Furazans and Furazan Oxides. Part II.[1] Preparation and Tautomerism of some Acyl Furoxans; Examples of Steric Hindrance to Conformational Mobility in Alicyclic Six-membered Rings

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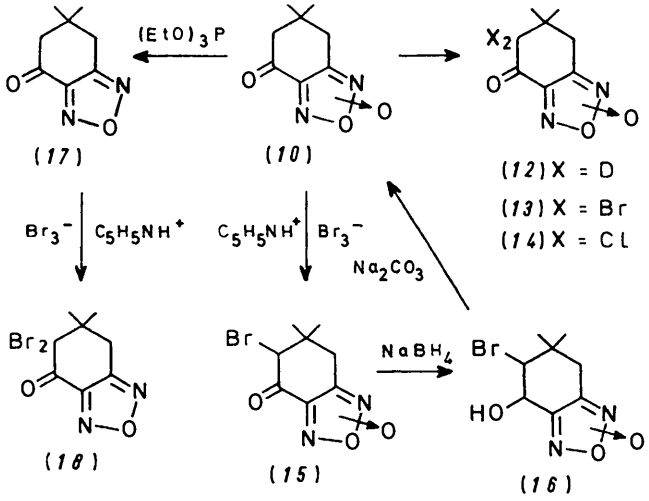
The dihydrobenzofurazan-4-one 1-oxides (*10a*)—(*15a*) are converted almost completely into the isomeric 3-oxides (*10b*)—(*15b*), respectively, on heating. Rate and equilibrium constants for the reaction have been determined. Some chemical transformations of the ketones are described. The dihalogeno-ketones (*13*) and (*14*) (*a* and *b*) display broadened n.m.r. signals at room temperature, due to slow equilibration between the 'half-chair' conformers.

THE effect of ring fusion and substituent variation on the position and rate of the furoxan equilibration reaction [(*1*) ⇌ (*2*)] has been of some interest to us in the past years. Simple furoxans (*1*) and (*2*) (R^1, R^2 = alkyl or aryl) have been investigated, both by Mallory and Cammarata [2] and by our group:[3] the position of equilibrium appears in the cases reported to be controlled mainly by steric effects, with the *N*-oxide oxygen preferring to occupy the less hindered site adjacent to the smaller group (in the examples so far reported, this has always been methyl, except for some isolated fused-ring cases [1]). In aminofuroxans electronic effects are paramount: Gagneux and Meier [4] have shown that there is a strong preference (>7 kJ mol^{-1}) for an amino-group to be adjacent to the N-5, rather than to the N-2 oxide. In the benzofuroxans [(*3*) ⇌ (*4*)], electron-withdrawing groups (R = NO_2,[5] CO_2H,[6] or CN [7]) show preference for conjugation with the *N*-oxide (*4*), but the effect is not large (*ca.* 1·7 kJ mol^{-1}). Pyridofuroxan [(*5*) ⇌ (*6*)] exists predominantly (ΔG° *ca.* 4·0 kJ mol^{-1}) in form (*5*), probably owing to a variety of effects working in concert.[8] We thought it of interest to study simple furoxans with electron-withdrawing substituents, and to this end have prepared some acyl furoxans [(*1*) and (*2*); R^1 = acyl, R^2 = alkyl].

Preparation of Compounds.—Dimedone (*7*) was converted into its isonitroso-derivative, and thence into the dioxime (*8*), by standard methods, and a similar sequence was carried out with dihydroresorcinol (*9*), although in much lower yield. Oxidation to the furoxans (*10*) and (*11*) was effected by potassium ferricyanide. In both cases a single isomer was formed, which proved to be the

