added over the course of 10 min. 3.8 ml. of phosphorus oxychloride. After 4 hr. of heating, the mixture was cooled and poured into ice water. The toluene layer was separated, washed with aqueous sodium bicarbonate, dried, and evaporated. The residual light tan gum was dissolved in hot ethanol, and was reprecipitated on cooling as an oil, which subsequently partially solidified. This material weighed 3.65 g. and had an infrared spectrum consistent with that expected for *1,4-diphenyl-2-naphthyl salicylate* with peaks at 3.03 (OH) and 5.91 μ (C=O).

This material (1.90 g.) was heated without further purification in an open test tube at 330–340° for 2 hr. Chromatography of the resultant material with benzene on alumina gave a yellow fraction. Evaporation of this fraction and sublimation of the residue at 170° (0.1 mm.) gave 52 mg. of crystals, m.p. 228–230°. Recrystallization of the product from ethanol gave 23 mg. of VIIb, m.p. 232–234°.

6-Phenyl-12H-benzo[b]xanthen-12-one (VIIIa). To a solution of 16.0 g. of 1-phenyl-2-tetralone[21] in 100 ml. of cymene was added 2.1 g. of 10% palladium on charcoal. The resulting suspension was refluxed for 10 hr., during which time the formation of water was observed in the condenser. The palladium was filtered off and the solvent was removed *in vacuo*. The residual oil was extracted three times with 30-ml. portions of 6% aqueous sodium hydroxide. Acidification of the aqueous solution gave 9.05 g. (58%) of *1-phenyl-2-naphthol* as a light brown oil, which soon crystallized, m.p. 63–67°. Recrystallization from water gave white needles, m.p. 65–67°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.04; H, 5.30.

To a boiling solution of 2.26 g. of salicyclic acid and 4.0 g. of 1-phenyl-2-naphthol in 60 ml. of toluene was added slowly 3.1 ml. of phosphorus oxychloride. After heating for 4 hr., the mixture was cooled and poured into ice water. The toluene layer was washed successively with sodium bicarbonate solution and water and then dried. Evaporation of the solvent left a residue which was recrystallized from ethanol to give *1-phenyl-2-naphthyl salicylate*, 3.70 g. (66%), as white crystals, m.p. 129–131°. Two additional recrystallizations gave white needles, m.p. 131–132°.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.10; H, 4.85.

In an open test tube, 2.00 g. of the ester was heated at 340–350° for 5 hr. The resulting gum was twice chromatographed by elution with chloroform on alumina. The bright yellow fraction was evaporated to dryness and the residue was sublimed. Recrystallization of the sublimate from acetone–water gave 110 mg. of *6-phenyl-12H-benzo[b]xanthen-12-one* (VIIIa) as yellow-green needles, m.p. 249–254°.

Acknowledgment. We are indebted to Dr. J. E. Lancaster and Mrs. M. Neglia for the n.m.r. spectra, to Mrs. R. Barritt for mass spectral measurements, to Dr. J. Deonarine and his staff for the microanalyses, to Mr. J. Koren for the measurement and plotting of some of the ultraviolet spectra, and to Mr. N. B. Colthup for aid in the measurement and interpretation of the infrared spectra.

(21) H. E. Zaugg, M. Freifelder, and B. W. Horrom, *J. Org. Chem.*, 15, 1197 (1950).

The Rates of Some Degenerate Rearrangements as Determined by Nuclear Magnetic Resonance Spectroscopy[1]

Frank B. Mallory,[2,3] Stanley L. Manatt,[4] and Clelia S. Wood[2]

Contribution from the Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania, and the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California. *Received July 22, 1965*

The rates and the activation parameters have been determined for the degenerate isomerizations of three different symmetrically disubstituted benzofurazan oxides in order to provide evidence for the mechanism of this type of interconversion. The rates of these very rapid processes were deduced from the line shapes of the n.m.r. spectra of the three compounds at various temperatures in the range from −40 to +50°. The positive entropies of activation (ranging from +4 to +6 e.u.), the relatively small energies of activation (ranging from 15.0 to 16.5 kcal./mole), and the correlation of the relative rates with the size of the substituents at the 4- and 7-positions flanking the N_2O_2 grouping are all considered to support an interconversion mechanism that involves ring opening of the furazan oxide to the corresponding o-dinitrosobenzene as the rate-determining step, followed by very rapid recyclization of this symmetrical intermediate to the heterocyclic N-oxide.

