symmetry-allowed concerted process in the *ground state.* The photoinduced reaction may be only a dark reaction in which electronically excited states internally convert to vibrationally excited ground states. Support for this view is found in the thermochromic behavior of **1a**. Thus, heating crystals of **1a**, up to 150°, developed the same blue color. Furthermore, thermal cycloaddition with TCNE or dimethyl acetylenedicarboxylate in toluene at 100° for 3 hr gave 60–70% yields of cycloadducts[10] having identical stereochemistry with the corresponding photoproducts. On the other hand, if the photochemical ring opening were to take a disrotatory course to form *anti*-**4** (Scheme I) thermal ring closure would be expected to take an opposite course to give the new *endo*-**1**. Such an exo–endo isomerization has not been observed to date. Examination of scale models suggests that the endo isomer of **1** is sterically unfavorable in general and impossible in the case of **1a** and **1c**. Indeed, our attempts to detect *endo*-**1a** in the synthesis[1a] of *exo*-**1a** or in its base-catalyzed epimerization[11] have been so far unsuccessful. To the extent that the formation of *endo*-**1a** appears unfeasible, a ground-state conrotatory course to and from *exo*-**1a** may be a more favored process. Complementary evidence for this view is found in the very low quantum yields of luminescence ($<10^{-3}$) from these photochromic aziridines or their colored intermediates even at 77°K. (The photocoloration can also be sensitized by triplet sensitizers of $E_T > 70$ kcal/mol.) Vibrationally excited ground states have been suggested by Ullman and Henderson[12] for the thermophotochromic system of indenone–benzopyrylium oxide which provides an excellent analogy to ours.

Acknowledgment. We thank Professor H. W. Heine for a generous supply of **1a** and for stimulating and timely discussions.

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(10) Heine, *et al.*,[1b] reported a similar reaction with diethyl acetylenedicarboxylate.

(11) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *J. Amer. Chem. Soc.*, 87, 1050 (1965).

(12) E. F. Ullman and W. A. Henderson, *ibid.*, 86, 5050 (1964).

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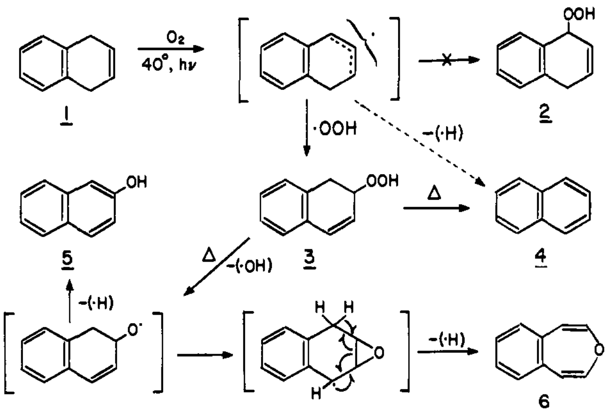
Autoxidation of 1,4-Dihydronaphthalene. Formation of 3-Benzoxepin *via* Pyrolysis of 1,2-Dihydronaphthalene 2-Hydroperoxide

Sir:

The considerable current interest in the chemistry[1a,b] and biochemistry[1c,d] of arene oxides and oxepins has prompted us to report a novel and convenient synthesis[2] of 3-benzoxepin (**6**). The route was discovered in the course of an attempt to prepare 1,4-dihydronaphthalene 1-hydroperoxide (**2**) by the reported autoxidation of 1,4-dihydronaphthalene (**1**). The latter reaction did not proceed as described,[3a,b] but led instead to 1,2-dihydronaphthalene 2-hydroperoxide (**3**) together with naphthalene (**4**), 2-naphthol (**5**), a polymeric mixture, and, quite unexpectedly, 3-benzoxepin (**6**) (Scheme I).

