Synthesis and Photolysis of Azido-benzo[*b*]thiophens, -benzothiazoles, -benzimidazoles, and -indazoles: Novel 6,7-Diamino-benzothiazoles, -benzimidazoles, and -indazoles and 6-Diethylamino-8*H*-thiazolo-[5,4-*c*]azepines

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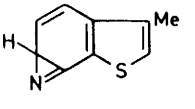
Irradiation of the 6-azidobenzothiazoles (4)—(9) (see Scheme) in the presence of an excess of a secondary amine gave either the corresponding 6,7-diaminobenzothiazole (14)—(20), a 6-amino-8*H*-thiazolo[5,4-*c*]azepine (21)—(24), a mixture of both, or intractable material [as in the case of azide (9)]. Irradiation of 7-azido-3-methylbenzo-[*b*]thiophen in an excess of diethylamine gave 7-amino-3-methylbenzo[*b*]thiophen and a trace of 3,3′-dimethyl-7,7′-azobenzo[*b*]thiophen. 6-Azidoindazole gave 7-amino-6-diethylaminoindazole (32) and 5(6)-azidobenzimidazole gave a mixture of 4(7)-amino-5(6)-diethylaminobenzimidazole (33) and 5(6)-amino-4(7)-diethylaminobenzimidazole (34). Photolysis of either 6-azidobenzothiazole or its 2-methyl derivative in a methoxide–methanol–dioxan mixture gave the corresponding 6-methoxy-8*H*-thiazolo[5,4-*c*]azepine, (30) or (31), respectively.

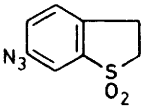
PHOTOLYSIS of 4-azidobenzo[*b*]thiophen in an excess of diethylamine gives 4-aminobenzo[*b*]thiophen and 4,4′-azobenzo[*b*]thiophen (triplet nitrene derived products),[1] 5-azidobenzo[*b*]thiophens give the corresponding 4-amino-5-diethylaminobenzo[*b*]thiophen,[1] whilst 6-azidobenzo[*b*]thiophens give the corresponding 7-amino-6-diethylaminobenzo[*b*]thiophen and/or 6-diethylamino-8*H*-thieno[2,3-*c*]azepine (singlet nitrene derived products) the latter by ring expansion.[2] It seemed of interest to explore the scope of these reactions of [6,5]-annelated heterocyclic systems further in order to determine the factors which control the course of reaction.

7-Azido-3-methylbenzo[*b*]thiophen was prepared from 7-amino-3-methylbenzo[*b*]thiophen [3] in the usual way [4] and photolysed in the presence of an excess of diethylamine in dioxan as a co-solvent because it has been shown to prolong the life of singlet nitrenes.[5] However, only triplet nitrene derived products were obtained, namely 7-amino-3-methylbenzo[*b*]thiophen (30%) and 3,3′-dimethyl-7,7′-azobenzo[*b*]thiophen (trace). Other α-azides † behave similarly.[1,6-8] These results can be rationalised by the fact that nucleophilic addition to the azirine intermediate (1), which is in equilibrium with the initially generated singlet nitrene, is hindered by the adjacent 5-membered ring (*cf.* ref. 1). Indeed, since the completion of this part of our work it has been shown that the use of TMEDA (*NNN′N′*-tetramethylethylenediamine),[9] which also prolongs the life of a singlet nitrene, and photolysis in a primary amine (less steric hindrance to nucleophilic addition at the azirine intermediate stage) [10] favour the formation of singlet-derived products in other systems carrying an α-azido-group.

6-Azido-2,3-dihydrobenzo[*b*]thiophen 1,1-dioxide (2) was prepared [4] next and irradiated in dioxan [5] in the presence of an excess of diethylamine, in order to study the effect of a reduced heterocyclic ring on the course of the reaction. This azide proved to be somewhat resistant to decomposition under these conditions, since traces of azide (i.r.) remained even after 45 h irradiation. Reaction mixtures were worked up after different reaction times but yielded only intractable material. Decomposition of azides normally occurs through



(1)



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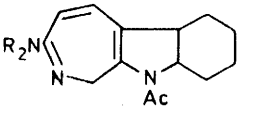


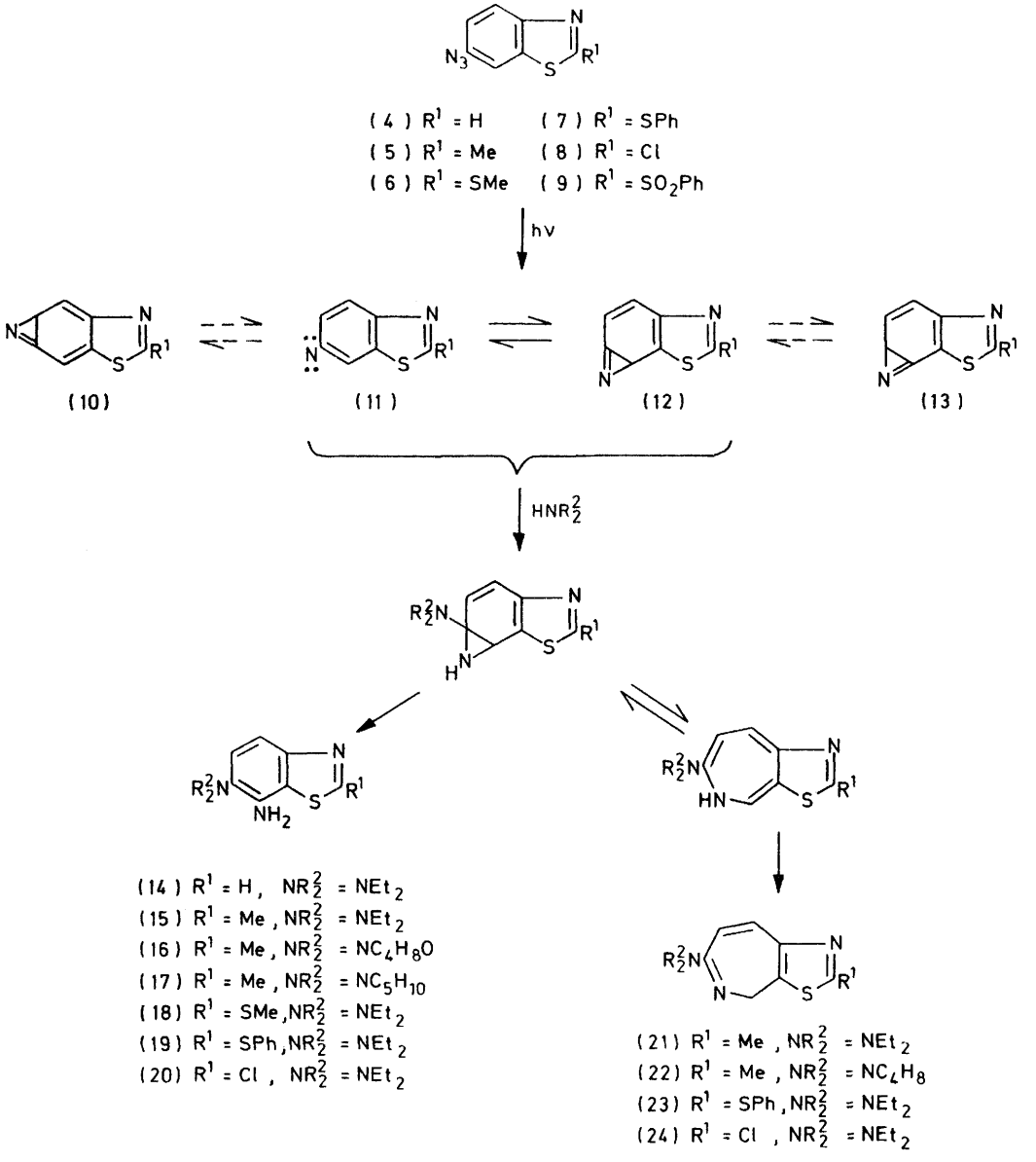
(3)

