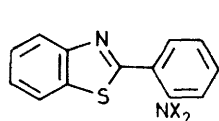


Competitive Cyclisations of Singlet and Triplet Nitrenes. Part 9.¹ 2-(2-Nitrenophenyl)-benzothiazoles and -benzimidazoles

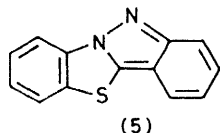
By David Hawkins, John M. Lindley, Ian M. McRobbie, and Otto Meth-Cohn,* The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

2-(2-Nitrophenyl)benzothiazole, produced by deoxygenation of the corresponding nitro-compound or by thermolysis or photolysis of the related azide, gives indazolo[3,2-*b*]benzothiazole by attack on the benzothiazole nitrogen. Similar attack of the nitrene in 2-(2-nitrophenyl)benzimidazoles gives benzimidazoindazoles in good yield. However, with an appropriate 1-substituent in the benzimidazole (e.g. Me or CHMe₂) the nitrene in its triplet state (generated by acetophenone-sensitised photolysis or by thermolysis of the azide bearing a 4-dimethyl-amino-group) preferentially attacks this substituent giving benzimidazoquinazolines.

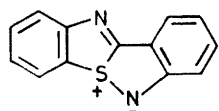
In previous papers in this series we demonstrated that suitably constructed aryl nitrenes can undergo efficient cyclisations, giving different products depending upon whether the singlet or triplet species was involved. We have also delineated methods whereby singlet or triplet pathways may be selected specifically and optimised. We now describe the application of these ideas to the 2-(2-nitrenophenyl)-benzothiazoles (1) and -benzimidazoles (12).²



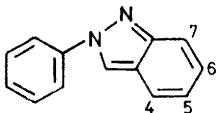
- (1) X = :
(2) X = H
(3) X = N
(4) X = O



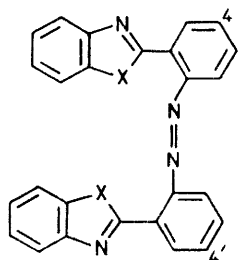
(5)



(6)



(7)



- (8) X = S
(9) X = NMe
(10) X = NPrⁱ
(11) X = NBu^t

(1) Reactions of 2-(2-Nitrenophenyl)benzothiazole (1). —2-(2-Aminophenyl)benzothiazole (2) is readily available in high yield by interaction of 2-aminothiophenol and anthranilic acid in polyphosphoric acid (PPA) at 250 °C for 4 h following the method of Hein.³ The usual sequence of diazotisation and treatment with buffered

sodium azide gave the azide (3). The corresponding nitro-compound (4) was also prepared by modification of the literature method⁴ (which we found ineffective), from 2-nitrobenzoyl chloride and 2-aminothiophenol. The resulting *S*-(2-nitrobenzoyl)-2-aminothiophenate was cyclised with acetic acid.

In principle, the singlet nitrene (1) has two sites for attack, at N or at S of the thiazole ring giving either (5) or (6). All our endeavours to encourage singlet nitrene reactions at S have, in the past, failed.⁵ This could be due to the potential reversibility of the sulphimide (6) to the nitrene (1).

Stable cyclic 5-membered sulphimides are well documented,⁶ although in the present case formation of (6) would seriously interfere with the aromaticity of the thiazole ring. The present series was no exception in that no evidence for products from attack at S was found. However, the indazolobenzothiazole (5) was available in high yield either by decomposition of the azide (3) or deoxygenation of the nitro-compound (4) (Table 1). That the structure (5) was correct was confirmed by desulphurisation with Raney nickel. 2-Phenylindazole (7) was isolated when the indazolobenzothiazole was desulphurised in refluxing ethanol † but, interestingly, 2-phenyl-4,5,6,7-tetrahydroindazole was the sole product on desulphurisation in refluxing toluene. Since 2-phenylindazole was unchanged under the latter conditions we presume that reduction of the quinonoid ring of the indazolobenzothiazole precedes desulphurisation. Other workers have noted more recently similar quinonoid reductions, which are in general unexploited.

Table 1 reveals that under singlet-promoting conditions (expts. 1–4) good yields of the indazolobenzothiazole (5) are formed. The virtue of photolyses in methylene chloride solution especially with added pyrene (a singlet photo-sensitiser and triplet quencher) for encouraging singlet reactivity have been emphasised by

† After the appearance of our preliminary publication,² Indian workers⁷ confirmed our nitrene cyclisations by thermolysis of the azide (3) and they also obtained the same result on desulphurisation.