Scheme I



In a typical experiment, 5 g of **1**[4] was maintained at 45° and irradiated with a 60-W fluorescent lamp while oxygen was passed through the liquid. After 48 hr, the mixture became too viscous for oxygenation to be continued. Dilution of the reaction mixture with 5 ml of ether was followed by precipitation of the polar components (3.2 g) with isopentane (50 ml), providing a preliminary separation. A small amount of **6** along with **1**, **4**, and **5** was found in the yellow isopentane solution. The hydroperoxide **3**, the major component in the viscous precipitate, was obtained as a colorless oil[5] by tlc on silica gel.[6] The mass spectrum of **3** shows a weak molecular ion (*m/e* 162, 3%) with fragments resulting from the loss of 16 (18%), 18 (42%), and 34 (100%) mass units. The nmr spectrum of **3** (1 $H_{1,ax}$ 2.95, 1 $H_{1,eq}$ 3.27, 1 H_2 4.73, 1 H_3 5.98, 1 H_4 6.75, and four aromatic protons 7.0–7.25; $^2J_{1,1} = 17.3$, $^3J_{1ax,2} = 6.1$, $^3J_{1eq,2} = 4.7$, $^3J_{2,3} = 4.4$, $^4J_{2,4} = 0.7$, and $^3J_{3,4} = 9.5$ Hz)[7] indicates a 3,4 double bond and quasiaxial substitution by oxygen at the 2 position. The structure of **3** was established by its chemical reactions. Decomposition by 20% Na_2CO_3 (100°, 5 min) gave **5** with only a trace of 1-naphthol, which presumably arose from a minor contaminant of **2**. Similarly, reduction of **3** with Pd and hydrogen gave 2-tetralol with only a trace of the 1 isomer.[8]

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(1) (a) C. H. Foster and G. A. Berchtold, *J. Amer. Chem. Soc.*, **93**, 3831 (1971); (b) L. A. Paquette and T. McCreadie, *J. Org. Chem.*, **36**, 1402 (1971); (c) B. R. Brodie, W. D. Reid, A. K. Cho, G. Sipes, G. Krishna, and J. R. Gillette, *Proc. Nat. Acad. Sci. U. S.*, **68**, 160 (1971); (d) P. L. Grover, P. Sims, E. Huberman, H. Marquardt, T. Kuroki, and C. Heidelberger, *ibid.*, **68**, 1098 (1971).

(2) For earlier syntheses, see K. Dimroth, G. Pohl, and H. Follmann, *Chem. Ber.*, **99**, 634 (1966); E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); and G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969).

(3) (a) H. Hock and F. Depke, *Chem. Ber.*, 83, 327 (1950); (b) M. Martan, J. Mangssen, and D. Votsi, *Israel J. Chem.*, 7, 751 (1969).

(4) No differences in yield or distribution of products were observed with **1** purified *via* its mercuric acetate complex; H. Donaldson, "The Chemistry and Technology of Naphthalene Compounds," E. Arnold and Co., London, 1958, pp 456–457. Also, autoxidation conditions identical with those used in ref 3 caused no change in products.

(5) Elemental analysis within 0.2% of theory. Low peroxide content (76% of theory) by the method of V. R. Kokatnur and J. Murray, *J. Amer. Chem. Soc.*, **63**, 1432 (1941), seemed due to acid-catalyzed decomposition of **3** during analysis.

(6) The plates were developed twice with benzene–toluene (9:1) at 4° in the dark, and the hydroperoxide was localized by uv fluorescence and acidic KI spray.

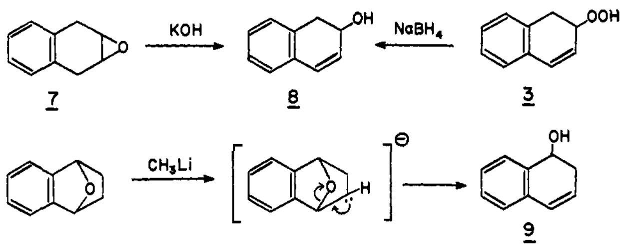
(7) All nmr spectra were run at 100 MHz in $CDCl_3$ and are reported with line positions in δ relative to TMS and coupling constants in hertz. Subscripts on hydrogens designate their position in the molecule.

