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Photoinduced Electron-Transfer Reactions of Some 1,4-Dialkylbicyclo[2.2.0]hexanes. Generation of Cyclohexane-1,4-diyl Radical Cations in Boat Form and Their Stereospecific $[\sigma^1s + \sigma^2s]$ Cleavage

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Abstract: The title reactions of *exo*- and *endo*-1,2,3,4,5,6-hexamethyl- and deuterium-labeled 1,4-dimethylbicyclo[2.2.0]hexanes **1–3** and of 3,5-dioxatricyclo[5.2.2]undecanes **4** are studied in the presence of a variety of electron acceptor sensitizers. Compound **1** undergoes virtually sensitizer-independent, highly stereospecific $[\sigma^1s + \sigma^2s]$ ring cleavage upon one-electron oxidation to give *erythro*-(*E*,*E*)-3,4,5,6-tetramethylocta-2,6-diene as the major product. Similar, but somewhat decreased stereospecificity is also observed in the reaction of **3**. The generation of *boat* cyclohexane-1,4-diyl radical cations which undergo the $[\sigma^1s + \sigma^2s]$ cleavage while retaining their configurations is proposed. The decreased stereospecificity of the reaction of **3** is attributed to the configurational instability of the resultant diene radical cation rather than to the incomplete stereospecificity of the ring cleavage process. In contrast, the composition of product derived from **2** is highly dependent on the sensitizer used and is found to be correlated with the reduction potential ($E_{1/2}^{\text{red}}$) of the latter. Thus **2** is predominantly isomerized to **1** by the sensitizers whose $E_{1/2}^{\text{red}}$s are more negative than −0.8 V vs SCE, while it affords primarily hexamethylcyclohexene (**5**) with the more readily reducible sensitizers. In addition to **1** and/or **5**, erythro-(*E*,*Z*)-diene **6** is invariably produced as the minor product, but the $[\sigma^1s + \sigma^2s]$ cleavage of **2** to give the erythro-(*Z*,*Z*)-diene is not detected. The stereochemistry and the sensitizer-dependency of the reaction of **2** are rationalized in terms of rapid ring flip of the incipient boat radical cation into the chair form to relieve steric repulsion among the four endo-methyl substituents. The chair intermediate subsequently rearranges to the radical cations of **5** and **6**, in competition with back electron transfer (ET) from the counter radical anion to give cyclohexane-1,4-diyl diradical, which, in turn, collapses to produce **1** and **6**. The rate of the back-ET is dependent on the $E_{1/2}^{\text{red}}$ of the sensitizer and so is the product composition. The different stereospecificities of the cleavage reactions of **1** and **2** rule out the operation of a concerted mechanism. The reaction of **4** affords a rearranged isomer as a primary product which is shown by a labeling experiment to be derived via intramolecular proton (or hydrogen) transfer subsequent to the $[\sigma^1s + \sigma^2s]$ cycloreversion, thus proving the occurrence of the ring cleavage in the single-electron-transferred radical cation. In accord with the experimental observation, the $[\sigma^1s + \sigma^2s]$ cleavage reactions of **1** and **3** are estimated to be slightly exothermic on the basis of available thermochemical data and calculated heats of formation. This is in marked contrast to the theoretically predicted and experimentally proved high endothermicity of the process in the parent system.

Introduction

Organic radical cations have recently attracted much attention because of their unusual structures and markedly enhanced reactivities compared to those of the corresponding neutral molecules.[1,2] Cyclohexane-1,4-diyl radical cation is a focus of current interest as a radical cation counterpart of the elusive cyclohexane-1,4-diyl diradical[3] and also as an intermediate associated with possible catalysis of the Cope rearrangement by electron transfer (ET).[4] As for its structure, preferential formation in a chair form has been observed upon ionization of both 1,5-hexadienes[4b,4f] and unsubstituted bicyclo[2.2.0]hexane,[5] suggesting that the corresponding boat form does not represent an energy minimum or corresponds only to a very shallow well at best on the potential energy surface and may not play a significant role in the reaction of cyclohexane-1,4-diyl radical cation. With regard to the energetics of its cleavage to give 1,5-hexadiene radical cation, theoretical calculations suggest the high endothermicity of the process for the parent system[4a] and, in fact, the rapid reverse cyclization of 1,5-hexadiene radical cations has been observed in a number of investigations.[4]

In the course of studies on the reactivity of strained polycyclic compounds, we have found that simple alkyl-substituted bicyclo[2.2.0]hexanes **1–4** relatively readily undergo one-electron oxidation for simple saturated alicyclic compounds to afford the corresponding cyclohexane-1,4-diyl radical cations, which efficiently undergo ring cleavage to give 1,5-hexadiene radical cations, in contrast with the behavior of the parent and some aryl-substituted systems reported to date;[4] thus the thermicity of ring cleavage reaction of cyclohexane-1,4-diyl radical cations may be

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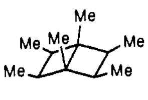

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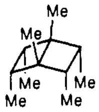

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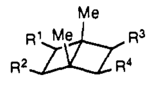
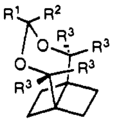


3

a, R^1 - R^4 = H
b, R^1 - R^4 = D_{4-n}/H_n (n = 0 ~ 4)



4

a, $R^1 = R^2 = R^3 = H$
b, R^1 = Me, $R^2 = R^3 = H$
c, $R^1 = R^2$ = Me, $R^3 = H$
d, $R^1 = R^2$ = Me, $R^3 = D$
e, $R^1 = R^2 = CH_2Cl$, $R^3 = H$

significantly affected by substituents. In addition, the observed [σ^1s + σ^2s] stereospecificity of the reactions of **1** and **3** indicates that the cyclohexane-1,4-diyl radical cations derived from those bicyclohexanes retain a boat conformation and do not undergo conformational flip to the chair forms to an appreciable extent prior to the ring cleavage, provided the boat form is not particularly strained sterically. In the present paper we report the full account of the above investigation.[6]

Results

Synthesis of Bicyclo[2.2.0]hexanes. *exo-* and *endo-*1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexanes **1** and **2** were prepared following the procedure of Van Rantwijk et al.[7] 1,4-Dimethylbicyclo[2.2.0]hexane (**3a**) and its deuterated derivative (**3b**) were obtained through reduction of 1,4-dimethyl Dewar benzene[8] by diimine and diimine-d_2,[9] respectively. In the 500-MHz ^1H NMR spectrum of **3a** in $CDCl_3$, the methylene protons appear as AA′XX′ multiplets at δ 1.80–1.90 and 1.95–2.05. The exo and endo protons were readily differentiated from each other by NOE experiments. Thus the former signal but not the latter was significantly enhanced in intensity upon irradiation of methyl protons at δ 0.973 and hence was assigned to the exo hydrogens and the latter to the endo hydrogens. The ratio of endo-H/exo-H in **3b** was (85 ± 2):(15 ± 2), which varied slightly from batch to batch. The ^2H NMR of **3b** at 76.7 MHz exhibited a single peak at δ 1.85, indicating >95% exo specificity of the deuterium addition to 1,4-dimethyl Dewar benzene, though the resolution was not sufficiently high to permit the detection of a small amount of endo-D. Therefore the majority, if not all, of exo-H in **3b** apparently resulted from the incomplete deuteration of the diimine. The NMR spectra of reaction products of **3b** were also consistent with the incorporation of on average 3.3 D into **3b**, i.e. 82% of the theoretical amount.[10] The reduction product **3b** thus was a mixture of bicyclohexanes bearing from four deuteriums down to none as suggested by the mass spectrum. However, this did not impede the study of stereospecificity of ring cleavage of **3**, because it was reasonably expected that the stereochemical outcome of the reaction should be essentially unaffected by the degree of deuterium substitution.

The bridged acetals **4** were prepared by LAH reduction of dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate (**5**)[11] followed by acetalization of the resultant diol. The $LiAlD_4$ reduction–acetalization of **5** provided **4d** in which the content of deuterium on the *O*-methylene carbons was >98%.

Electro- and Photochemical Measurements. Table I lists the oxidation peak potentials (E_p^{ox}) of bicyclo[2.2.0]hexanes which were measured using cyclic voltammetry at a sweep rate of 200 mV/s in acetonitrile containing tetraethylammonium perchlorate (0.1 M) as the supporting electrolyte. The anodic oxidation of bicyclohexanes was irreversible, so the peak potentials might be kinetically shifted relative to the reversible potentials owing to interference from the coupled chemical reaction.

Table I. Oxidation Peak Potentials (E_p^{ox}) of Bicyclo[2.2.0]hexanes and Related Substrates (V vs SCE)[a]

1	**2**	**3**	**7**	**10**[b]	**11a**
1.67	1.63	2.03	1.86	2.21	2.41

[a] Measured in deaerated acetonitrile at 25 °C. The substrate concentration was ca. 5 mM. [b] 1,4-Bis(methoxymethyl)bicyclo[2.2.0]hexane.

