

polarized (ap) line; rather the property distinguishing the two sets is the in-plane metal in group I and the out-of-plane metal in group II. Estimates of the metal displacement from the basal plane is obtained from structural determinations:<sup>9</sup> Zn, 0.33, 0.35;<sup>10</sup> Mg, 0.27; VO, 0.48; and Fe(III), 0.48 Å.

In agreement with previous studies<sup>4,5</sup> on heme-proteins, ap lines possessed a maximum  $\rho$  when the exciting light was absorbed by the visible bands, while the relative intensity of the polarized lines increased as shorter exciting wavelengths were employed.

Current interpretations<sup>2,4,5</sup> of heme resonance Raman spectra assign the polarized bands ( $\rho < 3/4$ ) to  $a_{1g}$  in-plane porphyrin skeletal vibrations and inverse polarized lines ( $\rho = \infty$ ) to  $a_{2g}$  vibrations. The dependence of the apparent value of  $\rho$  for the ap line upon exciting wavelength is consistent with  $a_{2g}$  vibronic coupling between the Q (visible) and B (Soret) electronic states. Increasing intensity of the polarized bands as the B band is approached by the exciting line is indicative of an  $a_{1g}$  vibration. The data reported here support a recent conclusion<sup>7</sup> that accidental degeneracy between the  $a_{2g}$  vibration and an  $a_{1g}$  mode rather than lowering of molecular symmetry is responsible for an appreciable parallel component to the ap lines at 1590  $\text{cm}^{-1}$  (group I) and 1574–1568  $\text{cm}^{-1}$  (group II). An ap line near 1313  $\text{cm}^{-1}$  also shows a slight shift in the  $I_{\text{p}}$  maximum at 457.9 nm as compared with 514.5 nm. This, too, is consistent with accidentally degenerate vibrations. The symmetry reductions from  $D_{4h}$  commonly encountered<sup>9</sup> in porphyrins are to  $D_{2d}$  or  $C_{4v}$  and could not account for the parallel ap components.

The present results emphasize the structural interpretation of heme-protein ap and polarized bands found in the 1550–1600- $\text{cm}^{-1}$  region. As long as the exciting wavelength is absorbed by the Q bands, resonant Raman spectra of metalloporphyrins displaying an ap line in the 1582–1609- $\text{cm}^{-1}$  region indicate an in-plane metal, e.g., low-spin Fe(III). In contradistinction, upon excitation into the Q band, a polarized line in this region with the concurrent shift<sup>11</sup> of the ap band to 1552–1574  $\text{cm}^{-1}$  is indicative of an out-of-plane metal.

The mechanism by which displacement of the metal from the porphyrin plane can cause this phenomenon is suggested<sup>7</sup> to be due to "doming" of the porphyrin skeleton and concomitant displacement of meso carbon atoms from the mean porphyrin plane. This explanation is attractive since it is independent<sup>12</sup> of the nature of the metal substituent, requiring only a distortion of the macrocycle. Verification of this mechanism must await studies on crystalline samples of metallotetra-phenylporphyrins, where structural information is available for a wide class of metals.

A polarized line at ca. 1500  $\text{cm}^{-1}$  evinces a less clear-cut correlation with metalloporphyrin structure. For the in-plane metals this line is observed between 1509

(9) Values are cited for *meso*-tetraphenylporphyrin complexes and a vanadyl deoxyphylloerythroetioporphyryl. See J. L. Hoard, *Science*, **174**, 1295 (1971); *Ann. N. Y. Acad. Sci.*, **206**, 18 (1973); E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).

(10) L. D. Spaulding, P. G. Eller, J. A. Bertrand, and R. H. Felton, *J. Amer. Chem. Soc.*, **96**, 982 (1974).

(11) MgOEP and ZnOEP did not display an ap line at 1565  $\text{cm}^{-1}$  when the 514.5-nm exciting light was used. Attempts to employ longer wavelength excitation directly into the Q band were foiled by excessive fluorescence. At shorter wavelengths  $\rho$  became smaller which would indicate both  $a_{1g}$  and  $a_{2g}$  vibrations are present.