[1] Part I, J. Ackrell, M. Altaf-ur-Rahman, A. J. Boulton, and R. C. Brown, *J.C.S. Perkin I*, 1972, 1587.
[2] F. B. Mallory and A. Cammarata, *J. Amer. Chem. Soc.*, 1966, **88**, 61.
[3] A. J. Boulton, P. Hadjimihalakis, A. R. Katritzky, and A. Majid Hamid, *J. Chem. Soc.* (*C*), 1969, 1901.
[4] A. R. Gagneux and R. Meier *Helv. Chim. Acta*, 1970, **53**, 1883.
[5] R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.*, 1963, 197.
[6] A. J. Boulton, A. R. Katritzky, M. J. Sewell, and B. Wallis, *J. Chem. Soc.* (*B*), 1967, 914.
[7] A. J. Boulton and R. C. Brown, unpublished work, 1968.
[8] A. J. Boulton, P. J. Halls, and A. R. Katritzky, *J. Chem. Soc.* (*B*), 1970, 636.

less stable (*a*). Isomerisation was almost quantitatively brought about by heating (to isomers *b*). Standard chemical methods produced the transformations outlined in the Scheme, which in most cases were performed with both isomeric series. The conditions were sufficiently mild to avoid equilibration of the furoxan ring, except when desired. Some of the reactions indicated (see Experimental section) were also performed in the dihydro-



SCHEME Series *a*, 1-oxides; series *b*, 3-oxides

resorcinol series, but the low yields caused early abandonment of work on these compounds.

H/D Exchange, in [$^2H_6$]acetone containing D_2O, took place exclusively adjacent to the keto-groups in the furoxans (*10a*) and (*10b*), to give the dideuterio-derivatives (*12a*) and (*12b*), respectively, as shown by the n.m.r. spectra. An attempt to prepare the epoxide from the bromohydrin (*16a*) was unsuccessful.

The exclusive formation of the unstable isomers (*10a*) and (*11a*) on oxidation of the dioximes is worthy of comment. We consider it most probable that internal hydrogen bonding (*19*) activates the keto-group *syn* to the oxime hydroxy-group. After nucleophilic addition of the hydroxylamine, elimination of water takes place to form a new oxime group with its stereochemistry controlled by the steric influence of the 2-substituent, to give the dioxime (*8*) of configuration 1-*E*,2-*E*. Oxidation takes place with minimum disturbance of the relative positions of the heavy atoms, so leading to the furoxans (*a*).

N.m.r. Spectra and Equilibria between Conformers.—

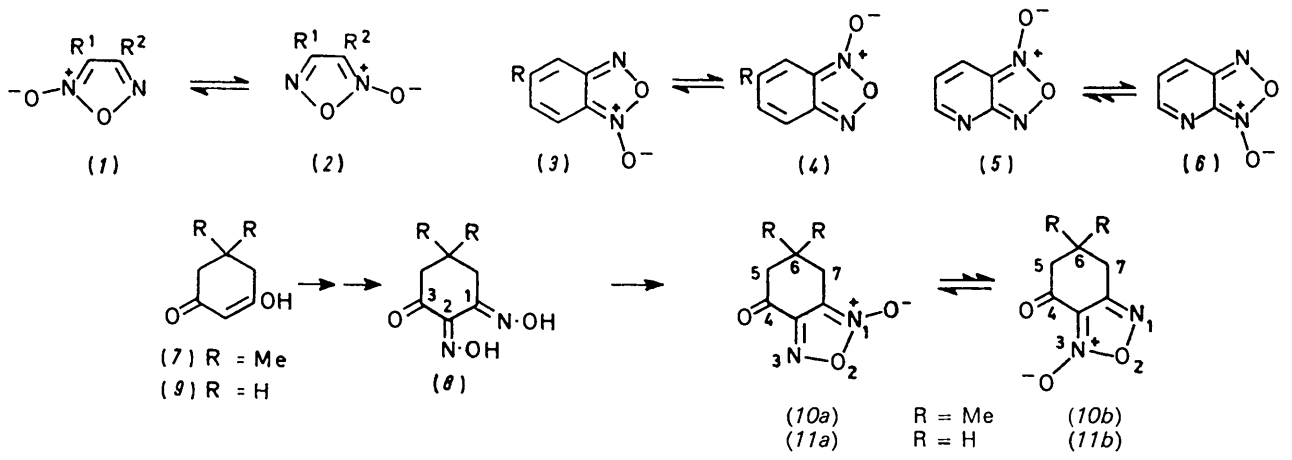
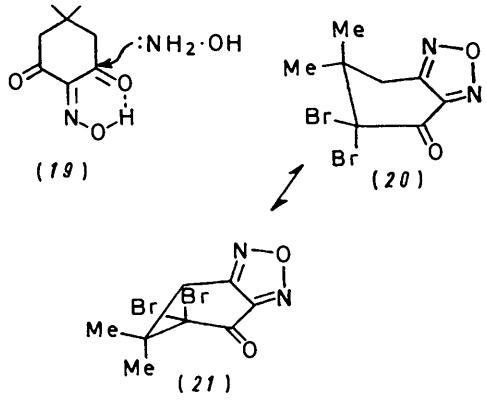


