

and sodium (0.53 g, 0.023 mol) in 45 ml of ethanol was added 1-bromopropane (3.7 g, 0.03 mol). The mixture was stirred under reflux for 20 hr and then poured into water and extracted with ether and the ether removed. The residue was refluxed for 21 hr with a mixture of 40 ml of acetic acid, 5 ml of sulfuric acid, and 25 ml of water. The solvents were removed, and the residue was extracted with ether, washed with dilute hydroxide, dried, and distilled. Ketone **4** was obtained as a colorless solid (2.5 g, 67%): mp 41°; nmr (CCl<sub>4</sub>)  $\delta$  0.93 (t, 3 H), 1.4 (m, 4 H), 2.0 (m, 3 H), 2.9 (t, 3 H), 7.2 (m, 3 H), 7.9 (m, 1 H); uv spectrum (hexane)  $\lambda_{\text{max}}$  326 nm,  $\epsilon_{\text{max}}$  38.

**$\alpha$ -(1-Adamantyl)acetophenone (5).** To a solution of 1-adamantaneacetic acid (Aldrich, 2.0 g, 0.01 mol) in 100 ml of anhydrous ether was added 2 equiv of phenyllithium. Aqueous work-up followed by distillation (135–137°, 0.2 mm) and chromatography on alumina gave 1.0 g (40%) ketone **5**: mp 64–65° (hexane); ir spectrum (CCl<sub>4</sub>) 1680 cm<sup>-1</sup>; nmr spectrum (CCl<sub>4</sub>)  $\delta$  1.65 (m, 12 H), 1.93 (m, 3 H), 2.60 (s, 2 H), 7.4 (m, 3 H), 7.8 (m, 2 H); uv spectrum (hexane)  $\lambda_{\text{max}}$  324 nm,  $\epsilon_{\text{max}}$  52.

**Cyclopentadiene-*d*<sub>6</sub>.** The most satisfactory of the several methods employed was the exchange reaction of cyclopentadiene in DMSO-D<sub>2</sub>O-NaOD.<sup>51</sup> After four exchanges mass spectral analysis (CEC 21-104 with an ionization voltage of 6.2 eV) showed 83.6% *d*<sub>6</sub>, 14.2% *d*<sub>5</sub>, 1.5% *d*<sub>4</sub>, <0.7% *d*<sub>3</sub>-*d*<sub>0</sub>.

***exo,exo*-5,6-Dideuterio-*endo*-2-benzoylnorbornane (8).** Catalytic deuteration of *endo*-5-benzoylnorbornene<sup>9</sup> (1.4 g, 0.0068 mol) in 15 ml of 95% ethanol over 0.06 g of 10% palladium on carbon followed by chromatography on silica gel (1% ethyl acetate-hexane) and evaporative distillation gave **8** as a colorless oil (0.7 g, 50%) (Table VIII).

**1,4,*exo*-5,*exo*-6,7,7-Hexadeuterio-*endo*-2-benzoylnorbornane (9).** Diels-Alder reaction of cyclopentadiene-*d*<sub>6</sub> with acrylic acid followed by treatment of the crude product with 2 equiv of phenyllithium gave 1,2,3,4,7,7-hexadeuterio-*endo*-5-benzoylnorbornane.

Catalytic hydrogenation of hexadeuterio-*endo*-5-benzoylnorbornene (1.36 g, 0.0065 mol) in 20 ml of 95% ethanol over 0.06 g of 10% palladium on carbon, after chromatography and distillation, gave **9** as a colorless oil (0.9 g, 66%) (Table VIII).

**1,4,5,5,6,6,7,7-Octadeuterio-*endo*-2-benzoylnorbornane (10).**

Catalytic deuteration of hexadeuterio-*endo*-5-benzoylnorbornene gave **10** as a colorless oil (Table VIII).

**Irradiation of 2-Propyl-1-tetralone (4).** A solution of 0.8 g of ketone in 80 ml of benzene was bubbled with argon and irradiated through Pyrex for 4.5 hr. Chromatography on silica gel (hexane-benzene) gave recovered starting material (10%), 1-tetralone (75%), and an alcoholic product (15%): ir spectrum (film) 3550 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\delta$  1.10 (d, 2 H, *J* = 7 Hz), 1.6–3.0 (m, 9 H), 7.2 (m, 4 H).