Introduction

Evidence that benzofurazan oxides undergo rapid equilibration of the Ia ⇌ Ib type in solution has been presented recently.[5] It is generally considered[5,6] that

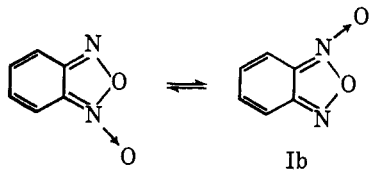
(1) Furazan Oxides. V. For part IV see F. B. Mallory, C. S. Wood, and B. M. Hurwitz, *J. Org. Chem.*, 29, 2605 (1964).

(2) This work was supported in part by Grant GP-1186 from the National Science Foundation to Bryn Mawr College.

(3) Alfred P. Sloan Research Fellow, 1964–1966.

(4) This paper represents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

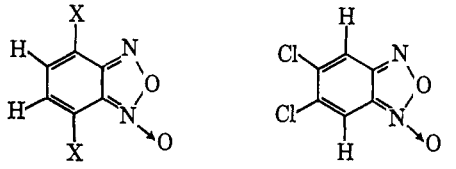
(5) (a) G. Englert, *Z. Elektrochem.*, 65, 854 (1961); (b) P. Diehl, H. A. Christ, and F. B. Mallory, *Helv. Chim. Acta*, 45, 504 (1962); (c) F. B. Mallory and C. S. Wood, *J. Org. Chem.*, 27, 4109 (1962);



Ia Ib

the most reasonable mechanistic pathway for this degenerate equilibration involves ring opening of the furazan oxide to give an *o*-dinitrosobenzene as a transient intermediate followed by very rapid recyclization of this intermediate to give either Ia or Ib. The present kinetic study was undertaken in an attempt to provide more decisive experimental support for this mechanism than has heretofore been available.

The rates of the interconversions of the Ia $\rightleftharpoons$ Ib type are sufficiently fast that they can be determined in the cases of certain symmetrically substituted benzofurazan oxides on the basis of observations of the line shapes of the n.m.r. spectra of the furazan oxides as a function of temperature. The particular cases we have studied are 4,7-dibromobenzofurazan oxide (II), 4,7-dichlorobenzofurazan oxide (III), and 5,6-dichlorobenzofurazan oxide (IV). Each of these compounds



II, X = Br
III, X = Cl

IV

possesses a simple, two-spin proton system whose n.m.r. spectrum changes from an AB quartet at low temperature (slow equilibration) to an A_2 singlet at high temperature (fast equilibration), a situation for which an adequate theory exists[7] that relates the spectral line shape to the average frequency with which the A and B protons exchange their magnetic environments. Moreover, this theory has been expressed[8] in a form that is readily applicable to the problem of deducing exchange rate constants from experimental spectra.

Results

The proton n.m.r. spectra of the benzofurazan oxides II, III, and IV were obtained at a series of regulated temperatures between -40 and $+50°$ with a Varian A-60 spectrometer equipped with a V-6040 variable temperature controller. Most of the spectra were determined using 0.5 *M* solutions of the benzofurazan oxide in acetone, although concentrations of 0.1 *M* were sometimes used at very low temperatures to avoid crystallization of the solute, and some spectra were also measured in carbon tetrachloride and in methanol solutions. Tetramethylsilane was added as an internal standard, and dissolved oxygen was removed from the solutions by flushing with high-purity nitrogen. For each compound at each temperature at least four spectra were obtained, and in some cases up to ten spectra were recorded on different days; line widths were generally reproduced to within 0.05 c.p.s. in such a series of repeated determinations. Sufficiently small radiofrequency fields were used (0.10 mgauss) that saturation effects were avoided.

The spectra at *ca.* $-40°$ were AB quartets with line widths approaching 0.4 c.p.s.[9]; the relative chemical shifts ($\nu_A - \nu_B$) and the coupling constants (J) for each compound were determined from these spectra and are given in Table I. As the temperature was raised, the spectra gradually changed through the following sequence: (a) the line widths increased with the two outer lines broadening more than the two inner lines such that the outer lines soon disappeared; (b) as the line widths of the two remaining lines continued to increase, the separation between them decreased until they coalesced to a single broad line; (c) the remaining single line then decreased in width toward a limiting value of 0.4 c.p.s. The experimentally observed line widths, $\Delta\nu$, and line separations at various temperatures are given in Table II.