Table 1 lists the chemical shifts of the protons of the heterocycles investigated. Distinction between the two isomers (series *a* and *b*) was made on the basis of the chemical shifts of the protons α to the heterocyclic ring. (For a summary of this criterion, see Part I.[1])

The αα-dihalogeno-ketones (*13*), (*14*), and (*18*) showed the expected two singlets (6H and 2H) at 80° in $CDCl_3$, but at 0° the methyl groups and methylene protons appeared as two singlets and an AB quartet, respectively. This is explained in terms equilibration of conformational [*e.g.* (*20*) ⟷ (*21*), in the case of compound (*18*)]. The increased energy barrier to ring inversion, compared with, *e.g.*, cyclohexene derivatives,[9] in which ΔG^* usually lies within the range 22—31 kJ mol^{-1}, undoubtedly arises from the high energy of the intermediate between the two equilibrium conformers, in which the



methyl groups and halogen atoms are eclipsed in pairs. Approximate energy barriers, obtained from the coales-

[9] F. A. L. Anet and M. Z. Haq, *J. Amer. Chem. Soc.*, 1965, **87**, 3147; F. R. Jensen and C. H. Bushweller, *ibid.*, 1965, **87**, 3285; 1969, **91**, 5774.

cence temperatures of the methyl signals,[6] † are listed in Table 2.

The spectrum of compound (*13a*), at *ca.* 50° in $(CD_3)_2CO$, showed the slow appearance of sharp signals above the broad, exchanging-type band envelope. These persisted after cooling, and proved to be caused by bromine–deuterium exchange between the dihalogeno-ketone and the solvent, forming the 5-bromo-5-deuterio-derivative of (*10a*).

Equilibria between Tautomers.—The compounds investigated were dissolved in dry bromoform, sealed in n.m.r. tubes with a little tetramethylsilane, and heated. The spectra were examined at intervals. Table 3 lists the free energy differences between the isomers, at the temperatures indicated, and the energies of activation for the reaction.

The ketones demonstrate what might have been expected, by comparison with the results from the benzofuroxans [5-8] and aminofuroxans,[4] that the more stable form, by a considerable factor, is that with the *N*-oxide adjacent to, and so in conjugation with, the keto-group [*cf.* (*22*)]. The conjugation effect is also noticeable in the carbonyl stretching frequency (Table 1).

These results contrast with those of Gasco *et al.*,[10] who found that the equilibrium (*23*) ⇌ (*24*) lies in favour of (*23*), by a small factor. In this case, we asume that steric effects are important, operating either directly, or indirectly, by impeding coplanarity and thus reducing conjugation, or both.