(12) An ap line at 1587  $\text{cm}^{-1}$  was found for metal-free H<sub>2</sub>OEP.

and 1534  $\text{cm}^{-1}$ , while it appears between 1480 and 1500  $\text{cm}^{-1}$  for the out-of-plane cases. The depolarized line encountered at 1664–1609  $\text{cm}^{-1}$  in our study has been proposed<sup>3,7</sup> as an "oxidation state marker" in the heme-proteins. Although this proposal may be correct for the heme-proteins, we find it does not apply to Co<sup>II</sup>-OEP, 1651  $\text{cm}^{-1}$ , as compared with Co<sup>II</sup>-OEP(ClO<sub>4</sub>), 1651  $\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub> solution).

Finally, as an application of the 1590- $\text{cm}^{-1}$  ap band as a structural probe, we note that replacement of ClO<sub>4</sub><sup>-</sup> by the strongly coordinating Br<sup>-</sup> ion in Co<sup>II</sup>-OEP<sup>+</sup> alters the resonant Raman spectrum in a manner indicative of a cobalt atom now displaced from the porphyrin plane.<sup>13</sup>

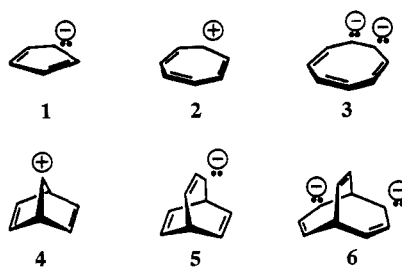
(13) NOTE ADDED IN PROOF. Classification of a metal as in- or out-of-plane is ambiguous for *slight* displacement from the basal nitrogen plane. Thus, in CO<sup>II</sup>-Etio NO the resonant Raman spectrum displays an ap line at 1604  $\text{cm}^{-1}$  which classifies it as in-plane; but a structural determination (W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8281 (1973)) on nitrosyltetraphenylporphyrinocobalt(II) yields a  $0.094 \pm 0.05$  Å displacement.

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## The Bicyclo[3.3.2]decatrienyl Dianion<sup>1</sup>

Sir:

One's current appreciation of the pericyclic  $4n + 2$  Hückel rule has been nourished by three preparative achievements: cyclopentadienide (1),<sup>2</sup> tropylium (2),<sup>3</sup> and the cyclooctatetraenide dianion (3).<sup>4</sup> The less exhaustively explored longicyclic topology now also has its characteristic rule.<sup>5</sup> A fully unsaturated bridged bicyclic ion is expected to be stabilized if any two of its three bridges differ in mode. Thus, if two each possess  $4n$   $\pi$  electrons (mode 0), the third must possess  $4n + 2$  (mode 2) and *vice versa*.



This topology now also has two ions whose roles recall those of 1 and 2. Like the cyclopentadienyl anion, the 7-norbornadienyl cation (4) was available as witness even before the rule was formulated.<sup>6</sup> Like the tropylium cation, the bicyclo[3.2.2]nonatrienyl

(1) Presented, in part, at the First Fall Organic Conference, Division of Organic Chemistry, American Chemical Society, Falmouth, Mass., Oct 3, 1973.

(2) J. Thiele, *Ber.*, **33**, 666 (1900).

(3) W. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3204 (1954).

(4) T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784, 3785 (1960).

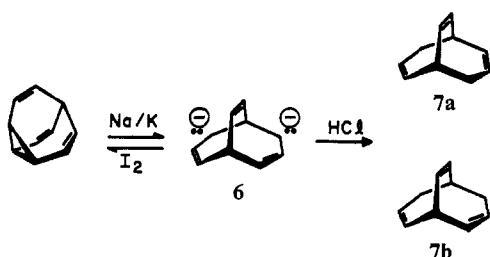
(5) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(6) S. Winstein and C. Ordonneau, *J. Amer. Chem. Soc.*, **82**, 2084 (1960).

anion (**5**) was first prepared<sup>7</sup> in response to the explicit prediction that it would be stabilized.<sup>8</sup>

We now complete the longicyclic trio by reporting the preparation of the bicyclo[3.3.2]decatrienyl dianion (**6**). Like the cyclooctatetraenyl, dianion **6** demonstrates how easily the topologically appropriate rule accommodates itself to coulombic repulsion—once again that of ten  $\pi$  electrons delocalized about eight trigonal carbons. A less fully unsaturated derivative provides an instructive contrast.

