

upon Na-NH₃-MeOH reduction of bullvalene^{14a} and of 1,4-dihydrobenzene from benzene.²¹ If only by analogy, such regioselectivity would appear to characterize two electron reductions that require protonation of the initially formed radical anion. In the bullvalene case, the more acidic reagents (NH₃-MeOH) can trap the radical anion before it acquires its second electron. In the case of dihydrobullvalene, acquisition of the second electron is sufficiently discouraged that protonation even by 1,2-dimethoxyethane (as well as dimerization) can intervene. Consistent with this view, DCI treatment of the dihydrobullvalene reaction solution incorporated less than 0.10 atoms of deuterium into either of the two products.

Potential exploitation of the bicyclo[3.3.2]decaatrienyl dianion as a template for the elaboration of C₁₁H₁₀O ketones,²² of C₁₂H₁₂ hydrocarbons,²³ and of novel organometallics is now under active investigation.

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(21) A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959); E. M. Kaiser, *Synthesis*, 391 (1972).

(22) M. J. Goldstein and S.-H. Dai, *Tetrahedron Lett.*, 535 (1974).

(23) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie-Academic Press, Weinheim, Germany, 1970, p 106.

(24) Schleuderberg Fellow, 1972-1973.

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Rearrangement of a Non-Arene Oxide via an NIH Shift Related Mechanism

Sir:

The chemical and metabolic isomerizations of various arene oxides to phenols have been demonstrated to occur *via* 1,2-hydride migrations, namely "NIH shifts."¹ Although a number of non-arene oxides are reported to undergo hydride or substituent migration in the epoxide-carbonyl rearrangement,² such migrations occur under thermal conditions or are catalyzed by Lewis acids.

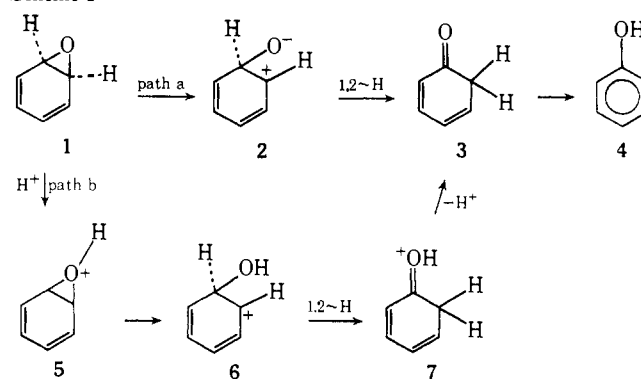
Recent investigations³ have established the existence of two independent pathways for the "NIH shift" in several unsubstituted arene oxides. For example, the rearrangement of benzene oxide (1) to phenol occurs *via* two competitive mechanisms, a spontaneous route

(1) (a) D. Jerina, J. Daly, B. Witkop, P. Zaltaman-Nirenberg, and S. Udenfriend, *Arch. Biochem. Biophys.*, **128**, 176 (1969); (b) D. M. Jerina, J. W. Daly, B. Witkop, P. Zaltaman-Nirenberg, and S. Udenfriend, *Biochemistry*, **9**, 147 (1970); (c) D. M. Jerina, J. W. Daly, B. Witkop, P. Zaltaman-Nirenberg, and S. Udenfriend, *J. Amer. Chem. Soc.*, **90**, 6523, 6525 (1968); (d) D. R. Boyd, D. M. Jerina, and J. W. Daly, *J. Org. Chem.*, **35**, 3170 (1970); (e) E. Boyland and P. Sims, *Biochem. J.*, **95**, 788 (1965).

(2) For a recent review of epoxide reactions, including the epoxide-carbonyl rearrangement, see J. G. Buchanan and H. Z. Sable in "Selective Organic Transformations," Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 1-95.

(3) (a) G. J. Kasperek and T. C. Bruice, *J. Amer. Chem. Soc.*, **94**, 198 (1972); (b) G. J. Kasperek, T. C. Bruice, H. Yagi and D. M. Jerina, *J. Chem. Soc., Chem. Commun.*, 784 (1972); (c) A third mechanism for the "NIH-shift" in several substituted arene oxides has been detected: G. J. Kasperek, T. C. Bruice, H. Yagi, N. Kanbisch, and D. M. Jerina, *J. Amer. Chem. Soc.*, **94**, 7876 (1972); H. Yagi, D. M. Jerina, G. J. Kasperek, and T. C. Bruice, *Proc. Nat. Acad. Sci. U. S. A.*, **69**, 1985 (1972).

Scheme I



(path a, Scheme I) and an acid-catalyzed route (path b, Scheme I). Dienone **3** has been suggested as an intermediate for both pathways.⁴ We wish to report the rearrangement of a non-arene oxide, cyclopentadiene oxide (**8**), by a spontaneous mechanism related to path a, Scheme I.

