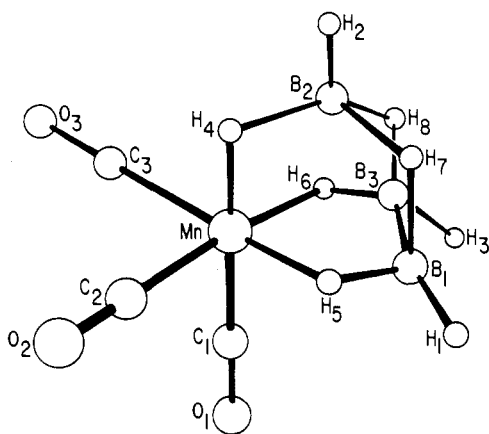


lowered. Upon decoupling  $^1\text{H}$ , a single very narrow resonance is observed, indicating magnetic equivalence of all three boron atoms. The  $^1\text{H}$  nmr spectrum of this complex consists of a broad signal of intensity 5 at  $\tau$  10.1 and a somewhat narrower signal of intensity 3 at  $\tau$  21.6. Decoupling  $^{11}\text{B}$  results in narrowing of these two broad resonances to sharp singlets. The presence of three protons far upfield from tetramethylsilane suggests that the  $\text{B}_3\text{H}_3^-$  ion is bound to the metal through three Mn-H-B bridge hydrogen bonds. The presence of a single type of hydrogen at lower field suggests that the hydrogens that are not involved in Mn-H-B bridge bonding are magnetically equivalent, most likely as a result of rapid intramolecular exchange (on the nmr timescale) around the periphery of the  $\text{B}_3$  triangle. Such exchange would also render the three boron atoms magnetically equivalent, as observed. Thus this new type of complex can be considered to be partially, or selectively, nonrigid. More important, however, this complex appears to be the first example in which the  $\text{B}_3\text{H}_3^-$  ion acts as a tridentate ligand. The proposed static structure for  $(\text{CO})_3\text{MnB}_3\text{H}_8$  is shown below.



Further studies of these and related new metal metalloboranes and their reactions are in progress and will be reported more fully later.

**Acknowledgments.** This work was supported in part by a grant from the National Science Foundation. S. J. H. thanks the E. I. du Pont de Nemours & Co. for a 1973 Summer Research Assistantship. The nmr and mass spectral facilities were provided in part by institutional grants from the National Science Foundation.

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### Photochemical Rearrangement of 4,4-Disubstituted-4-sila-2,5-cyclohexadienones

Sir:

Reports of photochemical skeletal rearrangements of silicon heterocycles are rare,<sup>1</sup> especially when compared

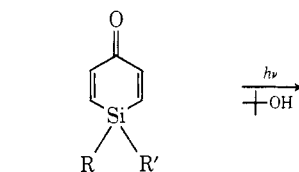
(1) The only photorearrangements of silicon heterocycles are the Norrish type I cleavages of silacyclohexan-2-ones and the ring contraction of 1,2,3-trisilacycloheptanes. M. Ishikawa and M. Kumada, *Chem. Commun.* 612 (1970); A. G. Brook, H. W. Kucers, and R. Pearce, *Can. J. Chem.*, **49**, 1618 (1971); A. G. Brook, R. Pearce, and J. B. Pierce, *ibid.*, **49**, 1622 (1971); H. Sakurai, Y. Kobayashi, and Y. Nakadaira, *J. Amer. Chem. Soc.*, **93**, 5272 (1971).

with the numerous photorearrangements of carbocycles and oxygen and nitrogen heterocycles. We wish to report a novel photochemical ring contraction of a silicon heterocycle to a carbocycle, the photorearrangement of 4,4-disubstituted-4-sila-2,5-cyclohexadienones to cyclopentenone derivatives.

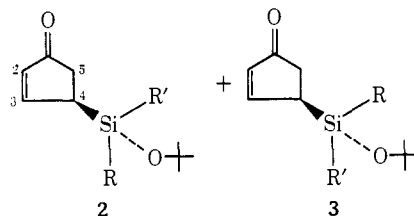
4,4-Dimethyl-4-sila-2,5-cyclohexadienone (**1a**) and 4,4-diphenyl-4-sila-2,5-cyclohexadienone (**1b**) were prepared by oxidation of the corresponding saturated ketones with DDQ as described by Felix and Weber.<sup>2</sup> 4-Methyl-4-phenyl-4-sila-2,5-cyclohexadienone (**1c**) was prepared by an analogous procedure.<sup>2,3</sup> Grignard reaction of allylmagnesium bromide with dichloromethylphenylsilane gave 4-methyl-4-phenyl-4-sila-1,6-heptadiene. Hydroboration-oxidation of the diene followed by Jones oxidation, esterification, Diekmann cyclization, decarboxylation, and DDQ oxidation gave the desired dienone **1c** in 4% overall yield.

