Ring Contraction of 1,2,4-Benzoxadiazines to Benzoxazoles[1]

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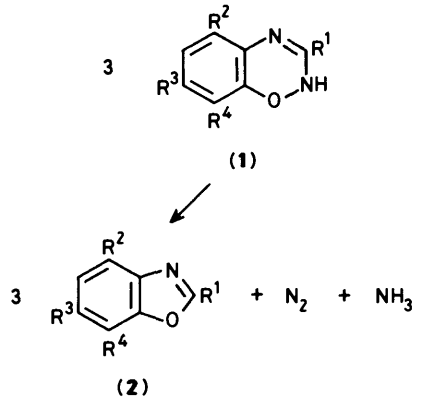
1,2,4-Benzoxadiazines (**1**) undergo a ring contraction to benzoxazoles (**2**) on heating. Other products of the reaction have been identified as nitrogen and ammonia. A mechanism is suggested for this reaction which involves (*i*) electrocyclic ring opening to an *o*-benzoquinone imine, (*ii*) recyclisation to a diaziridine, and (*iii*) extrusion of a nitrene fragment. Evidence is presented which is consistent with this proposal: thus, the benzoxazole (**7**) is produced on heating 3,5-di-t-butyl-*o*-benzoquinone with benzamidine and 4-nitrobenzoylnitrene is intercepted as the ylide (**11**) from the thermolysis of the substituted benzoxadiazine (**10**).

We have previously described two general routes to the little investigated 1,2,4-benzoxadiazine ring system and have revised some structures proposed for them in the early literature.[2] In the course of our work with 1,2,4-benzoxadiazines, some new examples of which are reported here, the most interesting reaction we uncovered was their thermal ring contraction to benzoxazoles.[1] We now provide details of the investigation of this reaction.

When 1,2,4-benzoxadiazines (**1**) were heated in chlorobenzene at reflux under nitrogen for 2 h, benzoxazoles (**2**) were formed by the thermal extrusion of nitrene (NH). The fate of this fragment was to become nitrogen and ammonia and the stoicheiometry shown in Scheme 1 is assumed.

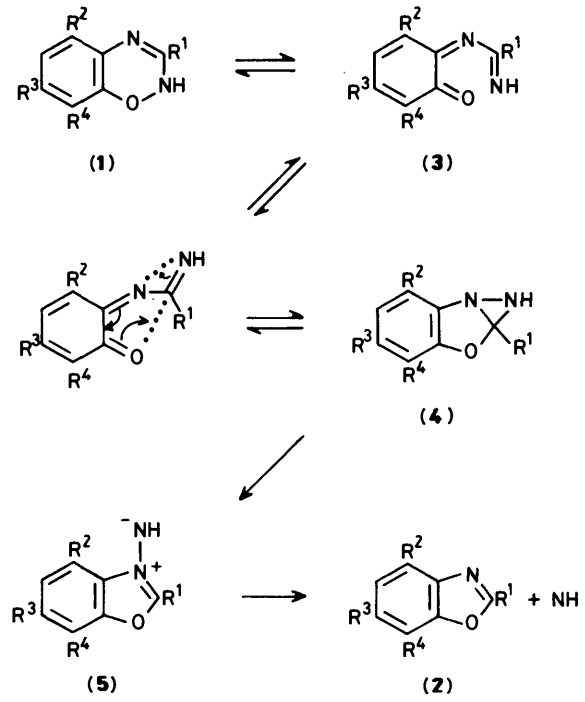


Scheme 1.

The results for this thermal reaction are summarised in Table 1. Yields were not optimised but, in the absence of side reactions, were often high. The reaction is of some preparative value, particularly for benzoxazoles with several substituents, since the starting material is a substituted aniline rather than the usual 2-aminophenol.