The kinetic data for the hydrolysis of **8** in aqueous buffer solutions between pH 5-9 fit eq 1. Values for

$$k_{\text{obsd}} = k_0 + k_{\text{H}^+}[\text{H}^+] + k_{\text{HA}}[\text{HA}] \quad (1)$$

k_0 , k_{H^+} , and k_{HA} are provided in Table 1. These data

Table I. Values of k_{H^+} , k_0 , and k_{HA} for the Hydrolysis of **8** at 25°^a

$k_{\text{H}^+} \times 10^{-3}$, M sec ⁻¹	8.3 ± 0.8 ^{b,c}
$k_0 \times 10^3$, sec ⁻¹	8.5 ± 0.3 ^{b,c}
$k_{\text{H}_2\text{PO}_4^-}$, M sec ⁻¹	0.093 ± 0.008 ^d
$k_{(\text{CH}_3)_2\text{AsO}_2\text{H}}$, M sec ⁻¹	0.038 ± 0.002 ^{d,e}

^a The appearance of **12** was monitored spectrophotometrically at 269 nm in the thermostated cell compartment (±0.1°) of a Gilford 2400 or Cary 16K spectrophotometer. ^b Obtained from a weighted least-squares plot of k_{obsd} vs. [H⁺]. Values of k_{obsd} were obtained from rates in buffered solutions, extrapolated to zero buffer concentration. ^c $\mu = 1.0$ (KCl). ^d Obtained from least-squares plots of k_{obsd} vs. [HA] at constant pH. The average of slopes at two different pH values is listed as k_{HA} . ^e $\mu = 1.0$ (NaCl).

reveal that the hydrolysis of cyclopentadiene oxide takes place by a spontaneous route (k_0) and an acid-catalyzed route (k_{H^+}), in addition to a general acid-catalyzed pathway (k_{HA}).

Product analyses carried out at pH 8.2,⁵ where the k_{H^+} term is negligible compared to the k_0 term, revealed that the pH-independent pathway (k_0) in the hydrolysis of **8** yields 33% of 3-cyclopentenone (**11**)⁶ and 32% of *cis*-2,4-pentadienal (**12**), in addition to 35% of a mixture of diols **9** and **10** (Scheme II).⁷ The rearrangement of **8** in D₂O at pD 7.6 yielded **11** without detectable incorporation of deuterium.⁸ Therefore, a 1,2-hydride

(4) A dienone intermediate has been isolated in the rearrangement of 8,9-indan oxide: G. J. Kasperek, P. Y. Bruice, T. C. Bruice, H. Yagi, and D. M. Jerina, *J. Amer. Chem. Soc.*, **95**, 6041 (1973).

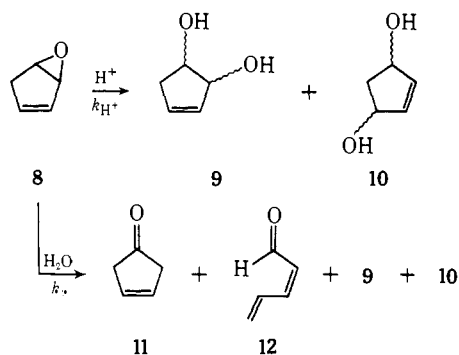
(5) Hydrolysis of **8** was carried out in dilute tris(hydroxymethyl)aminomethane solutions, 0.01 M total buffer. The yields of **11** and **12** were determined by a combination of uv and glpc.

(6) The infrared spectrum for **11** possessed $\nu_{\text{max}}^{\text{C=O}}$ 1750 cm⁻¹, and the unconjugated ketone was readily isomerized to 2-cyclopentenone.

(7) Previous investigations had reported only the formation of diols **9** and **10** from the hydrolysis of **8** in distilled water: (a) M. Korach, D. R. Nielsen, and W. H. Rideout, *J. Amer. Chem. Soc.*, **82**, 4328 (1960); (b) H. Z. Sable and Th. Posternak, *Helv. Chim. Acta*, **41**, 370 (1962). The nmr spectrum of the diol product mixture from hydrolysis of **8** in D₂O at pD 7.6 (phosphate buffer) indicated that the main product (ca. 45% of the diol mixture) was *trans*-1,4-diol, **10**. The ratio of 1,4-diols to 1,2-diols was ca. 55:45.

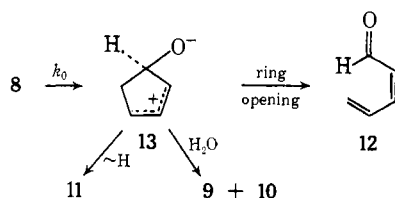
(8) The nmr spectrum of **11** isolated from rearrangement of **8** in D₂O at pD 7.6 (phosphate buffer) showed the ratio of the α -protons to the vinylic protons in **11** to be 2.0:1.0.