excitation of the aromatic ring and transmission of vibrational energy to the azide group.[11] It is possible in the case of azide (2) that either transmission of vibrational energy to the sulphone group or direct excitation of this group is occurring also with consequent further reactions.

At this stage of our work with [6,5]-annelated bicyclic heterocyclic ring systems 6-azidobenzo[*b*]thiophens substituted by electron-withdrawing groups in the thiophen ring were the only systems which had been shown to undergo ring expansion of the six-membered ring.[2] Azidoindoles, for example, either give the corresponding *o*-diamine (β-azides) or intractable products (α-azides), although irradiation of 9-acetyl-7-azido-1,2,3,4,4a,9a-

† The terms α and β are used by comparison with the α- and β-positions of naphthalene.

hexahydrocarbazole (a [6,5,6]-system) in various secondary amines yields the corresponding azepino-[3,4-*b*]indole (**3**).[8] We decided, therefore, to study 6-azidobenzothiazole and various of its 2-substituted derivatives in order to determine whether the character of the five-membered heterocyclic ring and the presence of an electron-withdrawing group in this ring are important features of these reactions.

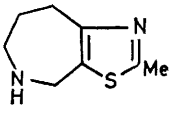


SCHEME

Photolysis of 6-azidobenzothiazole (**4**) (see Scheme) in dioxan [5] in the presence of an excess of diethylamine gave only 7-amino-6-diethylaminobenzothiazole (**14**) (33% yield). We had hoped to confirm the structure of this product through its conversion into 7-amino-4-diethylamino-1,2,3-benzothiadiazole by diazotisation and rearrangement of the resulting diazonium compound.[12-14] The isomeric diamine, namely 6-amino-7-diethylaminobenzothiazole, a possible product of the photolysis reaction (see later),[9] would not undergo such a rearrangement in the presence of only one equivalent of nitrous acid.[12] Indeed, this compound would be expected to yield only the corresponding phenol under our reaction conditions and this would be removed in our work-up procedure (see Experimental section).[12] Under the conditions used for such rearrangements the diamine (**14**) gave 6-diethylaminobenzothiazole (25% yield) and, surprisingly, 6-ethylaminobenzothiazole (12%) as the only isolable products. The ^{1}H n.m.r. spectra of the starting *o*-diamine (**14**) and each of the monoamine products are consistent with the proposed structures. Failure of diazotised 7-amino-6-diethylaminobenzothi-

azole (14) to rearrange may be a consequence of interaction of the diazonium group with the *ortho*-diethylamino-group. Nitrosative cleavage of tertiary amines to secondary amines is not unknown.[15]

Photolysis of 6-azido-2-methylbenzothiazole (5) in an excess of diethylamine (no dioxan) also gave an *o*-diamine (15) (18% yield) together with a lesser amount (8%) of 6-diethylamino-2-methyl-8*H*-thiazolo[5,4-*c*]-azepine (21). The only members of this ring system reported to date are compound (25) and two of its derivatives.[16] Compounds (15) and (21) may be assumed to arise from the azirine intermediate (12) (see Scheme), which is in equilibrium with the initially generated singlet nitrene (11). In the ^{1}H n.m.r. spectrum of the thiazoloazepine (21) there are two singlets at τ 5.80 and 7.34 for the methylene and methyl protons, respectively, a characteristic pair of doublets (J = 12.0 Hz) for the olefinic protons at τ 3.55 and 2.75, together with the



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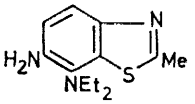

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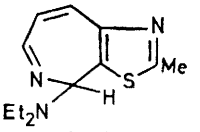

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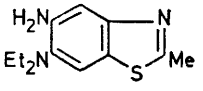

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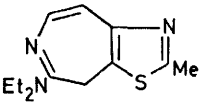

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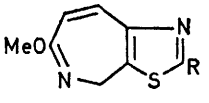
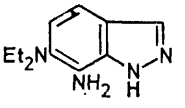


(30) R = H
(31) R = Me



(32)

usual triplet-quartet pattern for the two ethyl groups. In our opinion, establishing the structure of the thiazoloazepine produced in these reactions also establishes the structure of the related *o*-diamine (derived from a common azirine intermediate). If the azirine intermediate (12) had undergone a H-shift,[9] the *o*-diamine (26) and thiazoloazepine (27) would have been formed instead from the isomeric azirine intermediate (13).* Likewise, formation of the azirine (10) from the initially generated singlet nitrene (11) would give rise to the *o*-diamine (28) and thiazoloazepine (29). The ^{1}H n.m.r. spectrum of the isolated thiazoloazepine is consistent with structure (21) but inconsistent with structure (27), whilst the ^{1}H n.m.r. spectrum of the *o*-diamine isolated is consistent with structure (15) but inconsistent with structure (28). Formation of the thiazoloazepine (21) was unexpected in view of the result obtained with 6-azidobenzothiazole but may be a result of the shorter reaction time in this case (21.5 h compared with 32 h).

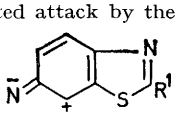
Irradiation of mixtures of 6-azido-2-methylbenzothiazole (5) and morpholine or piperidine similarly gave moderate yields of the *o*-diamines (16) (45% yield) and (17) (32%), respectively, but no thiazoloazepines were isolated in these cases (although this does not rule out their formation). Irradiation of this azide (5) in pyrrolidine, however, gave an isolated product (trace) whose ^{1}H n.m.r. spectrum was consistent with the thiazoloazepine (22).

When 6-azido-2-methylthiobenzothiazole (6) was irradiated in a mixture of diethylamine and dioxan, only a small amount of product was isolated. Its ^{1}H n.m.r. spectrum suggested that it was a 2 : 3 ratio (by integration of the methyl groups) of 7-amino-6-diethylamino-2-methylthiobenzothiazole (18) and the starting azide and this product was not examined further. Under the same conditions the 2-phenylthio-compound (7) gave both *o*-diamine (19) and thiazoloazepine (23) in low yields.

