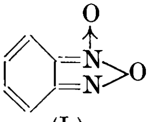
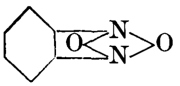
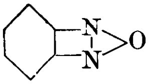
CCCCLVIII.—*The Constitution of Benzfurazan and Benzfurazan Oxide.*

By Dalziel Llewellyn Hammick, William A. M. Edwardes, and Ernest R. Steiner.

The substances of the general formula $X{<}N_2O_2$ originally prepared by Noelting and Kohn (*Chem.-Ztg.*, 1894, **18**, 1905) and by Zincke and Schwarz (*Annalen*, 1899, **307**, 28) by the action of heat on *o*-nitrobenzeneazoimides were regarded by these workers as being *o*-dinitroso-compounds. Forster and Fierz (J., 1907, **91**, 1942; where a complete list of references to previous work is given), however, drew attention to the relation of these substances to the corresponding *o*-quinonedioximes, from which they can readily be obtained by oxidation, and assigned to them a dioxime peroxide formula $X{\ll}\begin{array}{l}N{-}O\\ |\\ N{-}O\end{array}$. Green and Rowe (J., 1912, **101**, 2452) also emphasised their quinonoid nature and, on the basis of the possible mechanism of a new method of preparation that they had discovered (action of hypochlorite on *o*-nitro-amines), put forward the structure (I), benzfurazan oxide, benz*iso*oxadiazole oxide. In doing this they anticipated the structure for the dioxime peroxides established by Meisenheimer, Lange, and Lamparter (*Annalen*, 1925, **444**, 74). Green and Rowe, however, in a later paper (J., 1913, **103**, 897) abandoned the quinonoid structure for benzfurazan oxide and represented it as (II), giving the formula (III) to the benzfurazan obtained from it by reduction with hydroxylamine and elimination of water (Zincke and Schwarz, *loc. cit.*). (We find that the benzfurazans can readily be obtained from the benzfurazan oxides by reduction with methyl-alcoholic potash.) The reason for thus disregarding the evidence in favour of a quinonoid structure was the work of Forster and Barker (P., 1913, **29**, 152), who showed that the same naphthafurazan oxide is obtained from the decomposition of either 2-nitro-1-naphthylazoimide or 1-nitro-2-naphthylazoimide.

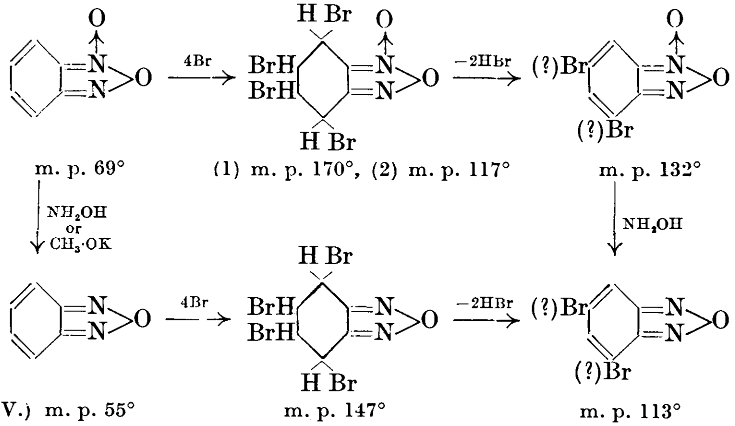

(I.)


(II.)


(III.)

An analogous result was obtained by Green and Rowe, who produced the same chlorobenzfurazan oxide by the action of hypochlorite on 5-chloro-2-nitroaniline and on 4-chloro-2-nitroaniline. This in their view could only mean that the N_2O_2 part of the molecule is symmetrical, which is not the case for a furazan oxide of the structure (I). In this view they agreed with Forster and Barker (J., 1913, **103**, 1918), who put forward further experimental evidence of a similar kind.

We have studied the action of bromine on benzfurazan oxide and on benzfurazan and obtained results that show that these substances possess the typically quinonoid property of forming with bromine addition compounds which readily lose hydrogen bromide to form dibromobenzfurazan oxide and dibromobenzfurazan. Thus we find that one molecule of benzfurazan oxide adds on four atoms of bromine to give a mixture of at least two isomeric *tetrabromotetrahydrobenzfurazan oxides*, which by the action of caustic potash readily lose two molecules of hydrogen bromide to give a single *dibromobenzfurazan oxide*. This dibromo-compound is reduced by hydroxylamine to a dibromobenzfurazan. Further, benzfurazan



itself adds on four atoms of bromine to give a *tetrabromo*-derivative, from which two molecules of hydrogen bromide are removed by alkalis, yielding a *dibromobenzfurazan* identical with that obtained from benzfurazan oxide after bromination, loss of hydrogen bromide and reduction. These results leave little doubt that the benzfurazans and benzfurazan oxides are quinonoid and that the sequence of reactions described above can be represented by the scheme on p. 3309.

