Only one absorption peak is obtained (at τ 8.77), which is further upfield than the methyl peak in pyruvic acid itself. A similar shift in the absorption in the methyl peak is known to accompany the formation of the hydrate of the parent acid.[16] Uncertainty in the assignment of a definite structure to product B results primarily from the absence of the acidic hydrogen in the nmr spectrum. For this reason a definite structure cannot be assigned to compound B at the present time, but we are certain that it is related to pyruvic acid. Infrared spectra were taken on a Perkin-Elmer infracord, and nmr spectra on a Varian A-56/60 nmr spectrophotometer in $CDCl_3$ which contained TMS. All pH measurements were made on a Beckman Model G pH meter.

(16) For a recent survey of the literature on nmr spectra of pyruvic acid and its hydrate, see N. Hellström and S.-O. Almqvist, *J. Chem. Soc. B*, 1396 (1970).

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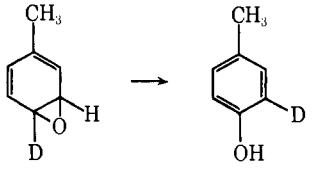
The Mechanism of the Aromatization of Arene Oxides

George J. Kasperek[1] and Thomas C. Bruice[2]*

Contribution from the Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106. *Received March 17, 1971*

Abstract: The kinetics of the aromatization of arene oxides has been studied at 30° (μ = 1.0) between pH 2.5 and 14.0. The pH–log k_{obsd} profiles for benzene oxide (**1**) and naphthalene oxide (**2**) are characterized by a straight line of slope −1.0 in the acid region in agreement with specific acid catalysis, and a plateau in the pH >7 region indicating a spontaneous aromatization. With phenanthrene oxide (**3**) only the acid-catalyzed portion was detected. For the spontaneous aromatization the entropy of activation ($\Delta S^{\pm}$ = −25.7), solvent deuterium kinetic isotope effect ($k_1^{H_2O}/k_1^{D_2O}$ = 1.33) at pH 12, and the established requirement of the NIH shift are in accord with a mechanism involving a rate-determining 1,2-hydride shift to form an enone which rapidly tautomerizes to the phenolic product. The detailed mechanism is discussed in light of the experimental data.

The oxidation to phenolic compounds is one of the most important biological reactions of aromatic hydrocarbons (*i.e.*, conversion of L-phenylalanine to L-tyrosine and the metabolism and detoxification of aromatic hydrocarbons by hydroxylases in the liver). Since it has been suggested that this oxidation proceeds through benzene oxides[3] (**1**) in the case of benzene, and 9,10-phenanthrene oxide[4] (**3**) in the case of phenanthrene, and proved to go *via* 1,2-naphthalene oxide[5] (**2**) in the case of naphthalene, the mechanism of the rearrangement of these arene oxides is of considerable interest. Any mechanism proposed for the aromatization of the arene oxides must incorporate the features of the NIH shift.[6] Thus, 3,4-epoxy-3,4-dihydrotoluene-*4*-^2H undergoes the NIH shift [7] (eq 1) on rearrangement to



(1)

4-hydroxytoluene-*3*-^2H in both the acid and neutral regions and naphthalene oxide-*1*-^2H also undergoes this shift[8] at pH 8. Although the aromatization of arene oxides[9] has been studied in some detail, there is little or nothing known about the catalysis of the reaction. It is stated, however, that proteins and even acetamide catalyze the formation of phenol from **1**,[3] but methanolic acetamide does not catalyze the formation of naphthol from **2**.[5c]

The present study deals with the dependence of the rates of the aromatization of **1**, **2**, and **3** upon lyate species and acetamide concentration.

Experimental Section

Materials. Benzene oxide was prepared by the method of Vogel[10] from 4,5-dibromocyclohexene oxide. The epoxidation of 4,5-dibromocyclohexene followed a modification of Van Tamelen's[11] method using *m*-chloroperbenzoic acid instead of perbenzoic acid. This brought the reaction time down from 1 month to 15 hr in refluxing chloroform. 1,2-Naphthalene oxide[12] and 9,10-phenanthrene oxide[13] were prepared as previously described.