To examine the effect of an electron-withdrawing 2-substituent we irradiated 6-azido-2-chlorobenzothiazole (8) in an excess of diethylamine. This gave a low yield of *o*-diamine (20) (2%) together with thiazoloazepine (24) (13%). Dioxan as a co-solvent [5] increased the yield of isolated thiazoloazepine (24) to 18%. Photolysis of this azide (8) in cyclohexylamine [10] in the presence of TMEDA as a singlet-stabilising reagent [9] gave an intractable product whilst its photolysis in triethylamine [17] gave only starting material (85% recovery after 20 h). A study with 6-azido-2-phenylsulphonylbenzothiazole (9) was limited by its insolubility in diethylamine or in a diethylamine–dioxan mixture. Addition of hexamethylphosphoric triamide to the latter mixture dissolved the azide, but work-up gave an intractable product.

Under the conditions used by Rigaudy *et al.*[18,19] for ring expansion of polycyclic aromatic azides, namely photolysis in a methoxide–methanol–dioxan mixture, 6-azido-2,3-dihydrobenzo[*b*]thiophen 1,1-dioxide (2) gave only a poor yield (9%) of 6-amino-2,3-dihydrobenzo[*b*]-thiophen 1,1-dioxide, the triplet nitrene derived product. Under these conditions 6-azidobenzothiazole (4) and its 2-methyl derivative (5) gave modest yields (37% and 22%, respectively) of the methoxythiazoloazepines (30) and (31), whilst 6-azido-2-chlorobenzothiazole (8) gave

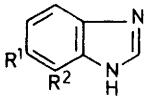
* The unprecedented conversion of azirines (12) ⇌ (13) can be avoided by postulated attack by the secondary amine on a



canonical structure of nitrene (11) (see R. S. Atkinson, in 'Aromatic and Heteroaromatic Chemistry', The Chemical Society, London, 1978, Vol. 6, p. 237; and B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Suschitzky, and P. T. Gallagher, *Angew. Chem. Internatn. Edn.*, 1980, **18**, 900.

only 6-amino-2-chlorobenzothiazole (33%) and 6-azido-2-methylthiobenzothiazole (6) gave only starting material and an intractable oil. Previously 3-azidopyridine has been shown to give 3-aminopyridine only under these conditions [20] whereas 3(and 4)-azidoquinolines do undergo ring expansion to give derivatives of benzo-1,4-diazepines.[21]

Irradiation of 6-azidoindazole in an excess of diethylamine gave only 7-amino-6-diethylaminoindazole (32). In order to establish that isomerization of the pyrazole ring to an imidazole ring had not occurred concurrently we irradiated 5(6)-azidobenzimidazole under the same conditions. This gave a mixture of two diamines, (33) and (34), both with properties different from those of (32). The structure of the *o*-diamine (33) was confirmed by its diazotization and treatment of the resulting diazonium compound with hypophosphorous acid, which gave 5(6)-diethylaminobenzimidazole. In the ^{1}H n.m.r. spectrum of this compound it was not possible to distinguish between H-4 and H-7 at 90 MHz due to their almost identical chemical shifts but a significant feature of the spectrum was a doublet of doublets for H-5 at τ 3.5 with $J_{4,5} = 9.0$ Hz and $J_{5,7} = 3.0$ Hz. The ^{1}H n.m.r. spectrum of 4(7)-diethylaminobenzimidazole would be expected to be different from that recorded for our product. Assuming that our two *o*-diamines arise from azirine intermediates similar to (12) and (13) (see footnote) [9] in the Scheme the other isolated compound must be (34). In the ^{1}H n.m.r. spectrum of this product, however, the two benzene ring protons produced signals overlapped by the $-NH_2$ and $-NH-$ group protons. Fortunately, deuteriation of the sample revealed two doublets for H-4 and H-5 with $J_{4,5} = 9.0$ Hz. 5(6)-Amino-6(5)-diethylaminobenzimidazole, which would arise if the azirine intermediate similar to (10) in the Scheme formed, would have a coupling constant in the order 0—2.0 Hz for $J_{4,7}$. The two *o*-diamines (33) and (34) have similar although slightly



(33) $R^1 = NEt_2$, $R^2 = NH_2$
(34) $R^1 = NH_2$, $R^2 = NEt_2$
(35) $R^1 = NEt_2$, $R^2 = H$

(36)

different u.v. spectra which are quite different from those of either 5(6)-diethylaminobenzimidazole or *o*-diamine (32).

Chapman and his co-workers [22,23] have suggested that the photochemical conversion of phenyl azide in the presence of bases to 2-substituted 3*H*-azepines proceeds *via* the formation of 1-azacyclohepta-1,2,4,6-tetraene (36). Evidence was presented for the formation of (36) in an argon matrix at 8 K. In our opinion, these results do not rule out a different mechanism in solution at higher temperatures. Indeed, we believe that, taken as a whole, all our results on polycyclic aromatic azides reported to date are more consistent with the mechanism shown in the Scheme than one involving intermediates similar to (36). Recent results by Rigaudy *et al.*[19] support this conclusion. On the basis of Chapman's suggestion it is difficult, for example, to rationalise the isolation of only 3-amino-4-ethylthiotoluene when 4-azidotoluene is photolysed in ethanethiol.[24,*]

Thus, so far, with [6,5]-annelated bicyclic heteroaromatic ring systems the only azides which have been shown to undergo the ring expansion reaction are those containing a S-atom in the heterocyclic ring, *e.g.* 6-azido-benzo[*b*]thiophens and -benzothiazoles. The nature of the substituent in the heterocyclic ring does not appear to be important since 6-azidobenzothiazoles containing either electron-donating or electron-withdrawing 2-substituents undergo the ring expansion reaction. Some of the factors which control the direction which the reaction takes are still not clear, however.

^{13}C *N.m.r. Spectra.*—A comparison of the ^{13}C n.m.r. spectra of the four isomers obtained by nitration of benzothiazole with those of benzothiazole and its 6-deuteriated derivative has allowed the assignments shown in Table 1 to be made.[25,26] We recorded the ^{13}C n.m.r. spectra of a number of the benzothiazoles prepared during the course of our work; the results are recorded in Table 1. For some of our compounds the results are in agreement with those recorded more recently in the literature.[27] In benzothiazoles the signal for C-2 is consistently the furthest downfield: C-3a and C-7a are readily identified by the absence of proton coupling. The signal for C-7a appears upfield of the signal for C-3a. For the remaining C-atoms our assignments were based on a comparison with the recorded spectra for benzothiazole, its 2-methyl derivative, and the four nitro-isomers mentioned before.[25,26]

The nitro-groups in 4-, 5-, 6-, and 7-nitrobenzothiazole deshield the C-atoms to which they are attached by 19.7, 20.7, 19.6, and 20.6 p.p.m., respectively (results from ref. 25). By summation of the substituent effects produced by the 2-methyl group in 2-methylbenzothiazole (relative to the parent heterocycle) with those produced by the 6-nitro-group in 6-nitrobenzothiazole (calculated from Table 1) the following calculated chemical shifts are obtained for 2-methyl-6-nitrobenzothiazole: for C-2, 173.7 (173.2); C-3a, 157.3 (157.2); C-4, 123.15 (122.7); C-5, 121.2 (121.5); C-6, 144.0 (144.9); C-7, 118.9 (118.0); and for C-7a, 136.9 (136.1) (the observed shifts are shown in parentheses).† A similar comparison can be made between the calculated and observed ^{13}C n.m.r. chemical shifts for 6-nitro-2-phenylthiobenzothiazole. In both cases good agreement is found for all the values. In the ^{13}C n.m.r. spectrum of the phenylthio-compound, C-7a and C′-2/6 (phenyl ring) have the same chemical shift, as demonstrated by

* *Note added in proof:* see the recent communication by I. R. Dunkin and P. C. P. Thompson, *J.C.S. Chem. Comm.*, 1980, 499.