The three 4-sila-2,5-cyclohexadienone derivatives all have  $n-\pi^*$  bands in the region of 350–400 nm. Consequently, the photoreactions were conducted in a Rayonet reactor equipped with 350-nm lamps. Additionally, the irradiation solutions were filtered with three concentric Pyrex filters to minimize light absorption by the photoproducts. With these irradiation conditions, 150-mg samples of the dienones in 100 ml of dry *tert*-butyl alcohol were irradiated under a nitrogen atmosphere for 2–3 hr, resulting in 65–70% destruction of dienones as indicated by glpc. Yields of isolated products based on starting materials destroyed were in the range of 20–40%. Photoproducts and unreacted starting materials were isolated by preparative glpc and medium pressure, silica gel, solid-liquid chromatography.

The photoproducts of **1a**, **1b**, and **1c** were characterized as 4-(*tert*-butoxydimethylsilyl)cyclopent-2-enone (**2a**), 4-(*tert*-butoxydiphenylsilyl)cyclopent-2-enone (**2b**), and two diastereoisomeric 4-(*tert*-butoxymethylphenylsilyl)cyclopent-2-enones (**2c** + **3c**), respectively, from



- 1a, R = R' = CH<sub>3</sub>  
b, R = R' = Ph  
c, R = CH<sub>3</sub>; R' = Ph



their spectroscopic data. The nmr spectra were recorded in the presence and absence of Euroshift F, tris-2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octane-

(2) R. A. Felix and W. P. Weber, *J. Org. Chem.*, **37**, 2323 (1972).

(3) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Org. Chem.*, **36**, 4060 (1971).

(4) The structural assignment for **1c** is consistent with the following spectroscopic evidence: nmr ( $\text{DCCl}_3$ )  $\delta$  0.57 (3 H, s), 6.8–7.1 (4 H, m), and 7.15–7.65 ppm (5 H, m); ir 6.08, 6.31, 6.38, and 6.72  $\mu$ ; mass spectrum,  $m/e$  200 (P, 29% of base).

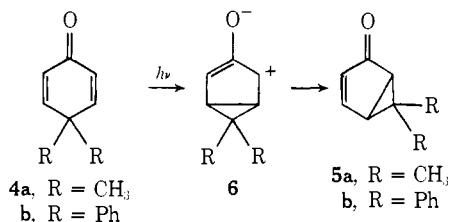
Table I. Nmr Spectra of Photoproduct 2a<sup>a</sup>

| Compound | Solvent           | Ring position   |  |  |   |
|----------|-------------------|---|--|--|---|
|          |                   | 2   | 3  | 4  | 5   |
| 2a       | DCCl <sub>3</sub> | 5.93–6.13<br>(m, 1 H)                                     | 7.67–7.83<br>(m, 1 H)                                      | 0.05 (s, 3 H)<br>0.08 (s, 3 H)<br>1.20 (s, 9 H)<br>2.43 (m, 1 H)   | 2.43 (m, 2 H)   |
|          |                   | 7.97<br>(d of d, 1 H)<br><i>J</i> = 2.5<br><i>J</i> = 5.5 | 8.35<br>(d of d, 1 H)<br><i>J</i> = 2.75<br><i>J</i> = 5.5 | 0.42 (s, 6 H)<br>1.38 (s, 9 H)<br>3.26 (c, 1 H)<br><i>J</i> = 2.5<br><i>J</i> = 2.75<br><i>J</i> = 1.5<br><i>J</i> = 6.0 | 4.41 (c, 1 H) <sup>b</sup><br>4.62 (c, 1 H) <sup>b</sup><br><i>J</i> = 19.5<br><i>J</i> = 6.0<br><i>J</i> = 1.5 |