Table I. Parameters from the 60-Mc. Proton N.m.r. Spectra of Some Benzofurazan Oxides[a]

Compd.	Substituents	$\nu_A - \nu_B$	J	$(\nu_A - \nu_B)/2$
II	4,7-Dibromo	10.33	7.62	456 (452)[b]
III	4,7-Dichloro	12.25	7.69	447 (444)[b]
IV	5,6-Dichloro	14.42	0.65	488 (478)[c]

[a] Parameters were measured in c.p.s. downfield from tetramethylsilane as an internal standard in acetone solution at *ca.* $-40°$ except where noted. The values of $\nu_A - \nu_B$ and J are averages of several determinations and are probably accurate to within ± 0.05 c.p.s. The uncertainty in the values of $(\nu_A - \nu_B)/2$ is estimated to be ± 0.5 c.p.s. [b] Measured at $+50°$. [c] Measured at $+30°$.

The method used to determine the exchange lifetimes given in Table II from the line shapes of the experimental spectra involved as the first step obtaining a set of theoretical spectra for each compound using an IBM 7094 computer with a program devised by Beauchamp[8] and based on the theory of Alexander[7] as recapitulated by Whitesides.[8] Thus, a theoretical spectrum for an exchanging AB system can be obtained in plotted form from the computer with this program by specifying four quantities: the chemical shift difference ($\nu_A - \nu_B$), the coupling constant (J), the relaxation time (T_2), and the exchange lifetime (τ), which is defined as the average time that elapses for a particular molecule between the exchange processes that simultaneously transpose the magnetic environments of the two protons. The values of the first two of these quantities were obtained experimentally (Table I) for each of the three compounds of interest. The value of T_2 was determined to be 0.8 sec. for both the A and B protons in each compound from the relationship $1/T_2 = \pi\Delta\nu_0$, where $\Delta\nu_0$, the line width in the absence of exchange, was found to be 0.4 c.p.s. in all cases.[9] Various different values of the fourth quantity (τ) were arbitrarily chosen for each compound in the range

(d) R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.*, 197 (1963).

(6) This pathway was first suggested by D. L. Hammick, W. A. M. Edwardes, and E. R. Steiner, *ibid.*, 3308 (1931).

(7) S. Alexander, *J. Chem. Phys.*, 37, 967 (1962).

(8) G. M. Whitesides, Ph.D. Thesis, California Institute of Technology, 1964; J. L. Beauchamp and J. D. Roberts, unpublished results.

(9) The tetramethylsilane resonance peak was observed to have a line width of 0.4 c.p.s. at all temperatures at the sweep rates employed (0.1–0.2 c.p.s. sec.$^{-1}$), and the resonance peaks of the benzofurazan oxides tended toward this limiting line width at both the high and the low temperature extremes used in these investigations.

Table II. Experimental Line Widths, Line Separations, and Exchange Lifetimes[a]

Compd.	Temp., °C.	$\Delta\nu$[b]	Sepn.[c]	$\Delta\nu$[c]	Lifetime (τ), sec.
II	50	0.75			0.0021
	40	1.22			0.0048
	30	2.47			0.0116
	20	5.88			0.030
	15		3.76	6.57[d]	0.051, 0.051
	10		4.61	1.99	0.078, ..., 0.081[e]
	0		4.99[f]	1.03	..., 0.23, 0.21[e]
	−10		5.14[f]	0.58	..., 0.67, 0.72[e]
III	50	0.74			0.0015
	40	1.22			0.0035
	30	2.67			0.0090
	20	6.03			0.021
	10		5.55	8.63[d]	0.056, ...
	0		6.60[f]	1.28	..., 0.17, 0.17[e]
	−10		6.75[f]	0.68[g]	..., 0.57, 0.53[e]
IV	30	0.53			0.00038
	20	0.69			0.00085
	10	1.18			0.0023
	0	2.48			0.0062
	−5	4.15			0.0104
	−10	7.28			0.0175
	−15	13.25			0.0285
	−20		11.4	18.4[d]	0.050, ...

