Evidence for the Transient Existence of 1,2-Dinitrosoalkenes[1]

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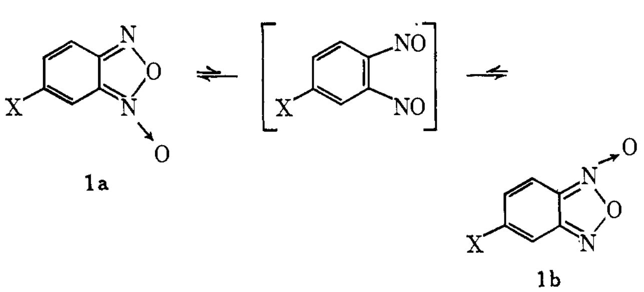
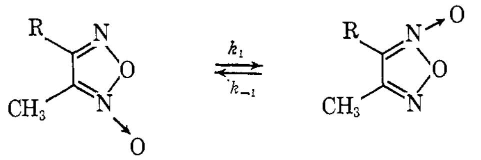
Abstract: Rates and activation parameters have been measured for the kinetically first-order interconversions in solution of the two methylphenylfurazan oxides and also the two ethylmethylfurazan oxides. N.m.r. spectral data were used to assign structures to these N-oxides. The kinetic results together with some energy calculations are interpreted as evidence for an interconversion mechanism that involves ring opening of the furazan oxides to give transient *cis*-1,2-dinitrosoalkenes.

In the preceding paper in this series[1a] kinetic evidence was presented in support of the long-standing belief[3] that the mechanism of the very rapid **1a** $\rightleftharpoons$ **1b** type of interconversion of benzofurazan oxides involves the formation of transient *o*-dinitrosobenzenes. As a further test of the validity and generality of this mechanism, we have carried out a rate study of the interconversions of some simple disubstituted furazan oxides (**2** and **3**) in order to determine whether the kinetic parameters are consistent with the hypothesis that these interconversions proceed by way of the corresponding dinitrosoalkenes (**4** and **5**, respectively).

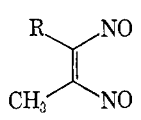


1a

1b



2a	(R = C_6H_5)	2b
3a	(R = C_2H_5)	3b



4 (R = C_6H_5)
5 (R = C_2H_5)

Benzofurazan oxide equilibrations of the **1a** $\rightleftharpoons$ **1b** type proceed so rapidly at room temperature[4] that it is not possible to isolate the individual isomers **1a** and **1b**, and the interconversion rates are measurable on the basis of n.m.r. spectral line shapes.[1a] In contrast, the interconversions of simple furazan oxides such as **2a** and **2b**, or **3a** and **3b**, are sufficiently slow that the isolation of each isomer is routine, and the equilibration rates are measurable by ordinary techniques in the temperature range of 125–140°.

Results

Methylphenylfurazan Oxides. The two previously obtained[5] methylphenylfurazan oxides, **2a** and **2b**, were prepared; their structures were assigned on the basis of n.m.r. spectroscopy (see below). Kinetic studies of the **2a** $\rightleftharpoons$ **2b** interconversion were carried out starting with 0.04 *M* solutions of either **2a** or **2b** in purified dimethylformamide in 4-mm. o.d. Pyrex tubes. The tubes were flushed with nitrogen and then sealed and placed in a constant temperature bath for various times at one of four different temperatures. The compositions of the resulting mixtures of **2a** and **2b** were determined by gas–liquid partition chromatography on a 2-ft. neopentylglycol succinate column (2% on Gaschrom P) at 105° using an F & M Model 400 gas chromatograph with flame ionization detection and disk integration; the retention times were 22 min. for **2b** and 28 min. for **2a**. No isomerization was detected for either isomer under the conditions of the g.l.p.c. analysis. No side reactions were observed; after equilibrium had been reached the composition of the solutions remained unchanged on prolonged heating. Data were collected for the approach to equilibrium from both directions at each temperature. The interconversions followed first-order kinetics as evidenced by the linearity of the plots[6] shown in Figure 1 of log $[(X_0 - X_{eq})/(X - X_{eq})]$ *vs.* time, where X is the mole fraction of **2a**, and X_0 and X_{eq} are the initial and equilibrium values, respectively, of X. The least-squares slopes of the lines shown in Figure 1 are equal to $(k_1 + k_{-1})/2.303$, where k_1 and k_{-1} are the first-order rate constants for the **2a** → **2b** and **2b** → **2a** reactions, respectively. From these slopes and the corresponding equilibrium concentration ratios, which are equal to k_1/k_{-1}, the values of k_1 were determined as given in Table I.