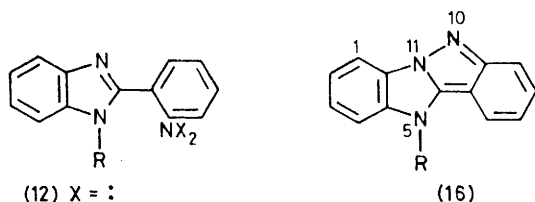
TABLE 1

Products from 2-(2-nitrenophenyl)benzothiazole (1)

Expt.	Conditions			Products (%)			S/T ^b
	Nitrene source	Solvent ^a	<i>hν</i> or heat (°C)	(5)	(2)	(8)	
1	-NO ₂	TEP-cumene	heat	54	4	0	13.5
2	-N ₃	cumene ^c	heat	79	1	0	79
3	-N ₃	CH ₂ Cl ₂	<i>hν</i>	53	7	8	3.5
4	-N ₃	CH ₂ Cl ₂ -pyrene	<i>hν</i>	75	0	0	v. high
5	-N ₃	PhAc	<i>hν</i> , 20	19	4	34	0.5
6	-N ₃	PhAc	<i>hν</i> , 107	69	0	17	4.1

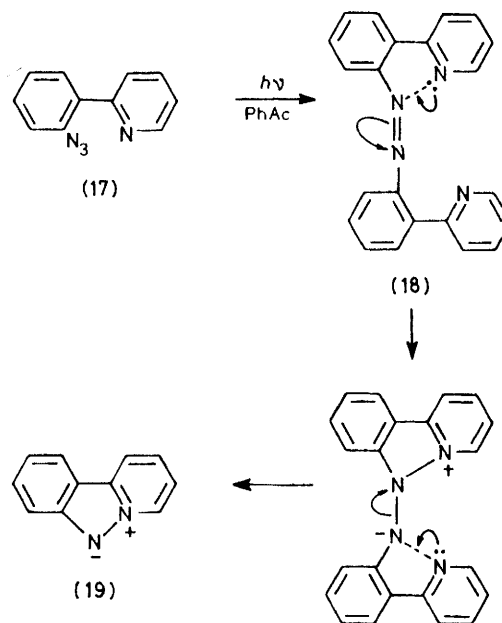
^a TEP = Triethyl phosphite; 1% solutions used. ^b S/T = ratio of singlet derived to triplet derived products. ^c Some bicumyl isolated.

us earlier.¹ The low yields of triplet-derived products [the amine (2) and the azo-compound (8)] is noteworthy. However, the photolyses in acetophenone require explanation since, in contradistinction to our earlier work, the apparent singlet-derived product (5) is formed (efficiently at 107 °C) under conditions of triplet-sensitisation. This paradox was made the more troubling when we investigated the chemistry of the 1-methyl-2-(2-nitrenophenyl)-benzimidazole (12a) and again made similar observations, since the benzimidazoindazole (16a) was again efficiently produced in hot acetophenone (see later). A possible explanation of these results follows from a recent suggestion of Boyer and Lai,⁸ who observed the quant-



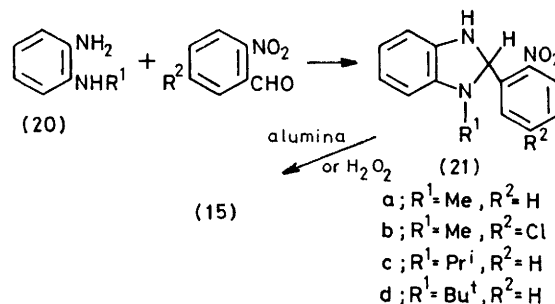
ative conversion of 2-(2-azidophenyl)pyridine (17) into the pyridoindazole (19) on photolysis in acetophenone (Scheme 1). They proposed that the azo-compound (18) was a key intermediate though did not attempt the suggested conversion. However, this attractive solution is untenable in our case (and probably also in Boyer and Lai's) since photolysis of the azo-compound (8) in acetophenone at 107 °C for 8 h was without effect on the azo-compound.