† In the arguments presented here we have ignored solvent effects.

an examination of the off-resonance proton decoupled spectrum in which only C′-2/6 appears as a doublet.

In 2-chlorobenzothiazole, the substituent effect produced by the chlorine atom at C-2 (−4.3 p.p.m.) is smaller and opposite in sign to that (+6.2 p.p.m.) produced by chlorine at C-1 in chlorobenzene [28] but this observation is in agreement with the substituent effect produced at C-3 in 3-chloroindazole (−1.2 p.p.m.).[29]

The ^{13}C n.m.r. spectra of the four 6-aminobenzothiazoles studied are remarkably similar (Table 1).

TABLE 1

^{13}C N.m.r. chemical shifts for benzothiazoles

Substituent(s)	Chemical shifts (δ p.p.m.) C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	2-Substituent
None [a]	155.2	153.2	123.1	125.9	125.2	122.1	133.7	
None [b]	155.5	152.6	122.1	125.1	125.8	122.7	133.2	
4-NO_2 [a]	161.1	149.4	142.8	122.4	125.6	128.8	137.2	
5-NO_2 [a]	160.9	152.8	118.2	146.6	119.8	124.0	140.9	
6-NO_2 [a]	163.0	156.6	123.6	121.4	144.8	119.6	134.6	
6-NO_2 [b]	162.3	156.1	123.1	120.8	144.3	119.2	134.1	
7-NO_2 [a]	160.7	155.4	130.5	127.2	122.4	142.7	130.5	
2-Me [c]	165.9	153.9	122.65	125.7	124.4	121.4	136.0	19.6 (Me)
2-Me [b]	166.3	152.6	121.5	125.6	124.3	121.5	134.9	19.6 (Me)
2-Me [d]	166.1	153.9	122.6	125.7	124.5	121.4	136.1	19.7 (Me)
2-SMe [e]	167.5	153.3	121.3	125.8	123.8	120.8	135.2	15.6 (SMe)
2-SMe [b]	167.4	152.5	120.7	126.0	123.9	121.4	134.2	15.5 (SMe)
2-SPh [e,f]	168.2	154.0	122.0	126.1	124.3	120.8	135.6	
2-Cl [c]	150.9	152.35	122.6	126.4	125.5	120.9	136.0	
2-Cl [b]	152.4	150.1	122.0	126.7	125.8	122.1	135.4	
2-Me,6-NO_2 [e]	173.2	157.2	122.7	121.5	144.9	118.0	136.1	20.6 (Me)
2-Me,6-NO_2 [b]	173.6	156.2	121.7	120.7	143.6	118.3	135.4	20.0 (Me)
2-SPh,6-NO_2 [e,g]	177.4	157.7	121.8	121.6	144.0	117.1	135.7	
6-NH_2 [e]	149.6	146.6	123.8	115.7	145.1	105.6	135.5	
6-NH_2 [b]	148.7	144.5	122.8	114.7	146.9	103.6	134.9	
2-Me,6-NH_2 [h]	162.4	146.5	122.7	115.1	144.2	105.8	137.3	19.7 (Me)
2-Me,6-NH_2 [b]	159.5	144.3	121.7	114.1	146.2	103.9	136.4	19.4 (Me)
2-SPh,6-NH_2 [h,i]	161.9	146.8	122.4	115.7	144.0	105.7	137.6	
2-Cl,6-NH_2 [h]	144.8	141.35	112.5	114.9	147.5	103.6	137.2	

[a] From J. Elguero, R. Faure, and E. J. Vincent, *Bull. Soc. chim. belges*, 1977, **86**, 95; solvent $(CD_3)_2SO$. [b] From S. N. Sawhney and D. W. Boykin, *J. Org. Chem.*, 1979, **44**, 1136; solvent $(CD_3)_2SO$. [c] Neat liquid. [d] From S. Florea, W. Kimpenhaus, and V. Fărcăşan, *Org. Magnetic Resonance*, 1977, **9**, 133; neat liquid. [e] In $CDCl_3$. [f] 130.75 (C′-1), 135.2 (C′-2/6), 129.85 (C-3/5), and 130.3 (C′-4). [g] 128.5 (C′-1), 135.7 (C′-2/6), 130.3 (C′-3/5), and 131.3 (C′-4). [h] In $(CD_3)_2SO$. [i] 131.8 (C′-1), 13.41 (C′-2/6), 129.7 (C′-3/5), and 130.9 (C′-4).

When the substituent effects produced by the amine group in 6-aminobenzothiazole are summated either with those produced by the 2-methyl group in 2-methylbenzothiazole or with those produced by the 2-substituent in 2-phenylthio- or 2-chloro-benzothiazole, good agreement is found between the calculated chemical shifts and those observed for 6-amino-2-methyl-, 6-amino-2-phenylthio-, and 6-amino-2-chloro-benzothiazole, respectively. The substituent effects produced by the amine group in the 6-aminobenzothiazoles on the C-atom to which it is attached and on C-4 (' *meta* '-position) are similar to the corresponding substituent effects in aniline [27] (+18.0 and +0.9 p.p.m.; respectively), but agreement is not quite as good when the substituent effects produced at C-5 and C-7 (' *ortho* '-positions) are compared with that produced at the *ortho*-position of aniline (−13.3).[27] However, in comparing the 6-aminobenzothiazoles with aniline, bond fixation and annelation to the heterocyclic ring have to be considered.

EXPERIMENTAL

The instruments used to record i.r., ^1H n.m.r., and mass spectra and the general experimental conditions were the same as those described in the preceding paper.[4] U.v. spectra were recorded with a Unicam SP 800A spectrometer whilst ^{13}C n.m.r. spectra were obtained using a Varian CFT20 instrument ($SiMe_4$ as an internal standard). Small-scale distillations were carried out with Kugelrohr micro-distillation apparatus and in these cases the ' b.p. ' temperatures cited are those of the oven at the point of distillation. Photolyses were performed under nitrogen through a Pyrex filter with a medium-pressure mercury vapour lamp emitting light predominantly at 254, 265, 297, 313, and 366 nm. All solutions were ' degassed ' with nitrogen gas prior to irradiation.