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(1) (a) Furazan Oxides. VI. For part V see F. B. Mallory, S. L. Manatt, and C. S. Wood, *J. Am. Chem. Soc.*, **87**, 5433 (1965); (b) this work was supported by Grant GP-1186 from the National Science Foundation; (c) presented in part before the Division of Organic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 17, 1965.

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

(3) D. L. Hammick, W. A. M. Edwardes, and E. R. Steiner, *J. Chem. Soc.*, 3308 (1931), and many subsequent papers by various authors.

(4) First-order rate constants for the isomerizations of some benzofurazan oxides were found[1a] to be in the range of 10^2–10^3 sec.$^{-1}$ at 30°.

(5) G. Ponzio, *Ber.*, **61**, 1316 (1928).

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 186.

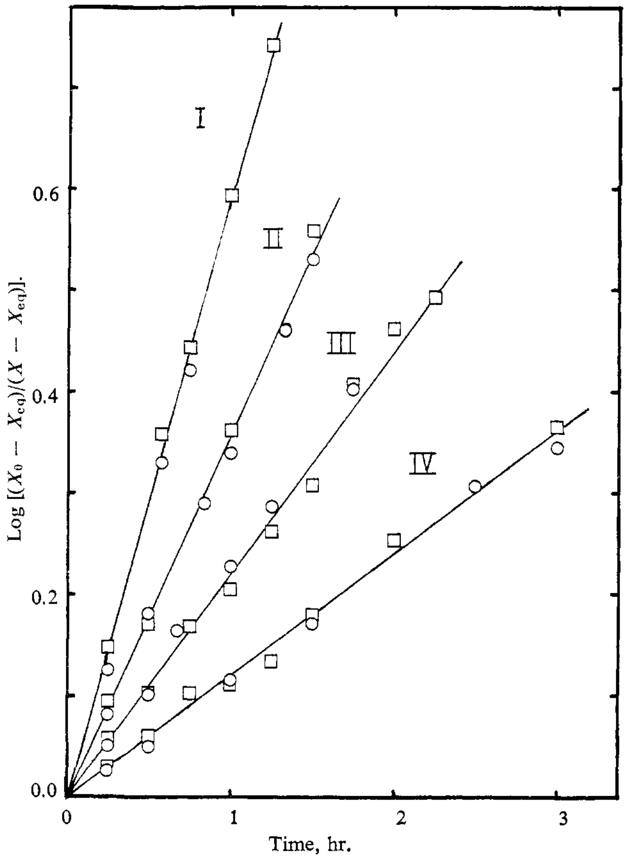

Figure 1. Plots of log $[(X_0 - X_{eq})/(X - X_{eq})]$ vs. time for the equilibration of 3-methyl-4-phenylfurazan oxide (**2a**) and 4-methyl-3-phenylfurazan oxide (**2b**) in dimethylformamide solutions starting either with pure **2a** ($X_0 = 1.000$, points shown as circles) or with pure **2b** ($X_0 = 0.000$, points shown as squares) at four temperatures: I, 140.2°; II, 135.3°; III, 130.3°; and IV, 125.0°.

The Arrhenius plot for the **2a** → **2b** reaction is shown in Figure 2, and the activation parameters, calculated by a least-squares analysis, are given in Table II.[7,8]

Table I. Equilibrium Concentration Ratios and Isomerization Rate Constants[a]

Temp., °C.[b]	Equil. [2b]/[2a]	Equil. [3b]/[3a]	10^5k_1, sec.$^{-1}$[c] 2a → 2b	10^5k_1, sec.$^{-1}$[c] 3a → 3b
125.0	0.564		2.79 ± 0.1	
130.3	0.567		5.08 ± 0.2	
135.3	0.569		8.31 ± 0.3	
140.2	0.572		13.7 ± 0.3	
130.9		0.790		5.06 ± 0.1
136.3		0.796		9.20 ± 0.2
140.8		0.801		14.7 ± 0.4

[a] Data for **2a** and **2b** were obtained in dimethylformamide solution; data for **3a** and **3b** were obtained in 1,1,2,2-tetrachloroethane solution. [b] Temperatures were maintained within ±0.2°. [c] The specified uncertainties are probable errors as determined by least-squares calculations.