The ring contraction proceeded cleanly, though slowly, in boiling benzene and was conveniently fast in chlorobenzene at 135 °C. It was insensitive to changes in solvent: benzoxadiazine (**1b**) was converted into benzoxazole (**2b**) by heating in xylene, chlorobenzene, butan-2-ol, hexafluorobenzene, or acetic anhydride, and by heating in the melt at 170 °C. There was no discernible acid catalysis since benzoxadiazine (**1a**) was unchanged in trifluoroacetic acid at room temperature and on heating the solution under reflux it was only slowly converted into the benzoxazole (**2a**). One of the volatile products, ammonia, was readily detected by smell and by Nessler's reagent and was estimated by titration and with an amino-acid analyser. The yield of ammonia, based on the stoicheiometry of Scheme 1, was high in the decomposition of compounds (**1b**) and (**1d**). The other product was shown to be nitrogen by mass spectrometry and its yield was estimated by collection with a Töpler pump.[3] Aniline was also detected in low yield as a product of a pyrolysis carried out in benzene: compound (**1b**) gave aniline (12%) when heated in benzene for 18 h. The formation of these products is consistent with the generation of a reactive intermediate capable of delivering an NH fragment to the solvent; this fragment was not intercepted, however, when reactions were performed in dimethyl sulphoxide or in the presence of dibenzoylethylene. Evidence for the formation of its dimer, di-imide (HN=NH), was sought by carrying out a reaction in the presence of dibenzoylacetylene and looking for reduction products, but they were not detected.

A possible mechanism for this unusual ring contraction is shown in Scheme 2. A quinone imine (**3**) is generated by



Scheme 2.

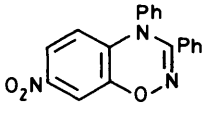
Table 1. Products of pyrolysis of benzoxadiazines (**1**)

	Benzoxadiazine (**1**)					
	R^1	R^2	R^3	R^4	Conditions[a]	Products (% yield)
a;	C_6H_4Me-4	H	H	H	PhCl/2 h	(**2a**) (80); NH_3 (18)
					PhH/37 h	(**2a**) (79)
					CF_3CO_2H aq./18 h	(**2a**) (38)
b;	C_6H_4Me-4	H	Cl	H	PhCl/2 h	(**2b**) (78); NH_3 (40)
					$C_6H_4(Me)_2$/2 h	(**2b**) (80); NH_3 (31)
					C_6F_6/21 h	(**2b**) (78)
					EtCH(OH)Me/18 h	(**2b**) (50); NH_3 (133)
					Ac_2O/15 min	(**2b**) (54)
					170 °C/2 h[b]	(**2b**) (50)
c;	C_6H_4Me-4	H	NO_2	H	PhCl/2 h	(**2c**) (33)
d;	C_6H_4Me-4	H	H	NO_2	PhCl/2 h	(**2d**) (80); NH_3 (88) N_2 (76)
e;	C_6H_4Me-4	Ph	H	H	PhCl/2 h	(**2e**) (77); NH_3[c]
f;	C_6H_4Me-4	Cl	H	NO_2	PhCl/2 h	(**2f**) (74)
g;	CO_2Et	H	H	H	PhCl/2 h	(**2g**) (16)
h;	CO_2Et	H	Cl	H	PhCl/2 h	(**2h**) (20)
j;	CO_2Et	H	NO_2	H	PhCl/2 h	(**2j**) (56)
k;	CO_2Et	Cl	H	H	PhCl/2 h	(**2k**) (15)
m;	CO_2Et	Br	H	H	PhCl/2 h	(**2m**) (60)
n;	CO_2Et	Cl	Cl	H	PhCl/2 h	(**2n**) (35)
o;	CO_2Et	Br	NO_2	H	PhCl/2 h	(**2o**) (60)

[a] All reactions in solution were carried out under reflux under N_2. [b] Pyrolysis of neat sample (melt) under N_2. [c] NH_3 was detected by means of Nessler's reagent.

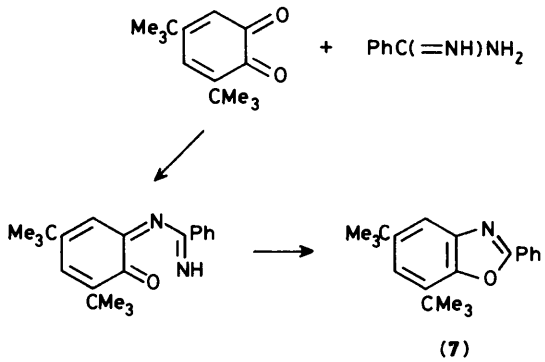
electrocyclic ring opening of the 2*H*- tautomer of the benzoxadiazine, the weak N–O bond being broken. This then rearranges as shown to the diaziridine (**4**) which can aromatise to the *N*-imide (**5**). The rearrangment of (**3**) to (**4**) could be a concerted intramolecular $_{\pi}4_a + {}_{\pi}2_a$ reaction, the new N–N and C–O bonds being formed as the C=NH bond is twisted out of the molecular plane. Antarafacial–antarafacial cycloadditions are rare but in this molecule the geometry for the reaction is quite favourable. A similar mechanism has been proposed for the rearrangement of octamethylcyclo-octatraene to octamethylsemibullvalene.[4] An analogy for the reverse of the conversion of (**3**) into (**4**) is provided by the pyrolysis of the adduct of phthalimidonitrene and benzofuran, in which an *ortho*-quinonoid system is generated.[5]