Table II. Calculated Free Energy Change for Electron Transfer for Relevant Pairs of Bicyclohexane and Electronically Excited Acceptor[a]

electron acceptor	$E_{1/2}^{red\ b}$ (V vs SCE)	ΔG_{ET} (kcal/mol)			
		1	**2**	**3**	**4**[c]
DCB	−1.60	−22 (4)	−23 (3)	−14 (12)	−10 (16)
CA	−1.39		−1		
DCN	−1.28	−13 (11)	−14 (10)	−5 (19)	
DCA	−0.89	−9 (19)	−10 (18)	−1 (27)	
TCB	−0.65	−36 (−8)	−37 (−9)		−24 (4)
TCA	−0.45	−17 (10)	−18 (9)	−9 (18)	−5 (22)
TCNQ	0.13	−26	−27	−18	

[a] Calculated for ET from **1–4** to the electron acceptors in the lowest excited singlet and triplet (in parentheses) states by using the Weller equation.[12] Excited-state energies of electron acceptors from refs 1b and 13. [b] $E_{1/2}^{red}$ of electron acceptors measured in acetonitrile.[14] [c] E_p^{ox} of **4** was assumed to be the same as that of **10**. [d] The lowest excited singlet energy was estimated from the absorption spectrum. The lowest triplet energy was not available.

Table III. Fluorescence Quenching Rate Constants[a] and Quantum Yields for Consumption of Bicyclohexanes

electron acceptor	k_q (10^{-9} M^{-1} s^{-1})			ϕ	
	1	**2**	**3**	**1**	**2**
DCB	13.8	15.3	11.5		
DCN	10.0	10.7		0.034[b]	0.067[b]
DCA	7.2	5.8	1.8	0.014[c]	0.029[c]
TCB	16.7	16.2		0.069[b]	0.12[b]
TCA	13.8	13.5	8.8	0.048[c]	0.14[c]

[a] Quenching experiments were carried out in deaerated acetonitrile at 25 °C. [b] At 313 nm. [c] At 365 nm.

Table IV. Photoinduced ET Reaction Products of **1**

electron acceptor	conversion (%)	yield (%)	composition of product		
			6	**7**	**9a**
		In Acetonitrile			
DCN	10	43	86	2	12
DCA	10	75	90	5	5
TCB	21	44	90	5	5
TCA	18	75	86	3	12
TCNQ	21	94	89	<2	11
		In Dichloromethane			
DCB	6	60	86	14	<2
DCB	17	60	88	12	<2
DCN	14	74	84	2	14
DCA	41	77	93	1	6
TCB	17	59	71	21	8
TCA	32	81	90	<2	10
TCNQ	24	89	95	<2	5

In Tables II and III are listed calculated free energy changes for ET (ΔG_{ET}) from the bicyclohexanes to electronically excited acceptors[15] and rate constants for the quenching of fluorescence

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(10) A percentage of deuterium incorporation calculated from the *endo*-H/*exo*-H ratio assuming that the deuteriums were exclusively introduced to the exo positions is 100(85 − 15)/85 = 82%.

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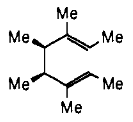
Table V. Photoinduced ET Reaction Products of **2**

electron acceptor	conversion (%)	yield (%)	composition of product 1	6	7	9a
		In Acetonitrile				
DCB	10	71	67	6	19	8
CA	17	59	82	<2	18	<2
DCN	20	78	66	2	27	5
DCA	17	73	72	3	25	<2
TCB	13	55	26	<2	12	62
TCA	17	83	15	<2	16	69
TCNQ	21	59	<2	<2	18	82
		In Dichloromethane				
DCB	21	59	72	<2	21	6
DCN	20	80	67	<2	27	4
DCA	28	56	80	<2	18	2
TCB	20	70	48	5	20	27
TCA	28	65	42	2	26	30
TCNQ	27	56	2	<2	28	70

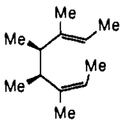
of the latter by the former (k_q), together with quantum yields for the consumption of **1** and of **2**.

Photoinduced Electron-Transfer Reactions of 1–4. The photoinduced ET reactions of **1–4** were carried out by employing a series of cyanoaromatics and TCNQ as electron-accepting sensitizers and irradiating solutions of substrate and sensitizer in acetonitrile or dichloromethane through Pyrex. The photolysates were analyzed by capillary GLC, and the major products were isolated and characterized on the basis of their spectroscopic properties and by comparison with authentic material in the case of known compounds.

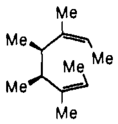
(a) *exo-* and *endo*-1,2,3,4,5,6-Hexamethylbicyclo[2.2.0]hexanes (1 and 2). The photoinduced ET reaction of **1** in acetonitrile was virtually independent of the sensitizer used and afforded erythro-(*E*,*E*)-diene **6**,[16,17] a [σ^1s + σ^2s] cycloreversion product, as the major product together with small amounts of erythro-(*E*,*Z*)-diene **7**[16] and hexamethylcyclohexene **9a** (Table IV). Since these products were liable to secondary photolysis under the reaction conditions, both the yield and apparent stereospecificity of cycloreversion deteriorated at the high conversion of **1**.[18] The reaction of **1** in dichloromethane was also largely stereospecific, but a significant amount of **7** was produced when sensitized by DCB or TCB.



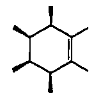
erythro-(*E*,*E*)
6

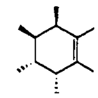


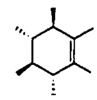
erythro-(*E*,*Z*)
7

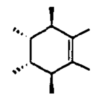


erythro-(*Z*,*Z*)
8


9a


9b


9c


9d

The sensitized photolysis of **2** was in striking contrast to that of **1**. The [σ^1s + σ^2s] cycloreversion to give erythro-(*Z*,*Z*)-diene **8**[16] was not detected. Moreover, the composition of the product which consisted of **1**, **7**, and **9a** was remarkably dependent on the electron acceptor employed, as summarized in Table V. A small amount of **6** detected in the product would most probably be derived via the secondary reaction of **1**, since extrapolation of the product composition to 0% conversion suggested that the formation of **6** as an initial product was negligible. In fact, in the TCNQ-sensitized reaction, where the isomerization of **2** to **1** was insignificant, the formation of **6** was not observed.

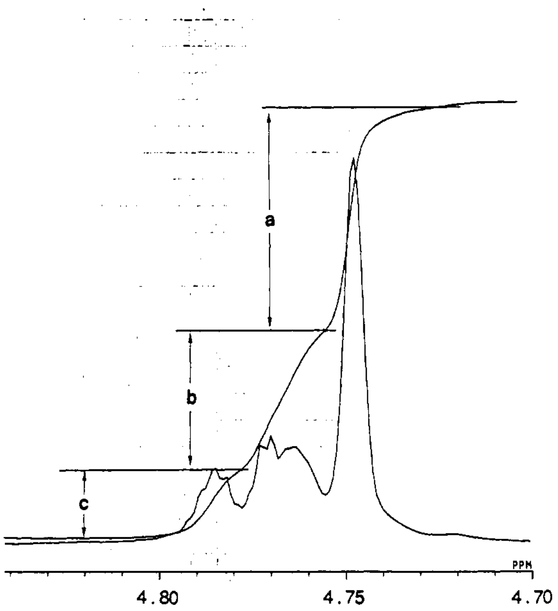
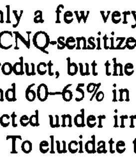


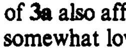
Figure 1. Typical, expanded 500-MHz ^{1}H NMR spectrum of **11b** in C_6D_6 in the vinylic region.

The isolated hexamethylcyclohexene was stereochemically homogeneous and exhibited only three methyl signals in its ^{1}H and ^{13}C NMR spectra, which were compatible with four stereoisomers (**9a–d**). Although its spectroscopic property did not permit rigorous stereochemical assignment, the all cis structure **9a** was tentatively assigned to the product, since the four methyl groups on the peripheral methine carbons are all cis with respect to the six-carbon framework in both **1** and **2** and **9a** seemed the most likely isomer to be produced irrespective of the mechanism of its formation, direct 1,3-H shift[4b] or consecutive 1,2-H shifts.[19] Under irradiation of phenanthrene in acetonitrile solution, both **1** and **2** were virtually inert, thus supporting the induction of their rearrangement by ET.[20]

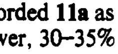
(b) 1,4-Dimethylbicyclo[2.2.0]hexane (3). Irradiation of DCB, DCA, or TCA in the presence of **3a** led to the cleavage of the latter to give **11a** almost exclusively in more than 70% yield in acetonitrile and in 80–90% yield in dichloromethane. Besides **11a**, only a few very minor volatile products were produced. The TCNQ-sensitized reaction of **3a** also afforded **11a** as a single major product, but the yield was somewhat lower, 30–35% in acetonitrile and 60–65% in dichloromethane. Compound **3** remained unaffected under irradiation of naphthalene in acetonitrile solution.