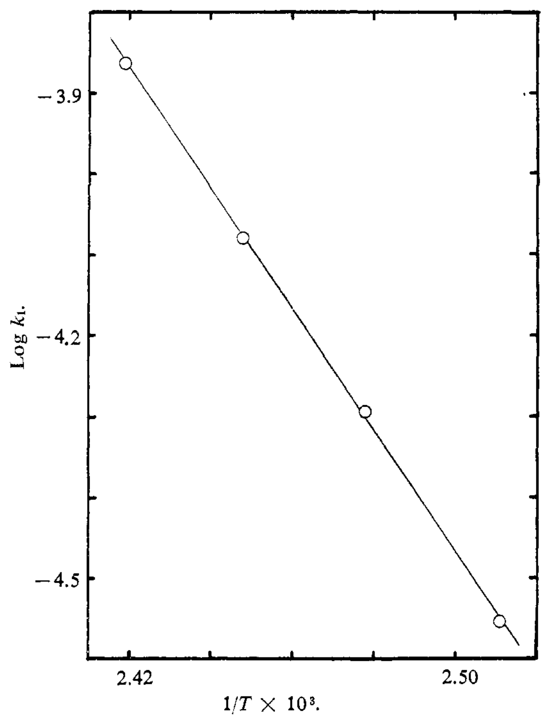

Figure 2. Plot of log k_1 vs. $1/T \times 10^3$, where k_1 is in sec.$^{-1}$ and T is in °K., for the **2a** → **2b** reaction in dimethylformamide solution.

The rate of approach to equilibrium at 129.6° starting with pure **2a** was found to be the same in three different solvents: dimethylformamide, ethylene glycol monomethyl ether, and 1,1,2,2-tetrachloroethane. The data are plotted in Figure 3 in terms of mole fractions of **2a**.

Table II. Activation Parameters[a]

Reaction	E_a, kcal./mole	log A	ΔS^*, e.u.[b]
2a → **2b**	34.2 ± 0.3	14.2 ± 0.2	+4
3a → **3b**	35.3 ± 0.4	14.8 ± 0.2	+7

[a] The specified uncertainties are probable errors as determined by least-squares calculations. [b] The values of ΔS^* were calculated for 135° from the absolute rate theory expression $\Delta S^* = 4.576 \log (A/T) - 49.2$, in which the transmission coefficient is taken as unity.

Ethylmethylfurazan Oxides. The mixture of the isomeric ethylmethylfurazan oxides, **3a** and **3b**, that was obtained by hypochlorite oxidation of the dioxime of 2,3-pentanedione was separated by preparative g.l.p.c.; the structures of **3a** and **3b** were assigned on the basis of n.m.r. spectroscopy (see below). The limited kinetic studies that were undertaken of the **3a** $\rightleftharpoons$ **3b** equilibration were carried out at three different temperatures starting with 1,1,2,2-tetrachloroethane solutions that were 0.02 M in a mixture of 97.1% **3a** and 2.9% **3b**. The data were obtained and analyzed in a similar way to that described above for the methylphenylfurazan oxides, except that the g.l.p.c. analysis involved the use of a 4-ft. tris(cyanoethoxy)propane

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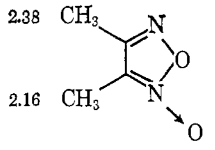
(7) (a) Evaluation of the Arrhenius pre-exponential factors, A, and consequently the entropies of activation, ΔS^*, is not necessarily straightforward. Thus, if the reaction proceeds by way of a high-energy intermediate (as opposed to a single transition state), and if the two transition states separating this intermediate from the two isomeric furazan oxides are of equal free energy, then the over-all rate constant for the reaction, k_1, is only half as large as the rate constant for surmounting the free-energy barrier whose height is of interest[7b]; under such circumstances, the values given in Table II for log A would be too small by 0.3, and those given for ΔS^* would be too small by 1.4 e.u.; (b) for a general discussion see 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.

(8) The results of an earlier rate study (M. Milone, *Gazz. chim. ital.*, 59, 829 (1929)) of the **2a** $\rightleftharpoons$ **2b** interconversion are not in good agreement with those reported here.

column (5% on Anakrom) at 90°; the retention times were 9 min. for **3b** and 12 min. for **3a**. Good linear plots were obtained of log $[(X_0 - X_{eq})/(X - X_{eq})]$ *vs.* time, with $X_0 = 0.971$ in all cases. The concentration ratios at equilibrium and the first-order rate constants for the conversion of **3a** to **3b** are given in Table I, and the activation parameters are in Table II.