Owing to the considerable differences between the parachor values to be expected for the structures that at various times have been put forward for the benzfurazans, it appeared to be worth while to undertake the necessary density and surface tension measurements. Our results (p. 3311) confirm, on the whole, the conclusions derived from the experimental evidence.

EXPERIMENTAL.

Addition of Bromine to Benzfurazan Oxide: Preparation of Tetrabromotetrahydrobenzfurazan Oxide.—Benzfurazan oxide (5 g.), prepared by the action of sodium hypochlorite on *o*-nitroaniline (Green and Rowe's method), was dissolved in 100 c.c. of dry carbon disulphide and 12 g. (4 atoms) of bromine in 20 c.c. of carbon disulphide were added, the mixture being left in bright daylight for 8 hours. No bromine then remained and large colourless crystals of the *tetrabromo*-addition product had separated; more was obtained on evaporation of the carbon disulphide (total yield, 17·3 g., which is theoretical for the addition of 4 atoms of bromine). After recrystallisation from alcohol or benzene the crystals that first separated from the reaction mixture melted at 170° (Found: C, 15·8; H, 1·0; N, 6·1; Br, 71·1. $C_6H_4O_2N_2Br_4$ requires C, 15·4; H, 0·9; N, 6·2; Br, 70·2%).

The solid obtained by evaporation of the carbon disulphide, after two recrystallisations from alcohol, melted at 117°. Analysis (Found: C, 6·2; H, 0·9; N, 6·2; Br, 70·8%) showed that it is an *isomeride* of the tetrabromide of m. p. 170°. Both substances on treatment with potassium hydroxide solution react instantly to give the same *dibromobenzfurazan oxide* (faintly yellow needles from alcohol), m. p. 132°, mixed m. p. 132° (Found: N, 9·4; Br, 53·9. $C_6H_2O_2N_2Br_2$ requires N, 9·5; Br, 54·4%).

Better yields of the lower-melting isomeride of tetrabromotetrahydrobenzfurazan oxide were obtained by brominating benzfurazan oxide in glacial acetic acid solution containing two molecules of anhydrous sodium acetate for each molecule of bromine present.

Addition of Bromine to Benzfurazan: Preparation of Tetrabromotetrahydrobenzfurazan.—5 G. of benzfurazan, prepared by the reduction of benzfurazan oxide with excess of 4% methyl-alcoholic potash and subsequent distillation in steam, were dissolved in 100 c.c. of dry carbon disulphide, to which 16 g. (4 atoms) of bromine in 25 c.c. of carbon disulphide were added, the mixture being kept in bright daylight for 8 hours. On removal of the solvent, 20 g. of *tetrabromotetrahydrobenzfurazan* (theoretical for the addition of 4 atoms of bromine, 20·5 g.) were obtained as colourless prisms, m. p. 147° after recrystallisation from alcohol (Found : C, 16·2; H, 0·9; N, 6·5; Br, 72·6. $C_6H_4ON_2Br_4$ requires C, 16·4; H, 0·9; N, 6·4; Br, 72·7%). No other tetrabromo-derivative was present in appreciable quantity.

On treating the tetrabromo-derivative with alkali, immediate loss of hydrogen bromide took place and *dibromobenzfurazan* (colourless needles from alcohol) was obtained, m. p. 113° (Found : N, 10·0; Br, 57·3. $C_6H_2ON_2Br_2$ requires N, 10·1; Br, 57·6%).

Benzfurazan is thus exactly analogous to benzfurazan oxide and must have the quinonoid structure (IV).

Reduction of Dibromobenzfurazan Oxide to Dibromobenzfurazan.—To 5 g. of dibromobenzfurazan oxide, m. p. 132°, in 75 c.c. of alcohol, 1·8 g. of hydroxylamine hydrochloride in 10 c.c. of water were added. A 25% aqueous solution of potassium hydroxide was added until nitrogen was no longer evolved. The mixture was then distilled in steam and 2 g. of fine needles were collected in the distillate. After recrystallisation from alcohol these melted at 113°, alone or mixed with the substance obtained from tetrabromotetrahydrobenzfurazan by the elimination of hydrogen bromide.