The free energies of activation for the equilibration of the ketones are lower than in the dialkyl and aryl alkyl furoxans studied by Mallory and Cammarata.[2] Since it is known [4] that the aminofuroxans are more readily isomerised than the simple compounds, we had expected that derivatives with electron-withdrawing substituents would be less so. Qualitatively, the results of Gasco *et al.*[10] ‡ suggest that this may be the case: they report

TABLE 1

N.m.r. and i.r. spectra of benzofurazan-4-ones and benzofurazan-4-one *N*-oxides

Compound	τ [a] 5	6 [c]	7	$\nu_{max.}$/cm^{-1} [b] C=O	Furazan (oxide)	
(*10a*)	7·42	8·81	7·30	1720	1650	1480, 1470
(*10b*)	7·46	8·81	7·10	1710	1600	1530
(*11a*)	7·0—7·4(m)	7·5—7·9(m)	7·0—7·4(m)	1720	1630	1480
(*11b*)	7·2—7·5(m)	7·6—7·9(m)	6·8—7·1(m)	1710	1600	1530
(*13a*) [d,e]		8·54	7·05	1740	1635	1480
(*13b*) [d]		8·50	6·60	1725	1615	1530
(*14a*) [d]		8·59	7·04	1745	1635	1480
(*14b*) [d]		8·60	6·85	1730	1610	1530
(*15a*)	5·72(d) [f]	8·75, 8·61	7·57 [f], 6·95 [g]	1730	1630	1485, 1470
(*15b*)	5·78(d) [f]	8·76, 8·62	7·33 [f], 6·73 [g]	1715	1605	1530
(*17*)	7·49	8·83	7·01	1720	1570	1470
(*18*) [d]		8·60	6·80	1730	1570	1470

[a] In $CDCl_3$ at 30°; singlets unless otherwise stated. [b] In $CHBr_3$. [c] 6-Me_2, except for (*11a,b*) (H_2). [d] N.m.r. at 60°. [e] N.m.r. in [$^2H_6$]acetone. [f] J_{AX} 1 Hz. [g] AB system; J_{AB} −17 Hz.

TABLE 2

Ring inversion [(*20*) ⇌ (*21*)] of dihalogeno-furazans and their oxides [a]

Compound	τ Values at *T* °C Me_a	Me_b	H_A	H_B [c]	*T*	T_c/K	$\Delta G^{\ddagger}$/kJ mol^{-1} [b]
(*13a*)	8·32	8·74	7·23	6·89	−10	317	66·5
(*13b*)	8·27	8·69	6·92	6·62	−10	318	66·5
(*14a*)	8·39	8·77	7·24	6·90	−20	308	64·5
(*14b*)	8·40	8·76	6·96	6·66	−20	303	63·5
(*18*)	8·28	8·78	7·29	7·14	−10	310	64·0

[a] In $CDCl_3$, except for (*13a*) ([$^2H_6$]acetone). [b] ±2 kJ. Calculated from T_c and $\delta(Me_a,Me_b)$ as described elsewhere.[5,6] [c] J_{AB} −17·5 to −18 Hz.

TABLE 3

Tautomerism (*a* ⇌ *b*) of furazan oxides

Compound pair	ΔG°/kJ mol^{-1} (*a* − *b*) [a]	E_A/kJ mol^{-1} [b,c]	*T*/°C (range) [d]
(*10*)	6·3	134	90—110
(*11*)	*ca.* 9	132	94—112
(*13*)	7·1	134	89—108
(*14*)	>9	133	89—109

