and 2 110 $cm^{-1}$ ($N_3$); *2-(4-azidobenzenesulphonamido)-4,6-dimethylpyrimidine* (1f) (*azidosulphadimidine*) (82%), m.p. 129—130 °C (Found: C, 47.9; H, 4.1. $C_{12}H_{12}N_6O_2S$ requires C, 47.5; H, 4.0%), $\nu_{max.}$ (KBr) 3 100—2 700br (bonded NH), 2 138, 2 120 and 2 100 $cm^{-1}$ ($N_3$); 2-azidobenzamide (1g) (93%), m.p. 135—136 °C (decomp.) (lit.,[19] m.p. 135—136 °C), and *4-azidobenzamide* (1 h) (84%), m.p. 136—137 °C (Found: C, 52.2; H, 3.8; N, 34.4. $C_7H_6N_4O$ requires C, 51.9; H, 3.7; N, 34.6%).

*Photolysis of Azides.*—*3-Carbamoyl-2-ethoxy-3H-azepine* (2b). A solution of 2-azidobenzamide (5.0 g) in ethanol (1 l) was photolysed through a quartz filter with a 100-W medium-pressure lamp in an Hanovia Photochemical Reactor until effervescence ceased. The ethanol was removed under vacuum and the oily residue was adsorbed onto aluminium oxide (20 g); the product was extracted from the solid and crystallised from benzene. The *azepine* (27%) had m.p. 153—155 °C (Found: C, 59.8; H, 6.5; N, 15.6. $C_9H_{12}N_2O_2$ requires C, 60.0; H, 6.7; N, 15.6%); δ($CDCl_3$) 1.25 (3 H, t, Me, *J* 6.6 Hz), 3.50 (1 H, d, 3-H), 4.18 (2 H, q, $CH_2$, *J* 6.6 Hz), 6.5—7.6 (3 H, m, 4-, 5-, and 6-H), 6.97 (1 H, d, 7-H, *J* 7.2 Hz). Similarly prepared, from the azide and the appropriate alcohol, were *3-carbamoyl-2-n-propoxy-3H-azepine* (2c) (23%), m.p. 124—125 °C (Found: C, 62.1; H, 7.2; N, 14.0. $C_{10}H_{14}N_2O_2$ requires C, 61.9; H, 7.3; N, 14.2%), *3-carbamoyl-2-n-butoxy-3H-azepine* (2d) (19%), m.p. 109—110 °C (Found: C, 63.7; H, 7.6; N, 13.4. $C_{11}H_{16}N_2O_2$ requires C, 63.4; H, 7.7; N, 13.5); *5-carbamoyl-2-methoxy-3H-azepine* (2e) (15%), m.p. 147—148 °C (Found: C, 57.8; H, 6.4; N, 17.2%; $M^+$, 166. $C_8H_{10}N_2O_2$ requires C, 57.8; H, 6.0; N, 16.9%; $M^+$, 166); δ([$^2H_6$]DMSO) 2.64 (2 H, d, 3-H, *J* 6.6 Hz), 3.53 (3 H, s, Me), 6.04 (1 H, t, 4-H, *J* 6.6 Hz), 6.38 (1 H, d, 6-H, *J* 8.0 Hz), and 6.98 (1 H, d, 7-H, *J* 8.0 Hz); and *2-methoxy-5-sulphamoyl-3H-azepine* (2g) (10%), m.p. 130—131 °C (Found: C, 41.1; H, 5.3; N, 13.9%; $M^+$, 202. $C_7H_{10}N_2O_3S$ requires C, 41.6; H, 5.0; N, 13.8%; $M^+$, 202); δ([$^2H_6$]DMSO) 2.76 (2 H, d, 3-H, *J* 7.2 Hz), 3.70 (3 H, s, Me), 6.10 (1 H, t, 4-H, *J* 7.2 Hz), 6.34 (1 H, d, 6-H, *J* 8.4 Hz), and 7.16 (1 H, d, 7-H, *J* 8.4 Hz).

The azepine (2g) (0.5 g) was boiled in piperidine (20 ml) for 4 h. Removal of the excess of piperidine gave an oil which was purified by chromatographic fractionation on an alumina column. The product, *5-carbamoyl-2-piperidino-3H-azepine* (2f) (46%), was eluted and crystallised from benzene and had m.p. 156—157 °C (Found: C, 65.6; H, 7.7; N, 19.3%; $M^+$, 219. $C_{12}H_{17}N_3O$ requires C, 65.7; H, 7.8; N, 19.2%; $M^+$, 219).