<sup>a</sup> The nmr spectra were measured at 60 MHz. Chemical shifts are given in parts per million relative to TMS on the  $\delta$  scale and coupling constants are reported in Hertz. The following abbreviations are used: s, singlet; d, doublet; m, multiplet; c, complex. <sup>b</sup> These protons appear as the AB portion of an ABX pattern. The X portion of the pattern is complicated by further coupling with olefinic protons at positions 2 and 3. Coupling constants and chemical shifts were verified by computer calculation.

dionatoeuropium(III), and the chemical shifts and coupling constants for 2a are shown in Table I. Similar but more complex nmr spectra were observed for 2b and 2c + 3c. Formation of approximately a 50:50 mixture of diastereoisomeric cyclopentenones 2c and 3c from the irradiation of 1c was evident from the appearance of two methyl singlets in the presence and absence of Euroshift F and two *tert*-butoxy singlets in the presence of Euroshift F in the nmr spectra. All the photoproducts gave parent ions in the mass spectrometer and characteristically fragmented by loss of isobutylene ( $P - 56$ ) followed by loss of the cyclopentenyl radical ( $P - 56 - 81$ ) to give  $(RR'SiOH)^+$  as the base peak. The photoproducts also showed strong infrared carbonyl absorption at  $5.88 \mu$  with additional bands of medium intensity at  $6.02$  and  $6.37 \mu$ .

Photochemical rearrangements of carbocyclic analogs of 1, 4,4-disubstituted-2,5-cyclohexadienones, have been extensively studied and reviewed over the past 15 years.<sup>5,6</sup> Classic examples are the type A photorearrangements of 4,4-diphenyl-2,5-cyclohexadienone (4a)<sup>7</sup> and 4,4-dimethyl-2,5-cyclohexadienone (4b)<sup>8</sup> to 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones (5a and 5b). These reactions have since been shown to be examples of a broad class of photoreactions known as di- $\pi$ -methane rearrangements.<sup>9</sup> The mechanism of the type A photorearrangement of 2,5-cyclohexadienones is thought to involve a zwitterionic intermediate 6.<sup>7</sup>



Application of the type A mechanism to the rearrangements of 1a, 1b, and 1c is shown in Scheme I. There are two paths which could lead to the observed products:

(5) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963); K. Schaffner, *ibid.*, 4, 81 (1966).

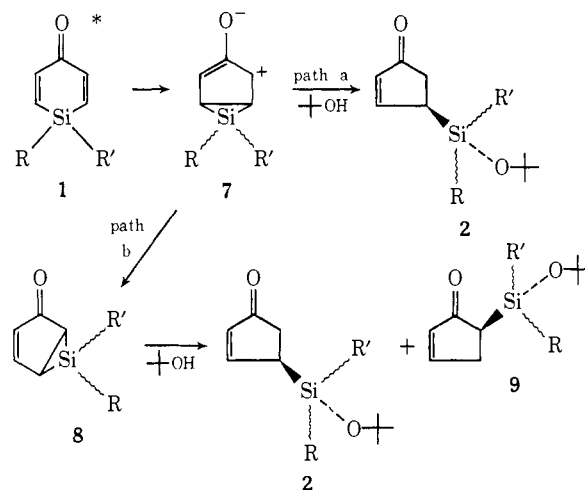
(6) P. J. Kropp in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.

(7) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 83, 4486 (1961); 84, 4527 (1962); H. E. Zimmerman and J. S. Swenton, *ibid.*, 86, 947 (1964); 89, 906 (1967).

(8) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *J. Amer. Chem. Soc.*, 90, 2990 (1968).

(9) S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 73, 531 (1973).

Scheme I



path a, reaction of *tert*-butyl alcohol directly with the zwitterion 7, and path b, reaction of *tert*-butyl alcohol with the type A product 8. The latter reaction path might be expected to yield two isomeric cyclopentenones 2 and 9. There is no experimental evidence for formation of positional isomeric cyclopentenones. The isolated photoproducts were assigned structure 2 rather than structure 9 based upon the nmr chemical shift changes after addition of Euroshift F. The methylene protons of 2 were consistently shifted down field more than the methine proton. This result is only consistent with the europium complexed with the carbonyl oxygen<sup>10</sup> and the methylene protons located adjacent to the carbonyl as in structure 2.<sup>11</sup> Thus mechanistic path a is preferred. Path a is similar to other reports of intramolecular and intermolecular nucleophilic attack on carbocyclic type A zwitterions (or protonated zwitterions) to give structurally related products.<sup>5,6</sup> Reaction of an intermediate such as 7 with *tert*-butyl alcohol to give the cyclopentenones (2) would not

(10) Although the ether oxygen is a better coordinating functional group than the carbonyl oxygen, the ether oxygen is sterically hindered by the adjacent quaternary atoms. H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971); J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, 94, 5325 (1972).