[a] The given values of $\Delta\nu$ are full line widths at half-peak heights. Line widths and line separations are given in c.p.s. Exchange lifetimes were obtained by graphical comparison of experimental spectra with computed spectra except where noted. [b] Coalesced line. [c] Inner lines. [d] The inner lines were not sufficiently resolved to permit measurement of $\Delta\nu$ for each line; the value given is the over-all width of the set. [e] These values of τ were calculated by the method of Beauchamp.[8] [f] These separations were too near those of the slow-exchange limit to serve as a reliable basis for the determination of τ. [g] The width of the outer lines was found to be 1.33 c.p.s.; this leads to $\tau = 0.57$ by graphical comparison with computed spectra, and to $\tau = 0.52$ by calculation using the method of Beauchamp.[8]

Table III. Theoretical Line Widths and Line Separations[a]

Compd.	τ, sec.	$\Delta\nu$[b]	Sepn.[c]	$\Delta\nu$[c]
II	0.003	0.91		
	0.006	1.42		
	0.015	3.11		
	0.030		2.15	5.88[d]
	0.060		4.34	6.84[d]
	0.150		5.11	1.32
	0.300		5.23	0.85
	0.600		5.25	0.62
III	0.003	1.11		
	0.006	1.85		
	0.015	4.33		
	0.030		3.35	8.04[d]
	0.060		5.89	3.47
	0.150		6.68	1.44
	0.300		6.78	0.91[e]
	0.600		6.83	0.65[f]
IV	0.0006	0.61		
	0.0015	0.91		
	0.003	1.39		
	0.006	2.42		
	0.015	5.92		
	0.030	14.05		
	0.060		12.23	17.56[d]
	0.150		14.05	2.85[g]
	0.300		14.20	1.91[g]
	0.600		14.05	1.48[g]

[a] Line widths and line separations are given in c.p.s. and are averages from two computed spectra. In all cases, $\Delta\nu_0$ was taken as 0.4 c.p.s. [b] Coalesced line. [c] Inner lines. [d] See ref. *d* of Table II. [e] $\Delta\nu$ for the outer lines was 2.08 c.p.s. [f] $\Delta\nu$ for the outer lines was 1.24 c.p.s. [g] These represent composite line widths of an inner and an outer line; the coupling constant is so small that these lines only begin to be resolved at $\tau = 0.6$ sec.

of 0.6 to 0.0006 sec. such that in each of the three cases the series of computed spectra ran the gamut of types from sharp AB quartets at large values of τ through broadened spectra at intermediate values of τ to sharp singlets at small values of τ. The line shape parameters measured from these theoretical spectra are given in Table III.

The theoretical line widths and line separations in Table III were plotted against the values of τ that were used to obtain the computed spectra. The plots of the widths of the coalesced lines against τ were nearly linear; the plots of both the widths and the separations of the inner lines against τ were curved. By interpolation into these empirical plots of the line shape parameters from the theoretical spectra, the values of τ were determined that correspond to the line widths and line separations that were obtained from the experimental spectra. These experimental lifetimes are given in Table II.

A relationship has been derived by Beauchamp[8] that permits the evaluation of τ near the low-temperature, slow-exchange limit. Thus, under these conditions

$$\tau = \frac{1 \pm J[(\nu_A - \nu_B)^2 + J^2]^{-1/2}}{\pi(\Delta\nu - \Delta\nu_0)}$$

where the plus sign is used for the outer lines and the minus sign is used for the inner lines of the AB quartet, and where we have taken $\pi\Delta\nu_0$ to represent $1/T_2$. This equation was employed to calculate some of the exchange lifetimes given in Table II.

From the data in Table II it can be seen that at a given temperature the exchange lifetimes for II and III are roughly comparable and are about thirty times larger than for IV.

A limited study was carried out of the temperature dependence of the spectra of 4,7-dichlorobenzofurazan oxide (III) in two other solvents, carbon tetrachloride and methanol. The chemical shifts and coupling constants in these two solvents, as determined from the spectra at −20°, were only slightly different from those determined in acetone solution. The line widths measured from the spectra at 30, 0, and −20° were such that the exchange lifetimes in carbon tetrachloride and methanol appeared to be roughly 20–40% smaller than those in acetone. Additional work will be required to substantiate this preliminary finding.

It was shown that the addition of a small amount of gaseous hydrogen chloride to an acetone solution of the 4,7-dichloro compound did not have an appreciable effect on the line width of the spectrum at 30°; this implies that there is no marked acid catalysis of the exchange process.