(2) *Reactions of 2-(2-Nitrenophenyl)benzimidazoles (12).*—A series of 1-alkyl-2-nitrophenylbenzimidazoles (15) was prepared by interaction of *N*-alkyl-*o*-phenylenediamines (20) with an *o*-nitrobenzaldehyde to give the dihydrobenzimidazoles (21) which were aromatised most effectively by elution through a column of alumina or by hydrogen peroxide (Scheme 2). The azides (14) were produced in the usual way and the nitro-compounds (15) and azides (14) were caused to react by deoxygenation



SCHEME 1

and by thermal or photodecomposition respectively. These systems have available both a nucleophilic site for the singlet nitrene to attack, as with the benzothiazoles, and an *N*-alkyl group to abstract hydrogen from in the case of the triplet species, making benzimidazoindazoles (16) and benzimidazoquinazolines (22) or (23) potentially available (Scheme 3). Indeed both of these goals were realised with appropriate examples (Table 2). Several significant points emerge from these results. (i) Whereas intramolecular hydrogen abstraction from a methyl group attached to an aromatic ring or an aliphatic nitrogen atom occurs readily during triplet-nitrene-mediated reactions,^{1,9} abstraction from an *N*-methyl group of a benzimidazole proceeds only with thermally excited triplet nitrenes. Indeed, only with the triplet nitrene produced thermally in refluxing bromobenzene (expt. 9) is this mode of reaction observed. Clearly the lack of mesomeric stabilisation of the *N*-CH₂• radical creates a significantly larger energy barrier to this pathway. This barrier is reduced by reintroducing mesomeric stabilisation by presenting a tertiary hydrogen for abstraction (expt. 12) under triplet-nitrene-producing conditions. This system gives significant yields of benzimidazoquinazolines (22) under hot photolysis con-



SCHEME 2

TABLE 2
Products from the nitro- and azido-phenylbenzimidazoles (15) and (14)

Expt.	X	R ¹	R ²	Conditions		Products (%)				
				Solvent	<i>hν</i> or heat (°C)	(16)	(22)	(23)	(13)	(9)–(11)
1	O	Me	H	Cumene/TEP	heat	83			Trace	
2	N	Me	H	Cumene	heat	96				
3	N	Me	H	PhAc	<i>hν</i> /20	15			26	7.5
4	N	Me	H	PhAc ^a	<i>hν</i> /107	42–63			11–13	3–22
5	N	Me	H	10% PhAc–PhCl ^b	<i>hν</i> /107	56–65			7–12	13–19
6	N	Me	H	10% PhAc–PhCl ^c	<i>hν</i> /97	51			23	0
7	N	Me	H	10% PhAc–PhCl ^d	<i>hν</i> /82	48			13	0
8	N	Me	H	10% PhAc–PhBr	<i>hν</i> /107	40			31	21
9	N	Me	NMe ₂	PhBr	heat			36	15	Trace
10	N	Me	NMe ₂	PhAc	<i>hν</i> /20				15	Trace
11	N	CHMe ₂	H	PhBr	<i>hν</i> /20	66			14	14
12	N	CHMe ₂	H	PhAc	<i>hν</i> /20		59		15	
13	N	CMe ₃	H	PhAc	<i>hν</i> /107	17				56

^a Based on four experiments. ^b Based on two experiments. ^c Azide (39%) recovered; yields based on reacted azides. ^d Azide (36%) recovered after 40 h irradiation (5 × longer than other examples); yields based on reacted azide.

ditions in acetophenone, unlike the *N*-methylbenzimidazole analogue. (ii) Apart from the decomposition of the azide bearing a *para*-dimethylamino-group (which we have shown earlier to be an efficient thermal route to triplet nitrenes¹) the apparent singlet-derived benzimidazoindazole (16) was generally the major product, even during triplet-sensitised reactions. Furthermore, whereas increasing temperature during triplet-sensitised photolysis in general leads to more efficient triplet reactivity, in the present series (expts. 5, 6, and 7) increasing temperature gives more of the supposed singlet-derived product (16a) (*cf.* expt. 2). The use of bromobenzene instead of chlorobenzene as a diluent for the acetophenone sensitizer, which as a 'heavy atom' solvent should aid any singlet → triplet conversion by collisional deactivation (expt. 8) does lead to slightly reduced yields of the benzimidazoindazole (16a) and increase in amine and azo-compound formation. These results taken together with those mentioned earlier in the decomposition of 2-(2-azidophenyl)benzothiazole (3) require a new rationalisation. It seems probable that the source of the apparent singlet-nitrene-derived pro-

ducts during triplet photosensitised reactions is from the triplet azide rather than the nitrene.*

EXPERIMENTAL

General conditions have been outlined in earlier papers in the series.¹

Benzothiazole Amines (2), Azides (3), and Nitro-compounds (4).—(a) 2-(2-Aminophenyl)benzothiazole (2). The amine (2) was prepared by the method of Hein, Alheim, and Leavitt³ in 80% yield, m.p. 127–128 °C (lit.,³ 126.7–127.7 °C).