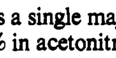
11
a, R^1 - R^4 = H
b, R^1 - R^4 = D_{4-n} / H_n
(n = 0 ~ 4)



12a



12b



12c

To elucidate the stereochemistry of cycloreversion of D-labeled **3b** requires observing the (*E*)- and (*Z*)-H of **11a**[17] as distinct signals in its ^{1}H NMR spectrum. The difference in the chemical

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(15) The electron accepting sensitizers employed in this study are *p*-dicyanobenzene (DCB), 9-cyanoanthracene (CA), 1,4-dicyanonaphthalene (DCN), 9,10-dicyanoanthracene (DCA), 1,2,4,5-tetracyanobenzene (TCB), 2,6,9,10-tetracyanoanthracene (TCA), and tetracyanoquinodimethane (TCNQ).

(16) Sinnema, A.; van Rantwijk, F.; de Koning, A. J.; van Wijk, A. M.; van Bekkum, H. *Tetrahedron* **1976**, *32*, 2269–2272.

(17) *E* denotes that the terminal substituent (CH_3 or D) and main alkyl chain residue are on opposite sides of the double bond, and *Z* denotes that they are on the same side.

(18) For example, the yield of product and its composition in the TCA-sensitized photolysis of **1** in acetonitrile changed with the progress of reaction as follows: 75% yield, **6**:**7**:**9a** = 86:3:12 at 18% conversion; 66%, 83:4:13 at 28% conversion; 59%, 82:5:13 at 35% conversion.

(19) Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1990**, *112*, 6647–6651.

(20) According to the Weller equation,[12] the ET from **1** or **2** to the lowest excited singlet phenanthrene is endothermic by 0.4–0.45 eV.

Table VI. Photoinduced ET Reactions of **3b**

entry	electron acceptor	solvent	concentration of **3b** (mM)	conversion (%)	**12a**:**12b** in **11b**[a]	endo-H:exo-H in recovered **3**[a,b]
1	DCB	MeCN	21	60	58:42	78:22
2		MeCN	228	10	69:31	
3		CH_2Cl_2	23	65	62:38	80:20
4	DCN	MeCN	226	10	74:26	
5	DCA	MeCN	21	15	86:14	
6		MeCN	22	80	74:26	83:17
7		MeCN	50	55	78:22	
8		MeCN	152	15	85:15	
9	TCA	MeCN	22	60	66:34	84:16
10		MeCN	234	10	72:28	
11		CH_2Cl_2	22	85	67:33	83:17
12	TCNQ	MeCN	189	15	83:17	
13		CH_2Cl_2	22	55	76:24	86:14

[a] Error involved in these ratios is ±2. [b] The ratio in the starting **3b** is (85 ± 2):(15 ± 2).

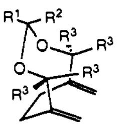
shifts of these protons is, however, extremely small in a variety of solvents, and the olefinic proton signal appears only as an overlapped singlet. Measurement in C_6D_6 provided the best resolution so far, and the olefinic protons were observed as two closely neighboring but well-resolved peaks at δ 4.764 and 4.784 in its 500-MHz ^1H NMR spectrum. Upon irradiation of allylic methylene protons at δ 2.08, a positive NOE was induced in the olefinic proton signal only in the higher field, which was accordingly assigned to the (*Z*)-H. In Figure 1 is shown a typical, expanded 500-MHz ^1H NMR spectrum due to the olefinic protons of partially deuterated **11b**, which was produced in the sensitized photolysis of **3b**. A broad singlet at δ 4.764 and a multiplet at δ 4.784 are due to the (*Z*)- and (*E*)-H of the nondeuterated olefinic methylene moiety (**12c**), respectively. Another multiplet at δ 4.770, which partially overlaps with the former signal, and a singlet at δ 4.746 are assigned to the geminally D-substituted (*E*)- and (*Z*)-H (**12b** and **12a**), respectively. It is well documented that deuterium substitution brings about an isotope-induced upfield shift of the resonance of the geminal proton of 0.01–0.02 ppm.[21] Accordingly, the statistic proportions of moieties **12a**, **12b**, and **12c** present in **11b** may be calculated using eq 1. Support for

$$\mathbf{12a}:\mathbf{12b}:\mathbf{12c} = \mathbf{a}:(\mathbf{b} - \mathbf{c}):\mathbf{c} \qquad (1)$$

the validity of this procedure to determine the geometrical distribution of deuterium in **11b** is provided by the observation that the signal intensity ratio of (**a** + **b** − **c**)/(**a** + **b**) = (**12a** + **12b**)/(**12a** + **12b** + **12c**) was virtually independent of the reaction conditions and was nearly equal to the extent of deuteration of **3b** (82%), whereas that of **a**/(**b** − **c**) = **12a**/**12b** varied depending on the electron acceptor and solvent used and also on the extent of conversion of **3b**. The results are summarized in Table VI.[22]

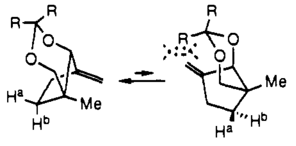
It is clearly noted that the ET-induced ring cleavage of **3** proceeded in a [σ^1s + σ^2s] manner but with only modest stereospecificity which deteriorated further with the progress of the reaction. The NMR spectrum of recovered **3b**, however, indicated that **3b** did not appreciably lose its stereochemical integrity, except for the DCB-sensitized reaction, even after the 55–85% consumption (Table VI).

(c) 1,4-Bridged Bicyclo[2.2.0]hexanes (4). The observed [σ^1s + σ^2s] stereospecificity of the ET-induced cleavage of **1** and **3** suggests that 1,4-bridging of the substrate will not impede the reaction. Sensitized photolysis of **4a** in acetonitrile, as expected, afforded **14a** as the major product (DCB, 75%; TCA, 70%; TCB, 80%), though the reaction was relatively slow. The DCB-sensitized photolysis of **4b** also produced **14b** in 42% yield. Compound **4c** reacted under irradiation of the electron acceptor in acetonitrile solution to give two products, one of which was isolated and assigned the structure of **15a** (DCB, 12%; TCA, 10%). The other product, however, was unstable and underwent complete decomposition during preparative GLC work. We reasoned that the lability of the latter product would be due to the acid-sensitive acetone acetal moiety and might be suppressed by replacing it with dichloroacetone acetal, which is far less sensitive to acid.[25] Accordingly, **4e** was prepared and subjected to sensitized photolysis under similar conditions, which led to the formation of **14e** and **15b** in 32% and 8% yield, respectively, with DCB as the electron-accepting sensitizer and in 17% and 14% yield, respectively, with TCA. Thus the unstable product produced in the reaction of **4c** would be **14c**, a strained nine-membered cyclic acetal.



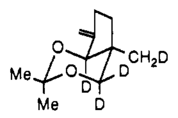
14

a, $R^1 = R^2 = R^3 = H$
b, $R^1 = Me$, $R^2 = R^3 = H$
c, $R^1 = R^2 = Me$, $R^3 = H$
d, $R^1 = R^2 = Me$, $R^3 = D$
e, $R^1 = R^2 = CH_2Cl$, $R^3 = H$



15 **a**, R = Me
b, R = CH_2Cl

16



17

The structural elucidation of **15a** and **15b** was primarily based on their ^1H NMR spectra, aided by decoupling and NOE experiments. The appearance of three methyl singlets at δ 0.78, 1.40,

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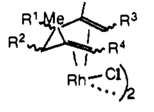
[21] (a) Allred, A. L.; Wilk, W. D. *J. Chem. Soc., Chem. Commun.* **1969**, 273. (b) Baird, M. C. *J. Magn. Reson.* **1974**, *14*, 117–120. (c) Khan, A. Y. *J. Math. Sci.* **1974**, *1*, 35–40; *Chem. Abstr.* **1975**, *82*, 56925r.

[22] ^2H NMR, resolution of which is greatly inferior to that of ^1H NMR, was not applicable to the examination of the (*E*)/(*Z*) distribution of deuterium in **11b**. Complexation of 1,5-hexadiene with rhodium salts is known to effect a large separation of (*E*)- and (*Z*)-proton signals in ^1H NMR.[23] In an attempt to directly determine the (*E*)-D/(*Z*)-D ratio in **11b** by ^2H NMR, stereoselectively (*E*)-deuterated **11b** which was obtained by the DCA-sensitized photolysis of **3b** was treated with rhodium(II) chloride to obtain **13**. The



13

$R^1 - R^4 = D_{4-n}/H_n$
($n = 0 \sim 4$)

intensities of well-separated (*E*)- and (*Z*)-H signals in its ^1H NMR spectrum, however, were nearly the same. Apparently, extensive geometrical isomerization of **11b** was under way during the formation of **13**. We also examined the use of lanthanide shift reagent. The addition of $Yb(fod)_3$ in combination with $Ag(fod)$[24] to the $CDCl_3$ solution of **11a** induced a remarkable downfield displacement of the olefinic proton signals, but they were not appreciably resolved and remained as a relatively broad singlet.