Scheme II



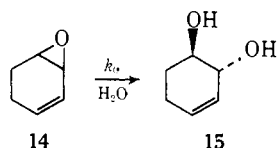
shift is required, and a mechanism whereby **11** is produced from an enol intermediate is eliminated as a major pathway. The rearrangement of **8** to **11** is therefore mechanistically analogous to the rearrangement of benzene oxide (**1**) to phenol *via* path a, Scheme I. Whether hydride migration occurs in the rate-determining step or subsequent to rate-determining formation of an intermediate zwitterion (Scheme III) has not been determined.⁹

Scheme III



Zwitterion **13** is potentially a common intermediate for all products obtained from the k_0 process. Of particular significance is the formation of significant amounts⁷ of cis and trans 1,4-diols, **10**, in addition to cis and trans 1,2-diols, **9**. This result is in marked contrast to that observed in the hydrolysis of 1,3-cyclohexadiene oxide (**14**), where the k_0 process yielded $\approx 98\%$ *trans*-3-cyclohexen-1,2-diol.¹⁰ Different mechanisms for diol formation from **14** and from **8** by the k_0 process therefore appear operative.

The presence of an hydroxide-catalyzed term in the hydrolysis of 1,3-cyclohexadiene oxide (**14**) at $\text{pH} > 12$



and the formation of predominantly *trans* 1,2-diol **15** strongly suggests nucleophilic displacement by water in the k_0 process for this epoxide. The formation of large amounts of 1,4-diols, **10**, and the absence of an hydroxide-catalyzed term in the hydrolysis of **8**¹¹ suggests a more delocalized intermediate such as **13**.¹²

(9) Studies of the rearrangement of naphthalene oxide show that hydride migration in the k_0 process occurs subsequent to rate-determining formation of a zwitterion. See ref 3b.

(10) D. L. Whalen, *J. Amer. Chem. Soc.*, **95**, 3432 (1973).

(11) The rate of hydrolysis of **8** did not change as the concentration of KOH was varied between 0.1 and 0.5 M.

(12) The similarity of the diol mixtures obtained from the k_0 process ($\text{pH} > 7.5$) and the k_{H^+} process ($\text{pH} < 5$) suggests a common intermediate. Protonation of the oxygen of zwitterion **13** might be expected to be fast relative to nucleophilic addition of water at the cationic center, thus leading to the same allylic cation intermediate formed by the k_{H^+} process.

The existence of a zwitterion intermediate is also suggested by the rearranged product **12**, which can potentially result from a concerted electrocyclic ring opening of **13**.

The acid-catalyzed hydrolysis of **8** at $\text{pH} \lesssim 4.0$, where the k_{H^+} term is much larger than the k_0 term, yielded less than 2% of either **11** or **12**.¹³ Instead, only a mixture of 1,2- and 1,4-diols, **14** and **15**, was obtained.¹⁴ The observation that the hydrolysis of **8** is general acid-catalyzed by a number of buffer acids is in line with our earlier suggestion that the hydrolyses of highly reactive epoxides are likely to exhibit such catalysis.¹⁰

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the American Cancer Society, Maryland Section, for support of this research.

(13) The epoxide samples used in these studies were contaminated with 3% of ketone **11** and 2% of aldehyde **12**. Glpc and uv analysis of the product mixture from hydrolysis of **8** at $\text{pH} 1-4$ indicated that the amounts of **11** and **12** present were, within experimental error, the same as were in the original epoxide sample.

(14) Nmr and glpc analyses of the diol mixture obtained from hydrolysis of **8** at $\text{pH} 2-8$ indicated that all four possible diols (cis and trans isomers of **9** and **10**) were obtained, the ratio of 1,4-diols to 1,2-diols being *ca.* 55:45. In a private communication, Dr. Henry Z. Sable informed us that he also obtained a mixture of all four diols from hydrolysis of **8** in distilled water.

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Mechanism of Stereoisomerization in Triarylboranes¹

Sir:

In previous studies concerning the mechanism of stereoisomerization in triarylboranes² and triarylcarbenium ions,³ the cumulative weight of circumstantial evidence has pointed to the two-ring flip mechanism as the mechanism of lowest energy (threshold mechanism). However, no experimental results have as yet appeared which rule out all alternatives to this mechanism. We wish to report the first direct evidence which establishes the two-ring flip as the threshold mechanism for triarylboranes and, by extension, for cognate systems.

Triarylboranes assume propeller conformations in the ground state, on the nmr time scale.² Although isomerizations of such molecules have commonly been discussed in terms of four flip mechanisms,^{2,3} each of which involves a reversal of helicity (sense of twist), there exist alternative nonflip rearrangements (in the permutational sense) in which isomerization is *not* accompanied by a reversal of helicity.⁴

Previous work^{2,3c,d} on boranes and carbenium ions, which showed that of the four flip mechanisms only the

(1) This work was supported by the National Science Foundation (GP-30257).

(2) J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7019 (1973).

(3) (a) I. I. Schuster, A. K. Colter, and R. J. Kurland, *J. Amer. Chem. Soc.*, **90**, 4679 (1968); (b) R. Breslow, L. Kaplan, and D. LaFollette, *ibid.*, **90**, 4056 (1968); (c) J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *ibid.*, **93**, 6522 (1971); (d) D. Gust and K. Mislow, *ibid.*, **95**, 1535 (1973).

(4) These nonflip rearrangements may be formally thought of as rotations of zero, one, two, or all three aryl rings by π radians, while the nonrotating rings remain fixed.