Structure Assignments. It has been reported[9] that the proton n.m.r. spectrum of dimethylfurazan oxide (**6**) consists of two peaks at 2.16 and 2.38 p.p.m.,[10] while that of dimethylfurazan (**7**) consists of a single peak at 2.31 p.p.m. Assignments for the former two peaks can be made by analogy with the results of previous work on azoxy compounds and also on benzofurazan oxide. Thus, it has been shown[11] that the methyl proton resonance peaks of some azoxy compounds of type **8** are at higher fields than the methyl proton resonance peaks of the corresponding azo compounds (**9**). Furthermore, it has been deduced[12] that the chemical shift of the proton at C-7 in benzofurazan oxide (**10**) is at higher field than that of the proton at C-4 by 0.25 p.p.m. Therefore, it seems reasonable to associate the 2.16-p.p.m. peak in the spectrum of **6** with the methyl group adjacent to the *N*-oxide oxygen, and consequently to associate the 2.38-p.p.m. peak with the methyl group remote from the *N*-oxide oxygen.



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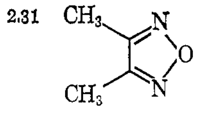

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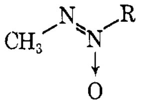

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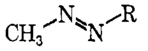

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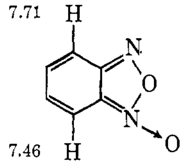

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In the 60-Mc. spectra of carbon tetrachloride solutions of the ethylmethylfurazan oxides (**3a** and **3b**), the unsplit methyl peaks are at 2.09 p.p.m. for the isomer with longer g.l.p.c. retention time, and at 2.32 p.p.m. for the isomer with shorter g.l.p.c. retention time. This is taken to indicate that the ring methyl group is adjacent to the *N*-oxide oxygen in the former isomer (**3a**) and remote from it in the latter isomer (**3b**). In accord with this assignment, the quartet attributed to the methylene group in the spectrum of **3b** is centered at higher field (2.53 p.p.m.) than the corresponding quartet in the spectrum of **3a** (2.67 p.p.m.).

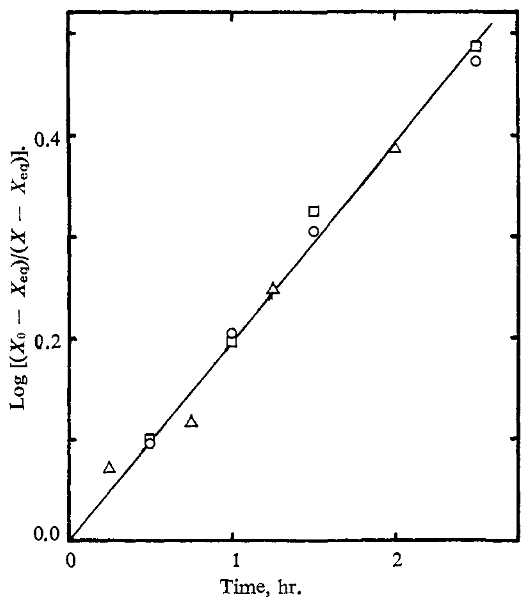
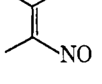


Figure 3. Plot of log $[(X_0 - X_{eq})/(X - X_{eq})]$ *vs.* time for the equilibrations of **2a** and **2b** at 129.6° in three different solvents: dimethylformamide (circles), ethylene glycol monomethyl ether (squares), and 1,1,2,2-tetrachloroethane (triangles). In all cases, $X_0 = 1.000$ and $X_{eq} = 0.638$.

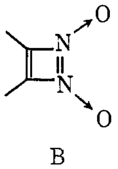
The methyl resonances in the 60-Mc. spectra of the methylphenylfurazan oxides (**2a** and **2b**) in deuteriochloroform solution are at 2.33 p.p.m. for the higher melting isomer, and at 2.53 p.p.m. for the lower melting isomer. This chemical shift difference of 0.20 p.p.m. is almost identical with that of 0.23 p.p.m. observed for the unsplit methyl resonances of **3a** and **3b**. In line with the assignments given above, the isomer with the higher field methyl resonance is considered to have structure **2a**, in which the methyl group is adjacent to the *N*-oxide oxygen; accordingly, the other isomer is assigned structure **2b**.