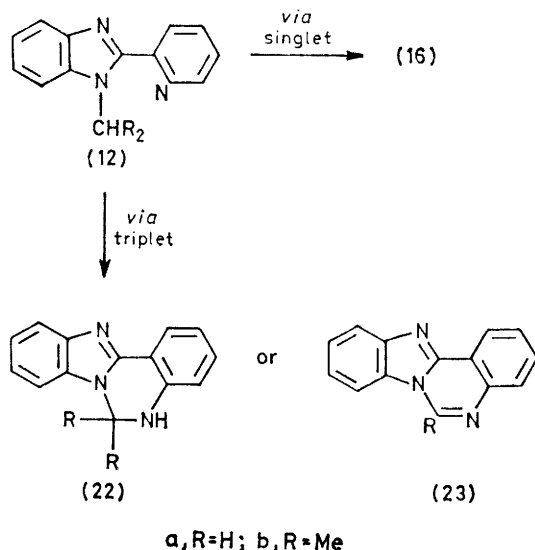
(b) 2-(2-Azidophenyl)benzothiazole (3). The above amine (2) (2.2 g) in a mixture of concentrated hydrochloric acid (8 ml), concentrated sulphuric acid (10 ml), and water (20 ml) was treated at 0 °C with sodium nitrite (0.7 g) in water (15 ml); this solution was then added dropwise to cooled saturated aqueous sodium acetate (50 ml) containing sodium azide (1.0 g). The precipitate was filtered off, washed with water, and eluted with dichloromethane through a column of alumina to give cream crystals of 2-(2-azidophenyl)benzothiazole (3) (1.7 g, 69%), m.p. 133–134 °C [from light petroleum (b.p. 80–100 °C)] (Found: C, 61.5; H, 3.3; N, 22.25. C₁₃H₈N₄S requires C, 61.2; H, 3.2; N, 22.2%), ν_{\max} (Nujol) 2140 cm⁻¹ (N₃), δ (CDCl₃) 8.74–7.10 (m, aromatic).

(c) 2-(2-Nitrophenyl)benzothiazole (4). A mixture of 2-nitrobenzoyl chloride (18.5 g) and 2-aminothiophenol (12.5 g) was refluxed in benzene (250 ml) for 30 min. After evaporation the residual yellow solid was dissolved in acetic acid (200 ml) and refluxed for 24 h. The cooled solution was poured onto ice (*ca.* 500 g) and the precipitate was filtered off, washed with water, and recrystallised from ethyl acetate to give the title compound as white needles (12.0 g, 47%), m.p. 122–123 °C (lit.,⁴ 121 °C).

Decomposition of the Benzothiazoles (3) and (4).—(a) The azide (3) (2.0 g) was thermolysed under nitrogen as a 1% solution by rapid addition of the azide in cumene (*ca.* 10 ml) to refluxing cumene (190 ml), followed by a further 18 h under reflux. Removal of the solvent gave a brown residue which was purified by chromatography on alumina as described below.

(b) Photolyses were conducted as described elsewhere⁹ using 1% solutions under nitrogen followed by work-up as described above.

(c) Deoxygenation of the nitro-benzothiazole (4) (4.9 g, 0.02 mol) with triethyl phosphite (8.4 g, 0.05 mol) in cumene



SCHEME 3

* For a discussion of such pathways see ref. 5.

(200 ml) for 72 h gave, after evaporation a brown oil which was purified as described above.

Elution with light petroleum gave *indazolo*[3,2-*b*]benzothiazole (5) which recrystallised from light petroleum (b.p. 80–100 °C) as white crystals, m.p. 145 °C (Found: C, 69.6; H, 3.5; N, 12.4. $C_{13}H_8N_2S$ requires C, 69.6; H, 3.6; N, 12.5%), δ (CDCl₃) 6.93–8.40 (m, aromatic), m/e 224 (M^+). Elution with toluene gave first 2,2'-bis(benzothiazol-2-yl)-azobenzene (8) as orange crystals from light petroleum (b.p. 80–100 °C), m.p. 273–275 °C (Found: C, 69.6; H, 3.5; N, 12.7. $C_{26}H_{16}N_4S_2$ requires C, 69.6; H, 3.6; N, 12.5%), m/e 448 (M^+), δ (hot CDCl₃) 7.0–8.7 (m, aromatic). This was followed by 2-(2-aminophenyl)benzothiazole, identical to the sample prepared above.