Attempts were made to substantiate the early steps in the mechanism of Scheme 2 by producing similar intermediates by independent routes and determining their fate. Three experiments of this type were carried out, as follows. (*i*) The first step in the proposed mechanism requires the 2*H*- tautomer of the benzoxadiazine for electrocyclic ring opening. This is supported by the much greater stability of 7-nitro-3,4-diphenyl-1,2,4-benzoxadiazine (**6**)* which was unchanged when heated in chlorobenzene under the standard conditions. It decomposed



(**6**)

slowly in boiling decalin but by a different pathway to yield benzonitrile as the volatile component. (*ii*) A reaction between 3,5-di-t-butyl-*o*-benzoquinone and benzamidine was designed to produce an *o*-quinone imine intermediate of the type shown in Scheme 2. When the two components were heated together in benzene, a compound which was identified as the benzoxazole (**7**) was produced. Since the *o*-quinone imine is a likely intermediate in the reaction (Scheme 3) this result is consistent



(**7**)

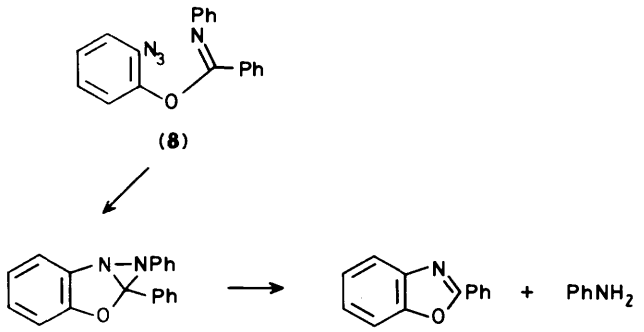
Scheme 3.

with the proposed mechanism. (*iii*) An attempt to model the diaziridine intermediate (**4**) was made by investigating the thermolysis of the azide (**8**). The products obtained were 2-phenylbenzoxazole and aniline, which are again consistent with the proposed mechanism, and which can be envisaged as being formed from a diaziridine intermediate (Scheme 4).

Finally in this proposed sequence is the conversion of the *N*-imide (**5**) into the benzoxazole (**2**) by heterolysis of the N–N bond. The NH fragment, presumably never free, has to trimerise, for example to HN=N–NH_2, and then cleave to give nitrogen and ammonia. Butan-2-ol (b.p. 98 °C) was chosen as a solvent for the decomposition of (**1b**) since there was then the possibility that the imide (**5**) could be reduced to benzoxazole (**2b**) and ammonia; indeed, in this reaction the yield of ammonia increased significantly, to 133% based on the stoicheiometry of Scheme 1.

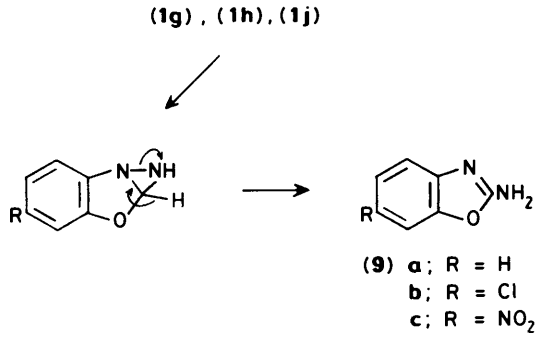
Further evidence for the mechanism of Scheme 2, and

* This compound is described as a 6-nitro-3,4-diphenyl-1,2,4-benzoxadiazine[6] but, for reasons discussed in ref. 2, it has been reassigned as the 7-nitro isomer