Kinetic Measurements. All experiments reported here were carried out in aqueous solution at 30° with μ = 1.0 (KCl) unless otherwise noted in the text. The rate of disappearance of **1** was followed by recording the decrease in optical density at 250 nm over the entire pH range studied. The rates of formation of 1-naphthol from **2** and 9-phenanthrol from **3** were followed at 235 and 250 nm, respectively, in the same manner. The pH was maintained by the addition of a potassium hydroxide solution controlled by a Radiometer pH-stat assembly. The reactions were followed in a thermostated, stirred cell with a 3-cm path length specifically

(1) Postdoctoral Fellow of the National Institutes of Health, 1969–present.
(2) To whom inquiries should be addressed.
(3) D. M. Jerina, J. W. Daly, B. Witkop, P. Zaltzman-Nirenberg, and S. Udenfriend, *Arch. Biochem. Biophys.*, **128**, 176 (1968).
(4) E. Boyland and P. Sims, *Biochem. J.*, **95**, 788 (1965).
(5) (a) D. M. Jerina, J. W. Daly, and B. Witkop, *Biochemistry*, **9**, 147 (1970); (b) D. M. Jerina, J. W. Daly, B. Witkop, P. Zaltzman-Nirenberg, and S. Udenfriend, *J. Amer. Chem. Soc.*, **90**, 6525 (1968); (c) D. R. Boyd, D. M. Jerina, and J. W. Daly, *J. Org. Chem.*, **35**, 3170 (1970).
(6) G. Guroff, J. W. Daly, D. M. Jerina, J. Renson, B. Witkop, and S. Udenfriend, *Science*, **157**, 1524 (1967).
(7) D. M. Jerina, J. W. Daly, and B. Witkop, *J. Amer. Chem. Soc.*, **90**, 6523 (1968).
(8) D. R. Boyd, J. W. Daly, and D. M. Jerina, personal communication of unpublished results.
(9) References 3–8 and references therein.
(10) E. Vogel, W. A. Boll, and H. Gunther, *Tetrahedron Lett.*, 609 (1965).
(11) E. E. Van Tamelen, *J. Amer. Chem. Soc.*, 77, 1704 (1955).
(12) E. Vogel and F. G. Klarner, *Angew. Chem., Int. Ed. Engl.*, 7, 374 (1968).
(13) M. S. Newman and S. Blum, *J. Amer. Chem. Soc.*, 86, 5598 (1964).

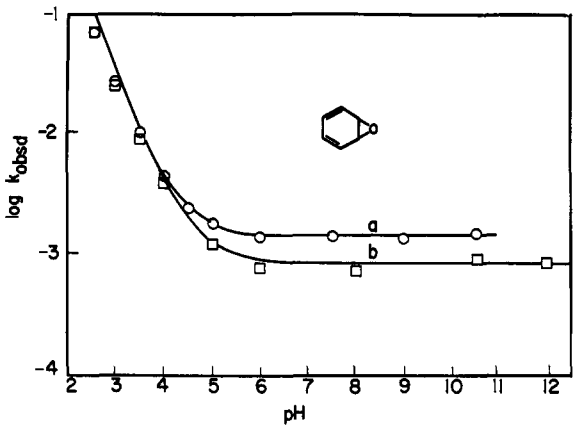


Figure 1. Plots of k_{obsd} *vs.* pH for the rearrangement of **1** at 30° in (a) water and (b) 10% aqueous acetamide. The points are experimental and the lines theoretical.