The following compounds were prepared by literature methods: 7-amino-3-methylbenzo[*b*]thiophen (31%), m.p. 54 °C [from light petroleum (b.p. 40—60 °C)] (lit.,[3] 56 °C); 6-nitro-2-phenylthiobenzothiazole (72%), m.p. 103.5—104 °C (lit.,[30] 104 °C); and 6-amino-2-chlorobenzothiazole (54%), m.p. 157—159 °C (lit.,[31] 155—157 °C) from 2-chloro-6-nitrobenzothiazole.[4]

6-Aminoindazole and 5(6)-nitrobenzimidazole were available commercially (Aldrich Chemical Company).

6-Nitro-2-phenylsulphonylbenzothiazole.—A solution of 6-nitro-2-phenylthiobenzothiazole (5.0 g, 17.4 mmol) in warm (60 °C) acetic acid (10 ml) was added during 10 min to a stirred mixture of hydrogen peroxide (30% w/v; 20 ml), acetic acid (20 ml), and concentrated sulphuric acid (1 drop) at ambient temperature, and the resulting mixture was stirred at 80 °C for 1 h, then diluted with water (50 ml) and poured into an aqueous solution of sodium sulphite. When the vigorous evolution of gas had subsided the mixture was diluted further with water and the precipitate filtered off, washed with water, and dried, to give 6-nitro-2-phenylsulphonylbenzothiazole (4.7 g, 85%), m.p. 215—217 °C, which was used without further purification.

6-Amino-2-phenylthiobenzothiazole.— 6-Nitro-2-phenylthiobenzothiazole (5.0 g, 17.4 mmol) was added during 45

min to a stirred mixture of iron powder (80%, 8.77 g, 125 mg-atom), ethanol (40 ml), water (50 ml), and acetic acid (2 ml) heated under reflux and the resulting mixture was heated under reflux for a further 45 min. More ethanol (50 ml) and charcoal (2 g) were added and the mixture was heated under reflux for 10 min, then filtered hot into water (150 ml), to give 6-*amino*-2-*phenylthiobenzothiazole* (3.3 g, 74%), m.p. 123—124 °C (from chloroform–hexane); $\nu_{max.}$ (Nujol) 3 200 and 3 330 cm^{-1} (NH_2); τ([$(CD_3)_2CO$]) 2.13—2.62 (m, 6 H, aromatic), 2.96 (d, 1 H, J 2.5 Hz, 7-H), 3.17 (dd, 1 H, $J_{4,5}$ 9.0 Hz, $J_{5,7}$ 2.5 Hz, 5-H), and 5.90br (s, 2 H, exchangeable, NH_2) (Found: C, 60.4; H, 3.9; N, 10.8%; M^+, 258. $C_{13}H_{10}N_2S_2$ requires C, 60.4; H, 3.9; N, 10.8%; M, 258).

6-*Amino*-2-*phenylsulphonylbenzothiazole* (7.2 g, 52%), m.p. 149—150 °C (from dichloromethane–n-pentane), $\nu_{max.}$ (Nujol) 3 370 and 3 470 cm^{-1}; τ[$CDCl_3$–$(Me)_2SO$] 1.9—2.4 (m, 6 H, aromatic), 2.90 (d, 1 H, J 2.0 Hz, 7-H), 3.10 (dd, 1 H, $J_{4,5}$ 9.0 Hz, $J_{5,7}$ 2.0 Hz, 5-H), and 4.20br (s, 2 H, exchangeable, NH_2) (Found: C, 53.4; H, 3.6; N, 9.6%; M^+, 290. $C_{13}H_{10}N_2O_2S_2$ requires C, 53.8; H, 3.5; N, 9.65%; M, 290): and 5(6)-aminobenzimidazole (71%), m.p. 163—164 °C [from ether–ethanol (4 : 1)] (lit.,[32] 164 °C) were prepared similarly.

Azides.—6-Azidobenzothiazole (4) and its 2-methyl (5) and 2-methylthio-derivatives (6) and 6-azido-2,3-dihydrobenzo[*b*]thiophen 1,1-dioxide (2) were prepared as described in the preceding paper and the following azides were prepared similarly: 7-*azido*-3-*methylbenzo*[b]*thiophen* (55%), m.p. 66—67 °C (from methanol); $\nu_{max.}$ (Nujol) 2 150 cm^{-1} (N_3); τ($CDCl_3$) 2.5—3.0 (m, 4 H, aromatic), and 7.55 (s, 3 H, Me); δ(^{13}C n.m.r.) ($CDCl_3$) 13.8 (q, Me) (Found: C, 57.1; H, 3.7; N, 22.4%; M^+, 189. $C_9H_7N_3S$ requires C, 57.1; H, 3.7; N, 22.2%; M, 189); 6-*azido*-2-*chlorobenzothiazole* (8) (65%), m.p. 114—115 °C (from light petroleum); $\nu_{max.}$ (Nujol) 2 100 and 2 120 cm^{-1} (N_3); τ($CDCl_3$) 2.13 (d, 1 H, J 10.0 Hz, 4-H), 2.64 (d, 1 H, J 2.5 Hz, 7-H), and 2.89 (dd, 1 H, $J_{5,7}$ 2.5 Hz, $J_{4,5}$ 10.0 Hz, 5-H) (Found: C, 39.9; H, 1.4; N, 26.5%; M^+, 210. $C_7H_3ClN_4S$ requires C, 39.9; H, 1.4; N, 26.6%; M, 210); 6-*azido*-2-*phenylthiobenzothiazole* (7) (55%), m.p. 50—51 °C (from n-pentane); $\nu_{max.}$ (Nujol) 2 100 and 2 125 cm^{-1} (N_3) (Found: C, 54.5; H, 2.8; N, 19.6%; M^+, 284. $C_{13}H_8N_4S_2$ requires C, 54.9; H, 2.8; N, 19.7%; M, 284); 6-*azido*-2-*phenylsulphonylbenzothiazole* (9) (29%), m.p. 172—174 °C (decomp.) (from hexane–chloroform); $\nu_{max.}$ (Nujol) 2 120 cm^{-1} (N_3) (Found: C, 49.2; H, 2.6; N, 18.2%; M^+, 316. $C_{13}H_8N_4O_2S_2$ requires C, 49.35; H, 2.55; N, 17.7%; M, 316): 6-azidoindazole (56%), m.p. 157—159 °C (from benzene) (lit.,[33] 161 °C); and 5(6)-azidobenzimidazole (54%), m.p. 176 °C (from aqueous ethanol) (lit.,[34] 175 °C).

Photolysis of 7-*Azido*-3-*methylbenzo*[b]*thiophen.*—A mixture of the azide (1.5 g, 7.94 mmol), diethylamine (40 ml), and dioxan (40 ml) was irradiated for 5 h. The solvent and excess of reagent were distilled off under reduced pressure and the residue chromatographed on alumina. Hexane eluted 7-azido-3-methylbenzo[*b*]thiophen (0.15 g, 10%), 3,3′-*dimethyl*-7,7′-*azobenzo*[b]*thiophen* (0.01 g, 0.8%), m.p. 248 °C (Found: M^+, 322.059 9; M^+ — 161, 161.029 9. $C_{18}H_{14}S_2N_2$ requires M, 322.059 8; C_9H_7SN, M — 161, requires 161.029 8), and 7-amino-3-methylbenzo[*b*]thiophen (0.38 g, 30%), identical (m.p. and i.r. and ^1H n.m.r. spectra) with an authentic sample.