[23] Winkhaus, G.; Singer, H. *Chem. Ber.* **1966**, *99*, 3593–3601, 3602–3609.

[24] Wenzel, T. J.; Sievers, R. E. *Anal. Chem.* **1981**, *53*, 393–399.

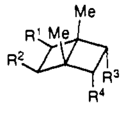
[25] (a) Bergstrom, R. G. In *The Chemistry of ethers, crown ethers, hydroxyl groups and their sulfur analogues*; Patai, S., Ed.; The Chemistry of Functional Groups, Supplement E; Wiley: New York, 1980; Chapter 20, pp 881–902 and references cited therein. (b) Prjanischnikow, N. D.; Leontowitsch, W. A. *Ber. Dtsch. Chem. Ges.* **1935**, *68*, 1866–1869.

and 1.46 and of only three protons geminal to either of the oxygens at δ 3.94 (s, 1 H) and 3.64 (AB q, $J = 12$ Hz, 2 H) in the spectrum of **15a** suggested its formation via hydrogen migration from the O-substituted methylene to one of the four-membered ring methylene carbons subsequent to the ring cleavage. Upon irradiation of the methyl protons at δ 0.78, the absorption intensities of the singlet signal at δ 3.94 and all four lines of the AB quartet centered at δ 3.64 were enhanced, indicating the cis fusion of the two rings and equatorial orientation of the methyl group with respect to the dioxane ring. The alternative conformer (**16**) would be disfavored owing to steric repulsion between the 1,3-diaxially oriented substituents.[26] The large difference in the chemical shifts of H^a and H^b ($\Delta\delta = 1.0$ ppm) also seems consistent with conformer **15**.[27]

In order to elucidate the mechanism of formation of **15** from **4**, the DCB-sensitized photolysis of deuterium-labeled **4d** was conducted in acetonitrile and the product corresponding to **15a** was isolated. In the ^1H NMR of the product, the signal of the bridgehead methyl protons appeared as a triplet, weakly split by coupling with the geminally substituted deuterium ($J = 1.8$ Hz) and having a relative intensity of about two protons. The O-substituted methylene and methine carbons retained the deuteriums, and transfer of the deuterium to positions other than the bridgehead methyl was not detected. The labeled rearranged product thus exhibited four peaks of nearly equal intensity at δ 0.79, 3.52, 3.73, and 3.94 in its ^2H NMR spectrum. These observations unambiguously demonstrate that the deuterium transfer occurred intramolecularly to give **17** without appreciable H–D exchange with the reaction medium.

DCB-sensitized photolysis of isolated **14e** in acetonitrile did not produce **15b** in a detectable yield, thus ruling out the formation of **15b** via the secondary reaction of **14e**.

(d) 1,5-Hexadiene Derivatives. The behavior of 1,5-hexadienes under photosensitization by the electron acceptors was briefly studied. Irradiation of DCB or DCN in the presence of **7** in dichloromethane led to the formation of **1**, **6**, and an isomer to which the structure of **18a** was tentatively assigned (DCB, 1:8:1, 48%; DCN, 3:4:3, 46%). As we will discuss later, the formation of **6** most probably results from the geometrical isomerization about the ionized π bond of the radical cation of **7**. Geometrical isomerization about the π bond should be reversible unless the equilibrium is strongly biased. Irradiation of a solution of **6** and TCA indeed led to the formation of **7** in 8–10% yield together with a few minor unidentified products.



18

a, R^1 - R^4 = Me

b, R^1 - R^4 = D_{4-n}/H_n ($n = 0 \sim 4$)

The main reaction of **11** under the photosensitized conditions was also geometrical isomerization about the π bond. Thus irradiation of DCB or TCA in the presence of stereoselectively (E)-deuterated **11b** ((Z)-H/(E)-H = 3–3.5) brought about a relatively rapid decrease in the (Z)-H/(E)-H ratio.[28] The cyclization of **11** to **3** was also detected, though the efficiency was much lower than that for the geometrical isomerization.

Discussion

All of the reactions investigated in this study are initiated by the electronic excitation of the electron acceptors, since the bicyclohexanes involved are transparent to the light filtered through Pyrex. ET from the bicyclohexanes to the excited sensitizers is energetically favorable, as estimated using the Weller equation[12] (Table II), and would most probably be involved in the subsequent efficient quenching of the latter by the former. In Figure 2 are shown log k_q vs ΔG_{ET} plots for the donor/acceptor pairs of **1**–**3** with the cyanoaromatics. The solid line is a Rehm–Weller plot drawn with the total reorganization energy $\lambda = 12$ kcal/mol and the broken one a Marcus plot with $\lambda = 22$ kcal/mol and $k_d(K_dZ)^{-1} = 0.04$.[29,30] Since the E_p^{ox}s of **1**–**3** might be kinetically shifted relative to the reversible potentials, the magnitude of the free energy change for the photoinduced ET process may differ to some extent from the values listed in Table II. The excellent fit of the plots to the curves, however, seems to provide good evidence that the bicyclohexanes are quenching the fluorescence of sensitizers via a single-electron-transfer (SET) process.

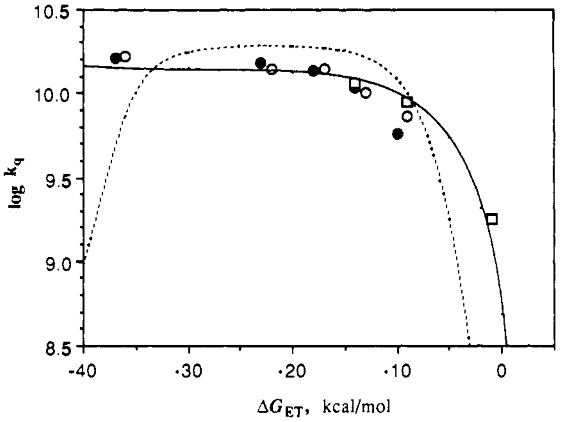
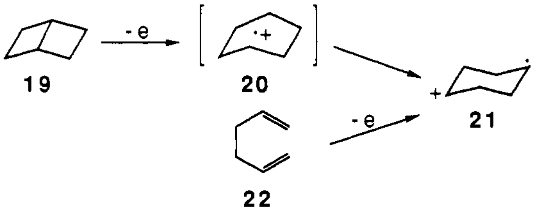


Figure 2. Plots of log k_q vs ΔG_{ET} from the data given in Table III: (○ 1; (●) 2; (□) 3. The solid line is a Rehm–Weller plot and the broken one a Marcus plot.

Scheme I



Both the experimental observations and theoretical calculations point to the initial formation of cyclohexane-1,4-diyl radical cations upon one-electron oxidation of bicyclo[2.2.0]hexanes. According to semiempirical AM1 MO calculations,[31] the HOMO of **3a** is mainly localized in the central bond and substitution of peripheral methylenes with methyl groups, i.e. to give **1** and **2**, does not affect the shape of the HOMO significantly. Moreover, the ring strain inherent in this ring system is largely relieved by the elongation of the central bond. In fact, it has recently been shown that the ionization of the parent bicyclohexane **19** leads to the formation of **21** (Scheme I).[5]

The stereospecific production of **6** from **1** demonstrates the generation of **23** in the boat form and its stereospecific cleavage in the [σ^1s + σ^2s] manner to give **24** which did not lose its stereochemical integrity before undergoing charge annihilation by back-ET (Scheme II). The formation of **7** as a minor product probably resulted from the secondary isomerization of **6**, since its relative amount in the product mixture increased with the advance of the sensitized photolysis and was found to be negligible

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(26) The ^1H NMR spectra of **15a** and **15b** were nearly superimposable, except for the absorptions due to the *gem*-dialkyl substituents, indicating a preference for the same conformer.

(27) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Oxford, England, 1969.