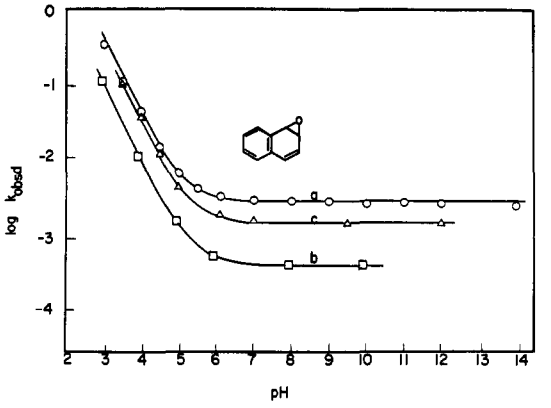


Figure 2. Plots of k_{obsd} *vs.* pH for the rearrangement of **2** at 30° in (a) water, (b) 30% aqueous ethanol, and (c) 10% acetamide. The points are experimental and the lines theoretical.

designed for the Cary-15 spectrophotometer.[14] Typically, 25 ml of 1.0 *M* potassium chloride was added to the cell; the pH was then adjusted to and maintained at the desired pH by the pH-stat assembly. The reaction was initiated by the addition of arene oxide from a concentrated solution ($0.1–10^{-3}$ *M*) in dioxane or tetrahydrofuran. The final concentrations in the aqueous solution were about 10^{-4} *M* in **1**, 10^{-5} *M* in **2**, and 4×10^{-7} *M* in **3**. In the reactions studied in 30% ethanol the concentration of **3** was raised to 5×10^{-6} *M*. Some kinetic runs were also made using 10^{-4} *M* **2** and these were followed at 305 nm. The glass electrode readings were corrected[15] to give readings of pH in the experiments conducted in 30% ethanol.

The observed OD *vs.* time curves were strictly first order and stable and reproducible infinity values were obtained. The values of the pseudo-first-order rate constants were calculated on an Olivetti-Underwood Programa 101 computer using a weighted least-squares analysis.

Product Analysis. At the end of each kinetic run the ultraviolet spectrum of the solution was taken, and this was compared with the spectrum of the expected phenolic product. In the case of **1**, **2**, and **3**, phenol, 1-naphthol, and 9-phenanthrol were the only products observed. Some 2-naphthol may be produced in the rearrangement of **2** which could not be detected by our method but it has been shown that only 2% of 2-naphthol is produced at pH 7 in aqueous solution.[4a]

Results

The pseudo-first-order rate constants for rearrangement of **1**, **2**, and **3** to phenol, 1-naphthol, and 9-phenanthrol, respectively, were determined over the pH range 2.5–14 at 30° in H_2O at $\mu = 1.0$ (with KCl). Examination of the log k_{obsd}–pH profiles for **1** and **2** (Figures 1 and 2) shows acid catalysis at low pH and a plateau in the pH >7 region. The solid lines which best fit the experimental points of Figures 1 and 2 are derived from eq 2. Values of k_1 and k_2 are presented

$$k_{obsd} = k_1 + k_2 a_H \qquad (2)$$

in Table I.

In the aromatization of **3** a spontaneous term was not detected (Figure 3) (no spectral change was observed in 24 hr at pH 10). Thus, if there is spontaneous rearrangement, k_1 for **3** is many orders of magnitude smaller than k_1 for **1** and **2**. Values of k_2 for **3** in H_2O can only be considered approximate because of its limited solubility and the inherent error associated with calculating rates from very small absorbancy changes ($\Delta OD < 0.1$). To overcome this the rate of rearrangement of **3** as a function of pH was measured in 30% aqueous ethanol at $\mu = 0.1$ (Figure 3b). The acid rate k_2 was lowered 4.3 times compared to k_2 in water. In order to compare **3** to the other arene oxides the rearrangement of **2** was also studied in 30% aqueous ethanol (Figure 2b). The ratio of k_2 in H_2O to k_2 in aqueous ethanol was found to be 4.3 for **2** as it is for **3**.