A copious, yellow-green, crystalline precipitate was obtained quite simply by the room temperature addition of a tetrahydrofuran or a 1,2-dimethoxyethane solution of bullvalene to sodium-potassium alloy.<sup>9</sup> This is presumed to be the dipotassium salt of **6**, in part because iodine oxidation regenerated bullvalene (92%). Carboxylation provided a mixture from which isomerically heterogeneous  $C_{14}H_{16}O_4$  dimethyl esters (78%)<sup>11,12a</sup> as well as  $C_{12}H_{14}O_2$  monomethyl esters (15%)<sup>11,12b</sup> were obtained. HCl protonation provided the isomeric bicyclic trienes<sup>13</sup> (**7a**<sup>14</sup> 47%; **7b**<sup>15</sup> 41%). Corresponding DCl treatment served to incorporate  $1.93 \pm 0.02$  atoms of deuterium into the first of these and  $1.96 \pm 0.06$  into the second.



The dilithium salt of **6** (unlike that of **3**<sup>4</sup>) was not obtained directly but rather by LiBr metathesis. Figure 1 compares its pmr and cmr spectra with those of monolithium bicyclo[3.2.2]nonatrienide (**5**).<sup>16</sup> As might be expected, the splitting pattern remains constant while the normalized areas change from 1:4:2:2 to 2:2:4:2.

(7) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2200 (1972).

(8) (a) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, p 71; (b) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

(9) Previous use of this reagent includes the preparation of, **5**<sup>7</sup> and the reduction of bicyclo[3.2.2]nona-2,6,8-triene to bicyclo[3.2.2]nona-2,6-diene.<sup>10</sup>

(10) M. J. Goldstein and S. Natowsky, *J. Amer. Chem. Soc.*, **95**, 6451 (1973).

(11) C and H analyses agreed with expectation to within  $\pm 0.3\%$ . Molecular weights were assigned mass spectrometrically. Reported yields are those of isolated products.

(12) (a) Ir(CCl<sub>4</sub>) 1748, 1720 cm<sup>-1</sup>; nmr OMe  $\tau$  (CCl<sub>4</sub>) 6.31, 6.33, 6.35, 6.37 ppm. (b) Ir (CCl<sub>4</sub>) 1740 cm<sup>-1</sup>; nmr OMe  $\tau$  (CCl<sub>4</sub>) 6.33, 6.35, 6.37 ppm.

(13) Chemical Abstract names: **7a**, bicyclo[3.3.2]deca-2,6,9-triene; **7b**, bicyclo[3.3.2]deca-2,7,9-triene; dihydro-**7a**, bicyclo[3.3.2]deca-2,6-diene; dihydro-**7b**, bicyclo[3.3.2]deca-2,7-diene.

(14) (a) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964); (b) mp 43°, lit.<sup>14a</sup> mp 45°;  $\tau$  (CCl<sub>4</sub>) 4.06 (sext, 2.03), 4.40 (m, 3.96), 7.28, 7.78 (m, 6.02) ppm; lit.<sup>14a</sup>  $\tau$  (CS<sub>2</sub>) 4.2 (sext, 2), 4.5 (m, 4), 7.3 (m, 2), 7.8 (m, 4) ppm.

(15) (a) J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schroder, *J. Amer. Chem. Soc.*, **89**, 612 (1967); (b) mp 38°;  $\tau$  (CCl<sub>4</sub>) 4.20 (m, 6.04), 7.05 (quart), 7.60 (m, 5.96) ppm; lit.<sup>15a</sup>  $\tau$  4.15 (6), 7.1 (2), 7.5 (4) ppm. The correct proton areas (6:1:5) become unambiguous upon deuteration.