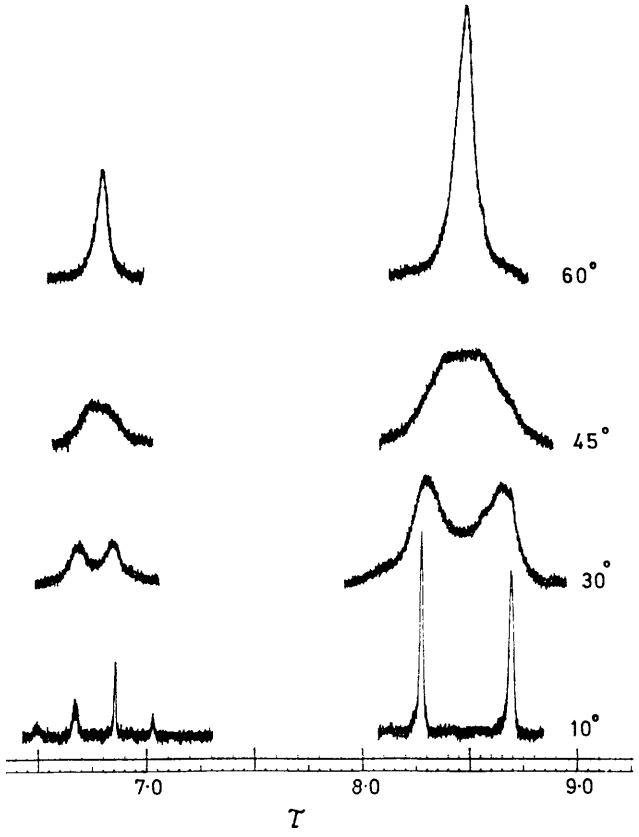
[a] ±0·5 kJ. In each case the *b* isomers are the favoured forms, at equilibrium. [b] ±2 kJ. Arrhenius parameter. *A* Values were subject to large experimental error, and are not quoted. [c] Figures for isomers *a*. For isomers *b*, $E_A \approx E_A(a) + \Delta G^{\circ}(a - b)$. [d] Temperature range for experiments; ΔG° is constant over this range, within experimental error.

† A more thorough investigation of this reaction, studying n.m.r. line shapes over a range of temperatures, is being undertaken by Mrs. A. Sinclair and N. Sheppard, of this department.

‡ More recent results confirm that the isomerisation (*23*) ⇌ (*24*) is about as sluggish as those studied by Mallory and Cammarata [2] (E_A *ca.* 145 kJ mol^{-1}) (A. Gasco, unpublished work).

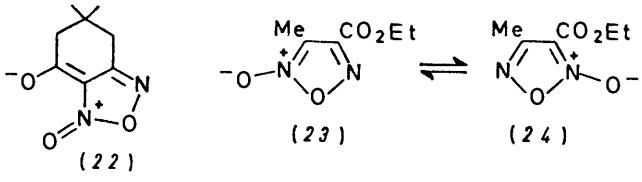
[10] A. Gasco, V. Mortarini, G. Ruà, G. M. Nano, and E. Menziani, *J. Heterocyclic Chem.*, 1972, **9**, 577.

equilibration at 180° for the conversion of (*23*) into (*24*). The isomerisation (*10a*) ⇌ (*10b*), however, went more easily than (*1*) ⇌ (*2*) (R = alkyl or aryl). The ready deuteriation of (*10a*), in $(CD_3)_2CO$–D_2O, at first suggested



N.m.r. spectra of 5,5-dibromo-6,7-dihydro-6,6-dimethylbenzofurazan-4(5*H*)-one 3-oxide (*13b*), in $CDCl_3$ at various temperatures

that interconversion could be proceeding *via* the enol, but such an explanation could not apply to the dihalogenoketones (*13*) and (*14*), which isomerised at much the same



(*22*) (*23*) (*24*)

rate as (*10*). There seems therefore to be no simple correlation between the electron-withdrawing power of the substituents and the ease of the isomerisation.

EXPERIMENTAL

Spectroscopic techniques and instrumentation were as described in Part I.[1] All new compounds described gave mass spectra in agreement with their assigned structures.

6,7-*Dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 1-*Oxide* (*10a*).—Aqueous sodium nitrite (7 g in 20 ml) was slowly added, with stirring, to a saturated solution of dimedone (14 g) in methanol at 0°, containing 10N-hydrochloric acid (20 ml). After 15 min at 0° aqueous hydroxyammonium chloride (7 g in 15 ml) was added, and the mixture was removed from the ice-bath and slowly titrated, with stirring, with saturated aqueous sodium acetate until a slight permanent darkening was observed. The temperature was kept at 5° for 2 h, after which the precipitated dioxime (*8*; R = Me) was collected and washed with a little ice-cold water. The dioxime was slurried with ethyl acetate (100 ml) and vigorously stirred with aqueous potassium ferricyanide (100 g in 250 ml) containing saturated aqueous sodium carbonate (15 ml). After 30 min the organic layer was separated, washed with brine, dried ($MgSO_4$), and decolourised by filtering through a short column of alumina (20 g). The solvent was removed *in vacuo*, the residue was dissolved in hot methylene chloride (30 ml), and boiling light petroleum (b.p. 40—60°; 100 ml) was added. The mixture was cooled to 0° to give the *furoxan* (*10a*) as plates (9·1 g, 50%), m.p. 118—120°, remelting after cooling at *ca.* 75° (Found: C, 52·8; H, 5·7; N, 15·2. $C_8H_{10}N_2O_3$ requires C, 52·7; H, 5·5; N, 15·4%), $\lambda_{max.}$ (MeOH) 213 (ε 11,800) and 308 nm (2000).