**Irradiation of  $\alpha$ -(1-Adamantyl)acetophenone (5).** A solution of 0.60 g of ketone in 50 ml of 1-propanol-benzene was bubbled with argon and irradiated for 45 min through Pyrex. Gc on a 5 ft  $\times$  1/8 in. column of 5% SF 96 on Chromosorb G at 210° showed >90% conversion to two products of shorter retention time than starting ketone. Chromatography on silica gel (2% ethyl acetate-hexane) resulted in elution of the product with longer gc retention time (**6**, 0.19 g, mp 82–83°) followed by the product with shorter gc retention time (**7**, 0.14 g, mp 106–107°). The ir spectra of **6** and **7** were similar and both showed only a free OH stretch at 3610 cm<sup>-1</sup> (0.03 *M*, CCl<sub>4</sub>). Nmr spectra (CCl<sub>4</sub>): for **6**,  $\delta$  1.4–2.2 (m, 15 H), 2.1 (d, H<sub>a</sub>), 2.2 (d, H<sub>b</sub>), 2.9 (m, H<sub>c</sub>), 2.3 (m, OH), 7.2 (m, 5 H); for **7**, 1.4–2.2 (m, 15 H), 1.95 (d, H<sub>a</sub>), 2.65 (d, H<sub>b</sub>), 2.5 (m, H<sub>c</sub>), 2.8 (m, OH), 7.2 (m, 5 H).

**Irradiation of *exo,exo*-5,6-Dideuterio-*endo*-2-benzoylnorbornane (8).** A solution of 0.2 g of ketone **8** in 25 ml of benzene was bubbled with argon and irradiated through Pyrex for 200 min. Analysis by gc showed ~50% conversion of starting ketone. Chromatography on silica gel (hexane-benzene) gave the photoelimination product as a colorless oil: nmr (CCl<sub>4</sub>)  $\delta$  1.6–2.7 (m, 6 H), 2.90 (t, 2 H), 5.62 (s, 1 H), 7.4 (m, 3 H), 7.8 (m, 2 H).

**General Procedures** for preparative irradiations, quantum yields, and rate constants are described in the accompanying manuscript. Viscosities of ketone-piperylene-cyclooctane solutions were measured using an Ostwald viscosimeter. A merry-go-round apparatus immersed in a thermostated water bath ( $\pm 0.5^\circ$ ) was used for the variable temperature studies.

**Acknowledgments.** The authors wish to thank Professors W. H. Saunders, Jr., M. S. Silver, M. A. Winnik, and J. Michl for stimulating discussions and C. Steel for informing us of his results prior to publication.

(51) S. McLean, C. J. Webster, and R. J. D. Rutherford, *Can. J. Chem.*, **47**, 1556 (1969).

## Photoisomerization of Cyclohexadienyl Cations. Stereochemistry of Bicyclohexenyl Cation Formation<sup>1</sup>

James W. Pavlik\*<sup>2</sup> and Robert J. Pasteris<sup>3</sup>

*Contribution from the Department of Chemistry, University of Wisconsin—River Falls, River Falls, Wisconsin 54022. Received January 30, 1974*

**Abstract:** The photoisomerization of cyclohexadienyl cations **1–5** has been studied under conditions which allowed direct observation of bicyclohexenyl cations **6–9** by nmr spectroscopy. Although most reported isomerizations of this type have been reported to yield the bicyclohexenyl cation with the larger group in the *endo* position, photolysis of cations **1** and **3** yielded cations **6** or **8** as a mixture of stereoisomers in which the *endo*-methyl cation predominates. Although increasing the size of R<sub>2</sub> had no effect on the stereochemistry of the ring closure in **2**, steric interaction in **4** was sufficient to favor formation of the *endo*-CCl<sub>3</sub> cation. This suggests that the stereochemistry of these ring closures is determined not only by interaction between R<sub>1</sub> and R<sub>2</sub> but also by repulsion between the C-1 OH group and R<sub>1</sub>. In view of this it was surprising that photolysis of **5** resulted in the *endo*-methyl cation as the major product. Molecular models suggest that hydrogen bonding between the C-1 OH and R<sub>1</sub> may affect the stereochemistry of the ring closure in **5**.