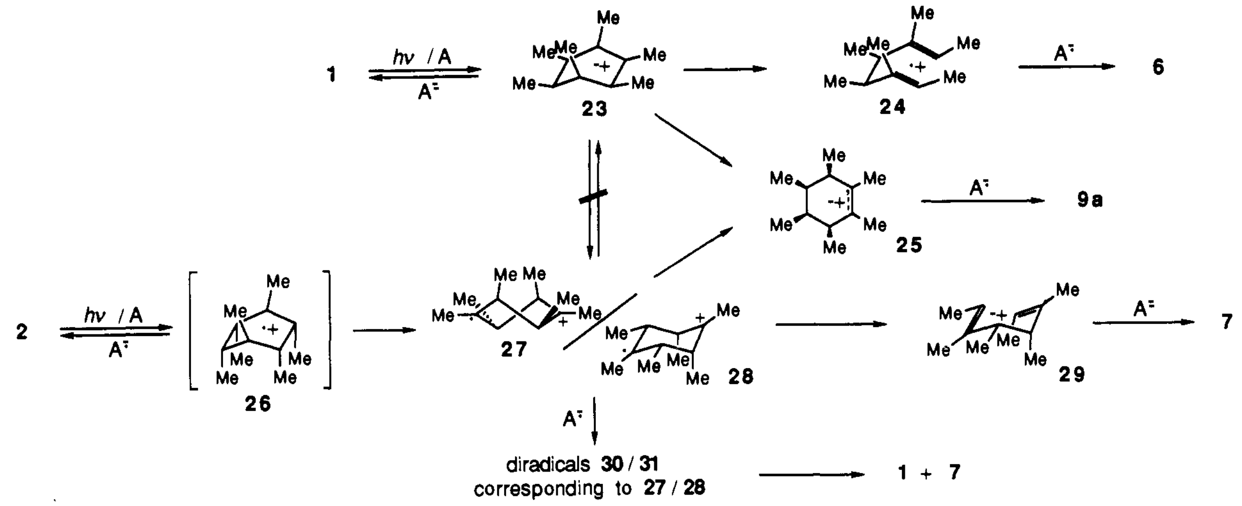
(28) For example, the ratio decreased from 3.5 to 2.1 upon irradiation of an **11b**/TCA mixture in acetonitrile for a period of 3 half-lives of **3** under comparable conditions.

(29) In both the plots the diffusion rate constant k_d is assumed to be 2×10^{10} M^{-1} s^{-1}. The diffusive equilibrium constant for formation of the donor/acceptor complex K_d and the frequency factor Z are assumed to be 0.86 and 6×10^{11} s^{-1}, respectively.[2]

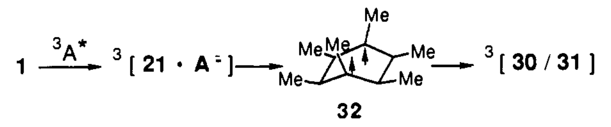
(30) It has recently been suggested that the magnitude of λ may be substantially higher than the values in the range of 10 kcal/mol usually assumed for photochemical ET processes since the proposal of Weller[12] and that, by assuming relatively high values of λ and Z, k_q may well be correlated with ΔG_{ET} by the Marcus equations. Legros, B.; Vandereecken, P.; Soumillion, J. Ph. *J. Phys. Chem.* **1991**, *95*, 4752–4761.

(31) MOPAC Version 5.00 (QCPE No. 445): Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10. Hirano, T. *JCPE Newsl.* **1989**, *1*, 36. Revised as Version 5.01 by J. Toyoda for Apple Macintosh.

Scheme II



Scheme III



when extrapolated to 0% conversion of **1**. In fact, **6** underwent geometrical isomerization to give **7**, though inefficiently, under the photolysis conditions. The stereospecific reaction pathway from **1** to **6** by way of **23** and **24** seems in good accord with recent theoretical calculations for [1 + 2] olefin cyclodimerization.[32]

When DCB or TCB was employed as the sensitizer for **1** in dichloromethane, a substantial amount of **7** was produced from the beginning of the reaction. As shown in Table II, the ET from **1** to TCB in the lowest triplet state is an exothermic process as well as that to the singlet excited TCB and might well take part in the reaction. The generation of a triplet radical ion pair in TCB-sensitized photo-ET is not unprecedented.[33] The boat triplet diradical (**32**) resulting from the ET from **1** to triplet TCB followed by rapid back-ET, being spin forbidden to collapse to the starting **1**, could not but undergo conformational relaxation to the skew boat form (**30**) and further to the chair form (**31**)[34] and, after intersystem crossing to the singlet state, would collapse to give **1** or cleave to produce **7** (Scheme III). Although ET from **1** to DCB in the lowest triplet state is slightly endothermic, it will not be unreasonable to assume that a small fraction of **1** reacted via the ET to ^{3}DCB* and afforded **7** as a primary product.[35] ET from **1** to the lowest triplet states of other sensitizers is substantially endothermic and hence would not take place to an appreciable extent.

Together with **6** and **7**, a small amount of **9a** was produced irrespective of electron acceptor and solvent used. This observation indicates that a fraction of **23** reacted through a reaction manifold, leading to **25** via hydride or hydrogen shift, in competition with the ring cleavage to give **24**. For the parent **21** in the chair form, it has been shown that the isomerization to cyclohexene radical cation is an exclusive unimolecular process.[4b,5]

The conspicuous features of the sensitized photolysis of **2** are the absence of stereospecific $[\sigma^1 s + \sigma^2 s]$ cleavage to afford **8**, the pronounced tendency to isomerize to **1**, and the remarkable dependency of product composition on the electron acceptors used. These characteristics may appear to suggest the direct transformation of **2** into a radical cation in skew boat (**27**) or chair form (**28**)[34] upon SET. Such a possibility, however, may be ruled out. As has been shown in a number of recent investigations, an ET quenching process involving a neutral donor and acceptor in a polar solvent such as acetonitrile leads to formation of either a contact radical ion pair or a solvent-separated ion pair.[36,37] That the measured quantum efficiencies for the consumption of **2** are substantially smaller than unity accordingly implies that the incipient radical cation retained a boat form and predominantly reverted to **2** via back-ET without loss of its stereochemical integrity. The back-ET to **27** or **28** should have resulted in the formation of **1** and **7** via recombination and ring cleavage, respectively, in preference to reversion to the sterically strained **2**. Interestingly, the E_p^{ox} of **1** is not much different from that of **2**. This suggests that the relief of strain in **2** upon SET to give the radical cation is not particularly large compared to that in **1**, in accord with the retention of the boat form in their incipient radical cations. The excellent fit of the k_q vs ΔG_{ET} plots for both **1** and **2** to the Rehm–Weller curve drawn with $\lambda = 12$ kcal/mol also suggests that the inner-sphere reorganization energies for the ionization of **1** and **2** are not particularly large and, hence, both compounds undergo relatively modest geometrical changes in going to their radical cations.[2]

The absence of stereospecific $[\sigma^1 s + \sigma^2 s]$ cleavage in the reaction of **2** in contrast to that of **1**, therefore, implies that the incipient radical cation in the boat form (**26**) would be conformationally labile and undergo rapid ring flip to give **27** and/or **28** prior to the ring cleavage, from which **1** and **7** were derived. The conformational instability of **26** in comparison with **23** is attributable to severe nonbonded repulsion among the four endo-methyl substituents. According to force field calculations (MM2),[38] the heat of formation of **2** is higher by 8 kcal/mol than that of **1** and a dihedral angle between the two rings in **2** is widened by ca. 10° compared to that in **1**. Semiempirical AM1 calculations[31] also

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(32) Pabon, R.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145–1146.

(33) Irie, M.; Tomimoto, S.; Hayashi, K. *J. Phys. Chem.* **1972**, *76*, 1419–1424.

(34) The skew boat intermediates **27** and **30** cannot be distinguished from the chair forms **28** and **31**, respectively, in the present reactions. The parent species **21** has been shown to possess a chair structure.

(35) Population of the triplet state of the cyanobenzenes requires an intersystem crossing process which might not be quite efficient. It should be noted, however, that the intersystem crossing of even a very small fraction of the excited singlet acceptor into the triplet state could result in substantially decreased stereospecificity, since the triplet radical ion pairs would provide **7** with high quantum efficiency, as discussed in the text, whereas the singlet pairs would mainly undergo charge annihilation via efficient back-ET only to revert to the starting materials, thus affording **6** with relatively low efficiency.

(36) (a) Knibbe, H.; Röllig, K.; Schäfer, F. P.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1184–1185. (b) Weller, A. *Z. Phys. Chem.* (*Wiesbaden*) **1982**, *133*, 93–98. Weller, A. *Pure. Appl. Chem.* **1982**, *54*, 1885–1888. (c) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255–1268. (d) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290–4301. (e) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068–2080.

(37) We were not able to detect any exciplex emission in acetonitrile for **2** and the electron acceptors used in this study. In polar solvents such as acetonitrile, exciplex emissions are rarely observed and the lack of emission is usually attributed to rapid dissociation of the initially formed contact ion pairs into solvent-separated ion pairs; it has also been suggested that the ET quenching results in the formation of the solvent-separated ion pair directly.[36]

(38) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134.