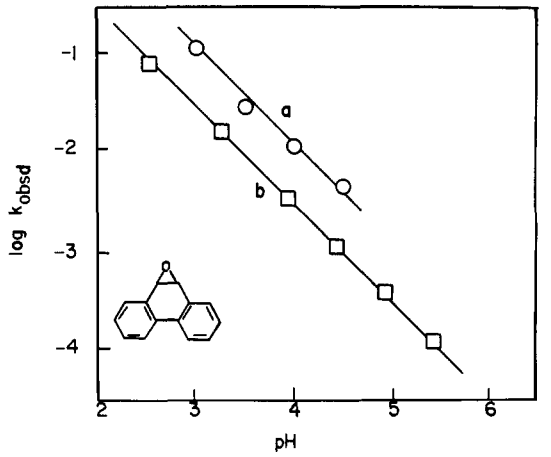


Figure 3. Plots of k_{obsd} *vs.* pH for the rearrangement of **3** at 30° in (a) water and (b) 30% aqueous ethanol.

Table I. Values of k_1 and k_2 for Various Arene Oxides[a]

Arene oxide	Solvent	$k_1 \times 10^3$ sec^{-1}	k_2, M^{-1} sec^{-1}
1	H_2O	1.40	32
1	10% acetamide	0.89	32
2	H_2O	3.00	470
2	30% EtOH[b]	0.42	110
2	10% acetamide	1.50	370
3	H_2O		130
3	30% EtOH[b]		30

[a] At 30° $\mu = 1$. [b] $\mu = 0.1$.

Benzene oxide is reported[3] to undergo acetamide and protein-catalyzed rearrangement to phenol. We found, however, no rate enhancement for the rearrangement of **1** or **2** on transfer from water to aqueous 10% acetamide solution (Figure 1b, 2c). Also, the rate of the rearrangement of **1** to phenol was not catalyzed by 10^{-4}

(14) J. R. Maley and T. C. Bruice, *Anal. Biochem.*, 34, 275 (1970).
(15) R. G. Bates, "Determination of pH," Wiley, New York, N. Y., 1964, p 224.

M lysozyme at pH 7. We cannot reconcile these differences but suggest the acetamide used by other workers may have been slightly acidic. Indeed, in our hands a 10% acetamide solution gave a pH of 5.4. Rate constants for the rearrangement of **2** in aqueous 0.01 *M* KOH at temperatures ranging from 20 to 50° are presented in Table II. The value of E_a is 14.0 ± 0.1 kcal/mol, and $\Delta S^{\pm}$ has a value of −25.7 ± 0.3 eu at 30°. The reported uncertainties were calculated from the standard error of a plot of ln k_{obsd} *vs.* $1/T$. The solvent deuterium kinetic isotope effect was determined to be $k_1^{H_2O}/k_1^{D_2O} = 1.33$ for aromatization of **2** at pH 12.

Table II. The Effect of Salt, Methanol, and Temperature on the Rearrangement of **2**[a]

T, °C	KCl, *M*	% MeOH	$k_{obsd} \times 10^3$ sec^{-1}
20	1.0	0	1.30
30	1.0	0	2.99
40	1.0	0	6.34
50	1.0	0	12.1
30	0.5	0	2.98
30	0.1	0	2.75
30	0.1	20	1.18
30	0.1	40	0.34

[a] At pH 12.

General acid catalysis by acetic acid could not be detected for **1**, **2**, or **3** (see Table III). Other attempts to find general acid catalysis of the rearrangement of **2** with imidazole and phosphate at pH 7 failed. Varying the salt concentration had little effect on the pseudo-first-order rate constants of the rearrangement of **2** at pH 12 (Table II). Adding methanol to the solvent also produced only a small effect at pH 12 (Table II).