The 5,6- and 4,7-dimethylbenzofurazan oxides were prepared in the hopes that the long-range coupling between the methyl protons and the ring protons would be sufficiently small that the spectra of the ring protons could be analyzed as being approximately simple AB types using the same methods as were used for the dihalo compounds. Unfortunately, these hopes were

not realized. Thus, the spectrum[10] of the ring protons of the 4,7-dimethyl compound had roughly the form of an AB quartet centered at 417 c.p.s. with $\nu_A - \nu_B = 9$ c.p.s. and $J = 7$ c.p.s., but the outer lines were quite broad (2–3 c.p.s.) and the inner lines were partially resolved into quartets with a splitting of about 1 c.p.s. arising from spin–spin interaction with the methyl groups. The spectrum[10] of the ring protons of the 5,6-dimethyl compound remained largely unresolved even at −40°, consisting of two peaks that were quite broad (4–5 c.p.s.) centered at about 430 and 444 c.p.s., respectively. In view of these complications in the spectra, it was not possible to determine the exchange lifetimes for the dimethyl compounds. However, it appears that these lifetimes are roughly in line with those determined for the dihalo compounds. Thus, the coalescence temperature (the temperature above which the exchange process is sufficiently fast that separate lines or groups of lines arising from the A and B protons are no longer observed in the spectrum, and at which, in each of the present cases, the spectrum changes from two broad lines to a single very broad line) for the 4,7-dimethyl compound is considerably higher than that for the 5,6-dimethyl compound (about 35° compared with about −15°); these coalescence temperatures are quite similar to those observed for the 4,7- and 5,6-dichloro compounds (about 20 and −15°, respectively). The implication is that for methyl as well as for chloro substituents, the 4,7-disubstituted compounds undergo the exchange process much less frequently than the 5,6-disubstituted compounds.

Discussion

The reciprocals of the exchange lifetimes given in Table II are the first-order rate constants for the exchange processes.[11] Whether or not these rate constants (k_{obsd}) are the appropriate ones (k) for use in constructing Arrhenius plots for these degenerate isomerizations depends on the isomerization mechanism. Thus, if the reaction pathway for exchange involves a single, transient, symmetrical intermediate then the relevant rate constant (k) would be $2k_{obsd}$ rather than k_{obsd}.[12] This factor of 2 arises because the free-energy barrier whose magnitude is of interest in such a case is that separating the furazan oxide from the intermediate, and the frequency with which this barrier is surmounted is twice the exchange frequency, owing to the fact that the intermediate would have equal probabilities of giving a furazan oxide with and without exchange of proton environments relative to the furazan oxide from which it had been formed. If more than one intermediate intervenes in the exchange process, then more complicated relationships would exist between k and k_{obsd} that depend on the ratios of the first-order rate constants for the forward and reverse reactions of the intermediates; however, except for certain special cases, such as those in which these ratios would all approach unity,[12b] these relationships simplify such that k is approximately equal to $2k_{obsd}$.

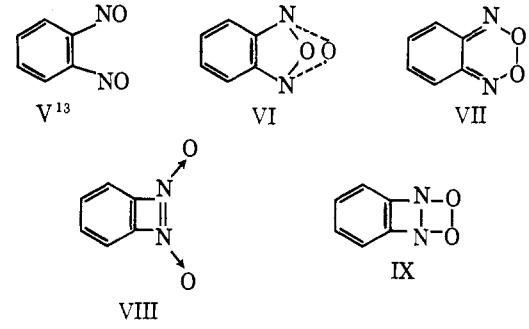
For reasons that will be elaborated below, our inclination is that a symmetrical intermediate is involved in the furazan oxide equilibrations under consideration, although there is presently no compelling experimental evidence in support of this notion. Accordingly, the Arrhenius plots shown in Figure 1 are plots of log $(2/\tau)$ against $1/T$. The slopes and intercepts of the three lines in Figure 1 were determined by least-squares analysis and led to the values of E_a, A, and ΔS^* given in Table IV. If the assumption that the exchange mechanism involves an intermediate is incorrect and the rate constants of interest are actually $1/\tau$ rather than $2/\tau$, then although the values of E_a remain unchanged, the values of k and A in Table IV are each too large by a factor of 2, and the values of ΔS^* are each too large by 1.4 e.u.

Table IV. Rate Constants and Activation Parameters

Compd.	k at 30°, sec.$^{-1}$	E_a, kcal./mole[a]	$10^{-14}A$, sec.$^{-1}$	ΔS^*, e.u.[b]
II	1.7×10^2	16.3[c]	1.0	+4
III	2.2×10^2	16.5	1.9	+5
IV	5.3×10^3	15.0	3.2	+6

[a] The probable errors in the values of E_a as determined by least-squares analysis of the data plotted in Figure 1 are ±0.1 kcal./mole for each of these compounds; perhaps a more realistic estimate of the uncertainty in these activation energies would be ±0.5 kcal./mole. [b] Evaluated at 30° from the absolute rate theory expression $\Delta S^* = 4.576 \log (A/T) - 49.2$, in which the transmission coefficient is taken as unity. [c] This activation energy has been reported previously to be 6 ± 2 kcal./mole on the basis of an n.m.r. study.[5a] The method used in this earlier work[5a] to deduce the exchange lifetimes from the spectra at various temperatures is apparently invalid.