Determinations of the Parachors.—Determinations were made by Sugden's method on benzfurazan oxide, tolufurazan oxide (4-methylbenzfurazan oxide), and benzfurazan. The results are given below.

* *Benzfurazan oxide*, (I): *M*, 136; m. p. 69°.

Temp.	$D_{4^\circ}^{t^\circ}$.	γ.	Parachor.
80°	1·280	44·14	273·8
96	1·264	42·25	274·0
110·5	1·250	40·55	274·6
127	1·234	38·53	274·6
		Mean	274·3

Tolufurazan oxide (as I): *M*, 150; m. p. 97°.

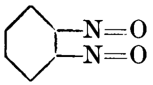
Temp.	$D_{4^\circ}^{t^\circ}$.	γ.	Parachor.
100·5°	1·1953	38·13	312·0
103·8	1·1922	37·83	312·0
108	1·1855	37·03	311·3
115	1·1822	36·18	311·2
120	1·1777	35·30	310·5
		Mean	311·4

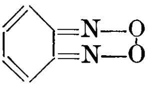
Benzfurazan (IV): *M*, 120; m. p. 55°.

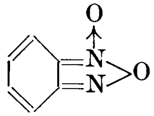
Temp.	$D_{4^\circ}^{t^\circ}$.	γ.	Parachor.
65°	1·1770	37·24	251·9
76	1·1655	36·18	252·5
80	1·1612	35·54	252·3
84°	1·1571	34·73	251·8
90·5	1·1503	34·13	252·1
98	1·1423	33·49	252·7
		Mean	252·2

* The data for benzfurazan oxide were very kindly determined for us by Dr. Sugden.

The structures that have hitherto been put forward for benzfurazan oxide are :—

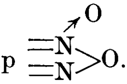






(V) $P_{\text{calc.}}$ = 284·3. (VI) $P_{\text{calc.}}$ = 258·0. (VII) $P_{\text{calc.}}$ = 267·2. (VIII) $P_{\text{calc.}}$ = 268·0

(The atomic and structural constants used in deriving the calculated parachor $P_{\text{calc.}}$ are taken from Sugden, "The Parachor and Valency," p. 38). It thus appears that the observed parachor agrees best with the value for the benzfurazan oxide structure (VIII), though it cannot distinguish between the structures (VII) and (VIII). The positive anomaly of 6·3 is high; a similar though smaller anomaly appears for the methylbenzfurazan oxide, where $P_{\text{calc.}} = 308{\cdot}6$, $P_{\text{obs.}} = 311{\cdot}4$ (anomaly = + 2·8). Benzfurazan itself gives, for the structure (IV), $P_{\text{calc.}} = 249{\cdot}6$; $P_{\text{obs.}} = 252{\cdot}2$ (anomaly = + 2·6).

Although the chemical and physical evidence appears to establish the quinonoid nature of benzfurazan and its oxide, the problem of why the same furazan oxide is always obtained from *o*-nitro-azoimides or *o*-nitroanilines substituted in the 4- or 5-positions still remains unsolved. The benzfurazan oxides resemble closely the benzildioxime peroxides in their volatility, ability to liberate iodine from potassium iodide, etc., and the structures of the benzildioxime peroxides are conclusively shown by the work of Meisenheimer, Lange, and Lamparter (*loc. cit.*) to contain the non-symmetrical group  $\overset{\nearrow O}{\begin{matrix}=N\\=N\end{matrix}}\!>O$. Two isomeric monosubstituted benzfurazan oxides ought therefore to exist, though neither we nor previous workers on these substances have succeeded in finding them. It is possible, however, that in the liquid state the benzfurazan oxide passes to some extent tautomerically into the symmetrical *o*-dinitroso-form, which would lead to the conversion of an unstable oxide into its stable isomeride and account for the apparent existence of only one form. There is some evidence for this view. When solutions of the benzfurazan oxides are heated, a distinct greenish-yellow colour is observed, which disappears on cooling. It may also be noted that the presence of *o*-dinitroso-molecules ($P_{\text{calc.}} = 284{\cdot}3$) in the molten benzfurazan oxide ($P_{\text{calc.}} = 268{\cdot}0$) would account for the positive anomaly in the observed parachor.

Summary.

The action of bromine on benzfurazan oxide and on benzfurazan yields by addition tetrabromo-derivatives. These lose hydrogen

bromide in the presence of alkali, giving substituted dibromo-derivatives. These reactions indicate that the benzfurazans are quinonoid in structure, as originally suggested by Green and Rowe.

Confirmation of this view is obtained from determinations of the parachors.

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