(11) The relative chemical shift changes of the protons at ring positions 4 and 5 of 2a, 2b, and 2c + 3c upon addition of Euroshift F were consistent with those observed for 2-methyl-2-cyclopentenone. The chemical shift assignments of the protons of 2-methyl-2-cyclopentenone were verified by double resonance experiments.

be unexpected in view of the susceptibility of silacyclopropanes to nucleophilic ring opening.<sup>12</sup>

Attempts to observe the type A product (8) at low temperature and in nonnucleophilic solvents have been unsuccessful. The dienones were photostable, neat at 77°K, and only polymeric products were observed in solvents other than *tert*-butyl alcohol.

**Acknowledgments.** The authors would like to thank Professors W. P. Weber and H. E. Zimmerman for helpful discussion regarding this work. Further the support of the General Medical Institute of the National Institutes of Health is gratefully acknowledged. One of us (J. A. S.) would like to extend special thanks to the National Science Foundation for its support of the Bowling Green State University Summer Institute for High School Teachers directed by Professor W. H. Hall.

(12) R. L. Lambert, Jr., and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 9246 (1972).

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### Photolysis of Arene Oxides at Low Temperatures. Oxygen Walks and Keto Tautomers of Phenols

Sir:

Walk reactions, rearrangements in which a divalent group (–O–, –NR–, CR<sub>2</sub>–) that is part of a three-membered ring undergoes migration along the surface of a cyclic  $\pi$  system, have been detected under a variety of conditions. Thermal isomerizations of substituted tropilidenes<sup>1</sup> and norcaradienes<sup>2</sup> occur with migration of the methylene group of a cyclopropane ring. Azepines undergo related thermal rearrangements.<sup>3</sup> In contrast to these thermal reactions, oxido-<sup>4–6</sup> and iminoannulenes<sup>4</sup> as well as arene oxides<sup>7–9</sup> undergo similar migrations of oxygen and substituted nitrogen probably by ionic pathways. Finally, several substituted norcaradienes<sup>10–12</sup> show this type of isomerization under the influence of light. The present study describes the photolysis of arene oxides at reduced temperature. An arene oxide in equilibrium with an oxepin (1), a K-region arene oxide (2), and a non-K-region arene oxide (3) have been examined as they represent the major classes of arene oxides.<sup>13</sup>

pin (1), a K-region arene oxide (2), and a non-K-region arene oxide (3) have been examined as they represent the major classes of arene oxides.<sup>13</sup>

Keto tautomers of phenols have been postulated<sup>14</sup> as nonenzymatic isomerization products of arene oxides since such tautomers readily explain the intramolecular migration and retention of aromatic ring substituents<sup>15</sup> (the NIH shift) observed during enzymatic hydroxylation. While the keto tautomer of phenol itself has never been detected, several reports of the chemical<sup>16–18</sup> and photochemical generation of keto tautomers of phenols bearing bulky substituents at the 2,6-positions have appeared.<sup>19,20</sup> Keto tautomers of naphthols and phenanthrols are unknown. In certain higher polycyclic systems, the keto tautomers predominate;<sup>21</sup> 9-anthrol has 89% of the keto form at equilibrium and only the keto form of 10-hydroxypentacene is known. Despite the fact that oxiranes with aryl substituents tend to undergo reactions other than C–O bond cleavage on photolysis,<sup>22</sup> arene oxides readily photoisomerize to phenols.<sup>23,24</sup> The isomerization is accompanied by the NIH shift.<sup>23</sup>

Photolysis of benzene oxide–oxepin (1) with 3100 Å light gives 2-oxabicyclo[3.2.0]hepta-3,6-diene,<sup>25</sup> while irradiation with 2537 Å light at –80° produces mainly phenol and only minor amounts of the above diene and benzene.<sup>24</sup> Under the latter conditions, sensitization by acetone (solvent) produced phenol exclusively. We have reexamined the photolysis of 1. After 30-min irradiation (2537 Å) of 1-3,6-*d*<sub>2</sub><sup>26,27</sup> in acetone-*d*<sub>6</sub> at room temperature in a quartz tube, nmr analysis indicated 40% of the sample had been converted to phenol. About 12% of the remaining oxide had undergone an oxygen migration to 1-1,4-*d*<sub>2</sub> as evidenced by the appearance of  $\beta$ -hydrogens as a broad apparent doublet at  $\delta$  5.83 and by increasing complexity of the signal at