Desulphurisation of Indazolobenzothiazole (5).—The title compound (1.0 g) and freshly prepared Raney nickel (from 25 g alloy, 1 : 1) was refluxed in either ethanol (250 ml) or toluene (250 ml) for 1 h. The nickel was filtered off and washed with dichloromethane and the organic phase evaporated. The residue was purified by elution with toluene through an alumina column to give (a), from the first experiment (in ethanol), 2-phenylindazole (7) (0.5 g, 59%), m.p. 82–84 °C (lit.,¹⁰ 83–84 °C), identical with an authentic specimen,¹⁰ and (b), from heating in toluene, 2-phenyl-4,5,6,7-tetrahydro-2*H*-indazole (0.3 g, 40%), m.p. 46 °C (lit.,¹¹ 47–48.5 °C), identical with an authentic sample.¹¹

Benzimidazole Nitro-Compounds (15), Amines (13), and Azides (14).—(a) *o*-Phenylenediamines (20). Reaction of 2-nitrochlorobenzene (63.0 g) with methylamine hydrochloride (27.0 g), potassium carbonate (55 g), and water (3 ml) in pyridine (300 ml) under reflux for 10 h gave after addition of water (100 ml) and extraction with chloroform (3 × 150 ml), 2-nitro-*N*-methylaniline (91%), m.p. 36 °C, (lit.,¹² 37 °C). 2-Nitrochlorobenzene (31.1 g) and isopropylamine (29.5 g) were heated and stirred together in an autoclave at 150 °C for 6 h. The solution was treated with ether and water, and the organic layer washed with water, dried, and evaporated to give an orange oil which was distilled to give 2-nitro-*N*-isopropylaniline (32.2 g, 89%), b.p. 144–146 °C at 11 mmHg (lit.,¹³ 141–145 °C at 11 mmHg). A mixture of 2-nitrofluorobenzene (14.1 g, 0.1 mol) and *t*-butylamine (18.25 g, 0.25 mol) in propanol (100 ml) was heated at 150 °C for 1 h in a rocking autoclave. The mixture was worked up as above and the orange oil distilled to give 2-nitro-*N*-(*t*-butyl)aniline (18.5 g, 95%) as an orange oil, b.p. 80–82 °C at 0.05 mmHg (lit.,¹⁴ 83 °C at 0.05 mmHg).

(b) The nitro-compounds were reduced to amines with reduced iron and ammonium chloride by the following typical procedure. A solution of 2-nitro-*N*-methylaniline (31.9 g, 0.21 mol) in propanol (100 ml) was added to a well stirred refluxing solution of ammonium chloride (25 g) in water (300 ml) containing reduced iron (25 g) and the reflux maintained for 3 h. The hot solution was filtered through Celite and the residue was washed well with chloroform. The filtrate was extracted with chloroform and the combined extracts were washed with water, dried (MgSO₄), and evaporated. The brown oil was distilled giving 2-amino-*N*-methylaniline (72%), b.p. 90–94 °C at 0.1 mmHg (lit.,¹² 245–248 °C at 736 mmHg). In a similar manner was obtained 2-amino-*N*-isopropylaniline (84%), b.p. 74–76 °C at 0.1 mmHg (lit.,¹³ 70–72 °C at 0.1 mmHg), and 2-amino-*N*-(*t*-butyl)aniline (68%), b.p. 106 °C at 0.3 mmHg (lit.,¹⁴ 70 °C at 0.2 mmHg).

(c) *Dihydrobenzimidazoles (21).* To the appropriate *o*-

phenylenediamine (0.1 mol) in methanol (50 ml) was added 2-nitrobenzaldehyde (15.1 g, 0.1 mol) or 5-chloro-2-nitrobenzaldehyde (18.55 g, 0.1 mol) and the mixture was refluxed for 1 h. On cooling, the product generally crystallised as deep red-orange crystals in high yield to give the following products: (i) 1-methyl-2-(2-nitrophenyl)-2,3-dihydrobenzimidazole (21a) (99.5%), m.p. 143–145 °C (lit.,¹⁵ 144 °C); (ii) 1-isopropyl-2-(2-nitrophenyl)-2,3-dihydrobenzimidazole (21c) as an orange oil which was used without further purification; (iii) 2-(2-nitrophenyl)-1-(*t*-butyl)-2,3-dihydrobenzimidazole (21e) (98%) obtained as a viscous dark red oil and used directly; and (iv) 2-(5-chloro-2-nitrophenyl)-1-methyl-1,2-dihydrobenzimidazole (21b) as orange crystals used directly without further purification.