The five principal types of symmetrical intermediate (or transition state) that are conceivable for the Ia ⇌ Ib type of interconversion are shown.



V[13] VI VII VIII IX

The fact that positive entropies of activation have been found experimentally (Table IV) for three examples of the Ia ⇌ Ib type of interconversion is consistent with the suggestion that the rate-determining step involves ring opening to give *o*-dinitrosobenzenes such as V. Furthermore, these positive values of ΔS^* tend to rule out the possibility that species of type VI are involved in these equilibrations (at least as the sole intermediates or transition states) since it is expected that the formation of these bicyclo[2.1.1]-hexane analogs from furazan oxides would have negative entropies of activation.

(10) See Table I, footnote *a*.

(11) Where more than one value of τ is listed in Table II for a given compound at a particular temperature, an average value of τ was used to calculate the rate constant.

(12) For general discussions see: (a) M. M. Kreevoy in "Technique of Organic Chemistry," Vol. VIII, Part II, 2nd Ed., S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 1372, 1373; (b) J. C. Giddings and H. Eyring, *J. Phys. Chem.*, **62**, 305 (1958).

(13) There are various possibilities for the *o*-dinitrosobenzene struc-

The relatively small magnitude of the energies of activation listed in Table IV does not seem consistent with the mechanistic involvement in these furazan oxide interconversions of such presumably high-energy species as types VII, VIII, and IX. Thus, VII lacks aromatic stability and also has a weak peroxidic bond, and VIII and IX are expected to possess considerable strain. *o*-Dinitrosobenzenes such as V, on the other hand, would have benzenoid aromaticity and no severe strain, and therefore appear to be sufficiently stable that their formation from the corresponding benzofurazan oxides with activation energies of only 15–16 kcal./mole is plausible.

We feel that these *o*-dinitrosobenzenes are more reasonably considered as intermediates than as transition states, in spite of the fact that all of the reported attempts at intercepting these presumed intermediates by reagents that react readily with model aromatic nitroso compounds have been unsuccessful or ambiguous.[14] We find no serious difficulty in rationalizing this apparent inconsistency by postulating that the unsuccessful bimolecular trapping reactions are not sufficiently rapid to compete effectively with the extremely rapid unimolecular recyclization of these *o*-dinitrosobenzenes to benzofurazan oxides.

The relative rates of equilibration of the furazan oxides II, III, and IV can also be interpreted readily[15] in terms of the intermediacy of the corresponding *o*-dinitrosobenzenes. Thus, a consequence of the ring opening of a benzofurazan oxide to an *o*-dinitrosobenzene would be an increase in the steric requirements of the N_2O_2 grouping.[16] The presence of large substituents at the 4- and 7-positions of the benzofurazan oxide might be expected, therefore, to retard the ring-opening reaction. In accord with this expectation, the relative isomerization rates for compounds II, III, and IV and the sizes of the 4- and 7-substituents in these three compounds, as judged roughly from van der Waals radii, follow qualitatively similar patterns as can be seen in Table V: thus, $k_{II} < k_{III} << k_{IV}$ and bromine is somewhat larger than chlorine which is in turn considerably larger than hydrogen. Further-