(13) See D. M. Jerina, H. Yagi, and J. W. Daly, *Heterocycles*, **1**, 267 (1973), for a review on the synthesis and chemistry of the arene oxide–oxepin system.

(14) D. R. Boyd, D. M. Jerina, and J. W. Daly, *Biochemistry*, **11**, 1961 (1972). Isomerization of either [1-<sup>2</sup>H]- or [2-<sup>2</sup>H]naphthalene 1,2-oxide to 1-naphthol at neutral pH occurs with 80% retention of deuterium from either substrate, a result which suggests the keto tautomer of 1-naphthol as the common intermediate from both substrates. Discussion of the involvement of keto tautomers in the aromatization of other arene oxides is available.<sup>13,15</sup>

(15) The NIH shift has been the subject of a recent review; J. W. Daly, D. M. Jerina, and B. Witkop, *Experientia*, **28**, 1129 (1972).

(16) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

(17) V. V. Ershov and A. A. Volo'Kin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 680 (1962); *Chem. Abstr.*, **57**, 12337c (1962).

(18) Isomerization of cyclohex-2-ene-1,4-dione to hydroquinone has been examined by E. W. Garbisch, *J. Amer. Chem. Soc.*, **87**, 4971 (1965).

(19) T. Matsuura and K. Ogura, *J. Amer. Chem. Soc.*, **89**, 3846 (1967); *Tetrahedron*, **24**, 6157 (1968).

(20) B. Miller, *J. Amer. Chem. Soc.*, **89**, 1685 (1967); *Chem. Commun.*, 574 (1971).

(21) For further discussion of the ketone–phenol equilibrium see H. A. Staab, "Einführung in die Theoretische Organische Chemie," Verlag Chemie, Weinheim 1959, p 104; E. Muller, "Neuere Anschauungen der Organischen Chemie," Springer Verlag, Berlin 1957, p 349; G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960, p 679.

(22) G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1971).

(23) D. M. Jerina, D. R. Boyd, and J. W. Daly, *Tetrahedron Lett.*, 457 (1970).

(24) J. H. Holovka and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 6390 (1967).

(25) E. Vogel and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(26) For the synthesis of 1-3,6-*d*<sub>2</sub>, 1,4-cyclohexadiene-3,3,6,6-*d*<sub>4</sub>, obtained from Merck, was converted to the desired oxide as previously described.<sup>27</sup> The nmr spectrum of the oxide in acetone showed two sharp singlets at  $\delta$  5.27 and 6.20 for the  $\alpha$ - and  $\gamma$ -hydrogens of 1.

(27) D. M. Jerina, J. W. Daly, B. Witkop, P. Zaltzman-Nirenberg, and S. Udenfriend, *Arch. Biochem., Biophys.*, **128**, 176 (1968).

(1) J. A. Berson and M. R. Willcott, *J. Amer. Chem. Soc.*, **88**, 2494 (1966).

(2) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, *J. Amer. Chem. Soc.*, **89**, 4076 (1967).

(3) L. A. Paquette, *Angew. Chem., Int. Ed. Engl.*, **10**, 11 (1971).

(4) V. Boekelheide, *Proc. R. A. Welch Found. Conf. Chem. Res., Org. Syn.*, **12**, 83 (1969).

(5) A. Shani and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 6310 (1967).

(6) E. Vogel and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); F. G. Klärner and E. Vogel, *ibid.*, **12**, 840 (1973).

(7) D. M. Jerina, N. Kaubisch, and J. W. Daly, *Proc. Nat. Acad. Sci. U. S. A.*, **68**, 2545 (1971).

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(10) G. W. Gruber and M. Pomerantz, *J. Amer. Chem. Soc.*, **91**, 4004 (1969).

(11) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **93**, 5128 (1971).

(12) H. E. Zimmerman and W. Eberbach, *J. Amer. Chem. Soc.*, **95**, 3970 (1973).