Nitrophenylbenzimidazoles (15).—The dihydrobenzimidazoles (21) were oxidised by elution of the dihydro-compound (10–20 g) through a column of alumina with toluene to give (i) 1-methyl-2-(2-nitrophenyl)benzimidazole (15a) (71%) as yellow crystals, m.p. 135–137 °C (lit.,¹⁵ 134–136 °C); (ii) 1-isopropyl-2-(2-nitrophenyl)benzimidazole (15b) (36%) as yellow crystals from ethanol, m.p. 140 °C (Found: C, 68.5; H, 5.8; N, 14.6. $C_{16}H_{13}N_3O_2$ requires C, 68.3; H, 5.4; N, 14.9%), δ (CDCl₃) 1.46d (*J* 7 Hz, 2Me), 4.25 septet (*J* 7 Hz, CH), and 7.0–8.1 (m, aromatic); (iii) 2-(2-nitrophenyl)-1-(*t*-butyl)benzimidazole (15c) (66%), as pale yellow crystals from ethanol, m.p. 191–192 °C (Found: C, 69.1; H, 5.6; N, 14.4. $C_{17}H_{17}N_3O_2$ requires C, 69.2; H, 5.8; N, 14.2%), δ (CDCl₃) 1.60s (Me) and 7.2–8.4 (m, aromatic); and (iv) 2-(5-chloro-2-nitrophenyl)-1-methylbenzimidazole (5-chloro derivative of 15a) (36%) as yellow crystals from ethanol, m.p. 144–145 °C (Found: C, 58.3; H, 3.6; N, 14.8. $C_{14}H_{10}ClN_3O_2$ requires C, 58.4; H, 3.5; N, 14.6%), δ (CDCl₃) 3.51s (Me) and 7.15–8.15 (m, aromatic).

2-(5-Dimethylamino-2-nitrophenyl)-1-methylbenzimidazole [5-NMe Derivative of (15a)].—A mixture of 2-(5-chloro-2-nitrophenyl)-1-methylbenzimidazole (11.5 g), dimethylamine hydrochloride (12.0 g) in water (5 ml), and sodium hydrogencarbonate (8 g) in pyridine (100 ml) was refluxed overnight. The solution was poured into ice-water and the precipitate was filtered off, washed well with water, and recrystallised from ethanol to give pale yellow crystals (11.2 g, 92.5%), m.p. 123–125 °C (Found: C, 64.6; H, 5.5; N, 18.8. $C_{16}H_{16}N_4O_2$ requires C, 64.85; H, 5.4; N, 18.9%), δ (CDCl₃) 2.88s (NMe₂), 3.71s (Me), and 6.8–8.1 (m, aromatic).

Azides.—(a) The above nitrophenylbenzimidazoles were reduced with reduced iron and ammonium chloride as described above to give the following amines: 2-(2-amino-phenyl)-1-methylbenzimidazole (87%) as white crystals from ethanol, m.p. 136–137 °C (lit.,¹⁶ 138 °C); 2-(2-amino-phenyl)-1-isopropylbenzimidazole (13b) (82%) as white crystals from ethanol, m.p. 134–135 °C (Found: C, 76.2; H, 6.7; N, 17.1. $C_{16}H_{17}N_3$ requires C, 76.5; H, 6.8; N, 16.7%); 2-(2-amino-phenyl)-1-(*t*-butyl)benzimidazole (13c) (92%) as white crystals from ethanol, m.p. 145–146 °C (Found: C, 76.75; H, 7.0; N, 15.7. $C_{17}H_{18}N_3$ requires C, 77.05; H, 7.2; N, 15.9%); 2-(2-amino-5-dimethylamino-phenyl)-1-methylbenzimidazole (5-NMe₂ derivative of 13a) (80%) as white crystals from ethanol, m.p. 118–120 °C (Found: C, 72.1; H, 6.8; N, 21.1. $C_{16}H_{18}N_4$ requires C, 72.2; H, 6.8; N, 21.0%).

(b) The above amines were converted into the azides by the following typical procedure. 2-(2-Aminophenyl)-1-isopropylbenzimidazole (7.0 g) in concentrated hydrochloric acid (15 ml) and water (50 ml) was diazotised with sodium