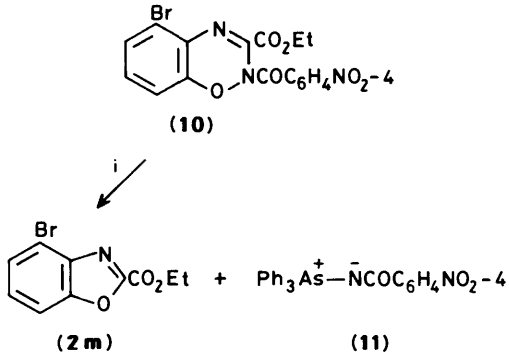
Scheme 4.

particularly for the intermediate (**4**; R^1 = H) is provided by the observation[2] that on mild basic hydrolysis and decarboxylation, ethyl 7-nitro-1,2,4-benzoxadiazine-3-carboxylate (**1j**) gave 2-amino-6-nitrobenzoxazole (**9c**) in high yield. This ring contraction with *retention* of both nitrogen atoms could proceed by the mechanism of Scheme 2 up to the diaziridine intermediate (**4**; R^1 = H) where there is now the possibility of aromatisation by hydrogen migration rather than by C–N bond cleavage (Scheme 5). We have shown that ethyl benzoxadiazine-3-carboxylate (**1g**) and its 7-chloro derivative (**1h**) also give the corresponding 2-aminobenzoxazoles (**9a**) and (**9b**) on treatment with aqueous sodium hydroxide at room temperature.



Scheme 5.

Clearly the mechanism of Scheme 2 would be strengthened by evidence for the *N*-imide intermediate (**5**). Benzoxazolium *N*-imides are unknown and our attempts to prepare them by reaction of 2-(*p*-tolyl)benzoxazole (**2a**) or benzoxazole itself with *O*-mesitylsulphonylhydroxylamine or with hydroxylamine-*O*-sulphonic acid followed by benzoyl chloride were unsuccessful. We decided therefore to study the thermolysis of a 1,2,4-benzoxadiazine bearing an electron-withdrawing substituent at N-2 which would stabilise the *N*-imide (**5**) or control its fate in a predictable way. Acylation of the benzoxadiazines was difficult because of their weak nucleophilicity, but a 4-nitrobenzoyl derivative (**10**) of the benzoxadiazine (**1m**) was isolated in moderate yield (60%) from a reaction carried out with 4-nitrobenzoyl chloride in pyridine over 3 days. Acylation was deemed to have taken place on the more nucleophilic N-2, rather than on N-4. The bulky substituent at C-5 can be expected to direct the substituent to N-2 [an attempted acylation of the benzoxadiazine (**1g**), with no substituent at C-5, gave a mixture of isomeric monoacylation products]. When heated in chlorobenzene for 3 h the benzoxadiazine (**10**) was converted into the benzoxazole (**2m**) and 4-nitrobenzamide, the latter being isolated in 78% yield. This is in accord with the mechanism of Scheme 2. Further evidence was provided by the thermolysis of compound (**10**) in the presence of copper bronze and triphenylarsine (Scheme 6). Besides the benzoxazole (**2m**),



Scheme 6. *Reagents*: i, Ph_3As, Cu

the imide (**11**) was isolated in good yield. This is the product to be expected from the interception of 4-nitrobenzoylnitrene by triphenylarsine.[7]

In summary, although we have not isolated any of the intermediates shown in Scheme 2, several experiments provide evidence in support of this route as the most likely one for this unusual ring contraction.

Experimental

The benzoxadiazines (**1a**)—(**1j**) were prepared as described earlier;[2] compounds (**1k**)—(**1o**), which have not previously been reported, were prepared by the oxidation of the corresponding amidoximes as described below.

Benzoxadiazines (**1m**), (**1n**), *and* (**1o**). *General Procedure.*—(a) *Ethyl (arylamino)hydroxyiminoacetates.* The appropriate (arylamino)oxoacetate was heated with phosphorus pentachloride to give the corresponding imidoyl chloride. This, without further purification, was added to a solution of hydroxylamine (in excess) in ethanol at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h then at 20 °C for 2 h. The solvent was distilled off and the residue was partitioned between water and dichloromethane. The organic solution was dried and the solvent was evaporated off to leave the residual title compound, which was purified by crystallisation.