Photolysis of cyclohexadienyl cations **1** and **5** has previously been shown<sup>4</sup> to result in the formation

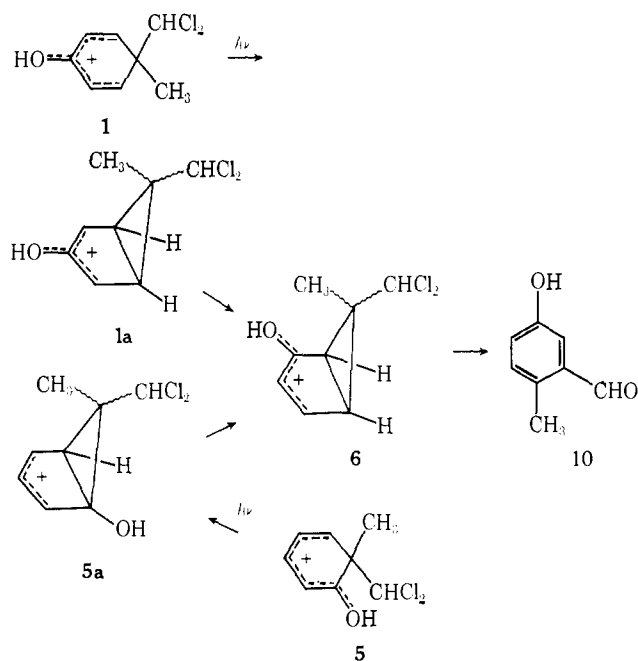
(1) Presented in part at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., Apr 1974.

(2) Department of Chemistry, Worcester Polytechnic Institute, Worcester, Mass. 01609.

(3) ACS-PRF Undergraduate Research Participant, 1972–1973.

of the same product, 5-hydroxy-2-methylbenzaldehyde, **10**. Although at that time the existence of bicyclohexenyl cation **6** was only postulated as a common intermediate in the conversion of **1** and **5** to **10**, similar work

(4) N. Filipescu and J. W. Pavlik, *J. Amer. Chem. Soc.*, **92**, 6062 (1970).



by Childs and Parrington<sup>5,6</sup> led to the direct observation of a number of bicyclohexenyl cations, including formation of **6** from **5**.

Since **6** exists in two stereoisomeric forms, their direct observation from both **1** and **5** remained of interest. In particular, since it has been shown that the groups attached to the migrating carbon atom maintain their relative positions during sigmatropic rearrangements of the type **1a** or **5a** to **6**,<sup>7-10</sup> then the isomeric distribution observed in **6** would reflect the effects of structure on the electrocyclic ring closure occurring upon conversion of **1** and **5** to **1a** and **5a**, respectively. Hart has proposed, for example, that when significant steric repulsion exists between the substituents on C-4 and those on the adjacent ring positions of the neutral 2,5-cyclohexadienone ring, then electrocyclic ring closure will occur in a manner that the larger groups on C-4 will move predominately into the endo position of the bicyclo[3.1.0] ring system.<sup>11</sup> Although this has been shown to be generally true with both cyclohexadienones<sup>12-15</sup> and cyclohexadienyl cations,<sup>16,17</sup> the reverse stereochemistry has been observed upon photolysis of neutral 4-methyl-4-trichloromethyl-2,5-cyclohexadienone.<sup>18</sup>

In order to further explore the effects of structure on

(5) B. Parrington and R. F. Childs, *Chem. Commun.*, 1581 (1970).

(6) B. Parrington, Ph.D. Dissertation, McMaster University, 1971.

(7) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **90**, 5612 (1968).

(8) T. M. Brennan and R. K. Hill, *J. Amer. Chem. Soc.*, **90**, 5614 (1968).

(9) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968).

(10) H. Hart, T. R. Rodgers, and J. Griffiths, *J. Amer. Chem. Soc.*, **91**, 754 (1969).

(11) T. R. Rodgers and H. Hart, *Tetrahedron Lett.*, 4845 (1969).

(12) T. Matsuura, *Bull. Chem. Soc. Jap.*, **37**, 564 (1964).

(13) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **89**, 1678 (1967).

(14) B. Miller, *J. Amer. Chem. Soc.*, **89**, 1690 (1967).

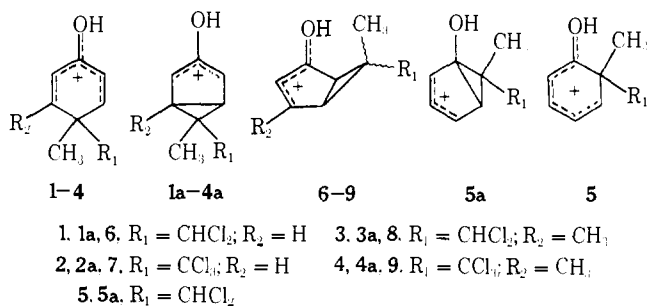
(15) K. Ogura and T. Matsuura, *Bull. Chem. Soc. Jap.*, **43**, 2891 (1970).