Discussion

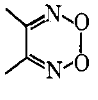
The most obvious mechanism for the type of interconversions under consideration involves ring opening of the furazan oxide to give a dinitroso intermediate (or transition state) (structure A) that rapidly cyclizes to give either the original or the isomeric furazan oxide. However, in addition to A, there are four other structures, B–E, whose possible involvement as intermediates (or transition states) in these interconversions can be considered for the sake of completeness.



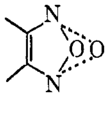
A



B



C



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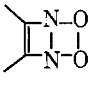

E

The relative energies of structures A, C, D, and E can be estimated by the use of bond energies[13]; in this way C, D, and E are calculated to have higher energy contents than A by 64, 78, and 100 kcal./mole, respectively. We believe that these energy values are so

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(9) G. Englert, *Z. anal. Chem.*, **181**, 447 (1961).

(10) All n.m.r. peak positions are given in p.p.m. downfield from tetramethylsilane as an internal standard.

(11) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

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

(13) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths and Co. (Publishers) Ltd., London, 1958. The specific values in kcal./mole used in the calculations are as follows: C=C, 146; C—C, 83; C=N, 147; C—N, 73; N=O, 145; N—O, 53; N—N, 39; and O—O, 35.

large, relative to the uncertainties in their magnitudes and also relative to the measured activation energies given in Table II, that C, D, and E can confidently be dismissed from consideration as having any mechanistic significance in furazan oxide interconversions. Appropriate bond energy values are not available for use in calculating the energy of the internal nitroso dimer structure B relative to the dinitroso structure A, but other data exist that allow a rough estimate of this quantity to be made. Thus, the dimers of some nitrosobenzenes have been determined to be stable with respect to dissociation to the monomers by less than 10 kcal./mole.[14] In the case of structure **B**, the strain energy is expected to be more than 30 kcal./mole,[15] so that we consider it likely that B is at least 20 kcal./mole higher in energy content than A. On the basis of these various energy considerations,[16] *cis*-1,2-dinitrosoalkenes (A) emerge as the only reasonable candidates for the intermediates (or transition states) in furazan oxide interconversions.[17]

The kinetic results described above for the **2a** $\rightleftharpoons$ **2b** and the **3a** $\rightleftharpoons$ **3b** equilibrations are consistent with the mechanistic involvement in these interconversions of the dinitrosoalkenes **4** and **5**, respectively. Thus, the observed first-order behavior is required for the postulated unimolecular mechanism. Also, the entropies of activation are positive, in accord with the expected ring-opened nature of the transition states compared to the furazan oxides from which they are derived. Finally, the lack of any appreciable solvent effect is in agreement with the "no-mechanism" character proposed for these isomerizations.

Although the interconversions of benzofurazan oxides and simple furazan oxides proceed at vastly different rates (the former reactions have been found[1a] to be about 10^8 times faster at 30° than the latter reactions are at 130°), they are considered to have closely analogous mechanisms. This mechanistic similarity is evidenced by the observation that the entropies of activation are the same, within experimental uncertainty, for the interconversion reactions of these two types of *N*-oxides.[1a] The energies of activation found in the present work are about 20 kcal./mole larger than those found previously in the benzofurazan oxide studies.[1a] This large difference in activation energies is viewed as a consequence of the aromatic resonance stabilization that exists for the dinitrosobenzenes but not for the dinitrosoalkenes. That is, the sacrifice in resonance energy is expected to be larger in the ring openings of simple furazan oxides, in which an aromatic benzene-like system is converted to an acyclic system, than in the ring openings of benzofurazan oxides, in which a naphthalene-like system is converted to a *bona fide* benzene system.

Experimental Section

Methylphenylfurazan Oxides (2a and 2b). A magnetically stirred solution prepared by dissolving 8.3 g. (0.36 g.-atom) of sodium in 1 l. of absolute ethanol was maintained at 0° during the dropwise addition of 48.4 g. (0.36 mole) of freshly distilled phenylacetone. Then 42.0 g. (0.36 mole) of freshly prepared *n*-amyl nitrite[18] was added over a period of 1.5 hr., and the mixture was allowed to stand overnight. The solvent was evaporated under reduced pressure and the residue was dissolved in 500 ml. of water. This solution was acidified with hydrochloric acid and cooled to give a precipitate that was collected and then recrystallized from 95% ethanol to give 43.6 g. (74%) of 1-phenylpropane-1,2-dione-1-oxime, m.p. 167.3–168.8° (lit.[19] m.p. 164–165°).