(16) (a) Bruker HX-90 spectrometer equipped with Digilab FTS/NMR pulser and data system; <sup>13</sup>C assignments were achieved by narrow band decoupling. (b) The spectrum of **5** is little affected by solvent change (tetrahydrofuran-dimethyl ether), lower temperatures ( $-141^\circ$ ), or cation, e.g., ambient temperature potassium salt spectra in 1,2-dimethoxyethane-*d*<sub>10</sub>: cmr  $\delta$  120.0, 111.5, ca. 58, 35.6 ppm; pmr  $\tau$  4.77, 5.04, 6.95, 7.70 ppm (lit.<sup>7</sup>  $\tau$  4.76, 5.02, 6.95, 7.71 ppm).

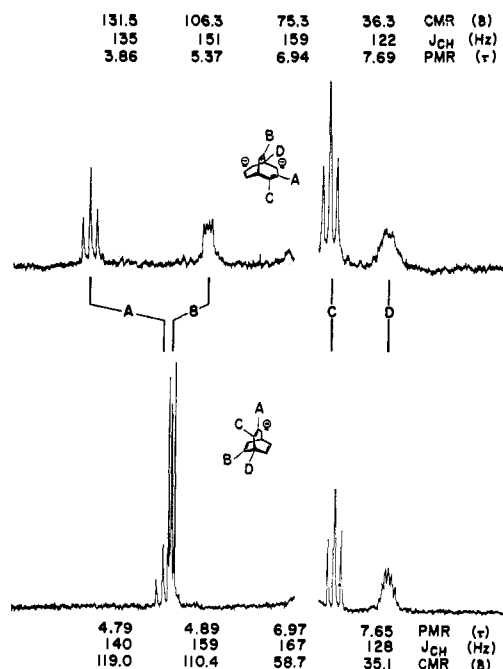


Figure 1. Pmr traces and nmr spectral assignments of dilithium bicyclo[3.3.2]decatrienide and lithium bicyclo[3.2.2]nonatrienide in 1,2-dimethoxyethane-*d*<sub>10</sub> at  $-20^\circ$ . Residual solvent proton absorption ( $\tau$  6.45–6.78 ppm) is deleted.

Rather more surprising, in the light of contemporary empiricism,<sup>7,17</sup> is that the acquisition of a second negative charge shifts the C carbon resonance to lower field but not that of the C proton. At A and at B, bonded carbon and hydrogen nuclei both shift but in opposite directions.

Hydrogenation of the two-carbon bridge is expected to have a more dramatic effect upon **6** (which is not bicycloaromatic) than upon either of the singly charged ions, **4** or **5** (which are).<sup>5</sup> These last two are thus transformed to homoaromatic ions, also expected to be quite stabilized, if not to the degree of their bicycloaromatic precursors. The quantitative experiments needed to confirm this prediction have now been successfully done.<sup>6,10,17a,18</sup>

By contrast, the bicyclo[3.3.2]decadienyl dianion should be homoaromatic—highly reactive if indeed it could ever be obtained. Appropriately then, identical treatment of dihydrobullvalene<sup>14a,19</sup> with sodium-potassium alloy provided a homogeneous solution rather than a crystalline precipitate. From this, a dimeric  $C_{20}H_{26}$  (39%)<sup>11</sup> as well as a monomeric  $C_{10}H_{14}$  (42%)<sup>11</sup> hydrocarbon fraction was isolated. Although such yields proved sensitive to experimental detail, the monomer fraction remained exclusively dihydro-**7a**, contaminated by less than 10% of dihydro-**7b**.<sup>13,20</sup> This last result recalls the exclusive formation of **7a**

(17) (a) M. V. Moncur and J. B. Grutzner, *J. Amer. Chem. Soc.*, **95**, 6449 (1973); (b) P. J. Garratt, "Aromaticity," McGraw-Hill, London, 1971.

(18) Note, however, that a first attempt has failed to detect laticyclic stabilization beyond the homoaromatic level: L. A. Paquette and I. R. Dunkin, *J. Amer. Chem. Soc.*, **96**, 1220 (1974).

(19) M. Meréni, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964).