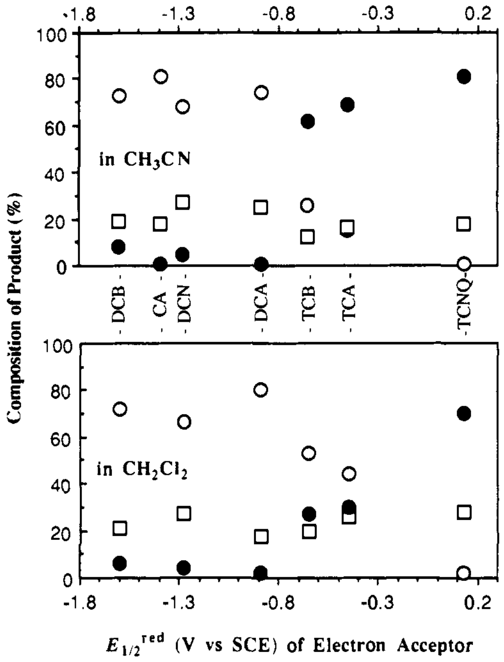


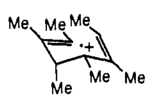
Figure 3. Correlation of product composition with E_{red} of electron acceptors in the reaction of 2: (○) (1 + 6); (□) 7; (●) 9a.

indicate the presence of similar differences in the geometry and the heat of formation between 1 and 2. The different stereospecificities of the ET-induced cleavage reactions of 1 and 2 unambiguously demonstrate that a concerted, single-step mechanism was not operative and that 23 and 27/28 did not interconvert to an appreciable extent within their lifetimes.

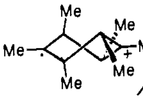
As listed in Table V, the results of the sensitized photolysis of 2 were markedly dependent on the electron acceptors used. These seemingly variant product compositions were found to be nicely correlated with the reduction potentials of electron acceptors $E_{1/2}^{\text{red}}(\text{A/A}^-)$, as illustrated in Figure 3. It is clearly noted that a dramatic change in the product composition occurred at $E_{1/2}^{\text{red}}(\text{A/A}^-) \sim -0.7$ V vs SCE in acetonitrile and at a slightly more positive $E_{1/2}^{\text{red}}(\text{A/A}^-)$ in dichloromethane. Thus the isomerization of 2 to 1 predominated the reactions in acetonitrile when sensitized with electron acceptors such as DCN and DCA whose $E_{1/2}^{\text{red}}$s are more negative than -0.8 V, whereas the formation of **9a** became the major process with TCA and TCNQ whose $E_{1/2}^{\text{red}}$s are more positive than -0.5 V. The ring cleavage of 2 to give 7, on the other hand, was relatively independent of the $E_{1/2}^{\text{red}}$ of the electron acceptor and invariably comprised 15–20% of the reactions.

The observed correlation between the product composition and $E_{1/2}^{\text{red}}(\text{A/A}^-)$ suggests the involvement of a back-ET process in the product-determining stage. The rate of back-ET is primarily determined by the thermicity of the process, $\Delta G_{\text{BET}} = E_{1/2}^{\text{red}}(\text{A/A}^-) - E_{1/2}^{\text{ox}}(\text{D/D}^+)$. The redox potentials for **27**/**30** and **28**/**31** couples are not available, but a $E_{1/2}^{\text{ox}}$ of 0.09 V vs SCE has recently been reported for *t*-Bu radical.[39] If the $E_{1/2}^{\text{ox}}$ value for **30** (or **31**) is assumed not to be greatly different from that value, ΔG_{BET} for **27** (or **28**) and the electron acceptors used in this study should be in the range -1.4 to 0.1 eV. In this range of ΔG_{BET}, the back-ET process is reasonably expected to be in the Marcus "normal" region; hence the higher the exothermicity of back-ET is the faster the process will tend to be.[1,2] Accordingly, when the $E_{1/2}^{\text{red}}$ of the acceptor used was <-0.8 V vs SCE, the dominant reaction pathway for **27**/**28** would be charge neutralization by back-ET to give **30**/**31**, which, in turn, afforded a mixture of **1** and **7**. The formation of **1** and **7** upon thermolysis of **2**, which is presumed to proceed via **30**/**31**, has already been disclosed by Van Rantwijk and his co-workers.[16] The back-ET to **27**/**28** would become slower as it becomes less exothermic and would eventually be overshadowed by the competing transformation into **25** and **29**. The propensity of **21** for isomerizing to cyclohexene radical cation has been documented.[4b,5] The invariably observed production of **7** thus demonstrates that it was derived through the two channels via the ring cleavage of **27**/**28** followed by the charge neutralization and via the back-ET to **27**/**28** followed by bond fission in the resultant **30**/**31**.[40]

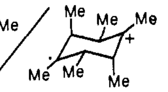
As described in the previous section, the photoinduced ET reaction of **7** led to the formation of **1**, **6**, and **18a**. This suggests that **7** underwent cyclization via **29** and **33** to give **27**/**28** and



33



34



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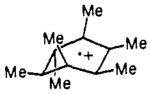

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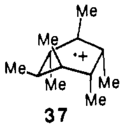

37

34/**35**, from which **1** and **18a** were derived, respectively, via back-ET–recombination. It should be noted that these products could not be derived via the cyclization of **7** to the boat intermediates **36** and/or **37**. Thus it appears that, in the ET-induced cyclization of **7**, the production of chair or skew boat cyclohexane-1,4-diyl radical cations is kinetically favored to that of the boat forms.

The photoinduced ET reaction of **3** afforded **11** as a single major product. The predominant formation of (*E*)-deuterated **11b** from exo-deuterated **3b** is in accord with the generation of the radical cation intermediate in the boat form (**38**) and its stereospecific cleavage in the [σ^1s + σ^2s] manner. The stereospecificity, however, was dependent on the electron acceptors used and also on the extent of conversion of **3b** and, above all, was not very high. The observed deterioration of apparent stereospecificity at the high conversion of **3b** is attributable to the secondary geometrical isomerization in the primarily produced **11b** under the photolysis conditions. The proportion of (*E*)-D in **11b**, however, was only 69–86% even at a low conversion of 15% or lower. If the incomplete stereospecificity of cycloreversion of **3b** had arisen from the partial leakage of **38** into **39** in the chair form prior to the cleavage,[41] the stereochemical distribution of deuterium in the recovered **3b** should have been disturbed, because **39** would undergo efficient reduction by back-ET in competition with the ring cleavage and a part of the resultant diradical, at the least, would collapse to give a mixture of **3b** and **40**. Thermolysis of **3b**, in fact, led to extensive distribution of the deuterium to the endo position in the recovered starting material along with the production of **11b** in which the (*E*)- and (*Z*)-positions were substituted with the deuterium to nearly the same extent, in support of the intermediacy of the chair diradical and its partial reversion to **3b** and **40**.[42] The endo-H/exo-H ratio in the **3b** recovered from the photosensitized reaction, however, remained unchanged within an experimental error, except for the DCB-sensitized reaction, even after 55–85% conversion (Table VI). We suspect that the incomplete stereospecificity would result from the stereochemical instability of **41** rather than the conformational lability of **38**.

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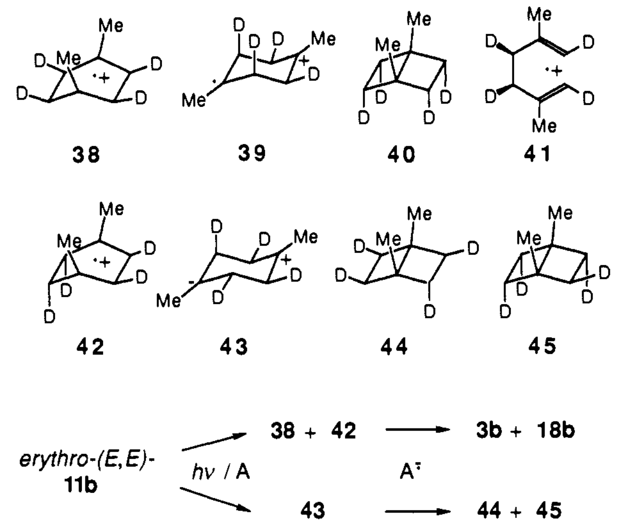
[39] Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132–137.

[40] The alteration in the product composition of **2** in dichloromethane at a more positive $E_{1/2}^{\text{red}}(\text{A/A}^-)$ compared with that for the reaction in acetonitrile seems in accord with the above scheme. Charge annihilation within radical ion pairs by back-ET tends to be more exothermic in dichloromethane than in acetonitrile, since, in less polar dichloromethane, $E_{1/2}^{\text{ox}}(\text{D/D}^+)$ tends to be more positive and $E_{1/2}^{\text{red}}(\text{A/A}^-)$ more negative.

[41] The chair intermediate **39** cannot be distinguished from the corresponding skew boat form in this study, as is the case in the reactions of hexamethyl derivatives **1** and **2**. The skew boat form was omitted from the scheme for clarity.