(8) Analysis by vpc on 15% SE-30 at 130–140°; less than 2% 1-tetralol or 1-naphthol (as the trimethylsilyl ether) was present in the samples.

The origin of hydroperoxide **3** during the radical-chain autoxidation of **1** cannot as yet be stated with certainty; either **3** forms directly from the rearranged allylic radical (Scheme I), or the hydroperoxide **2** is first formed and rearranged to **3**. Although the rearrangement of allylic hydroperoxides in dilute solutions is quite facile, such isomerization is strongly inhibited by 2,6-di-*tert*-butyl-4-methylphenol.[9] The presence of **2** in the crude autoxidation mixture could not be established from the nmr spectrum of the mixture determined in deuterioacetone containing this inhibitor. Thus, we favor the arguments of Howard and Ingold[10] for the direct formation of **3**.

Hydroperoxide **3** was reduced with $NaBH_4$ in ethanol (0°, 2 hr) to 2-hydroxy-1,2-dihydronaphthalene (**8**) (78%, mp 20–25°).[11] The assigned structure of **8** (Scheme II) is consistent with its nmr and mass spectra.[12] This "naphthalene hydrate" **8** was also prepared by the base-catalyzed rearrangement (ethanolic KOH at room temperature for 1 week) of 1,4-dihydronaphthalene 2,3-oxide. First reported in 1895,[13] this reaction seems to be the most facile example of such epoxide rearrangements studied to date.[14] The isomeric "hydrate," 1-hydroxy-1,2-dihydronaphthalene **9**, was prepared (Scheme II) by the action of methyllithium on 1,2,3,4-tetrahydronaphthalene 1,4-oxide (28°, 10 days, 10%) and was readily distinguished from **8** by its nmr spectrum.[15] Both **8** and **9** were stable at neutral and basic pH, but readily dehydrated (k_{obsd} = 1.92×10^{-3} sec^{-1} and 3.57×10^{-4} sec^{-1}, respectively) to naphthalene in *n*-butyl alcohol which was 10 m*M* acid with concentrated HCl at 25°.

Scheme II



Perhaps the most interesting reaction of hydroperoxide **3** is thermal decomposition. While **1** is autoxidized at 40°, the resulting **3** spontaneously rearranges to oxepin **6** (Scheme I). Pyrolysis of pure, neat **3** (40°, 12 hr) converted half the material to polymeric peroxides along with a mixture of 60% **4**, 13% **5**, and 27% **6** as volatile components. The proportion of **6** is not increased when solutions of **3** are heated. Sublimation of crude **3** (5 g, 100° (5 mm), 1 hr) gave a mixture of compounds (1 g) from which 0.36 g of pure **6** was isolated by column chromatography on silica gel.[16] Although we do not exclude the possibility of a heterolytic process, formation of **6** seems likely to occur *via* the homolytic mechanism shown in Scheme I. Heterolytic decomposition of hydroperoxides most often occurs under acidic conditions and is typified by alkyl migration to oxygen.[17] In contrast, treatment of **3** with acid (0.5 *M* $HClO_4$ in 50% dioxane) gave naphthalene.

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[9] W. F. Brill, *J. Amer. Chem. Soc.*, 87, 3286 (1965).

[10] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 45, 785 (1967).

[11] Separated by tlc on silica gel developed with $CHCl_3$; R_f 0.5.

[12] The mass spectrum of 8 showed a weak molecular ion at *m/e* 146 (16%) with the base peak resulting from loss of 18 (100%) while the nmr spectrum was assigned as 2 H_1 2.98, 1 H_2 4.42, 1 H_3 6.06, 1 H_4 6.49, and four aromatic protons 6.9–7.3; $^3J_{1,2}$ = 6.0, $^3J_{2,3}$ = 4.4, and $^3J_{3,4}$ = 9.5 Hz.