Table III. Observed First-Order Rate Constants for the Rearrangement of Arene Oxides in the Presence of Acetic Acid at pH 3.77[a]

Acetic acid at pH 3.77, total acetate, *M*	Benzene oxide, $k_{obsd} \times 10^{-3}$ sec^{-1}	Naphthalene oxide, $k_{obsd} \times 10^2$ sec^{-1}	Phenanthrene oxide, $k_{obsd} \times 10^2$ sec^{-1}
1.0	6.75	7.09	2.40
0.8	6.75		2.49
0.6	6.67	6.55	2.42
0.4	6.76	6.87	2.59

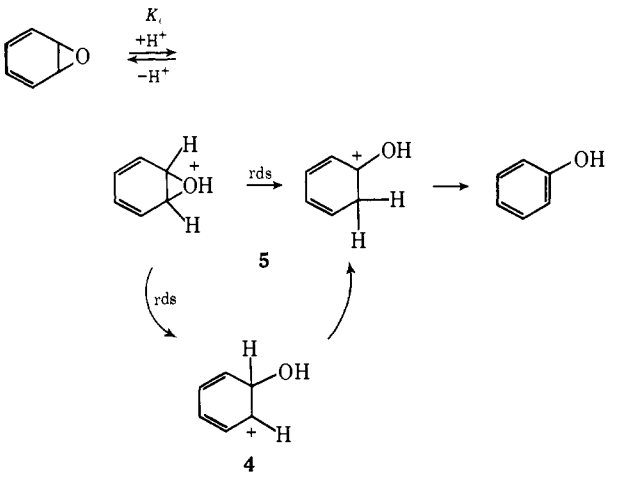
[a] At 30° μ = 1.0.

Discussion

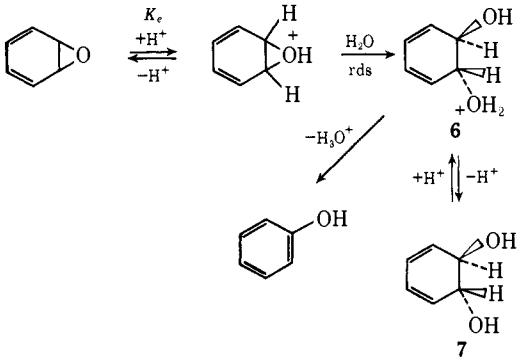
The rearrangement of arene oxides shows two distinct regions in their dependence on pH; an acid-catalyzed region and a pH-independent region. The mechanism of this rearrangement will be discussed in light of the kinetic data and the established requirement of the NIH shift both at acid and neutral pH.

Acid-Catalyzed Regions. Since general catalysis was not detectable the mechanism operating below pH 7 must be specific acid catalysis (either A-1 (Scheme I) or A-2 (Scheme II)). In the A-1 mechanism the protonated intermediate is converted to carbonium ion **4**, or alternatively yields **5** in a concerted 1,2-hydride shift. In the A-2 mechanism attack by water forms **6** which then rapidly dehydrates to form the phenol.

Scheme I



Scheme II



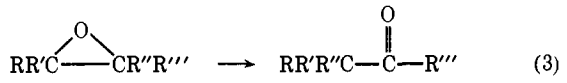
In the A-2 mechanism a buildup of **7** would be predicted because diols of this type are dehydrated very slowly under these conditions.[16] Since no buildup of an intermediate is detected, the A-2 mechanism is ruled out. This leaves only the A-1 mechanism in which the carbonium ion **4** could undergo a 1,2-hydride shift to form **5** or alternatively **5** could be produced directly by a concerted mechanism and thus show the NIH shift. The A-1 mechanism for arene oxide aromatization finds support by analogy to the established A-1 catalyzed hydration of epoxides.[17] A further analogy can be found in the A-1[18] catalyzed hydrolysis of acetals which also involves carbon–oxygen bond cleavage. Choosing between the concerted and stepwise A-1 process (Scheme I) is more difficult. The concerted mechanism is preferred because it is difficult to imagine **4** undergoing a hydride shift, necessary for the NIH shift, in preference to aromatizing to the phenol. The concerted mechanism is also supported by its analogy to the rearrangement of epoxides to form aldehydes or ketones (eq 3) which have been shown to go *via* a concerted mechanism.[19]

(16) J. N. Smith, B. Spencer, and R. T. Williams (*Biochem. J.*, 47, 284 (1950)) have shown that the half-life for the dehydration of 5,6-dihydroxy-2-chloro-1,3-cyclohexadiene is 48 hr in 1 *N* HCl at 19°.