(b) *Oxidative cyclisation.* A solution of *N*-chlorobenzotriazole (1.7 g, 0.11 mol) in dichloromethane (30 ml) was added dropwise during 15 min to a solution of the oxime (0.10 mol) in dichloromethane (50 ml) at −78 °C. The solution was stirred for 1 h and then warmed to room temperature and stirred for a further 2 h. It was filtered through Celite and the filtrate was evaporated to dryness. The residual benzoxadiazine was purified by column chromatography (silica), the product being eluted with chloroform–acetone (19:1).

The following were prepared by this procedure:

*Ethyl 5-bromo-*4H-1,2,4-*benzoxadiazine-3-carboxylate* (**1m**). (a) *Ethyl (2-bromophenylamino)hydroxyiminoacetate.* This was prepared (60%) from ethyl (2-bromophenylamino)oxoacetate[8] as described above, and had m.p. 135—136 °C (from ethanol) (Found: C, 41.6; H, 3.8; N, 9.6. $C_{10}H_{11}BrN_2O_3$ requires C, 41.8; H, 3.8; N, 9.8%).

(b) The amidoxime gave, by the procedure described above, yellow needles of the *benzoxadiazine* (**1m**) (1.70 g, 60%), m.p. 76—77 °C (from dichloromethane–hexane) (Found: C, 42.5; H, 3.3; N, 9.9. $C_{10}H_9BrN_2O_3$ requires C, 42.1; H, 3.2; N, 9.8%); $\nu_{max.}$(Nujol) 3 400 (NH) and 1 720 cm^{-1} (C=O); δ($CDCl_3$) 1.40 (3 H, t, *J* 7 Hz), 4.45 (2 H, q, *J* 7 Hz), and 6.50—7.40 (4 H, m).

*Ethyl 5,7-dichloro-*4H-1,2,4-*benzoxadiazine-3-carboxylate* (**1n**). (a) *Ethyl (2,4-dichlorophenylamino)hydroxyiminoacetate.* This was prepared (45%) from ethyl (2,4-dichlorophenylamino)oxoacetate,[9] and had m.p. 182 °C (from ethanol) (Found:

Table 2. Benzoxazoles (**2**)

	R¹	R²	R³	R⁴	M.p. (°C)[a]	Formula	Found (required) C	H	N
(2a)	C_6H_4Me-4	H	H	H	116—117[b]				
(2b)	C_6H_4Me-4	H	Cl	H	126	$C_{14}H_{10}ClNO$	69.3 (69.0)	4.4 (4.1)	5.7 (5.75)
(2c)	C_6H_4Me-4	H	NO_2	H	159—161	$C_{14}H_{10}N_2O_3$	65.7 (66.1)	4.1 (3.9)	
(2d)	C_6H_4Me-4	H	H	NO_2	156	$C_{14}H_{10}N_2O_3$	65.9 (66.1)	4.1 (3.9)	11.0 (11.0)
(2e)	C_6H_4Me-4	Ph	H	H	131	$C_{20}H_{15}NO$	83.9 (84.2)	5.4 (5.3)	5.0 (4.9)
(2f)	C_6H_4Me-4	Cl	H	NO_2	222—223	$C_{14}H_9ClN_2O_3$	58.1 (58.2)	3.4 (3.1)	9.5 (9.7)
(2g)	CO_2Et	H	H	H	101[c]				
(2h)	CO_2Et	H	Cl	H	68—70[d]	$C_{10}H_8ClNO_3$	53.4 (53.2)	3.6 (3.6)	6.2 (6.2)
(2j)	CO_2Et	H	NO_2	H	99—100	$C_{10}H_8N_2O_5$	50.4 (50.8)	3.5 (3.4)	11.9 (11.9)
(2k)	CO_2Et	Cl	H	H	74—75[d]	$C_{10}H_8ClNO_3$	52.9 (53.2)	3.2 (3.6)	5.8 (6.2)
(2m)	CO_2Et	Br	H	H	86[d]	$C_{10}H_8BrNO_3$	44.7 (44.5)	3.1 (3.0)	4.9 (5.2)
(2n)	CO_2Et	Cl	Cl	H	92	$C_{10}H_7Cl_2NO_3$	45.9 (46.2)	2.8 (2.7)	5.3 (5.4)
(2o)	CO_2Et	Br	NO_2	H	109	$C_{10}H_7BrN_2O_3$	37.8 (38.1)	2.3 (2.2)	8.8 (8.9)

[a] Purified by crystallisation from ethanol, except where indicated. [b] Lit. m.p. 116—117 °C: S. Skraup, *Justus Liebigs Ann. Chem.*, 1919, **419**, 1. [c] Lit. m.p. 101 °C: K. Dichore, K. Sasse, and K.-D. Bode, *Justus Liebigs Ann. Chem.*, 1970, **733**, 70. [d] Purified by sublimation.