(16) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968).

(17) I. S. Isaev, V. I. Mamatyuk, L. I. Kuzubova, and T. A. Gordimova, and V. A. Koptuyug, *Zh. Org. Khim.*, **6**, 2482 (1970).

(18) D. I. Schuster, K. Vasanth Prabhu, S. Adcock, J. van der Veen, and H. Fujiwara, *J. Amer. Chem. Soc.*, **93**, 1557 (1971).

the stereochemistry of this ring closure in cationic systems, we have studied the photolysis of cations **1-5**



- 1, 6.**  $R_1 = \text{CHCl}_2$ ;  $R_2 = \text{H}$     **3, 3a, 8.**  $R_1 = \text{CHCl}_2$ ;  $R_2 = \text{CH}_3$   
**2, 2a, 7.**  $R_1 = \text{CCl}_3$ ;  $R_2 = \text{H}$     **4, 4a, 9.**  $R_1 = \text{CCl}_3$ ;  $R_2 = \text{CH}_3$   
**5, 5a.**  $R_1 = \text{CHCl}_2$

under conditions which allow direct observation of the bicyclohexenyl cations **6-9** by nmr spectroscopy.

## Results and Discussion

Figures 1 and 2 show the changes in the nmr spectra of the 4,4-disubstituted cations **1** and **2** upon photolysis. Each figure shows the conversion of the starting cyclohexadienyl cation to a mixture of diastereomeric bicyclohexenyl cations. Thus Figure 1 shows the formation of two new methyl signals at  $\delta$  1.63 and 1.90 ppm, two new dichloromethyl signals at  $\delta$  5.68 and 5.80 ppm, and signals associated with the two bridgehead protons and the  $\alpha$ -vinyl proton at  $\delta$  3.70, 4.17, and 6.90 ppm, respectively. Because the bicyclohexenyl cations are also photolabile under the conditions of the experiment,<sup>19</sup> Figure 1 also shows absorptions at  $\delta$  2.83 and 7.7 ppm due to the formation of protonated **10**.<sup>20</sup>

Figure 2 shows that although the concentration of the bicyclohexenyl cations achieved from **2** was not as great as in the former case, both bridgehead protons at  $\delta$  4.0 and 4.4 ppm and the two new methyl signals at  $\delta$  1.80 and 2.05 ppm are readily observable. Continued photolysis in this instance gave rise to additional signals at  $\delta$  2.70 and 7.7 ppm. Neutralization of the solution after these latter signals reached maximum intensity yielded a crystalline solid whose melting point and nmr spectrum were consistent with the photoproduct analogous to **10**, 2-methyl-5-hydroxybenzoic acid.<sup>21</sup>

The upfield methyl signals in Figures 1 and 2 have been assigned to isomers **6a** and **7a**, respectively, in which the methyl groups are in the endo positions. Shielding of *endo*-methyl groups by the cyclopentenone ring in neutral bicyclo[3.1.0] ring systems has been adequately established<sup>12-15,23</sup> and our present observations show that this generalization can also be extended to these bicyclohexenyl cations. Thus in the nmr spectra of neutral bicyclohexenones obtained by neutralizing  $\text{H}_2\text{SO}_4$  solutions of **6a** and **6b**, the ratios of the upfield to downfield methyl groups were identical to the ratios observed in the nmr spectra of the acid solutions before neutralization. This verifies that the relative chemical shifts of the *endo*- and *exo*-methyl groups in bicyclohexenyl cations are the same as in the neutral bicyclohexenones.

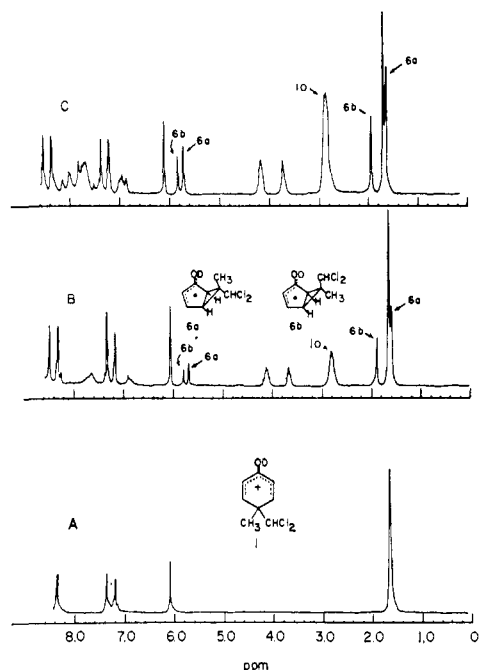
(19) 4,4-Disubstituted-2,5-cyclohexadienyl cations and the corresponding bicyclo[3.1.0]hexenyl cations have principal absorption maximum at approximately 260 nm.