(17) (a) F. A. Long and J. G. Pritchard, *J. Amer. Chem. Soc.*, 78, 2663 (1956); (b) J. G. Pritchard and F. A. Long, *ibid.*, 78, 2667 (1956); (c) F. A. Long, J. G. Pritchard, and F. E. Stafford, *ibid.*, 79, 2362 (1957).

(18) E. H. Cordes, *Progr. Phys. Org. Chem.*, 4, 1 (1967).

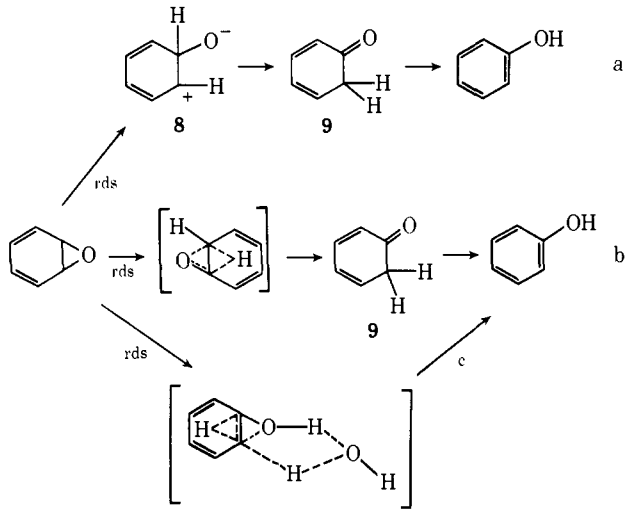
(19) H. O. House and D. J. Reif, *J. Amer. Chem. Soc.*, 77, 6525 (1955).



(3)

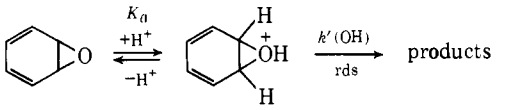
pH-Independent Region. There are three distinct types of mechanisms not involving participation of H^+ or HO^- possible for the rearrangement of arene oxides. The first, as shown in Scheme III (path a), in-

Scheme III



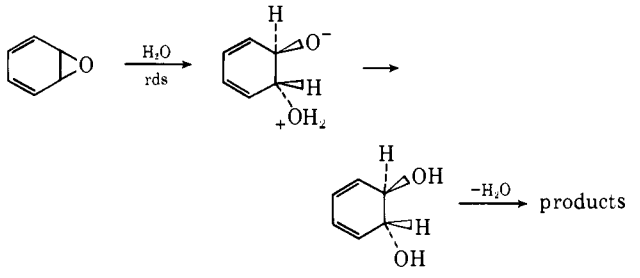
volves a unimolecular ring opening to a zwitterion **8**, or possibly a hydride shift concerted with ring opening as in Scheme III (path b). It is also possible to envision a totally concerted process as in III (path c) where the dienone **9** is never formed. A kinetically equivalent mechanism (Scheme IV) could involve preequilibrium

Scheme IV



protonation followed by rate-determining hydroxide attack. A final mechanism (Scheme V) worthy of

Scheme V



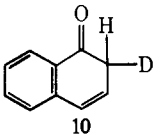
consideration involves a nucleophilic attack by water to form a diol which rapidly dehydrates to form phenol.