C, 43.1; H, 3.5; N, 10.0. $C_{10}H_{10}Cl_2N_2O_3$ requires C, 43.3; H, 3.6; N, 10.1%).

(b) Oxidation of this amidoxime gave the *benzoxadiazine* (**1n**) (65%), m.p. 80 °C (from ethanol) (Found: C, 43.7; H, 3.1; N, 10.3. $C_{10}H_8Cl_2N_2O_3$ requires C, 43.7; H, 2.9; N, 10.2%); $\nu_{max.}$(Nujol) 3 400 (NH) and 1 718 cm^{-1} (C=O); δ($CDCl_3$) 1.40 (3 H, t, *J* 7 Hz), 4.42 (2 H, d, *J* 7 Hz), 6.60 (1 H, d, *J* 2 Hz), and 6.89 (1 H, d, *J* 2 Hz).

*Ethyl 5-bromo-7-nitro-*4H-1,2,4-*benzoxadiazine-3-carboxylate* (**1o**). (a) *Ethyl (2-bromo-4-nitrophenylamino)hydroxyiminoacetate.* Ethyl (2-bromo-4-nitrophenylamino)oxoacetate was prepared by the method of ref. 9 and, without characterisation, was converted (60%) into the *oxime*, m.p. 186 °C (from ethanol) (Found: C, 36.3; H, 3.2; N, 12.4. $C_{10}H_{10}BrN_3O_5$ requires C, 36.2; H, 3.0; N, 12.6%).

(b) Oxidation of the amidoxime gave the *benzoxadiazine* (**1o**) (80%), m.p. 150 °C (from ethanol) (Found: C, 36.4; H, 2.5; N, 12.6. $C_{10}H_8BrN_3O_5$ requires C, 36.4; H, 2.4; N, 12.7%); $\nu_{max.}$(Nujol) 3 400 (NH) and 1 718 cm^{-1} (C=O); δ($CDCl_3$) 1.43 (3 H, t, *J* 7 Hz), 4.52 (2 H, q, *J* 7 Hz), 7.1—7.4 (1 H, br), 7.57 (1 H, d, *J* 2 Hz), and 8.10 (1 H, d, *J* 2 Hz).

*Ethyl 5-chloro-*4H-1,2,4-*benzoxadiazine-3-carboxylate* (**1k**). Ethyl (2-chlorophenylamino)hydroxyiminoacetate was prepared from 2-chloroaniline and ethyl chloroglyoxylate oxime by the method described in ref. 2; it was not characterised. Oxidation gave the *benzoxadiazine* (**1k**) (60%), m.p. 70 °C (from ethanol) (Found: C, 50.1; H, 3.8; N, 11.4. $C_{10}H_9ClN_2O_3$ requires C, 49.9; H, 3.8; N, 11.6%); δ($CDCl_3$) 1.40 (3 H, t, *J* 7 Hz), 4.45 (2 H, q, *J* 7 Hz), and 6.50—7.00 (4 H, m).

Pyrolysis of the Benzoxadiazines in Chlorobenzene. General Procedure.—A solution of the benzoxadiazine (1.0 mmol) in chlorobenzene (20 ml) under nitrogen was heated under reflux for 2 h (and for a further 2 h if any starting material was detected by t.l.c.). The solvent was then distilled off and layer chromatography (silica) with chloroform–acetone (50:1) as the eluant was used to isolate the benzoxazoles, which were obtained in the yields shown in Table 1. M.p.s and analytical data for these benzoxazoles are listed in Table 2.

Determination of Nitrogen Evolved.—The benzoxadiazine (**1d**) (0.144 g, 0.53 mmol) in chlorobenzene (5 ml) was heated in an evacuated sealed tube at 140 °C for 3 h. The reaction mixture was cooled and the non-condensable gases (liquid nitrogen cooling) were collected in the gas burette of a Töpler pump;[3] the volume at S.T.P. was 2.3 ml. The gas was identified as nitrogen by mass spectrometry. Layer chromatography of the residue gave 7-nitro-2-(*p*-tolyl)benzoxazole (**2d**) (0.085 g, 80%) and recovered benzoxadiazine (0.035 g). On the basis of the mass of benzoxadiazine consumed and the stoicheiometry of Scheme 1 the yield of nitrogen was 76%.