(20) The identity of these signals was confirmed by comparison with the nmr spectrum of authentic 5-hydroxy-2-methylbenzaldehyde in 98%  $\text{D}_2\text{SO}_4$ .

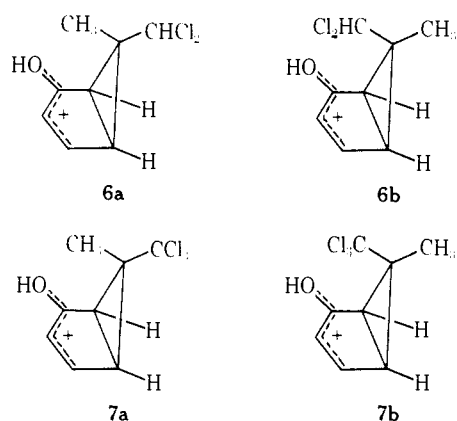
(21) Mp 184-185° (lit.<sup>22</sup> 185°); nmr (acetone- $d_6$ )  $\delta$  2.24 (s, 3 H), 6.84-7.14 (m, 2 H), 7.45 (d,  $J = 3$  Hz, 1 H), 7.75 (broad, 1 H).

(22) D. Peltier, *C. R. Acad. Sci.*, **236**, 1972 (1953).

(23) H. Hart and D. W. Swatton, *J. Amer. Chem. Soc.*, **89**, 5075 (1967).



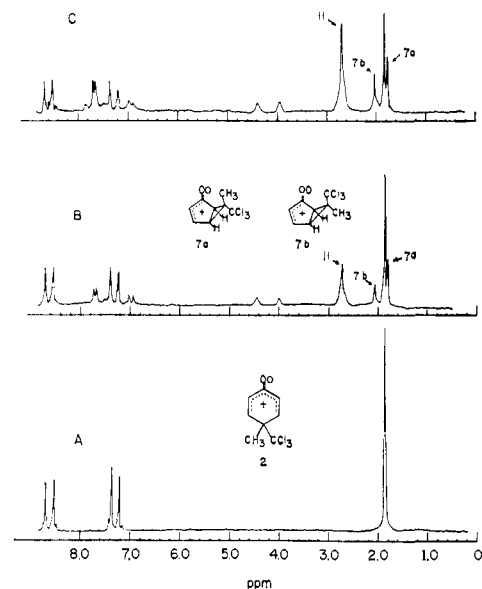
**Figure 1.** Nmr spectrum of **1** in 98%  $D_2SO_4$ : (A) before irradiation; (B) after 4-hr irradiation; (C) after 6-hr irradiation.



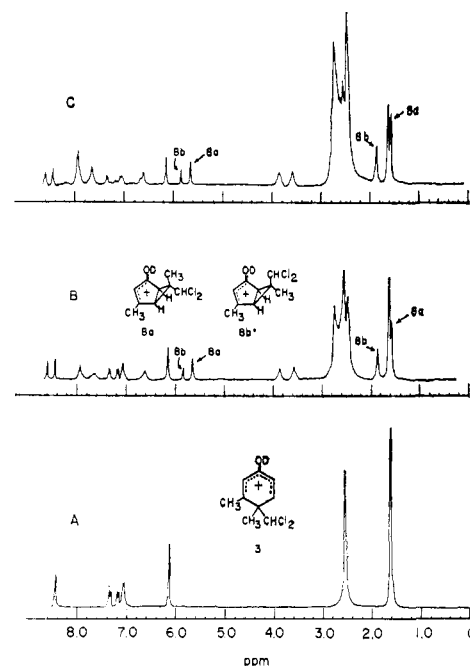
Integration of the methyl regions in Figures 1 and 2 reveals an isomeric ratio of 1.4:1 for **6a**:**6b** and 1.1:1 for **7a**:**7b**. Thus in both instances electrocyclic ring closure has occurred with the smaller C-4 substituent moving predominately into the endo position of the bicyclohexenyl ring system rather than into the exo position as generally observed.