Although ring opening of epoxides to form diols was shown to occur by nucleophilic attack of water in the pH-independent region,[17b,20] we can eliminate Scheme V for the following reasons. (1) If H_2O were acting as a nucleophile, one would expect to see a hydroxide rate at higher pH as with the simple epoxides,[17b] since OH^- is a better nucleophile than H_2O. (2) No diol was detected, and the respective *trans*-1,2-diols of benzene and naphthalene are stable enough to be detected under these conditions.[3,5] Scheme IV may also be eliminated since it would require

$$k' = \frac{(k_{obsd})(K_a)}{K_w}$$

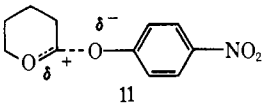
Knowing k_{obsd} and K_w, and estimating the pK_a to be less than -2,[21] it is clear that k' would be beyond diffusion control.

This leaves only the mechanisms of Scheme III. The totally concerted mechanism of Scheme III (path c) is made unlikely because a solvent isotope effect of $(k_{H_2O}/k_{D_2O}) = 2$–4 is expected[22] when a proton is transferred from the solvent in the transition state, and k_{H_2O}/k_{D_2O} is only 1.33 for the rearrangement of **2**. Finally, this mechanism is unlikely because Jerina[8] found both naphthalene oxide-*1*-^2H and 1,2-naphthalene oxide-*2*-^2H give 1-naphthol with 72–75% deuterium in the 2 position at pH 8. This requires an intermediate such as **10** proposed by Jerina[8] in



which the hydrogen and deuterium are equivalent. This is clearly not the case in the transition state in Scheme III (path c).

Choosing between the mechanisms depicted in Scheme III (paths a and b) is more difficult, since they differ only in the timing of the hydride shift and would both be expected to show about the same solvent isotope effect. Although we cannot unequivocally state which mechanism is operating, IIIb is preferred for the following reasons. (1) Fife[23] found $\Delta S^{\ddagger} = +2.2$ eu for the pH-independent hydrolysis of 2-(*p*-nitrophenoxy)tetrahydropyran, which he proposed to go by way of a transition state like **11**, which is



analogous to **8**. Thus, if Scheme III (path a) were operating, a $\Delta S^{\ddagger}$ of about 0 would be expected. The $\Delta S^{\ddagger}$ of -25.7 eu for the rearrangement of **2** is not consistent with a mechanism involving **8**, but is consistent with the highly ordered transition state in Scheme III (path b). (2) The small change in rate with solvent and ionic strength variation indicates the transition state is not differently charged than the reactants, consistent with a concerted mechanism. (3) Finally, the concerted mechanism is preferred by its analogy to the rearrangement of epoxides[19] and the acid-catalyzed rearrangement of the arene oxides.

Since no spontaneous rate of rearrangement of **3** could be detected under the conditions used for **1** and **2** a different mechanism is suspected. Indeed Boyland

(20) J. G. Pritchard and F. A. Long, *J. Amer. Chem. Soc.*, 78, 6008 (1956).

(21) E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 223 (1963). The pK_a's of many ethers are listed. These vary from -2.08 for tetrahydrofuran to about -6.45 for anisole.

(22) F. H. Westheimer, *Chem. Rev.*, 61, 265 (1960).

(23) T. H. Fife and L. H. Brod, *J. Amer. Chem. Soc.*, 92, 1681 (1970).

and Sims[4] have shown that **3** refluxed in 60% aqueous acetone for 36 hr produced a large amount of *trans*-9,10-dihydroxy-9,10-dihydrophenanthrene. This is consistent with SN2 attack by water on the epoxides. Unfortunately, because of its symmetry the question of the importance of the NIH shift on **3** cannot be detected. Thus, **3** most certainly hydrolyzes in an analogous manner to simple epoxides.