Determination of Ammonia Evolved.—(a) *Pyrolysis in chlorobenzene.* The benzoxadiazine (**1d**) (0.387 g, 1.50 mmol) was heated in dry chlorobenzene (60 ml) under reflux for 1 h. A stream of nitrogen was passed through the solution and through two tubes each containing sulphuric acid (0.1M; 5.0 ml). Titration of the combined acid solutions with standard aqueous sodium hydroxide (0.05M) required 31.2 ml; thus the amount of ammonia evolved was 0.44 mmol (88% based on the relationship in Scheme 1).

(b) *Pyrolysis in xylene.* An analogous pyrolysis of the benzoxadiazine (**1d**) (0.387 g, 1.50 mmol) in xylene (60 ml) for 2 h gave 0.46 mmol (92%) ammonia.

(c) *Pyrolysis in butan-2-ol.* The benzoxadiazine (**1b**) (0.302 g, 1.17 mmol) in dry butan-2-ol (50 ml) gave, after heating under reflux for 18 h, 0.52 mmol ammonia (133% based on the stoicheiometry shown in Scheme 1; 44% based on an equimolar relationship). The solution also gave, after evaporation and

layer chromatography, 6-chloro-2-(*p*-tolyl)benzoxazole (**2b**) (0.140 g, 50%).

Pyrolysis of Benzoxadiazine (**1b**) *in Benzene: Determination of Aniline.*—The benzoxadiazine (**1b**) (0.059 g, 0.23 mmol) was heated in dry benzene (8 ml) at 80 °C for 18 h under nitrogen. Aniline was detected and was estimated (2.4 mg, 12%) by g.l.c. comparison with an authentic specimen (Pye 104 chromatograph; Carbowax column; N_2 carrier gas; 110 °C).

Reaction of 3,5-*Di-t-butyl*-o-*benzoquinone with Benzamidine.*—Benzamidine (0.73 g, 6.1 mmol) and 3,5-di-t-butyl-*o*-benzoquinone[10] (0.98 g, 5.0 mmol) were dissolved in dry benzene. The solution was heated under reflux for 4 h under nitrogen and in the absence of light. Layer chromatography gave [with chloroform–hexane (1:1)] a blue oil which slowly solidified to crystals, m.p. 60—61 °C (from methanol) (Found: N, 4.8. $C_{21}H_{25}NO$ requires N, 4.8%); δ($CDCl_3$) 1.39 (9 H), 1.55 (9 H), 7.20—7.75 (5 H, m), and 8.10—8.40 (2 H, m); *m/z* 307 (M^+). The compound was identified as *2-phenyl-5,7-di-t-butylbenzoxazole* (**7**) by comparison with a specimen prepared (50%) from 3,5-di-t-butyl-*o*-benzoquinone and benzylamine.[11]

2-Azidophenyl N-*Phenylbenzimide* (**8**).—A solution of 2-azidophenol (1.35 g, 10.0 mmol) and *N*-phenylbenzimidoyl chloride (2.4 g, 11.0 mmol) in pyridine (20 ml) was stirred at 20 °C for 12 h. The reaction mixture was poured into an excess of hydrochloric acid (2M) and the precipitate was filtered off, washed, and dried. Chromatography (silica) of this and elution with chloroform gave the *azide* (**8**) (1.00 g, 35%), m.p. 89 °C (from ethanol) (Found: C, 72.3; H, 4.5; N, 18.1. $C_{19}H_{14}N_4O$ requires C, 72.6; H, 4.5; N, 17.8%); *m/z* 314 (M^+), 286 ($M^+ - N_2$), 195, and 180 (base).

Pyrolysis of the azide (0.32 g, 1.0 mmol) in the melt at 140 °C for 8 h under nitrogen gave 2-phenylbenzoxazole (0.11 g, 55%) and aniline (0.055 g, 60%). Pyrolysis in solution in chlorobenzene gave the same products.

2-Aminobenzoxazole (**9a**).—The benzoxadiazine (**1g**) (100 mg) was stirred at room temperature for 12 h in aqueous NaOH (0.2M; 5 ml). The solution was neutralised and extracted with dichloromethane to give 2-aminobenzoxazole (**9a**) (45 mg, 69%), m.p. 129 °C (from aqueous ethanol), which was identified by comparison with an authentic specimen.