Replacement of the C-3 hydrogen with a methyl group, as in **3** and **4**, results in a greater potential for steric interference between this methyl group and the groups on C-4 as the latter atom moves up or down during electrocyclic ring closure. Thus the magnitude of this interference should be reflected in the ratio of the isomeric bicyclohexenyl cations formed from either **3** or **4** relative to the analogous ratio formed from **1** where steric interference is at a minimum.

Figure 3 shows the changes in the nmr spectrum of **3** upon irradiation. Although two pairs of diastereomeric bicyclohexenyl cations are possible from **3**, the appearance of two bridgehead protons of equal intensity at  $\delta$  3.88 and 3.58 ppm is consistent with the formation of **8**, the more stable cation. Integration reveals no significant difference between the ratios of the two new dichloromethyl signals at  $\delta$  5.67 and 5.83 ppm

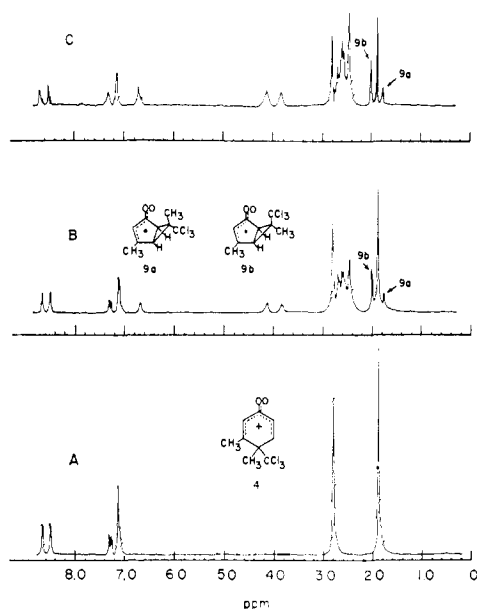


**Figure 2.** Nmr spectrum of **2** in 98%  $D_2SO_4$ : (A) before irradiation; (B) after 0.5-hr irradiation; (C) after 1-hr irradiation.



**Figure 3.** Nmr spectrum of **3** in 98%  $D_2SO_4$ : (A) before irradiation; (B) after 8-hr irradiation; (C) after 13-hr irradiation.

or the two new methyl signals at  $\delta$  1.60 and 1.90 ppm and the analogous signals in Figure 1. The equality of these ratios shows that the relative amounts of *endo*- and *exo*-bicyclohexenyl cations formed upon photolysis of either **1** or **3** are not significantly different. This being the case, steric interference between the C-3 methyl and C-4 dichloromethyl groups during ring closure of **3** must be no more significant than between the latter group and the C-3 hydrogen during ring closure of **1**. Continued photolysis of **3** is also accompanied by formation of two broad, partially unresolved methyl signals of unequal intensity at  $\delta$  2.48 and 2.75 ppm and two aldehyde proton signals of unequal intensity at  $\delta$  9.82 and 9.92 ppm. Thus it appears that bicyclohexenyl cation **8** is photochemically converted



**Figure 4.** Nmr spectrum of **4** in 98%  $D_2SO_4$ : (A) before irradiation; (B) after 1-hr irradiation; (C) after 1.5-hr irradiation.

to two aromatic aldehydes, presumably 2,5-dimethyl-3-hydroxy- and 2,3-dimethyl-5-hydroxybenzaldehyde.

Figure 4 shows the results of increasing the size of the substituent at C-4 from  $CHCl_2$  to  $CCl_3$  while retaining the methyl group at C-3. Although, as with trichloromethyl cation **2**, it was again not possible to achieve a large concentration of the intermediate bicyclohexenyl cations, both bridgehead protons at  $\delta$  3.58 and 3.85 ppm and the  $\alpha$ -vinyl proton at 6.71 ppm of **9** are clearly visible after short duration irradiation. Furthermore the changes in the nmr spectrum of **4** show dramatic changes in the ratio of the two new methyl signals at  $\delta$  1.78 and 2.02 ppm as compared to the ratios observed in either Figures 2 or 3. Thus, in this instance, the bicyclohexenyl isomer with the C-4 methyl group in the *exo* position predominates by a ratio of 2:1.