[13] E. Bamberger and W. Lodter, *Justus Liebigs Ann. Chem.*, **288**, 100 (1895). Formation of a benzylic carbanion facilitates the reaction.

[14] More current examples can be found in the rearrangement of acyclic epoxides (J. K. Crandall and L. C. Lin, *J. Org. Chem.*, 33, 2375 (1968)) and of cyclohexene epoxides (J. Starosick and B. Rickborn, *J. Amer. Chem. Soc.*, 93, 3046 (1971)) to form the "hydrate of benzene" analogous to the "naphthalene hydrates" reported here.

[15] The mass spectrum of 9 showed a molecular ion at *m/e* 146 (39%) with the base peak resulting from loss of 18 (100%): the nmr spectrum was assigned as 1 H_1 4.80, 2 H_2 2.58, 1 H_3 6.00, 1 H_4 6.56, and four aromatic protons 7.0–7.5; $^3J_{1,2}$ = 5.6, $^3J_{2,3}$ = 4.3, $^4J_{2,4}$ = 1.8, and $^3J_{3,4}$ = 9.5 Hz.

[16] The 3-benzoxepin eluted from the column with isopentane and had nmr and mass spectra and melting point identical with authentic material.[2]

[17] See, for example, A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, pp 147–150, and P. A. S. Smith in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Wiley, New York, N.Y., 1963, pp 573–577. The acid-catalyzed rearrangement of 3-hydroperoxycyclohexene to adipaldehyde is the closest analogy to the system studied here.

[18] NATO Postdoctoral Fellow, 1970–1971.

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Cyclopentenyl Cation. A New Degenerate Rearrangement of an Allyl Cation

Sir:

Cyclopentenyl cation has not previously been reported as a stable species even though several alkylated cyclopentenyl cations have been prepared and studied in 96% H_2SO_4 by Deno and his coworkers.[1,2] We wish to report the preparation and properties of solutions of the cyclopentenyl cation and the observation of a new degenerate rearrangement process. 3-Chlorocyclopentene (prepared from cyclopentadiene and HCl gas at Dry Ice temperatures[3]) was treated with an excess of SbF_5 using a new apparatus in which molecular beams of the reagents are formed and impinge on a liquid nitrogen cooled surface in a highly evacuated chamber.[4] With this molecular beam apparatus, the polymerization which ordinarily occurs, using the standard procedure for preparing cations,[5] with unsaturated precursors due to attack of the cation on the unreacted allyl chloride, is almost completely eliminated.

The nmr spectrum of the ion with SO_2ClF added as a solvent, taken at room temperature, is shown in Figure 1. Proton 1 at τ 1.53 is coupled to proton 2 at −0.99 (J = 4 Hz). Proton 2 is coupled to proton 3 at τ 5.87 with a much smaller coupling constant as expected.[6] When peak 3 is spin decoupled, peak 2 becomes a clear doublet (J = 4 Hz). We believe that the sharp peak at τ 0.20 is due to a trace of HF or HCl.

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[1] N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. Hodge, and J. Houser, *J. Amer. Chem. Soc.*, 85, 2998 (1963).

[2] N. C. Deno, N. Friedman, J. Hodge, J. Houser, C. Pittman, and H. Richey, *ibid.*, 85, 2991 (1963).

[3] R. B. Moffet, "Organic Syntheses," Collect. Vol. 1, Wiley, New York, N. Y., 1963, p 238.

[4] M. Saunders and D. Cox, manuscript in preparation.

[5] M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, 90, 2436 (1968).

[6] Assuming a planar allyl cation form, the dihedral angle between H-2 and -3 would be 60°, which would be predicted to produce a small coupling constant.