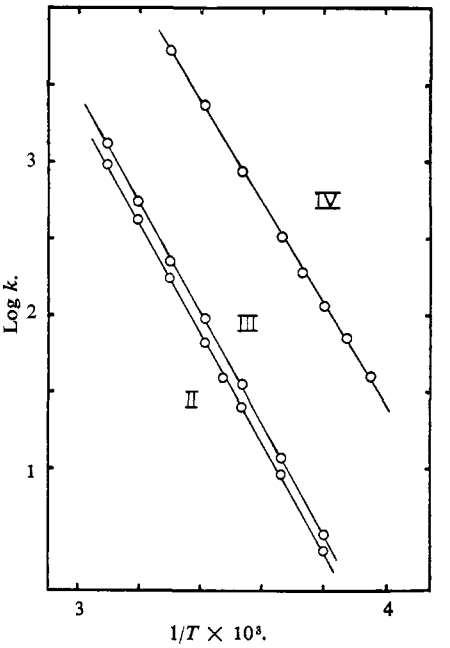
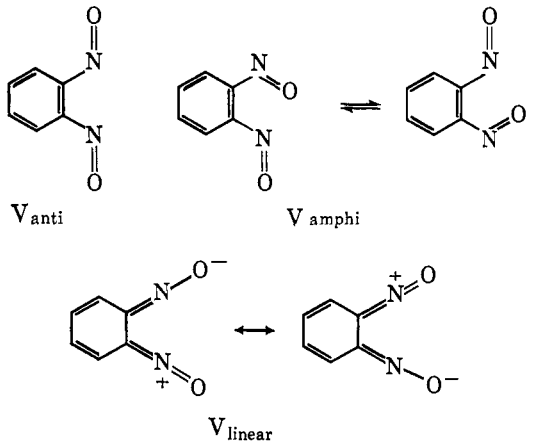


Figure 1. Plots of log k *vs.* $1/T$ (where $k = 2/\tau$ in sec.$^{-1}$ and T is in °K.) for the isomerizations of 4,7-dibromobenzofurazan oxide (II), 4,7-dichlorobenzofurazan oxide (III), and 5,6-dichlorobenzofurazan oxide (IV).

ture (V), among which are the following limiting cases. Two additional



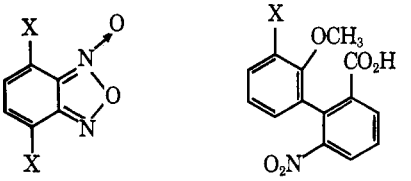
structures, V_{cis} and V_{trans}, would have the oxygens out of the plane of the aromatic ring, either on the same side or on opposite sides of this plane, respectively. The structure with abnormal CNO bond angles has been suggested previously for benzofurazan oxide (I): see J. H. Boyer in "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 462.

(14) See ref. 5c for pertinent references.

(15) In suggesting an interpretation for the relative rates we are assuming, of course, that the different substituents effect the magnitudes of the rate constants (k) without making any gross change in the mechanism such as altering the number of intermediates.

(16) This increase in the effective volume of the N_2O_2 grouping would result primarily from the substantial nonbonded interaction in the dinitroso intermediate between the nitrogen and the oxygen that are bonded together in the related furazan oxide.

Table V. Relative Rate Comparisons



X	Rel. isomerization rate of A[a]	Rel. racemization rate of B[b]	van der Waals radius, Å.[c]
Br	1.0	1.0	1.95
Cl	1.3	1.5	1.80
H	31[d]	87	1.2

[a] In acetone solution at 30°. [b] In acetone solution at 25°: S. L. Chien and R. Adams, *J. Am. Chem. Soc.*, **56**, 1787 (1934); C. C. Li and R. Adams, *ibid.*, **57**, 1565 (1935). [c] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260. [d] For this case the substituents at the 5- and 6-positions of A are chlorines rather than hydrogens.

more, the similarity of the substituent effects on the relative rates of racemization of certain biphenyls (structure B, Table V) and on the relative rates of interconversion of the correspondingly substituted furazan oxides (structure A, Table V) also supports the suggestion that the latter reactions involve rate-determining ring openings to *o*-dinitrosobenzenes, since the steric compression on the substituents X in structures A and B should be similar in the transition states for the two reactions. In terms of this type of steric argument,

the relative reactivity order II < III << IV is not compatible with a mechanism that would involve the rate-determining formation of species of type VI, since the steric requirements of the N_2O_2 grouping would be smaller in such species than in the corresponding furazan oxides.

Although it has been possible in this discussion to interpret the relative isomerization rates of II, III, and IV in terms of a simple steric argument without having to consider the electronic properties of the different substituents, this does not require the nonexistence of an electronic substituent effect on the rates of this type of interconversion. We are examining this point by extending these studies to include some benzofurazan oxides having substituents that are electronically less innocuous than bromine and chlorine.

Experimental Section

4,7-Dibromobenzofurazan Oxide (II). Benzofurazan oxide[17] was brominated in aqueous acetic acid solution and the resulting tetrabromide[18] was dehydrobrominated by chromatography on alumina. The crude material was recrystallized from 95% ethanol to give 4,7-dibromobenzofurazan oxide melting at 133.4–133.8° (lit.[18] m.p. 133.0–133.5°).