Although the stereochemical course of the electrocyclic ring closure in **1** and **2**, which leads predominately to the formation of the isomer with the smaller C-4 substituent in the *endo* position, is apparently not subject to simple steric control, the increased yield of the *exo*-methyl isomer obtained from **2** relative to **1** is consistent with Hart's hypothesis.<sup>11</sup> Thus as the second substituent on C-4 is increased in size from  $CHCl_2$  to  $CCl_3$ , it is consistent with steric considerations that the smaller group on C-4 would more readily pass across the plane of the C-3 and C-5 hydrogens into the *exo* position. Replacement of the C-3 hydrogen with a  $CH_3$  group, as in **4**, thus magnifies this steric effect to the extent that it becomes the predominate factor in controlling the stereochemical course of the ring closure.

Although no information is available concerning the formation of bicycloketones from neutral 4-methyl-4-dichloromethyl-2,5-cyclohexadienones, it is interesting to compare the stereochemistry of the ring closure of cation **2** with that observed from the photolysis of neutral 4-methyl-4-trichloromethyl-2,5-cyclohexadienone. In the latter case, Schuster observed stereospecific ring closure leading to the *endo*-methylbicyclohexenone.<sup>18</sup> Failure to observe any of the *endo*-trichloromethyl isomer in this case suggests that the steric

interference experienced as the larger trichloromethyl group moves past the C-3 and C-5 hydrogens into the *exo* position is less important in controlling the stereochemical course of the ring closure than the repulsion that the negative oxygen would exert on the trichloromethyl group if it would move into the *endo* position of the intermediate zwitterion. Since photolysis of the analogous cyclohexadienyl cation **2** (Figure 2) results in an almost equal distribution of the two bicyclic products, it appears that protonation of the negative oxygen reduces this repulsion so that the stereochemical course of the ring closure is more equally affected by these two opposing interactions. As we have observed in the case of cation **4**, Schuster found that replacement of the C-3 hydrogen with methyl increases the relative importance of steric effects on the stereochemistry of the electrocyclic ring closure of neutral 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone. Again, however, the stereochemistry of the ring closure in cation **4** (Figure 4) was found to be more sensitive to steric control than the corresponding neutral dienone from which the *endo*-methylbicyclohexenone predominated by a ratio of 15:1.

Considering the effects of steric hindrance and electrostatic repulsion on the stereochemistry of the electrocyclic ring closure in 2,5-cyclohexadienyl cations, it might be expected that both of these factors would be particularly pronounced in the case of 6-methyl-6-dichloromethyl-2,4-cyclohexadienyl cation, **5**. Movement of the dichloromethyl group into the *exo* position would not only require the larger C-6 group to pass across the plane of the C-1 hydroxyl and C-5 hydrogen, but also into a position of maximum repulsion between the C-OH and C- $CHCl_2$  dipoles. Thus both factors would be operating in the same direction.

In view of this the changes in the nmr spectrum of **5** upon photolysis were somewhat surprising. Figure 5 shows that despite these factors, photolysis of **5** results in the formation of a mixture of bicyclohexenyl cations **6a** and **6b** in which the *exo*-dichloromethyl isomer predominates by a ratio of 1.8:1.

The greater concentration of **6a** and **6b** achieved in this case is due to the longer wavelength of the excitation light which although strongly absorbed by **5** is only weakly absorbed by the bicyclohexenyl cations. When **5** was irradiated under conditions identical with those used for the photolysis of **1** (see Experimental Section), the concentration of **6a** and **6b** achieved was less than shown in Figure 5 but the ratio of the two stereoisomers remained the same. Thus the difference in the stereochemistry of the ring closures of **1** and **5** is not due to any difference in excitation wavelength.

Since bicyclohexenyl cations **6a** and **6b** are photolabile under the photolysis conditions employed, these measured ratios depend not only on their relative rates of formation from **1** and **5**, but also on their relative rates of conversion to **10**. In order to evaluate how these latter rates affect the observed ratios, an equimolar mixture of cations **6a** and **6b** were irradiated in the absence of the starting cyclohexadienyl cations. Nmr analysis of the mixture before and after consecutive irradiations showed that while 50% of each starting cation was converted to **10**, no experimentally significant change in their ratio could be detected. Thus the stereoisomeric ratios of **6a** and **6b** formed from

either **1** or **5** are not affected by the subsequent photochemical reaction.

