in the ultraviolet, free hydroxyl in the infrared but no carbonyl (lit.,[2,9a] m.p. 226–228° $[\alpha]^{20}D$ −12°).

Anal. Calcd. for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found: C, 77.64; H, 10.38.

The diacetate (acetic anhydride–pyridine, steam bath, 2 hr.) was obtained as plates from methanol, m.p. 218–220°, $[\alpha]^{20}D$ −9°, acetate but no free hydroxyl bands in the infrared (lit.,[2,9b] m.p. 223–225°, $[\alpha]^{20}D$ −8°.

Anal. Calcd. for $C_{31}H_{48}O_5$: C, 74.36; H, 9.66; acetyl, 17.1. Found: C, 74.29; H, 9.56; acetyl, 16.3

The bis-3,5-dinitrobenzoate (3,5-dinitrobenzoyl chloride–pyridine, 3 hr., steam bath) was obtained as plates from acetone–methanol, m.p. 186–187°, $[\alpha]^{20}D$ +35°.

Anal. Calcd. for $C_{41}H_{48}O_{13}N_4$: C, 61.18; H, 6.01; N, 6.96. Found: C, 61.29; H, 6.14; N, 6.85.

22,26-Oxido-$\Delta^{5,17(20)}$-cholestadiene-3β,16ξ-diol (IIb).—The lithium aluminum hydride reduction of 22,26-oxido-$\Delta^{5,17(20)}$-cholestadiene-3β,22-diol-16-one (Ib) carried out exactly as in the preparation of IIa gave IIb in a yield of 65% as needles after recrystallization from methanol, m.p. 236–237°, $[\alpha]^{20}D$ −80° (lit.,[7,9c] m.p. 236–237°, $[\alpha]^{20}D$ −81.3°).

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 78.28; H, 10.10.

The diacetate (acetic anhydride–pyridine, 2 hr., steam bath) was obtained as rectangular plates from chloroform–methanol, m.p. 258–260°, $[\alpha]^{20}D$ −71° (lit.,[7,9d] m.p. 260–262° $[\alpha]^{20}D$ −70.7°).

Anal. Calcd. for $C_{31}H_{46}O_5$: C, 74.66; H, 9.29; acetyl, 17.3. Found: C, 74.53; H, 8.99; acetyl, 17.1.

The bis-3,5-dinitrobenzoate (3,5-dinitrobenzoyl chloride–pyridine 3 hr., steam bath) was obtained as thin plates from acetone–methanol, m.p. 206–207°, $[\alpha]^{20}D$ −1°.

Anal. Calcd. for $C_{41}H_{46}O_{13}N_4$: C, 61.34; H, 5.77; N, 6.97. Found: C, 61.52; H, 5.72; N, 6.77.

22,26-Oxido-$\Delta^{17(20)}$-cholestene-3,16-dione (III).—To a stirred solution of 300 mg of 22,26-oxido-$\Delta^{17(20)}$-cholestene-3β,16ξ-diol (IIa) in 200 ml. of acetone at 20°, was added dropwise, an 8 *N* solution of chromic acid in dilute sulfuric acid (*ca.* 40%) until a persistent orange-brown coloration indicated oxidation was complete. The mixture was diluted with water and the crystalline precipitate was collected, washed with water, and dried to yield 280 mg. of III, m.p. 182–188°. Recrystallization from ethanol raised the melting point to 195–197°, $[\alpha]^{20}D$ −78°, λ_{max} 236 (ϵ 10,400), ν^{CHCl_3} 1706 cm.$^{-1}$ strong (3-ketone and 16-ketone) and 1666 cm.$^{-1}$, strong (double bond in conjugation with a carbonyl).

Anal. Calcd. for $C_{27}H_{40}O_3$: C, 78.59; H, 9.77. Found: C, 78.82; H, 9.54.

The monoöxime (hydroxylamine hydrochloride, methanol–pyridine, water, steam bath, 2 hr.) was obtained as plates from ethanol, m.p. 234–237°, with slight decomposition.

Anal. Calcd. for $C_{27}H_{41}O_3N$: C, 75.83; H, 9.67, N, 3.28. Found: C, 75.70; H, 9.50; N, 3.33.

Reduction of III with lithium aluminum hydride gave the original diol IIa in a yield of 60%.

Acknowledgment.—We are indebted to Dr. G. Rosenkranz, Syntex, S.A., Mexico, for a generous supply of kryptogenin.

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(9) (a) Considered previously to be IVa; (b) acetate of IVa; (c) considered previously to be IVb; (d) acetate of IVb.