Photolysis of 6-*Azido*-2,3-*dihydrobenzo*[b]*thiophen* 1,1-*Dioxide* (2).—(a) *In diethylamine–dioxan.* When this azide was treated in the manner described in the preceding experiment, it gave only an intractable tar from which we failed to isolate compounds by chromatography on alumina (see Discussion).

(b) *In dioxan–methanol in the presence of potassium methoxide.* A mixture of the azide (1.9 g, 9.1 mmol), dioxan (40 ml), and 3M-potassium methoxide in methanol (40 ml) was irradiated for 33 h. Concentrated hydrochloric acid in methanol (1 : 3) was added to neutralise the mixture and the precipitate of potassium chloride was filtered off. Distillation of the solvents under reduced pressure gave a

TABLE 2

Photolyses of 6-azidobenzothiazoles; reaction conditions and products

	Reaction conditions					*o*-Diamine			8*H*-Thiazolo[5,4-*c*]-azepine		
Azide No.	Azide (mmol)	Dioxan (ml)	Amine (ml)	Reaction Time (h)	Elution solvent(s) (Ratios) [a]	No.	Yield (%)	B.p. (°C/mmHg) M.p. (°C)	No.	Yield (%)	M.p. (°C)
(4)	10	40	$HNEt_2$ (4)	32	$CHCl_3$-L.P. (1 : 9)	(14) [b]	33	157 at 0.4			
(5)	10		$HNEt_2$ (76)	21.5	$CHCl_3$-L.P. (3 : 7)	(15) [c]	18	146—148 at 0.4	(21) [d]	8	70—71
(5)	8.4		HNC_4H_8O (80)	20	$CHCl_3$-L.P. (2 : 8)	(16) [e]	45	192—193			
(5)	10		HNC_5H_{10} (70)	15	$CHCl_3$-L.P. (2 : 8)	(17) [f]	32	113.5—114			
(5)	10		HNC_4H_8 (80)	20	$CHCl_3$-L.P. (1 : 9)				(22) [g]	<1	
(6)	10	40	$HNEt_2$ (40)	22	Et_2O-L.P. (2 : 8)	(18) [h]					
(7)	11.4	40	$HNEt_2$(40)	10	$CHCl_3$-n-hexane (3 : 7)	(19) [i]	4	195 (decomp) at 0.3	(23) [i]	7	64—66
(8)	4.75		$HNEt_2$ (70)	16	$CHCl_3$-L.P. (2 : 8)	(20) [j]	2		(24) [d]	13	84—85
(8)	10	40	$HNEt_2$ (40)	24	$CHCl_3$-L.P. (3 : 17)				(24) [d]	18	84—85
(8) [k]	4.75		NEt_3 (80)	20	$CHCl_3$-n-hexane (1 : 9)						
(8) [l]	10.2		$H_2N{\cdot}C_6H_{11}$ (75)	15	$CHCl_3$-n-hexane						
(9) [m]	4.7	40	$HNEt_2$ (40)	18	$CHCl_3$-L.P. (2 : 8)						

[a] L.P. = light petroleum (b.p. 60—80 °C). [b] *N*-Benzoyl derivative (81%), m.p. 127—129 °C (from n-pentane–ether); ν_{max} (Nujol) 1 655 (CO) and 3 400 cm^{-1} (NH) (Found: C, 66.2; H, 6.0; N, 13.0%; M^+, 325. $C_{18}H_{19}N_3OS$ requires C, 66.4; H, 5.9; N, 12.9% M, 325). [c] *NN*-Diacetyl derivative (37%), m.p. 104—105 °C (from hexane); $\nu_{max.}$ (Nujol) 1 700 and 1 720 cm^{-1} (CO) (Found: C, 59.8; H, 6.6; N, 13.0%; M^+, 319.1354. $C_{16}H_{21}N_3O_2S$ requires C, 60.1; H, 6.6; N, 13.15%; M, 319.1354). [d] Recrystallised from n-pentane. [e] Recrystallised from chloroform–light petroleum (b.p. 60—80 °C). [f] Recrystallised from n-hexane. [g] See Discussion. [h] Not isolated; see Discussion. [i] Column chromatography yielded a mixture of (19) and (23) which was separated by preparative t.l.c. ($CHCl_3$). [j] Identified only by its i.r. and ^1H n.m.r. spectra (Table 2). [k] Starting material recovered (85%). [l] TMEDA (5 ml) added; the product was intractable. [m] Hexamethylphosphoric triamide (1 ml) was added to dissolve azide; the product was intractable.

residue which was chromatographed on alumina. Chloroform eluted starting material (10 mg) and 6-amino-2,3-dihydrobenzo[*b*]thiophen 1,1-dioxide (0.15 g, 9%), identical (m.p. and i.r. spectrum) with an authentic sample (see preceding paper).

petroleum (7 : 93) eluted 6-azidobenzothiazole (0.44 g, 37%) and, with a changed solvent ratio (1 : 9), 6-*methoxy*-8H-*thiazolo*[5,4-c]*azepine* (30) (0.29 g, 37%, based on azide consumed), m.p. 54—55 °C (from n-pentane) (see Table 4 for analytical data).

TABLE 3

Analytical data for 6,7-diaminobenzothiazoles

Product no.	$\nu_{max.}$ (NH_2) [a] (cm^{-1})	Chemical Shifts (Hz) [b] 4-H	5-H	$J_{4,5}$ (Hz)	2-Substituent	2 × CH_2 (q)	2 × CH_3 (t)	J (Hz)	NH_2 [c]	Found (%) C	H	N	Formula	Required (%) C	H	N
(14) [d]	3 300, 3 420	2.35 (d)	2.70 (d)	9.0	1.10 (s, 1 H, 2-H)	7.0	9.05	7.0	5.55	59.2	7.0	19.0	$C_{11}H_{15}N_3S$	59.7	6.8	19.0
(15) [e]	3 350, 3 450	2.56 (d) [f]	2.63 [f]	9.0	7.2 (s, 3 H, 2-Me)	7.1	9.1	7.0	5.7							
(16) [g]	3 330, 3 420	2.57 (d) [f]	2.83 (d) [f]	9.0	7.2 (s, 3 H, 2-Me)				5.8	57.6	6.0	17.1	$C_{12}H_{15}N_3SO$	57.8	6.1	16.85
(17) [h]	3 325, 3 425	2.63 (d) [f]	2.87 (d) [f]	10.0	7.25 (s, 3 H, 2-Me)				5.8	63.1	7.1	17.0	$C_{18}H_{17}N_3S$	63.1	6.9	17.0
(19) [i]	3 330, 3 440					7.35	9.35	7.0	6.0							
(20)	3 340, 3 440	2.60 [f]	2.85 [f]	9.0		7.1	9.1	7.0	5.8							