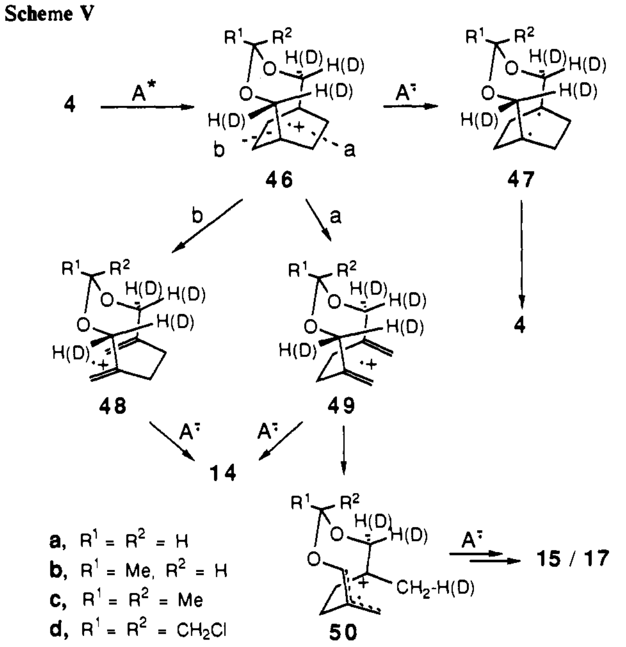
[42] Thus the *endo*-H/*exo*-H ratio dropped from 85:15 in the starting **3b** to 62:38 in the recovered **3** after 75% conversion. The ratio of **12a**:**12b** in the produced **11b** was 52:48.

Scheme IV



Experimental observations[43] as well as theoretical calculations[44] indicate that increasing alkyl substitution on olefinic carbons of an alkene radical cation results in less twist around the double bond and an increased rotational barrier through 90°. According to semiempirical calculations by Clark and Nelsen,[44] the barrier to rotation around the π bond in 2-methylpropene radical cation is 5.8 kcal/mol. By taking this value as the barrier to rotation through 90° for **41** and assuming 10^{13} as the preexponential factor,[45] the rate of (*E*)/(*Z*) isomerization is calculated to be $3.5 \times 10^8\ s^{-1}$ at 12 °C (temperature at which **3b** was photolyzed). The theoretical barrier refers to the radical cation in vacuum, and the actual rate in acetonitrile, therefore, may be considerably different. With this degree of rate for the rotation about the π bond, however, it is reasonable to assume that **41** partly underwent the (*E*)/(*Z*) isomerization prior to charge neutralization via back-ET. In a trisubstituted alkene radical cation, e.g. 2-methyl-2-butene radical cation, the predicted barrier to rotation amounts to 10.6 kcal/mol and the rate of rotation about the π bond at 12 °C is estimated to be $7 \times 10^4\ s^{-1}$, which is considerably slower than rates of various reaction processes expected for simple alkene radical cations. It is thus concluded that the stereospecific production of **6** from **1** is materialized by the stereospecific cleavage of **23** in the $[\sigma^1s + \sigma^2s]$ manner complemented by the high configurational stability of resultant **24**.[46]

Scheme V



The DCB-sensitized photolysis of **3b** resulted not only in the substantially lower stereospecificity of ring cleavage but also in the appreciable distribution of the deuterium to the endo position in the recovered **3**, as can be seen from the decreased endo-H/exo-H ratio. The endo/exo scrambling of deuterium in the recovered **3** may be rationalized in terms of reversibility of the ring cleavage of 1,4-dimethylcyclohexane-1,4-diyl radical cation. The most highly exothermic back-ET from DCB radical anion to **41** may be situated deep in the Marcus "inverted" region and hence relatively slow, and a small portion of **41** might undergo recyclization to give cyclohexane-1,4-diyl radical cation in boat and/or chair form, which can eventually revert to **3** via back-ET. Such recyclization of selectively (E)-labeled **41** is expected to produce a mixture of labeled **3** in which the deuteriums are extensively distributed to the endo positions statistically, irrespective of the form (boat or chair) of the intermediate (Scheme IV). In fact, the DCB-sensitized photolysis of selectively (E)-labeled **11b** led to the formation of D-labeled **3** along with the much faster (Z)-D/(E)-D equilibration. Thus the DCB-sensitized reaction of **3b** resulted in the least stereospecific ring cleavage and the most extensive stereorandomization of deuterium substituents in the recovered **3**. When the electron acceptors other than DCB were used as the sensitizer, the back-ET to **41** was relatively fast and hence both the geometrical isomerization and the recyclization of **41** were less extensive.[48]

There seems to be no doubt that the formation of **15** in the photoinduced ET reaction of **4** resulted from the proton or hydrogen migration subsequent to the ring cleavage. This implies that the cleavage of **4** was induced in the fully single-electron-transferred radical cation rather than in an exciplex which bears significant locally-excited-state character, since the ring cleavage in the latter would directly lead to **14** in its ground state. The occurrence of hydrogen transfer subsequent to back-ET to give diradicaloid **47** is also readily ruled out.[49] For a multistep process

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(43) (a) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963–5970. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *Chem. Phys. Lett.* **1984**, *107*, 86. (c) Shiotani, M.; Nagata, Y.; Sohma, J. *J. Phys. Chem.* **1984**, *88*, 4078–4082. (d) Eierdanz, H.; Potthoff, S.; Bolze, R.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 526–527. (e) Fujisawa, J.; Sato, S.; Shimokoshi, K.; Shida, T. *J. Phys. Chem.* **1985**, *89*, 5481–5486. (f) Abelt, C. J.; Roth, H. D. *J. Am. Chem. Soc.* **1985**, *107*, 6814–6818. (g) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 1265–1270.

(44) Clark, T.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 868–870.

(45) Assumed to be the same in magnitude as that for the thermal geometrical isomerization of simple alkenes. See: Willcott, M. R.; Cargill, R. L.; Sears, A. B. *Prog. Phys. Org. Chem.* **1972**, *9*, 25–98.

(46) If the rate of (*E*)/(*Z*) isomerization in **41** is assumed independent of the electron acceptors used, the extent of loss of stereochemical integrity in the produced **11b** should be in inverse proportion to the rate of back-ET to **41** which, in turn, primarily depends upon exothermicity of the process in a manner consistent with the Marcus relationship. The back-ET process is exothermic by 2.3–4.0 eV for the five electron acceptors and **3** investigated in this study, with the order of increasing exothermicity being TCNQ < TCA < DCA < DCN < DCB, whereas the stereospecificity of ring cleavage of **3b** increases in the order of DCB < TCA < DCN < TCNQ < DCA. No simple correlation between the return-ET exothermicity and the reaction stereospecificity is recognized from the experimental observations. The kinetics of return-ET, however, is suggested to be very sensitive to small structural changes.[36d,47] It should be noted that the electron acceptors used in this study greatly differ in molecular dimension and property, from the 'one-ring' cyanoaromatic to the 'three-ring' anthracene derivatives and nonaromatic TCNQ. The lack of an apparent relationship between the reaction stereospecificity and the values of ΔG_{BET}, therefore, is not necessarily in conflict with the above argument.

(47) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 1991–1993.

(48) In the above discussion we surmised that the charge neutralization of **41** proceeded via the back-ET from the sensitizer radical anions, despite the feasibility of ET from **3** which is exothermic by ca. 8 kcal/mol and hence at least energetically favorable. If the reduction of **41** to **11** occurred primarily after the diffusive separation of geminate radical ion pairs and the latter process participated to an appreciable extent, the stereospecificity of ring cleavage of **3** should be dependent on its concentration. The dilution of concentration of **3b** by a factor of 7.5, however, did not lead to an appreciable decrease in the stereospecificity (Table VI, entries 5 and 8), suggesting the occurrence of back-ET largely within the geminate radical ion pairs.

(49) The cleavage of singlet **47** should directly provide **14** in its ground state. It is highly unlikely that **15** was produced via hydrogen migration in triplet **14** resulting from back-ET within triplet radical ion pairs. The lowest triplet states of simple alkenes lie 4.1–4.3 eV above the ground state,[50] and the cleavage of triplet **47** into triplet **14** is estimated to be highly endothermic.