Furazan Oxides. II. Evidence for Equilibria of Benzofurazan Oxides with *o*-Dinitrosobenzenes[1]

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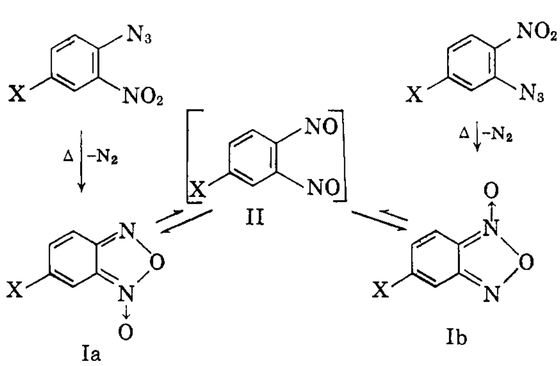
The fact that the pyrolysis of either of the substituted nitroazides of the type shown below yields a single compound X—$C_6H_3N_2O_2$ rather than two separate isomeric benzofurazan oxides such as Ia and Ib was originally thought[2] to indicate a symmetrical configuration of the N_2O_2 grouping. However, recent n.m.r.[3,4] and X-ray[5] results have demonstrated the validity of the unsymmetrical *N*-oxide formulation I for this class of compound. These results require the existence of an equilibration Ia ⇌ Ib such that only the more stable isomer is isolated. This type of equilibration was originally postulated by Hammick[6] and has recently been demonstrated by n.m.r. studies.[3,4] For example, the proton resonance pattern of the parent benzofurazan oxide (I with X = H) is a complicated ABCD type at low temperatures but changes to a symmetrical A_2B_2 pattern at higher temperatures when the rate of the Ia ⇌ Ib interconversion is sufficiently rapid that only the average proton environments are detected. Similarly, the two peaks of the O^{17} n.m.r. spectrum of I (X = H) at room temperature coalesce to a single peak above 45°.[4]



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[1] Presented before the Organic Division at the National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13, 1962.

[2] M. O. Forster and M. F. Barker, *J. Chem. Soc.*, **103**, 1918 (1913).

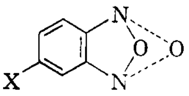
[3] G. Englert, *Z. anal. Chem.*, **181**, 447 (1961); F. B. Mallory and C. S. Wood, *Proc. Natl. Acad. Sci.*, **47**, 697 (1961); G. Englert, *Z. Naturforsch*, **16b**, 413 (1961); A. R. Katritzky, S. Øksne, and R. K. Harris, *Chem. Ind.* (London), 990 (1961).

[4] P. Diehl, H. A. Christ, and F. B. Mallory, *Helv. Chim. Acta*, **45**, 504 (1962).

[5] D. Britton and W. E. Noland, *Chem. Ind.* (London), 563 (1962).

[6] D. L. Hammick, W. A. M. Edwards, and E. R. Steiner, *J. Chem. Soc.*, 3308 (1931).

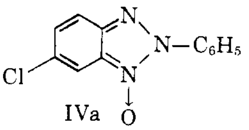
This type of interconversion has been assumed[3,4,6] on plausibility grounds to proceed by way of an *o*-dinitrosobenzene[7] such as II. However, it is conceivable, although less likely, that the equilibration occurs by way of a bicyclic configuration of heteroatoms, such as in III.[8]



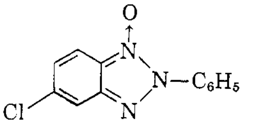
III

Two pieces of evidence are now available to help distinguish between these two mechanisms. First, from the results of the recent kinetic study[4] which was based on the temperature dependence of the proton and O^{17} n.m.r. spectra of benzofurazan oxide a value of 10 ± 4 e.u. can be calculated for the activation entropy of the process Ia $\rightleftharpoons$ Ib (with $X = H$). Although there is considerable uncertainty in the magnitude of this value there is reasonable assurance that the sign is positive, which is in accord with the mechanism of ring opening to *o*-dinitrosobenzene as a transient intermediate (or transition state). On the other hand, the Ia $\rightleftharpoons$ III $\rightleftharpoons$ Ib mechanism would be expected to have a negative activation entropy.

Further support for the mechanism involving the dinitroso form II as opposed to the bicyclic form III has been obtained from a study of the analogous benzotriazole oxides IVa and IVb.

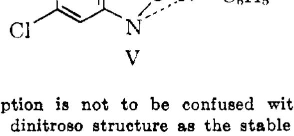


IVa



IVb

In contrast to the substituted benzofurazan oxides, where rapid equilibration precludes isolating both isomers, the corresponding compounds IVa and IVb have each been prepared and shown to be nonidentical crystalline solids. Furthermore, IVa and IVb did not interconvert on heating as liquids at 145°. This indicates that the bicyclic configuration V, which would provide a path for the interconversion IVa $\rightleftharpoons$ V $\rightleftharpoons$ IVb, is not readily accessible. This negative result lends indirect support to the hypothesis that the analogous bicyclic form III is not involved in the benzofurazan oxide equilibrations.