nitrite (3.0 g) in water (10 ml) at 0 °C. This solution was run into an ice-cold solution of sodium azide (4.0 g) and sodium acetate (20 g) in water (150 ml). The oil formed was extracted with ether and the extract was washed, dried (MgSO_4), and evaporated, and the residue chromatographed on alumina. Elution with dichloromethane gave 2-(2-azidophenyl)-1-isopropylbenzimidazole (14b) (5.6 g, 72.5%) as an oil, ν_{max} (liquid film) 2120 cm^{-1} (N_3), $\delta(\text{CDCl}_3)$ 1.52 (d, J 7 Hz, Me), 4.27 (septet, J 7 Hz, CH), and 6.9–8.0 (m, aromatic). In a similar manner was obtained 2-(2-azidophenyl)-1-methylbenzimidazole (14a) (78%), m.p. 98–100 °C (Found: C, 67.4; H, 4.5; N, 28.1. $\text{C}_{14}\text{H}_{11}\text{N}_3$ requires C, 67.5; H, 4.45; N, 28.1%), ν_{max} (Nujol) 2100 cm^{-1} (N_3); 2-(2-azidophenyl)-1-(*t*-butyl)benzimidazole (14c) (61%), m.p. 143–144 °C (decomp.) (Found: C, 70.15; H, 5.9; N, 24.35. $\text{C}_{17}\text{H}_{17}\text{N}_3$ requires C, 70.2; H, 5.9; N, 24.1%), ν_{max} (Nujol) 2150 and 2075 cm^{-1} (N_3); 2-(2-azido-5-dimethylaminophenyl)-1-methylbenzimidazole (5-NMe₂ derivative of 14a) (79%), m.p. 139–140 °C (decomp.) (Found: C, 65.6; H, 5.35; N, 29.1. $\text{C}_{16}\text{H}_{18}\text{N}_4$ requires C, 65.7; H, 5.5; N, 28.75%); ν_{max} (Nujol) 2120 cm^{-1} (N_3).

Decomposition of Azides and Deoxygenation of Nitro-compounds.—The methods described above for the azido- and nitro-benzothiazoles were adopted, giving the products indicated in Table 2. The products were obtained by elution of the reaction mixtures (after removal of reaction solvents) through an alumina column using solvents increasing in polarity from toluene to diethyl ether to chloroform. The products, in order of elution, showed the following characteristics.

(a) From 1-methyl-2-(2-nitrophenyl)- (15a) or 2-(2-azido-phenyl)-1-methylbenzimidazole (14a). 5-Methyl-5H-benzimidazo[3,2-*b*]indazole (16a) was eluted with toluene as yellow crystals, m.p. 183–184 °C (from ethyl acetate) (Found: C, 75.9; H, 5.2; N, 19.0. $\text{C}_{14}\text{H}_{11}\text{N}_3$ requires C, 76.0; H, 5.0; N, 19.0%), $\delta(\text{CF}_3\text{COOD})$ 4.39 (s, Me) and 7.4–8.4 (m, aromatic). Elution with toluene-diethyl ether (1 : 1 v/v) gave 2-(2-aminophenyl)-1-methylbenzimidazole, while chloroform gave 2,2'-bis-(1-methylbenzimidazol-2-yl)azobenzene (9), m.p. 253–255 °C [orange crystals from light petroleum (b.p. 80–100 °C)] (Found: C, 76.1; H, 5.0; N, 18.9. $\text{C}_{28}\text{H}_{22}\text{N}_6$ requires C, 76.0; H, 5.0; N, 19.0%), $\delta(\text{CDCl}_3)$ 3.43 (s, Me) and 7.03–7.97 (m, aromatic), m/e 442 (M^+).

(b) From 2-(2-azidophenyl)-1-isopropylbenzimidazole (14b). Elution with toluene gave 5-isopropyl-5H-benzimidazo[3,2-*b*]indazole (16b), m.p. 125–126 °C [from light petroleum (b.p. 80–100 °C)] (Found: C, 76.9; H, 6.0; N, 17.0. $\text{C}_{16}\text{H}_{15}\text{N}_3$ requires C, 77.1; H, 6.1; N, 16.85%), $\delta(\text{CDCl}_3)$ 1.50 (d, J 7 Hz, Me), 4.68 (septet, J 7 Hz, CH), 6.95–7.5 (m, 4 aromatic H), and 7.6–8.2 (m, 4 aromatic H). Elution with toluene-diethyl ether (1 : 1 v/v) afforded 2-(2-amino-phenyl)-1-isopropylbenzimidazole. Elution with toluene gave 6,6-dimethyl-5,6-dihydrobenzimidazo[1,2-*c*]quinazoline (22), m.p. 128–130 °C [from light petroleum (b.p. 80–100 °C)] (Found: C, 77.4; H, 5.9; N, 16.7. $\text{C}_{16}\text{H}_{15}\text{N}_3$ requires C, 77.1; H, 6.1; N, 16.85%), ν_{max} (Nujol) 3340 cm^{-1} (NH), δ 1.84 (s, Me), 5.3 (br, NH), 6.4–8.0 (m, aromatic). Elution with chloroform gave 2,2'-bis-(1-isopropyl-

benzimidazol-2-yl)azobenzene (10), m.p. 222–224 °C [orange crystals from light petroleum (b.p. 80–100 °C)] (Found: C, 77.0; H, 6.1; N, 16.9. $\text{C}_{32}\text{H}_{30}\text{N}_6$ requires C, 77.1; H, 6.1; N, 16.85%), $\delta(\text{CDCl}_3)$ 1.47 (d, J 7 Hz, Me), 4.35 (septet, J 7 Hz, CH), and 7.07–7.94 (m, aromatic), m/e 498 (M^+).