(20) Authentic samples<sup>11</sup> of dihydro-**7a** (mp 77°,  $\tau$  (CDCl<sub>3</sub>) 4.30 (m, 3.97), 7.42 (m, 2.00), 7.70 (m, 4.02), and 8.10 (m, 4.01) ppm) and dihydro-**7b** (mp 77°,  $\tau$  (CDCl<sub>3</sub>) 4.27 (m, 4.04), 7.13 (m, 1.14), 7.71 (broad s, 4.91), and 8.17 (m, 3.93) ppm) were obtained by separate diimide reductions of **7a** and **7b**.

upon Na-NH<sub>3</sub>-MeOH reduction of bullvalene<sup>14a</sup> and of 1,4-dihydrobenzene from benzene.<sup>21</sup> 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 (NH<sub>3</sub>-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 C<sub>11</sub>H<sub>10</sub>O ketones,<sup>22</sup> of C<sub>12</sub>H<sub>12</sub> hydrocarbons,<sup>23</sup> and of novel organometallics is now under active investigation.

**Acknowledgment.** Partial financial support was provided by U. S. Public Health Research Grant No. 10495 from the National Cancer Institute. Patient nmr instruction and maintenance was provided by H. S. Hair.

(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."<sup>1</sup> Although a number of non-arene oxides are reported to undergo hydride or substituent migration in the epoxide-carbonyl rearrangement,<sup>2</sup> such migrations occur under thermal conditions or are catalyzed by Lewis acids.

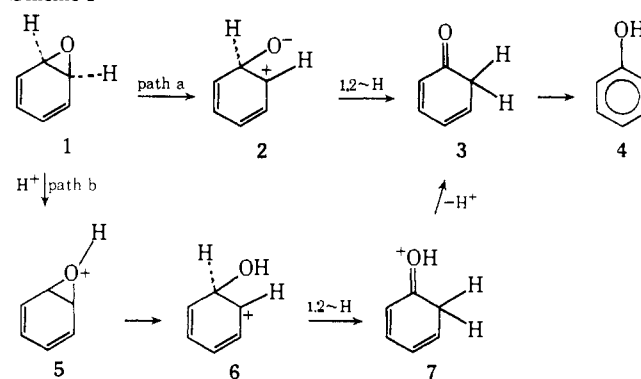
Recent investigations<sup>3</sup> have established the existence of two independent pathways for the "NIH shift" in several unsubstituted arene oxides. For example, the rearrangement of benzene oxide (1) to phenol occurs *via* two competitive mechanisms, a spontaneous route

(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.<sup>4</sup> 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

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

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

**Table I.** Values of  $k_{\text{H}^+}$ ,  $k_0$ , and  $k_{\text{HA}}$  for the Hydrolysis of 8 at 25°<sup>a</sup>

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

<sup>a</sup> 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. <sup>b</sup> Obtained from a weighted least-squares plot of  $k_{\text{obsd}}$  vs. [H<sup>+</sup>]. Values of  $k_{\text{obsd}}$  were obtained from rates in buffered solutions, extrapolated to zero buffer concentration. <sup>c</sup>  $\mu = 1.0$  (KCl). <sup>d</sup> Obtained from least-squares plots of  $k_{\text{obsd}}$  vs. [HA] at constant pH. The average of slopes at two different pH values is listed as  $k_{\text{HA}}$ . <sup>e</sup>  $\mu = 1.0$  (NaCl).

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

Product analyses carried out at pH 8.2,<sup>5</sup> where the  $k_{\text{H}^+}$  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)<sup>6</sup> and 32% of *cis*-2,4-pentadienal (12), in addition to 35% of a mixture of diols 9 and 10 (Scheme II).<sup>7</sup> The rearrangement of 8 in D<sub>2</sub>O at pD 7.6 yielded 11 without detectable incorporation of deuterium.<sup>8</sup> 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<sup>-1</sup>, 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 D<sub>2</sub>O 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 D<sub>2</sub>O at pD 7.6 (phosphate buffer) showed the ratio of the  $\alpha$ -protons to the vinylic protons in 11 to be 2.0:1.0.