*2-Amino-4,6-dimethylpyrimidine.* Photolysis of 2-(4-azidobenzenesulphonamido)-4,6-dimethylpyrimidine in methanol as above yielded the aminopyrimidine (15%), m.p. 148—149 °C (lit.,[20] 153 °C); δ($CDCl_3$) 2.28 (6 H, s, 2 × Me), 6.0 (2 H, br s, $NH_2$), and 6.38 (1 H, s, 5-H).

*5-Sulphamoyl-3H-azepin-2(1H)-one* (9a).—4-Azidobenzenesulphonamide (2.9 g) was dissolved in redistilled tetrahydrofuran (370 ml) and water (630 ml). The mixture was photolysed (as above) for 20 h and the solution was vacuum-evaporated to give a brown solid (2.4 g). A methanol solution of the solid was chromatographically fractionated on a neutral alumina column and a pale yellow band was eluted with toluene–methanol (10 : 3). Evaporation of solvent afforded the crude *azepinone* (1.9 g) which crystallised from water as cream prisms, m.p. 176—178 °C (decomp.) (Found: C, 38.4; H, 5.0; N, 14.7%; $M^+$, 188. $C_6H_8N_2SO_3$ requires C, 38.3; H, 4.9; N, 14.9%; $M^+$, 188); $\nu_{max.}$ (KBr) 3 260br (bonded NH), 1 665 $cm^{-1}$ (CO); δ([$^2H_6$]DMSO) 2.93 (2 H, d, 3-H, *J* 7 Hz), 6.09 (1 H, d, 6-H, *J* 9 Hz), 6.35 (1 H, t, 4-H, *J* 7 Hz), 6.53 (1 H, d, 7-H, *J* 9 Hz), 7.3 exchangeable (3 H, br s, $NH_2$ and NH).

T.l.c. examination of the photolysate on silica-gel plates (0.25 mm) employing toluene–acetone (7 : 3) as developing solvent confirmed the absence of sulphanilamide (8a), azobenzene-4,4′-disulphonamide (8b), or hydrazobenzene-4,4′-disulphonamide (8c).

*5-N-Amidinosulphamoyl-3H-azepin-2(1H)-one* (9b). Photolysis of 4-azidobenzenesulphonylguanidine (as above) afforded the *amidinosulphamoylazepinone* (9b) (60%) which crystallised from water as buff flakes, m.p. 190—192 °C (decomp.) (Found: C, 36.4; H, 4.7; N, 24.4%; $M^+$, 230. $C_7H_{10}N_4SO_3$ requires C, 36.5; H, 4.4; N, 24.35%; $M^+$, 230); $\nu_{max.}$ (KBr) 3 470, 3 440, 3 370, 3 280, and 3 200 (NH), and 1 670 $cm^{-1}$ (CO), δ([$^2H_6$]DMSO) 2.88 (2 H, d, 3-H, *J* 7 Hz), 6.02 (1 H, d, 6-H, *J* 9 Hz), 6.29 (1 H, t, 4-H, *J* 7 Hz), 6.45 (1 H, d after $D_2O$ shake, 7-H, *J* 9 Hz), 6.73 (4 H, br s, 4 × NH), 9.93 (1 H, d before $D_2O$ shake, N-1, *J ca.* 4 Hz).

*Decomposition of the Azides in Hydrazine.*—(i) 4-Azidobenzenesulphonamide (1.0 g) was refluxed in ethanol (50 ml) with hydrazine hydrate (10 ml) for 2 h. The solvent was removed by vacuum evaporation to leave a gum which solidified slowly. Crystallisation of the solid from water gave benzenesulphonamide (45%), m.p. 145—147 °C identical (i.r.) with an authentic sample.

(ii) A profuse effervescence occurred when 4-azidobenzenesulphonamide (2.0 g) was warmed with hydrazine hydrate (10 ml). The vigorous exothermic reaction was maintained at 105 °C by external heat for 5 min and water (30 ml) was added. The precipitated benzenesulphonamide (85%) was identical (i.r.) with the sample prepared above.

(iii) Decomposition of *N*-acetyl-4-azidobenzenesulphonamide in hydrazine hydrate as in (ii) afforded benzenesulphonamide (73%).

(iv) No effervescence occurred when 4-azidobenzenesulphonamide was heated in excess of phenylhydrazine for 5 min at 75 °C. When hydrazine hydrate was added to the hot solution a vigorous effervescence ensued.

(v) No reaction occurred and starting material was recovered (>95%) when 4-azidobenzenesulphonamide and hydrazine (1 mol equiv.) were boiled in either tetrahydrofuran or toluene for 2 h.

(vi) Decomposition of 4-azidobenzenesulphonylguanidine or 4-azidobenzamide in hot hydrazine hydrate as in (ii) above afforded benzenesulphonylguanidine (67%) and benzamide (78%), respectively.

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