A solution of 43.6 g. (0.27 mole) of 1-phenylpropane-1,2-dione-1-oxime, 21.6 g. (0.54 mole) of sodium hydroxide, and 18.9 g. (0.27 mole) of hydroxylamine hydrochloride in 400 ml. of water was heated on a steam bath for 1 hr. and then allowed to stand overnight. The precipitate was collected by filtration, suspended in boiling 95% ethanol for 15 min., and collected again to give 38.0 g. (80%) of methylphenylglyoxime, m.p. 237.5–238.2° (lit.[5] m.p. 238–239°), to which the *anti* configuration has been assigned.[5]

To a solution of 38.0 g. (0.21 mole) of methylphenylglyoxime and 17.6 g. (0.44 mole) of sodium hydroxide in 400 ml. of water maintained at 0° was added 300 ml. of cold, 5% aqueous sodium hypochlorite (Clorox). The precipitate was collected and dried to give 30.0 g. (80%) of a mixture of the two methylphenylfurazan oxides. Separation of this mixture and purification of the individual isomers by several recrystallizations from 95% ethanol according to a previously described procedure[5] gave 3-methyl-4-phenylfurazan oxide (**2a**), m.p. 95.2–95.8° (lit.[5] m.p. 96°), and 4-methyl-3-phenylfurazan oxide (**2b**), m.p. 61.6–62.4° (lit.[5] m.p. 62°). The infrared spectra of both isomers agreed with those previously reported.[20] The 60-Mc. n.m.r. spectra[21] in deuteriochloroform solution exhibited the following peaks: a singlet of relative area 3.0 at 2.33 and a complex multiplet of relative area 5.0 at 7.47–7.77 p.p.m. for **2a**; a singlet of relative area 3.0 at 2.53 and a complex multiplet of relative area 5.0 at 7.45–8.22 p.p.m. for **2b**.

Ethylmethylfurazan Oxides (3a and 3b). Ethylmethylglyoxime, prepared from 2,3-pentanedione and hydroxylamine, was treated with aqueous sodium hypochlorite (Clorox) in alkaline solution at 0°. The crude product was purified by molecular distillation at *ca.* 30 mm. The pale yellow distillate[22] was separated by g.l.p.c. using an Aerograph Model A-90-C gas chromatograph with a 4 ft. × $^1/_4$ in. tris(cyanoethoxy)propane column (5% on Anakrom) at 100° to give samples of 3-ethyl-4-methylfurazan oxide (**3b**; retention time 15 min.) and 4-ethyl-3-methylfurazan oxide (**3a**; retention time 19 min.) that were each nearly free from contamination with the other isomer. The ratio of **3b** to **3a** in the molecular distillate was approximately 3:2. N.m.r. spectra[21] of the two samples were obtained at 60 Mc. in carbon tetrachloride solution. The spectrum of **3a** consisted of a triplet centered at 1.33 and a quartet centered at 2.67 p.p.m. (J = 7.5 c.p.s.) associated with the ethyl group, and a singlet at 2.09 p.p.m. associated with the ring methyl group. The spectrum of **3b** consisted of a triplet centered at 1.22 p.p.m. and a quartet centered at 2.53 p.p.m. (J = 7.5 c.p.s.) associated with the ethyl group, and a singlet at 2.32 p.p.m. associated with the ring methyl group.

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(14) V. v. Keussler and W. Lüttke, *Z. Elektrochem.*, **63**, 614 (1959).

(15) The strain energy of cyclobutadiene has been estimated to be 32.8 kcal./mole by M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 87, 3255 (1965).

(16) Entropy considerations would also favor structure A over structures B–E.

(17) Similar calculations and arguments can be used to provide additional support for the earlier conclusion[1a] that the interconversions of benzofurazan oxides proceed by way of *o*-dinitrosobenzenes as opposed to species with structures analogous to B, C, D, and E.

(18) W. A. Noyes, *J. Am. Chem. Soc.*, **55**, 3888 (1933).

(19) H. Rheinboldt and O. Schmitz-Dumont, *Ann.*, **444**, 113 (1925).

(20) A. Dornow, K. J. Fust, and H. D. Jordan, *Ber.*, **90**, 2124 (1957).

(21) These n.m.r. spectra were obtained with a Varian A-60 spectrometer at Rutgers University through the courtesy of Dr. D. B. Denney.

(22) In an earlier preparation (R. Scholl, *Ber.*, 23, 3490 (1890)) a b.p. of 115–116° (16.5 mm.) was reported, and satisfactory elemental analyses were obtained.