Ring closure in **5** is thus favored by association of the C-1 hydroxyl and C-6 dichloromethyl groups rather than by a pathway which allows for their maximum separation as was observed in the case of **1**. Inspection of molecular models offers a plausible explanation for this observation. Unlike the 4,4-disubstituted-2,5-cyclohexadienyl cation **1**, intramolecular hydrogen bonding is quite possible between the C-1 hydroxyl hydrogen and the chlorine atom of the C-6 dichloromethyl group in the 2,4-cyclohexadienyl cation **5**. Furthermore, although hydrogen bonding between these two groups is able to remain intact during movement of the dichloromethyl group into the *exo* position, passage of this group into the *endo* position must be accompanied by a disruption of these stabilizing forces.

### Experimental Section

**Preparation of Cyclohexadienyl Cations.** All cyclohexadienyl cations were prepared by slow addition of 0.015 g of the corresponding cyclohexadienone to 0.5 ml of rapidly stirred, chilled 96% H<sub>2</sub>SO<sub>4</sub> or 98% D<sub>2</sub>SO<sub>4</sub>. The thermal stability of these cations was demonstrated by quantitative recovery of the cyclohexadienones upon neutralization of the acid solutions after prolonged standing of the solutions at room temperature.

**Preparation of Cyclohexadienones.** Dichloromethyl-substituted cyclohexadienone precursors of cations **1** and **5** were prepared by method III of von Auwers and Keil.<sup>24</sup> Trichloromethyl-substituted cyclohexadienone precursors of cations **2-4** were prepared according to the method of Neuman.<sup>25</sup>

**Photolysis of Cyclohexadienyl Cations.** All solutions were irradiated in a water-jacketed quartz tube between 17 and 20° under a continuous fine stream of nitrogen. Cyclohexadienyl cations **1-4** were irradiated using two Rayonet 3000-Å lamps through a Corex filter. Cyclohexadienyl cation **5** was irradiated through a Pyrex filter using two 100-W spot lamps.

**Photolysis of Bicyclohexenyl Cations 6a and 6b.** A 1:1 mixture of *exo*- and *endo*-6-methyl-6-dichloromethylbicyclo[3.1.0]hexenone (0.044 g) in 0.5 ml of CCl<sub>4</sub> was added dropwise to 0.3 ml of rapidly stirred, chilled 98% D<sub>2</sub>SO<sub>4</sub>. After the mixture was stirred several minutes the CCl<sub>4</sub> layer was removed and the acid solution irradiated as above for cyclohexadienyl cations **1-4**. Nmr analyses were carried out before irradiation and after 15, 30, 60, 120, and 150

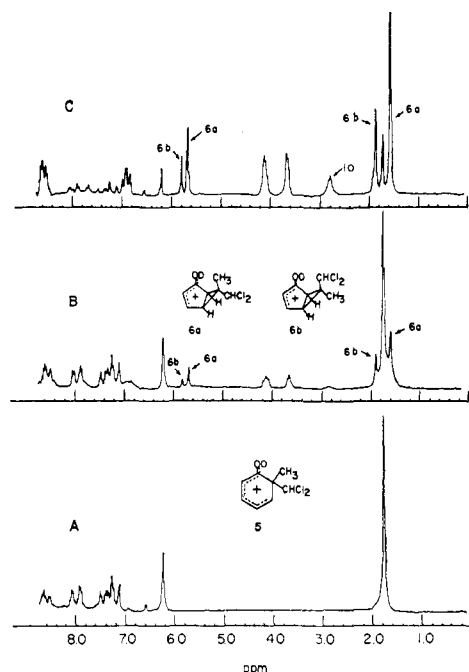


Figure 5. Nmr spectrum of **5** in 98% D<sub>2</sub>SO<sub>4</sub>: (A) before irradiation; (B) after 2-hr irradiation; (C) after 6-hr irradiation.

min of photolysis. Integration of the *exo*- and *endo*-methyl and dichloromethyl signals gave *exo*:*endo* ratios of 0.98, 1.02, 1.02, 1.03, and 1.02, respectively.

**Nmr Spectra.** All spectra were recorded on a Varian T-60 nmr spectrometer at ambient temperature. The chemical shifts ( $\delta$ ) are reported in parts per million downfield from TMS using methylene chloride ( $\delta$  5.30) as the secondary standard. No differences in the spectral changes were observed when the photolyses were carried out in 96% H<sub>2</sub>SO<sub>4</sub> or 98% D<sub>2</sub>SO<sub>4</sub>. Spectra illustrated in this paper were recorded in 98% D<sub>2</sub>SO<sub>4</sub>.

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(24) K. von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902).

(25) M. S. Neuman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).