[a] Liquids as films; solids as Nujol mulls. [b] In $CDCl_3$, unless stated otherwise. [c] All broad singlets; protons exchangeable on deuteriation; [d] *N*-Benzoyl derivative (81%), m.p. 127—129 °C (from ether–n-pentane); $\nu_{max.}$ (Nujol) 1 655 (CO) and 3 400 cm^{-1} (NH) (Found: C, 66.2; H, 6.0; N, 13.0%; M^+, 325. $C_{18}H_{19}N_3OS$ requires C, 66.4; H, 5.9; N, 12.9%; M, 325). [e] Found: M^+, 235.1152. $C_{12}H_{17}N_3S$ requires M, 235.1143; characterised as its *NN*-diacetyl derivative—see Table 2 for data. [f] Cannot be assigned unambiguously on evidence available. [g] τ 6.03—6.24 (m, 4 H, CH_2OCH_2) and 7.03—7.18 (m, 4 H, CH_2NRCH_2). [h] τ 7.05—7.3 (m, 4 H, CH_2NRCH_2) and 8.2—8.5 (m, 6 H, piperidine ring 3 × CH_2). [i] τ 2.4—3.2 (m, 7 H, aromatic protons) (Found: M^+, 329.1016. $C_{17}H_{19}N_3S_2$ requires M, 329.1027).

Photolyses of 6-Azidobenzothiazoles in the Presence of Amines: General Method.—A mixture of the azide, dioxan or TMEDA (if present), and the amine was deoxygenated by bubbling through it nitrogen or argon for 15 min, and then irradiated at ambient temperature. The solvent and excess of reagent were distilled off under reduced pressure and the product chromatographed on alumina. The reaction conditions and results are summarised in Table 2 whilst analytical data are presented in Tables 3 and 4.

Photolysis of 6-Azidobenzothiazole (4) *in Dioxan–Methanol Containing Potassium Methoxide.*—A mixture of the azide (4) (1.2 g, 6.8 mmol), dioxan (40 ml), and 3M-potassium methoxide in methanol (40 ml) was irradiated at ambient temperature for 8 h. Concentrated hydrochloric acid in methanol (1 : 3) was added to neutralise the mixture and the precipitated potassium chloride was filtered off. Distillation of the solvents under reduced pressure gave a black oil, which was chromatographed on alumina. Ether–light petroleum (1 : 19) eluted starting material (0.15 g) and, with a changed solvent ratio (8 : 92), 6-*methoxy*-2-*methyl*-8H-*thiazolo*[5,4-c]*azepine* (31) (0.44 g, 22%), m.p. 68—69 °C (from n-pentane) (see Table 4 for analytical data).

Similar treatment of 6-azido-2-methylbenzothiazole (10.0 mmol) and work-up as described in the preceding experiment gave a residual product which was chromatographed on alumina. Ether–light petroleum (1 : 19) eluted starting material (0.15 g) and, with a changed solvent ratio (8 : 92), 6-*methoxy*-2-*methyl*-8H-*thiazolo*[5,4-c]*azepine* (31) (0.44 g,

6-Azido-2-chlorobenzothiazole (8) (10.0 mmol) similarly gave, after elution of the product from an alumina column with ether–light petroleum (3 : 17), 6-amino-2-chlorobenzothiazole (0.60 g, 33%), identical (m.p. and i.r. spectrum) with an authentic sample, whilst 6-azido-2-methylthiobenzothiazole (6) (6.8 mmol) gave, after elution of the crude product from an alumina column with ether–light petroleum (1 : 9), starting material (6), identical (m.p. and i.r. and ^1H n.m.r. spectra) with an authentic sample, and an intractable oil.

TABLE 4

Analytical data for 8*H*-thiazolo[5,4-*c*]azepines

Product no.	ν_{max} (Nujol) cm^{-1}(C=N)	Chemical Shifts (τ) [a] 4-H(d)	5-H(d)	J(Hz)	8-CH_2 (s)	2 × CH_2 (q)	2 × CH_3(t)	J (Hz)	2-Substituent	Found (%) C	H	N	Formula	Required (%) C	H	N
(21) [b]	1 610	2.75	3.35	12.0	5.8	6.7	8.9	7.0	7.3 (s, 3 H, 2-Me)	60.9	7.5	17.6	$C_{12}H_{17}N_3S$	61.2	7.3	17.8
(23) [c]	1 610		3.34	12.0	5.85	6.8	8.9	6.5								
(24) [d]	1 620	2.85	3.37	12.0	5.9	6.8	9.0	7.0		51.6	5.6	16.4	$C_{11}H_{14}ClN_3S$	51.6	5.5	16.4
(30) [e]	1 650	2.65	3.35	12.0	5.6				1.35 (s, 1 H, 2-H)	53.5	4.3	15.5	$C_8H_8N_2OS$	53.3	4.5	15.5
(31) [f]	1 640	2.85	3.71	12.0	5.7				7.4 (s, 3 H, 2-Me)	55.3	5.0	14.8	$C_9H_{10}N_2OS$	55.6	5.2	14.4

[a] In $CDCl_3$, unless stated otherwise. [b] $\lambda_{max.}$ (MeOH) (ε) 220 (4.147) and 307 nm (3.833). [c] τ 2.2—2.8 (m, 6 H, aromatic protons) (Found: M^+, 329.1019. $C_{17}H_{19}N_3S_2$ requires M, 329.1021). [d] In CCl_4. [e] τ 6.3 (s, 3 H, OCH_3). [f] $\lambda_{max.}$ (MeOH) (ε) 218 nm (4.067); τ (CCl_4) 6.45 (s, 3 H, OCH_3).