6,7-*Dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 3-*Oxide* (*10b*).—The furazan 1-oxide (*10a*) (1 g) was refluxed for 4 h in light petroleum (b.p. 100—120°; 9 ml) and toluene (1 ml). After cooling, the product was filtered off and recrystallised from CH_2Cl_2–light petroleum (b.p. 40—60°). The residues from the mother liquors were combined and reheated, to give a small second crop. The *furoxan* (0·6 g, 60%) formed small octahedral prisms, m.p. 85—86° (Found: C, 52·9; H, 5·5; N, 15·3%), $\lambda_{max.}$ (MeOH) 215 (ε 11,700), 250 (3500), and 284 nm (3500).

The dideuterio-ketone (*12a*) formed an *oxime*, m.p. 132—135° (softening 125°), as micro-needles, from ether–hexane [Found: C, 48·5; H, 5·7. $C_8H_9D_2N_3O_3$ requires C, 48·2; H, 5·6% (gas analysis)], τ [$(CD_3)_2SO$] 8·97 (6H), 7·43 (2H), and 7·25 p.p.m. (*ca.* 0·2H; residual H at C-5).

6,7-*Dihydrobenzofurazan*-4(5H)-*one* 1-*Oxide* (*11a*).—This furoxan was prepared from dihydroresorcinol (*9*) (0·1 mol) in the same way as its dimethyl derivative, except that the nitrosation was carried out at −10°, and the oxidation of the (much smaller yield of) dioxime was performed with less ferricyanide (25 g in 100 ml) and carbonate (5 ml). The *furoxanone* (*11a*) was obtained as plates (0·5 g, 3%) (from methylene chloride–light petroleum), m.p. 115°, remelting after cooling at *ca.* 70° (Found: C, 46·7; H, 3·9; N, 18·2. $C_6H_6N_2O_3$ requires C, 46·8; H, 3·9; N, 18·2%), $\lambda_{max.}$ (MeOH) 212 (ε 6100) and 268 nm (4300).*

6,7-*Dihydrobenzofurazan*-4(5H)-*one* 3-*Oxide* (*11b*).—Rearrangement of the 1-oxide (*11a*), as for the dimethyl derivative (*10a*), gave the *furazan* 3-*oxide* (*11b*) (0·6 g, 60%) as needles, m.p. 71° [from methylene chloride–light petroleum (b.p. 40—60°)] (Found: C, 46·6; H, 4·5; N, 18·2%), $\lambda_{max.}$ (MeOH) 215 (ε 9000), 252 (2000), and 284 nm (4000).

5,5-*Dibromo*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 1-*Oxide* (*13a*).—The furoxanone (*10a*) (0·3 g) in acetic acid (10 ml) was treated with pyridinium hydrobromide perbromide (1·2 g). After 24 h at 20° the solution was poured into water and the precipitate was collected and dissolved in cold acetone. Water was added to produce a slight turbidity, and the solution was cooled to 0°. The *dibromoketone* (*13a*) slowly separated as needles (0·5 g, 90%), m.p. 138°, solidifying and remelting *ca.* 150° (Found: C, 28·2;

* The difference between the u.v. spectra of this compound and its 6,6-dimethyl derivative (*10a*) is probably due to predominant hemiacetal formation in the case of (*11a*). In cyclohexane solution the spectrum of (*11a*) ($\lambda_{max.}$ 217 and 312 nm) closely resembles that of (*10a*).