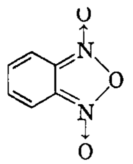


V

In view of the supposition of the transient existence of *o*-dinitrosobenzenes in equilibrium with the corresponding benzofurazan oxides, it is surprising that chemical properties of nitroso groups have not been observed in the studies of these compounds. For example, benzofurazan oxide (I with $X = H$) does not give an azo compound on treatment with aniline[9] and is not oxidized to *o*-dinitrobenzene by nitric acid,[10] peracetic acid,[11] or performic acid.[11]

These observations may be rationalized by assuming that molecules in the *o*-dinitroso form undergo ring closure to benzofurazan oxides at rates which are much faster than the rates of any reactions characteristic of isolated aromatic nitroso groups. Alternatively, it might be that the two nitroso groups are never free from a strong mutual interaction which could alter the normal properties of such groups.

The one seeming exception to this behavior involves the reported oxidation of I ($X = H$) with peroxytrifluoroacetic acid to give *o*-dinitrobenzene in low yield.[12] Although this may represent a reaction taking place by way of *o*-dinitrosobenzene, which is presumed to be present in extremely low concentration at equilibrium, it is also possible that this reaction proceeds by oxidation of the furazan oxide to benzofurazan dioxide (VI). This dioxide has been shown[13] to be unstable with respect to ring opening to *o*-nitronitrosobenzene which would be oxidized under the reaction conditions to *o*-dinitrobenzene.



VI

Experimental[14]

4-Chloro-2-nitroazobenzene.—A solution of 1.9 g. (0.01 mole) of 4-chloro-2-nitronitrosobenzene[13] and 1.0 ml. (0.9 g., 0.01 mole) of freshly distilled aniline in 50 ml. of glacial acetic acid was stirred magnetically at room temperature in the dark for 5 hr. The solution was diluted with 100 ml. of water, and cooled in an ice bath. The crude brown precipitate was collected by suction filtration, washed with 100 ml. of water, and sublimed[15] at 85° (0.05 mm.) to give 2.4 g. (92%) of dark red crystals, m.p. 91.8–92.5°. The sublimate was recrystallized twice from 95% ethanol in the dark to give orange needles, m.p. 92.2–92.5°.

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[7] This assumption is not to be confused with the erroneous assignment of the dinitroso structure as the stable configuration of benzofurazan oxides by Boyer. See J. H. Boyer in "Heterocyclic Compounds," R. C. Elderfield, ed., John Wiley & Sons, Inc., New York, N. Y., 1961, p. 462.

[8] This type of structure also was once mistakenly considered to be the stable configuration of benzofurazan oxides. See A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **103**, 897 (1913), and ref. 2.

[9] P. Ruggli and F. Buchmeier, *Helv. Chim. Acta*, **28**, 850 (1945).

[10] P. Drost, *Ann.*, **307**, 49 (1899).

[11] A. S. Bailey and J. R. Case, *Tetrahedron*, **3**, 113 (1958).

[12] J. H. Boyer and S. E. Ellzey, Jr., *J. Org. Chem.*, **24**, 2038 (1959).

[13] F. B. Mallory, K. E. Schueller, and C. S. Wood, *ibid.*, **26**, 3312 (1961).

[14] All melting points are uncorrected. Analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[15] F. B. Mallory, *J. Chem. Ed.*, **39**, 261 (1962).

Anal. Calcd. for $C_{12}H_8ClN_3O_2$: C, 55.08; H, 3.08. Found: C, 55.28; H, 3.34.

5-Chloro-2-nitroazobenzene.—The procedure was as described above. From 1.9 g. (0.01 mole) of 5-chloro-2-nitronitrosobenzene[13] and 1.0 ml. (0.9 g., 0.01 mole) of aniline was obtained after sublimation 2.4 g. (92%) of bright red needles, m.p. 92.6–94.2°. The sublimate was recrystallized from 95% ethanol to give 2.2 g. (84%) of orange needles, m.p. 93.6–94.2° (lit.,[16] m.p. 94°).