(c) From 2-(2-azidophenyl)-1-(*t*-butyl)benzimidazole. With toluene-diethyl ether (3 : 1 v/v) 5-(*t*-butyl)-5H-benzimidazo[3,2-*b*]indazole (16c) was eluted as a pale straw oil which was further purified by preparative t.l.c. on silica (Found: C, 77.6; H, 6.65; N, 15.9. $\text{C}_{17}\text{H}_{17}\text{N}_3$ requires C, 77.5; H, 6.5; N, 16.0%), $\delta(\text{CDCl}_3)$ 2.0 (s, Me) and 7.25–8.65 (m, aromatic). With diethyl ether as eluant was obtained 2,2'-bis-[1-(*t*-butyl)benzimidazol-2-yl]azobenzene (11), m.p. 282–283 °C (orange crystals from toluene) (Found: C, 77.7; H, 6.6; N, 16.0. $\text{C}_{34}\text{H}_{34}\text{N}_6$ requires C, 77.5; H, 6.5; N, 16.0%), $\delta(\text{CF}_3\text{COOD})$ 1.89 (s, Me) and 7.2–8.3 (m, aromatic).

(d) From 2-(2-azido-5-dimethylaminophenyl)-1-methylbenzimidazole [5-NMe₂ derivative of (14a)]. With toluene as eluant a trace of an orange solid, m.p. 193–195 °C [m/e 528 (M^+)] which was probably 2,2'-bis-(1-methylbenzimidazol-2-yl)-4,4'-bis(dimethylamino)azobenzene [4,4'-(NMe₂)₂ derivative of (9)] was eluted, followed by 2-dimethylamino-benzimidazo[1,2-*c*]quinazoline, as white crystals from light petroleum (b.p. 80–100 °C), m.p. 207–208 °C (Found: C, 73.2; H, 5.4; N, 21.4. $\text{C}_{16}\text{H}_{14}\text{N}_4$ requires C, 73.3; H, 5.4; N, 21.35%), m/e 262 (M^+), $\delta(\text{CDCl}_3)$ 3.05 (s, NMe₂), 6.98–8.1 (m, aromatic), and 8.77 (s, H-6). Further elution with diethyl ether gave 2-(2-amino-5-dimethylaminophenyl)-1-methylbenzimidazole, identical with the sample reported above (m.p., mixed m.p., and i.r. spectrum).

[0/196 Received, 4th February, 1980]

REFERENCES

- Part 8, J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1980, 982.
- Preliminary communication (in part), I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 929.
- D. W. Hein, R. J. Alheim, and J. J. Leavitt, *J. Amer. Chem. Soc.*, 1957, **79**, 427.
- F. S. Babichev, L. A. Kirpianova, and T. A. Dashevskaya, *Ukrain. khim. Zhur.*, 1966, **32**, 706 (*Chem. Abs.*, 1966, **65**, 13,681).
- B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Suschitzky, and P. T. Gallagher, *Angew. Chem. Internat. Edn.*, 1979, **18**, 900.
- E. g. P. K. Claus, P. Hofbauer, and W. Reider, *Tetrahedron Letters*, 1974, 3319.
- G. S. Reddy and K. K. Reddy, *Current. Sci.*, 1976, **45**, 535.
- J. H. Boyer and C.-C. Lai, *J.C.S. Perkin I*, 1977, 74.
- J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1977, 2194.
- J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.
- I. I. Grandberg, A. N. Kost, and L. S. Yaguzhinskii, *Zhur. obschei Khim.*, 1959, **29**, 2537.
- O. Fischer and H. O. Veiel, *Ber.*, 1905, **38**, 320.
- A. Rossi, A. Hunger, J. Kebrle, and J. Hoffmann, *Helv. Chim. Acta*, 1960, **43**, 1298.
- J. W. Clark-Lewis and J. Moody, *Austral. J. Chem.*, 1970, **23**, 1229.
- A. V. El'tsov and Kh. L. Muravich-Aleksandr, *Zhur. org. Khim.*, 1965, **1**, 1307.
- F. Montanari and R. Passerini, *Bull. sci. facolta chim. ind. Bologna*, 1953, **11**, 42 (*Chem. Abs.*, 1954, **48**, 6437).