H, 2·6; N, 8·0. $C_8H_8Br_2N_2O_3$ requires C, 28·3; H, 2·4; N, 8·2%), $\lambda_{max.}$ (MeOH) 222 (ε 9400) and 322 nm (1500).

5,5-*Dibromo*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 3-*Oxide* (*13b*).—The furoxan (*13a*) (1·0 g) was isomerised by refluxing in toluene for 4 h. The cooled solution was decolourised by passing through a short column of alumina (5 g), eluting with ether. The solvents were removed and the residue was crystallised from acetone–light petroleum (1 : 4), giving the *dibromo-ketone* (*13b*) as octahedral prisms (0·8 g, 80%), m.p. 150—151° (Found: C, 28·2; H, 2·4; N, 8·3%), $\lambda_{max.}$ (MeOH) 222 (ε 7600), 248 (4800), and 296 nm (4700).

Bromination of the furoxan (*10b*) (0·07 g) at 70° for 3 h, otherwise under the same conditions as described for the isomer (*10a*), gave the dibromo-compound (*13b*) directly (75%).

5,5-*Dichloro*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 1-*Oxide* (*14a*).—The furoxan (*10a*) (1·4 g), in acetic acid (20 ml) containing 10N-HCl (2 ml) and pyridine (1 ml), was treated with chlorine (6% in acetic acid; 40 ml) for 8 h at 40°. The mixture was then poured into water (100 ml), and after 12 h at 0° the *dichloro-ketone* was filtered off and recrystallised from aqueous methanol, giving prisms (1·0 g, 50%), m.p. 112°, remelting, after heating to 140° and cooling, at 125—126° (Found: C, 38·05; H, 3·2; N, 10·9. $C_8H_8Cl_2N_2O_3$ requires C, 38·3; H, 3·2; N, 11·2%), $\lambda_{max.}$ (MeOH) 221 (ε 9900), 267 (1580), and 318 nm (1200).

5,5-*Dichloro*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 3-*Oxide* (*14b*).—The furoxan (*14a*) (0·5 g) was refluxed for 12 h in toluene. The solvent was removed *in vacuo* and the residue was recrystallised from acetone–light petroleum, giving prisms of the isomeric *furoxan* (*14b*) (0·35 g, 70%), m.p. 126—127° (Found: C, 38·0; H, 3·2; N, 11·1%), $\lambda_{max.}$ (MeOH) 222 (ε 8000), 249 (3400), and 293 nm (3900).

5-*Bromo*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 1-*Oxide* (*15a*).—The furoxan (*10a*) (0·8 g) was treated with pyridinium hydrobromide perbromide (1·4 g) in acetic acid (10 ml) for 2 h at 20°. The mixture was then poured into water, and the crude *bromo-ketone* was filtered off and washed with water. After decolourisation (Al_2O_3; ether elution) the product was crystallised from chloroform–light petroleum, to form needles, m.p. 127—128°, remelting, after cooling, at *ca.* 95° (Found: C, 36·6; H, 3·4; N, 10·7. $C_8H_9BrN_2O_3$ requires C, 36·8; H, 3·5; N, 10·7%).

5-*Bromo*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* 3-*Oxide* (*15b*).—The furoxan (*15a*) was isomerised in refluxing toluene, as described for the dibromo-derivative (*13a*). The *isomer* (*15b*) formed prisms (70%), m.p. 100—102° (from chloroform–light petroleum) (Found: C, 36·7; H, 3·6; N, 10·7%).