Diazotization of 7-Amino-6-diethylaminobenzothiazole (14).—Sodium nitrite (0.207 g, 3.0 mmol) in water (1.25 ml) was added to a stirred mixture of the *o*-diamine (14) (0.60 g, 2.7 mmol) in 50% sulphuric acid (10 ml) at 0 °C, and the resulting mixture was stirred at 0 °C for a further 30 min; it was then allowed to warm up to ambient temperature and stirred for a further 7.5 h at this temperature. The mixture was warmed slowly to 70 °C, during which gas evolution occurred. In the belief that the diazonium salt would preferentially rearrange to give 7-amino-4-diethylamino-1,2,3-benzothiadiazole, the resulting mixture was made alkaline by addition of 2M-sodium hydroxide and the product extracted with ether to give a deep-red oil which was chromatographed on alumina. Gradient elution with hexane–ether gave 6-diethylaminobenzothiazole (0.14 g, 25%), b.p. (Kugelrohr apparatus) 104—106 °C at 0.5 mmHg; $\nu_{max.}$ (liquid film) 1 600 cm^{-1} (C=N); $\tau(CDCl_3)$ 1.35 (s, 1 H, 2-H), 2.05 (d, 1 H, *J* 9.0 Hz, 4-H), 2.90 (d, 1 H, *J* 2.0 Hz, 7-H), 3.10 (dd, 1 H, $J_{4,5}$ 9.0 Hz, $J_{5,7}$ 2.0 Hz, 5-H), 6.60 (q, 4 H, *J* 7.0 Hz, 2 × CH_2), and 8.80 (t, 6 H, *J* 7.0 Hz, 2 × CH_3) [Found: M^+, 206.087 7; $M^+ - NEt_2$, 134.006 3. $C_{11}H_{14}N_2S$ requires *M*, 206.087 8 and C_7H_4NS, $M - NEt_2$, requires 134.006 5] and 6-ethylaminobenzothiazole (0.060 g, 12%), b.p. (Kugelrohr apparatus) 115—117 °C at 0.4 mmHg; $\nu_{max.}$ (liquid film) 1 600 (C=N) and 3 335 cm^{-1} (NH); $\tau(CDCl_3)$ 1.30 (s, 1 H, 2-H), 2.10 (d, 1 H, *J* 9.0 Hz, 4-H), 3.00 (d, 1 H, *J* 2.0 Hz, 7-H), 3.20 (dd, 1 H, $J_{4,5}$ 9.0 Hz, $J_{5,7}$ 2.0 Hz, 5-H), 6.40br (s, 1 H, exchangeable, NH), 6.80 (q, 2 H, *J* 7.0 Hz, CH_2), and 8.75 (t, 3 H, *J* 7.0 Hz, CH_3) [Found: M^+, 178.056 5; $M^+ - NEt$, 135.014 2, $M^+ - NHEt$, 134.006 4. $C_9H_{10}N_2S$ requires *M*, 178.056 5; C_7H_5NS, $M - NEt$, requires 135.014 2; C_7H_4NS, $M - NHEt$, requires 134.006 5].

Photolysis of 6-Azidoindazole.—A stirred, deoxygenated (dry nitrogen) solution of the azide (2.5 g, 15.7 mmol) in diethylamine (70 ml) was irradiated for 7 h and then the excess of reagent was distilled off under reduced pressure and the residue chromatographed on alumina. Chloroform eluted 7-*amino*-6-*diethylaminoindazole* (32) (1.64 g, 51%), m.p. 152—153 °C (from n-hexane–ether); $\nu_{max.}$ (Nujol) 3 160 (NH) and 3 350, 3 450 cm^{-1} (NH_2); $\lambda_{max.}$ (MeOH) (ε) 223 (4.151) and 296 nm (3.953); $\tau(CDCl_3)$ 1.98 (s, 1 H, 3-H), 2.85 (d, 1 H, *J* 9.0 Hz, aromatic), 3.05 (d, 1 H, *J* 9.0. Hz, aromatic), 7.03 (q, 4 H, *J* 7.0 Hz, 2 × CH_2), and 9.05 (t, 6 H, *J* 7.0 Hz, 2 × CH_3) (Found: C, 64.7; H, 8.0; N, 27.4%; M^+, 204. $C_{11}H_{16}N_4$ requires C, 64.7; H, 7.9; N, 27.4%; *M*, 204).

Photolysis of 5(6)-Azidobenzimidazole.—A stirred, deoxygenated (dry nitrogen) solution of the azide (2.5 g, 15.7 mmol), diethylamine (40 ml), and dioxan (40 ml) was irradiated for 9 h; the excess of reagent and the solvent were then distilled off under reduced pressure and the residue chromatographed on alumina. Ethanol–ether (2 : 98) eluted 4(7)-*amino*-5(6)-*diethylaminobenzimidazole* (33) (0.72 g, 22%), m.p. 222—224 °C (from ether–ethanol); $\nu_{max.}$ (hexachlorobutadiene) 3 340 and 3 440 cm^{-1} (NH_2); $\lambda_{max.}$ (MeOH) (ε) 223 (4.005) and 296 nm (3.495); τ[$CDCl_3$ + $(CD_3)_2SO$] 2.2 (s, 1 H, 2-H), 2.8 (d, 1 H, *J* 9.0 Hz, aromatic), 3.3 (d, 1 H, *J* 9.0 Hz, aromatic), 4.15br (s, 3 H, exchangeable, NH_2m NH), 6.82 (q, 4 H, *J* 7.0 Hz, 2 × CH_2), and 9.03 (t, 6 H, *J* 7.0 Hz, 2 × CH_3) (Found: C, 64.6; H, 8.0; N, 27.2%; M^+, 204), whilst ethanol–ether (4 : 96) eluted 5(6)-*amino*-4(7)-*diethylaminobenzimidazole* (34) (0.55 g, 17%), m.p. 220—221 °C; $\nu_{max.}$ (hexachlorobutadiene) 3 350 and 3 465 cm^{-1} (NH_2); $\lambda_{max.}$ (MeOH) (ε) 222 (4.065), 261 (3.750), and 289 nm (3.530); $\tau(CDCl_3)$ 2.15 (s, 1 H, 2-H), 2.98 (d, 1 H, *J* 9.0 Hz, aromatic), 3.18 (d, 1 H, *J* 9.0 Hz, aromatic), 2.4—4.0br (s, 3 H, exchangeable, NH_2, NH), 7.05 (q, 4 H, *J* 7.0 Hz, 2 × CH_2), and 9.05 (t, 6 H, *J* 7.0 Hz, 2 × CH_3) (Found: M^+, 204.137 5. $C_{11}H_{16}N_4$ requires *M*, 204.137 5).

Deamination of 4(7)-Amino-5(6)-diethylaminobenzimidazole (33). A solution of sodium nitrite (0.15 g, 2.17 mmol) in water (1.0 ml) was added dropwise during 10 min to a stirred solution of the *o*-diamine (33) (0.37 g, 1.81 mmol) in 5M-hydrochloric acid (5 ml) at 0 °C. Then, 50% hypophosphorous acid (4 ml) was added at room temperature and the mixture was stirred for a further 2 h at this temperature. 2M-Sodium hydroxide (45 ml) was added and extraction with chloroform gave 5(6)-*diethylaminobenzimidazole* (35) (0.21 g, 61%), m.p. 143—144 °C (from chloroform–light petroleum); $\nu_{max.}$ (hexachlorobutadiene) 2 400—2 900 cm^{-1} (NH); $\lambda_{max.}$ (MeOH) (ε) 223 (4.049) and 279 nm (3.660); $\tau(CDCl_3)$ 2.2 s, 1 H, 2-H), 2.8—3.2 (m, 2 H, 4-H and 7-H), 3.50 (dd, 1 H, $J_{4,5}$ 9.0 Hz, $J_{5,7}$ 3.0 Hz, 5-H), 6.55 (q, 4 H, *J* 7.0 Hz, 2 × CH_2), and 9.05 (t, 6 H, *J* 7.0 Hz, 2 × CH_3) (Found: C, 69.8; H, 7.7; N, 22.2%; M^+, 189. $C_{11}H_{15}N_3$ requires C, 69.8; H, 8.0; N, 22.2%; *M*, 189).

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