2-Amino-6-chlorobenzoxazole (**9b**).—The benzoxadiazine (**1h**) (120 mg) was stirred with aqueous NaOH (0.2M; 5 ml) for 18 h. The solution was neutralised and extracted with dichloromethane to give the benzoxazole (**9b**) (54 mg, 64%), m.p. 184—185 °C (from aqueous ethanol), (lit.,[12] 184—185 °C).

Ethyl 5-Bromo-2-(4-nitrobenzoyl)-1,2,4-benzoxadiazine-3-carboxylate (**10**).—A solution of the benzoxadiazine (**1m**) (0.57 g, 2.0 mmol) and 4-nitrobenzoyl chloride (0.75 g, 4.0 mmol) in dry pyridine (20 ml) was kept at room temperature for 3 days. The solution was then poured into an excess of aqueous hydrochloric acid and the precipitate was filtered off. Chromatography (silica) of this and elution with chloroform–acetone (50:1) gave colourless needles of the *benzoxadiazine* (**10**) (0.52 g, 60%), m.p. 139—140 °C (from ethanol) (Found: C, 47.0; H, 2.9; N, 9.4. $C_{17}H_{12}BrN_3O_6$ requires C, 47.0; H, 2.8; N, 9.7%); $\nu_{max.}$(Nujol) 1 725 and 1 695 cm^{-1} (C=O).

Pyrolysis of the Benzoxadiazine (**10**).—(a) *In chlorobenzene.* A solution of the benzoxadiazine (**10**) (0.22 g, 0.51 mmol) in dry chlorobenzene (5 ml) was heated under reflux in a nitrogen atmosphere for 3 h. Chromatography (silica) of the crude product gave [with chloroform–acetone (50:1)] ethyl 4-bromobenzoxazole-2-carboxylate (**2m**) (0.070 g, 51%) and (with ethyl acetate) 4-nitrobenzamide (0.066 g, 78%).

(b) *With triphenylarsine and copper.* A mixture of the benzoxadiazine (**10**) (0.13 g, 0.30 mmol), triphenylarsine (0.30 g, 0.98 mmol), and copper bronze (0.1 g) was heated under nitrogen at 130 °C for 3 h. The mixture was cooled, extracted with dichloromethane, and filtered. The filtrate was evaporated to dryness and the residue was triturated with ether. The mixture was again filtered; addition of hexane to the filtrate gave triphenylarsine *N*-4-nitrobenzoylimide (**11**) (0.11 g, 80%), m.p. 193 °C (from toluene), which was identical (i.r. and mixed m.p.) to an authentic specimen.[7] The filtrate gave, by layer chromatography, the benzoxazole (**2m**) (0.060 g, 74%).

In the absence of copper bronze the products were the benzoxazole (**2m**) (53%) and 4-nitrobenzamide (60%).

References

1 Preliminary communication of part of this work, T. L. Gilchrist, C. J. Harris, M. E. Peek, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1975, 962.
2 T. L. Gilchrist, C. J. Harris, F. D. King, M. E. Peek, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2161.
3 H. Kienitz, in 'Methoden der Organischen Chemie' (Houben–Weyl), vol. 2, Georg Thieme Verlag, Stuttgart, 1953, p. 733.
4 R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 781.
5 D. W. Jones, *J. Chem. Soc., Perkin Trans. 1*, 1972, 225.
6 A. Werner and T. Herberger, *Chem. Ber.*, 1899, **32**, 2686.
7 J. I. G. Cadogan and I. Gosney, *J. Chem. Soc., Perkin Trans. 1*, 1974, 466.
8 J. J. Batch, K. P. Parry, C. F. Rowe, D. K. Lawrence, and M. J. Brown, Ger. Offen. Pat. 2,819,879.
9 R. J. Cremlyn, *J. Chem. Eng. Data*, 1974, **19**, 288.
10 W. Flaig, T. Ploetz, and H. Biergans, *Justus Liebigs Ann. Chem.*, 1955, **597**, 196.
11 E. J. Corey and K. Achiwa, *J. Am. Chem. Soc.*, 1969, **91**, 1429.
12 J. Sam and J. N. Plampin, *J. Pharm. Sci.*, 1964, **53**, 538.

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