5-*Bromo*-4,5,6,7-*tetrahydro*-6,6-*dimethylbenzofurazan*-4-*ol* 1-*Oxide* (*16a*). The bromo-ketone (*15a*) (0·24 g) in dioxan (4 ml) was treated with sodium borohydride (0·1 g) at 20°. The solution turned first orange, then colourless. It was poured into water and extracted with ether. The extract was dried ($MgSO_4$) and evaporated, and the residue was crystallised from methylene chloride–light petroleum to give the *bromohydrin* (*16a*) as prisms (0·15 g, 60%), m.p. 123—124° (Found: C, 36·4; H, 4·2; N, 10·8. $C_8H_{11}BrN_2O_3$ requires C, 36·5; H, 4·2; N, 10·65%), $\nu_{max.}$ 3400 and 1620 cm^{-1} ($CHBr_3$), τ 8·73 and 8·69 (2 × CH_3), 7·60 and 7·18 (AB, *J* −18 Hz, H-7, -7′), 6·76 (d, *J* 11 Hz, H-5), 5·56 (d, *J* 4 Hz, HO), and 4·85 (dd, *J* 11 and 4 Hz, H-4).

In the hope of preparing the 4,5-epoxide, the bromohydrin (*16a*) was treated with sodium carbonate in dimethylformamide for 12 h at 20°. On dilution with water, the ketone (*10a*) was the only product (*ca.* 80%) isolated.

6,7-*Dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* (*17*).—(*a*) The furoxan (*10a*) was refluxed for 2 h in trimethyl phosphite. Hydrolysis of the excess of ester (H_2O–HCl). extraction with ether, evaporation of solvent, and azeotropic drying (C_6H_6) gave the *furazan* (*17*) (70%) as flat needles, m.p. 66—68° (from ether–light petroleum) (Found: C, 57·7; H, 6·0; N, 16·6. $C_8H_{10}N_2O_2$ requires C, 57·8; H, 6·1; N, 16·9%), $\lambda_{max.}$ (MeOH) 233 nm (ε 3050), qualitatively similar in cyclohexane—probably coincidentally, since the furazan (*17*) formed a hemiacetal with methanol ($\nu_{max.}$ 3400—3000, no ν_{CO} at 1720 cm^{-1}).

(*b*) The triketone dioxime (*8*) (6 g) was refluxed for 6 h with acetic anhydride (30 ml) and sodium acetate (5 g). After cooling, the mixture was poured into water, stirred to hydrolyse the anhydride, and extracted with ether. The extract was dried ($MgSO_4$) and distilled, giving 4-*acetoxy*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*, b.p. 83° at 0·2 mmHg; needles, m.p. 31° (from light petroleum) (Found: C, 57·9; H, 5·8; N, 13·3. $C_{10}H_{12}N_2O_3$ requires C, 57·7; H, 5·8; N, 13·45%), τ 8·79 (6H), 7·79 (3H), 7·14 (2H), and 4·22 (1H), $\nu_{max.}$ 3040, 1780, 1730w, and 1650 cm^{-1}. The enol acetate was decomposed by stirring for 30 min with potassium carbonate (4 g) in methanol (40 ml), followed by pouring into water, ether extraction, and azeotropic drying and purification as described in (*a*), to give the furazan (*17*) (2·9 g, 55%).

The most convenient preparation of the furazan (*17*) was by the following modification of the method of Tokura *et al.*[11]

(*c*) The dioxime (*8*) (2 g) was suspended in methylene chloride (50 ml), and stirred at 20° while thionyl chloride (1 ml) was added dropwise over 1 h. The mixture was poured on ice and extracted with ether. The extracts were washed with aqueous sodium hydrogen carbonate, then dried ($MgSO_4$), with subsequent isolation and purification as before; yield 1·2 g (65%).

5,5-*Dibromo*-6,7-*dihydro*-6,6-*dimethylbenzofurazan*-4(5H)-*one* (*18*).—The furazan (*17*) (0·1 g) was brominated in acetic acid, by the method described for the furoxan (*10b*). The *dibromo-derivative* (*18*) (1·6 g, 80%) formed cubic prisms, m.p. 130—131° (from ether) (Found: C, 29·4; H, 2·65, N, 8·6. $C_8H_8Br_2N_2O_2$ requires C, 29·65; H, 2·5; N, 8·6%).

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