6-Chloro-2-phenylbenzotriazole Oxide.—A solution prepared by warming 2.6 g. (0.01 mole) of 4-chloro-2-nitroazobenzene in 10 ml. of 95% ethanol was stirred magnetically and a solution of 9.6 g. (0.04 mole) of sodium sulfide nonahydrate in 30 ml. of water was added all at once. After stirring at room temperature for 17 hr. the mixture was cooled in an ice bath and the light tan solid was collected by suction filtration. The crude material was sublimed at 125° (0.05 mm.) to give 2.4 g. (97%) of pale yellow crystals. Two recrystallizations from 95% ethanol (Norit) gave 2.2 g. (90%) of white needles, m.p. 141.6–142.4°. A small sample which had been recrystallized twice more from ethanol melted at 142.2–142.8°.

Anal. Calcd. for $C_{12}H_8ClN_3O$: C, 58.67; H, 3.28. Found: C, 58.91; H, 3.15.

5-Chloro-2-phenylbenzotriazole Oxide.—The procedure was as described above. From 2.6 g. (0.01 mole) of 5-chloro-2-nitroazobenzene and 9.6 g. (0.04 mole) of sodium sulfide nonahydrate was obtained after sublimation 2.3 g. (94%) of light yellow crystals. Two recrystallizations from 95% ethanol (Norit) gave 2.0 g. (82%) of white needles, m.p. 139.8–140.4° (lit.,[16] m.p. 142.5°).

Attempted Isomerization of Benzotriazole Oxides.—Separate 0.1-g. portions of 6-chloro-2-phenylbenzotriazole oxide and 5-chloro-2-phenylbenzotriazole oxide were heated for 2.5 hr. in an oil bath maintained at 145°. The 5-chloro isomer became dark on heating while the 6-chloro compound underwent no visible change. In each case, the infrared spectrum of the sample after heating was identical with that of the pure compound.

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[16] C. Willgerodt and L. Ellon, *J. prakt. Chem.*, **44**, 67 (1891).

Naphthalene as a Photoquencher

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Received July 3, 1962

Our interest in a photoadduct between naphthalene and maleic anhydride was intensified by reports of an analogous reaction proceeding with benzene.[1–3] Preliminary evaluation led us to the conclusion the former reaction should proceed in the same manner as the latter and, as a consequence, the reaction would be of lesser significance. However, upon further consideration it was observed that a decision could be made between a 1,2- and a 1,4-addition as the initial reaction of maleic anhydride with naphthlene if the reaction occurred. An analogy could then be made to the benzene photoproduct formation. Two quite different products would be expected depending on the mode of the first addition.

Upon irradiation of naphthalene and excess maleic anhydride in tetrahydrofuran, no photoadduct was found. Naphthalene was recovered quantitatively and the maleic anhydride nearly so with an uncharacterized polymeric material. In an irradiation under identical circumstances without naphthalene, the polymer was obtained exclusively.

On the basis of these results we conclude that naphthalene has a quenching effect on the photoinduced polymerization of maleic anhydride. A similar observation has recently been reported by Moore and Ketchum[4] for the influence of naphthalene on the photoreduction of benzophenone.

Experimental

The following reaction solutions were irradiated simultaneously in identical quartz vessels with a 140-watt Hanovia high pressure mercury arc lamp.

Irradiation of Naphthalene and Maleic Anhydride.—A solution of 5.6 g. (0.057 mole) of maleic anhydride and 1.44 g. (0.011 mole) of naphthalene in 30 cc. of purified tetrahydrofuran was irradiated for 8 hr. Distillation of the reaction mixture provided 4.88 g. (87%) of maleic anhydride. Chromatography of the residue on alumina produced 1.40 g. (97%) of naphthalene. On further elution a gum appeared which was not completely eluted until ether was passed over the column.

Irradiation of Maleic Anhydride.—The above procedure was duplicated omitting the naphthalene. Distillation provided no maleic anhydride and alumina chromatography failed to yield material other than an amorphous gum.

Acknowledgment.—The financial support received from the Research Corporation which made this research possible is gratefully acknowledged.

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[1] E. Grovenstein, Jr., D. V. Rao, and J. W. Taylor, *J. Am. Chem. Soc.*, **83**, 1705 (1961).

[2] G. O. Schenkt and R. Steinmetz, *Tetrahedron Letters*, **21**, 1 (1961).

[3] H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960).

[4] W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

Formation of Dibenzothiophene by a Disulfide Ring Closure[1]

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Disulfides, derived by oxidation of β-aryl-α-mercaptoacrylic acids, have been shown in earlier reports[2,3] to undergo cyclization in the presence of a Lewis acid to give the corresponding condensed

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[1] This research was supported in part by the U. S. Army Research Office (Durham) under contract No. DA-33-008-ORD-1916.

[2] E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 39 (1956).

[3] E. Campaigne and W. E. Kreighbaum, *J. Org. Chem.*, **26**, 1326 (1961).