4,7-Dichlorobenzofurazan Oxide (III). The addition of 61 g. (0.3 mole) of 2,5-dichloroacetanilide to 180 ml. of fuming nitric acid (*d* 1.52) maintained at −5 to 0° gave 69.4 g. (92%) of a mixture of isomeric dichloronitroacetanilides from which there was obtained, after acidic hydrolysis and steam distillation, 11.6 g. (19%) of 3,6-dichloro-2-nitroaniline, m.p. 64.0–66.5° (lit.[19] m.p. 68°).

A solution of 4.1 g. (0.02 mole) of 3,6-dichloro-2-nitroaniline in 25 ml. of glacial acetic acid and 16 ml. of concentrated sulfuric acid was maintained at 0–5° and treated with 1.5 g. (0.022 mole) of sodium nitrite. To the resulting solution of the diazonium ion was added 3.0 g. (0.045 mole) of sodium azide in 7 ml. of water. The reaction mixture was stirred at room temperature for 2.5 hr. and was then diluted with 25 ml. of water. The precipitate was collected, washed with water, and air dried. This crude 3,6-dichloro-2-nitroazidobenzene was dissolved in 6 ml. of diethylene glycol and heated at 140–145° for 1 hr. and then the solution was poured with stirring onto crushed ice. The crude product was collected, washed with water, sublimed, and finally recrystallized from 95% ethanol to give 2.15 g. (53%) of 4,7-dichlorobenzofurazan oxide, m.p. 95.4–96.7°. A sample that was recrystallized three times from methanol and finally sublimed melted at 96.6–97.0°.

Anal. Calcd. for $C_6H_2Cl_2N_2O_2$: C, 35.15; H, 0.98; N, 13.67. Found: C, 35.07; H, 1.18; N, 13.54.

5,6-Dichlorobenzofurazan Oxide (IV). A solution of 1.24 g. (0.006 mole) of 4,5-dichloro-2-nitroaniline and 4.0 g. (0.06 mole) of potassium hydroxide pellets in 50 ml. of 95% ethanol was stirred magnetically and maintained at 6–10° during the dropwise addition of 92 ml. of 5% aqueous sodium hypochlorite.[20] The precipitate was collected, washed with water, recrystallized from 95% ethanol, and finally sublimed to give 0.74 g. (60%) of 5,6-dichlorobenzofurazan oxide, m.p. 129.7–131.4°. A small sample that was purified by chromatography on alumina and by several recrystallizations from methanol melted at 130.8–131.2°.

Anal. Calcd. for $C_6H_2Cl_2N_2O_2$: C, 35.15; H, 0.98; N, 13.67. Found: C, 35.43; H, 0.91; N, 13.59.

4,7-Dimethylbenzofurazan Oxide. A solution of 25 g. (0.15 mole) of 2,5-dimethylacetanilide in 50 ml. of concentrated sulfuric acid was nitrated at 50° with a mixture of 15 g. of concentrated nitric acid and 15 g. of concentrated sulfuric acid. After acidic hydrolysis and steam distillation there was obtained 6.42 g. (25%) of 3,6-dimethyl-2-nitroaniline, m.p. 31–32° (lit.[21] m.p. 33–36°).

3,6-Dimethyl-2-nitroaniline (3.3 g., 0.02 mole) was diazotized, the resulting diazonium ion solution was treated with sodium azide, and the nitroazide was pyrolyzed as described above for the preparation of III. After purification of the crude product by one sublimation and two recrystallizations from methanol there was obtained 1.8 g. (55%) of 4,7-dimethylbenzofurazan oxide, m.p. 80.5–81.2°. Two further recrystallizations from methanol gave material melting at 80.9–81.2°.

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.66; H, 4.73; N, 16.98.

5,6-Dimethylbenzofurazan Oxide. A solution of 4.98 g. (0.03 mole) of 4,5-dimethyl-2-nitroaniline and 2.15 g. (0.033 mole) of potassium hydroxide pellets in 300 ml. of 95% ethanol was treated with 440 ml. of aqeuous sodium hypochlorite[20] over a period of 45 min.; the temperature of the reaction mixture reached 50°. After the addition was complete the mixture was cooled in ice. The precipitate was collected, washed with water, and air dried to give 4.39 g. (89%) of 5,6-dimethylbenzofurazan oxide, m.p. 138.0–139.7°. Purification by three sublimations and three recrystallizations from 95% ethanol gave material melting at 139.4–139.7°.

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.54; H, 4.89; N, 17.24.

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