A Novel Route to Racemization of Sulfoxides

G. Modena,* U. Quintily, and G. Scorrano

Contribution from Centro C.N.R. Meccanismi di Reazioni Organiche, Istituto di Chimica Organica, Universita' di Padova, 35100 Padua, Italy.
Received February 22, 1971

Abstract: Optically active *sec*- and *tert*-alkyl phenyl sulfoxides undergo racemization together with fragmentation in aqueous perchloric acid. A detailed investigation of *tert*-butyl phenyl sulfoxide (**1**) showed that the racemization is neither due to nucleophilic substitution at sulfur nor to pyramidal inversion. The rates of racemization (k_r) and fragmentation (k_d) reactions follow the same kinetic law, both depending on the concentration of the protonated sulfoxide, and they are similarly affected by the acidity of the medium. Similar rates (k_d/k_r = 2–3) and similar energies of activation were found for the two reactions. Experiments with ^{18}O-labeled **1** and with (R_S,R_C)-α-phenylethyl phenyl sulfoxide showed that racemization at sulfur does not occur *via* oxygen exchange and it is accompanied by partial racemization of carbon chiral center ($k_{SO}/k_{alkyl} \sim 3.5$). The results are discussed on the basis of two alternative mechanisms, one involving a reversible S → O shift of the alkyl group, the other an alkyl cation sulfenic acid ion–molecule pair.

The rates of reduction and of racemization of sulfoxides are very sensitive to the steric requirements of the groups attached to the sulfur atom.[1-3]

Mislow, *et al.*,[1] reported that methyl *p*-tolyl sulfoxide racemizes in a 2:1 v/v mixture of dioxane and 12 *M* aqueous HCl more than 10^5 times faster than the tertiary butyl derivative.

Andersen, *et al.*,[2] found a ratio $k_{Me}/k_{tert\text{-}Bu}$ greater than 10^3 for the reduction with sodium iodide in aqueous perchloric acid of phenyl alkyl sulfoxides.

We studied[3,4] the reduction with sodium iodide and the racemization with sodium chloride and sodium bromide in aqueous perchloric acid of phenyl alkyl sulfoxides, and found[3] a decrease in reactivity from the methyl to the isopropyl derivative ($k_{Me}/k_{i\text{-}Pr}$ about 60) similar to that observed by Mislow[1] and Andersen.[2]

However, we have not been able to make any direct comparison with the tertiary butyl derivative, since, in our conditions, the rate of loss of optical activity of (+)-*tert*-butyl phenyl sulfoxide appears to be independent of halide ion concentration. This reaction, in fact, occurs in the absence of any added salt. It suggests a peculiar behavior of this substrate and we observed as reaction products large amounts of diphenyl disulfide and phenyl benzenethiolsulfonate, together with racemized sulfoxide.

Diphenyl disulfide and phenyl benzenethiolsulfonate often appear as decomposition products of organosulfur compounds.[5] The most intriguing fact, however, is the observed racemization of the sulfoxide in the absence of any nucleophile.[6] We now report a detailed study of this reaction. Some preliminary results have been published elsewhere.[7]

Results

The reactions were run in aqueous perchloric acid solutions at 25°.

Product Analysis. *tert*-Butyl phenyl sulfoxide (**1**) (250 mg) was allowed to react for 35 days in aqueous perchloric acid, 6 *M*. After work-up the following products were isolated: diphenyl disulfide (**2**) (55 mg), phenyl benzenethiolsulfonate (**3**) (34 mg), and **1** (29 mg). When **1** was kept for 64 hr in 8.9 *M* perchloric acid, only **1** and **2** were found as major reaction products; **3** was present only in trace amounts as evidenced by thin-layer chromatography.

The stoichiometric eq 1 requires a 1:1 ratio of **2** and **3**.

$$\underset{\mathbf{1}}{4\text{PhSO-}tert\text{-Bu}} + 2H_2O \longrightarrow \underset{\mathbf{2}}{Ph_2S_2} + \underset{\mathbf{3}}{PhSSO_2Ph} + tert\text{-BuOH} \quad (1)$$

Even in the less concentrated solution we used, we found **2** in a greater amount than **3**. This is not surprising since it is reported that phenyl benzenethiolsulfonate suffers hydrolysis in acid media[5] to give diphenyl disulfide and sulfinic or sulfonic acids. We did not succeed in isolating any amount of the above acids from the strongly acidic reaction mixture.

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