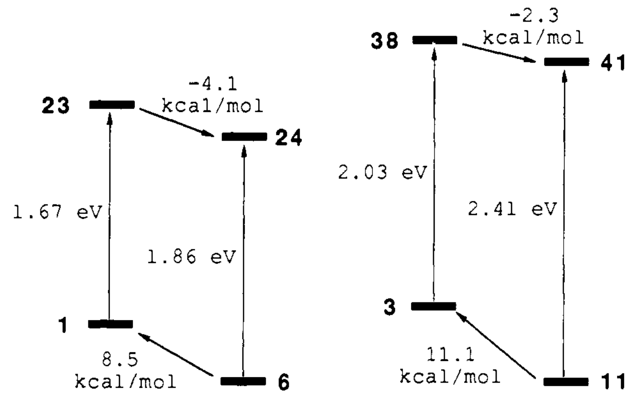


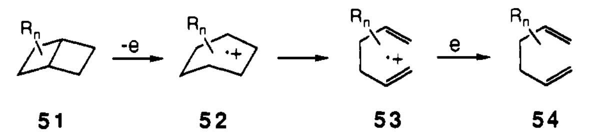
Figure 4. Thermochemical cycles to estimate the ring fission energies of **23** and **38**.

involving radical ion pairs, it is often difficult to specify on which stage charge annihilation via back-ET occurs. The formation of **15**, however, demonstrates that the ET-induced ring fission of **1**, **3**, and **4** in the supra,supra fashion is indeed a radical cation process, occurring in boat cyclohexane-1,4-diyl radical cations prior to back-ET.[51] It should be noted that the acetals **4** are the substrates least susceptible to one-electron oxidation among the bicyclohexanes studied in this investigation.

Force field calculations and also examination of molecular models indicate puckering of the seven-membered ring of **4**, as depicted in Scheme V and suggest the persistence of a similar conformation in the central-bond-elongated radical cation intermediate **46**. The stereospecific [$\sigma^1s + \sigma^2s$] cleavage involving bond a in **46** leads to **49**, in which one of each pair of allylic methylene protons is oriented inward and thus disposed quite favorably toward transfer to the terminal methylene carbon of the opposite π bond to afford **50**. It is well documented that alkene radical cations are extremely strong Brønsted acids[52] and an intramolecular protonation reaction in **49** might well provide **50**. Alternatively, the rearrangement could be mechanistically a radical reaction and abstraction of the allylic hydrogen by the opposite olefinic methylene carbon might product **50**, since spin in the 1,1-disubstituted alkene radical cation is largely localized on the unsubstituted carbon.[43,44] Subsequent back-ET from the counter radical anion to **50** followed by recombination provides **15**/**17**. The deuterium distribution in **17** is nicely accommodated by this mechanism.

The rearranged products **15**/**17** were obtained from **4c**–**e** but not produced in a detectable amount in either of the reactions of the less substituted acetals (**4a** and **4b**). We surmise that the intermediates **49a** and **49b** derived from these acetals are conformationally more flexible than **49c** and **49d** and undergo rapid relaxation to the more stable conformer(s) in which the allylic protons are no longer favorably disposed toward the intramolecular transfer to give **50**. The cleavage of bond b in **46** should provide **48**, in which the allylic C–H bonds are relatively remote from the opposite olefinic methylene carbon and, moreover, unfavorably oriented toward the proton or hydrogen transfer to that carbon, and thus appears less likely to lead to the formation of **15**. The regioselectivity of bond cleavage in **46** might somehow be affected by the substituents on the acetal ring, and the lower substitution of the acetal ring of **4** might result in the preferential cleavage of bond b, leading to the diminished yield of **15** in the reactions of **4a** and **4b**, though such a possibility seems relatively remote.

Scheme VI



It has been reported that parent 1,5-hexadiene (**22**) rapidly cyclizes upon ionization to give cyclohexane-1,4-diyl radical cation in the chair form (**21**),[4b,5] in accord with theoretically predicted high exothermicity of the process.[4a] The presently observed ET-induced cleavage of the substituted bicyclohexanes suggests that alkyl substitution, on C-1 and C-4 of **19** in particular, significantly affects the relative thermodynamic stabilities of bicyclo[2.2.0]hexane (cyclohexane-1,4-diyl) radical cation and its ring-cleaved 1,5-hexadiene counterpart. In Figure 4 are shown thermochemical cycles which were constructed on the basis of available thermochemical data and force field calculations to estimate thermicity for the interconversions between **23** and **24** and between **38** and **41**. The heats of formation (ΔH_f^0) of **1** and **3a** are greater than those of **6** and **11a** by 8.5 and 11.2 kcal/mol, respectively, according to the MM2 calculations.[53] The free energy change for the ring cleavage (ΔG_{RC}) of **52** to give **53** is given by eq 2, where F is the Faraday constant and E^0 is the

$$-\Delta G_{RC} = [\Delta H_f^0(\mathbf{51}) - \Delta H_f^0(\mathbf{54})] + F[E^0(\mathbf{51}/\mathbf{52}) - E^0(\mathbf{54}/\mathbf{53})] \quad (2)$$

standard redox potential for the given couple (Scheme VI). In order to calculate the ΔG_{RC} associated with the process, the values of E^0 were estimated from the E_p^{ox} values. Thus the cleavage reactions of both **23** and **38** would be slightly exothermic, in agreement with the experimentally observed high efficiency, though the calculated ΔG_{RC} values are subject to inaccuracy arising from the estimation of ΔH_f^0 and E^0 values.

The relatively inefficient production of **3** in the photoinduced ET reaction of **11** is in accord with the calculated modest endothermicity for the transformation of **41** into **38**. The sensitized photolysis of **6** also led to the formation of a mixture of bicyclohexanes in low yield. Taking the ready cyclization of **22** upon ionization into consideration, it seems that the methyl substituents on C-2 and C-5 of **11** stabilize the corresponding radical cation **41** more effectively than those on the bridgehead carbons of **3** stabilize **38**, thus reversing the relative thermodynamic stabilities of the diene radical cation and its cyclized form. Stabilization of a one-electron σ bond by a methyl substituent may be less effective than that of a one-electron π bond by the same group.

Conclusion

The generation of cyclohexane-1,4-diyl radical cations in the boat form (**52**) as discrete intermediates was confirmed for the first time. The boat structure, which is probably retained in its form by virtue of a one-electron 1,4-σ bond,[54] appears conformationally stable. When suffering from particular steric strain, however, it may undergo conformational flip to the skew boat and/or chair form. The energetics of the cleavage of **52** to give the corresponding 1,5-hexadiene radical cations **53** are markedly affected by alkyl substituents, and 1,4-dialkyl-substituted intermediates undergo the ring cleavage efficiently, in contrast to the behavior of the parent radical cation: the cleavage of the 1,4-dialkyl derivatives is estimated to be slightly exothermic, in contrast to the high endothermicity theoretically predicted for the parent

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(50) Kropp, P. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Chapter 1, pp 1–142.

(51) Miyashi and his co-workers have recently proposed the intermediacy of boat 1,4-cyclohexane-1,4-diyl radical cation (A) in photo-ET-induced equilibration between 2,5-diaryl-1,5-hexadiene (B) and 1,4-diarylbicyclo[2.2.0]hexane (C) to give a photostationary mixture involving C as a major component.[4f] The production of C has been postulated to be preceded by the generation of the corresponding bicyclohexane radical cation which would be in equilibrium with A. The interconversion between B and C, however, has been interpreted by considering rearrangement only on the radical cation surface, neglecting the diradical channel, i.e. by way of chair cyclohexane-1,4-diyl diradical, as a probable process for the formation of B and C. Their argument for the boat intermediate, therefore, seem inadequate.

(52) (a) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 50–187. (b) Bordwell, F. G.; Chen, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867–2872, 2872–2877. (c) Bordwell, F. G.; Chen, J.-P.; *J. Am. Chem. Soc.* **1989**, *111*, 1792–1795.

(53) The MM2 calculations indicate that ΔH_f^0s of **6**–**8** will not differ by more than 1 kcal/mol.

(54) For the bridged structures of cycloalkane-1,3-diyl radical cations, see: (a) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456–6457. (b) Williams, F.; Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835–1837.

system. The cleavage reaction proceeds in the stereospecific [σ^1s + σ^2s] manner. The overall stereospecificity of ET-induced ring cleavage, however, may be spoiled to some extent, owing to the instability of intermediate alkene radical cations toward geometrical isomerization when the double bond bears only one or two alkyl substituents.

Experimental Section

General Information. ^{1}H and ^{13}C NMR were recorded on Hitachi R-1900 and JEOL FX-100 and FX-500 spectrometers in $CDCl_3$ unless otherwise indicated. Chemical shifts are reported in parts per million relative to $(CH_3)_4Si$ as the internal standard. IR spectra were taken on Hitachi Model 215 and 270-30 grating spectrometers. Mass spectra were recorded on JEOL JMS-HX 110 and JMS-DX 303 spectrometers with an ionization voltage of 70 eV unless otherwise indicated. Fluorescence spectra were measured on a JASCO FP-770 spectrofluorometer. Analytical GLC was performed on a Hitachi 163 or Shimazu GC-14A gas chromatograph equipped with a flame ionization detector. Preparative GLC was performed on a Hitachi 063 gas chromatograph. The following columns were used: A, OV-1 bonded, small bore, 50 m; B, OV-1701 bonded, small bore, 50 m; C, poly(ethylene glycol) 20M 5%, 1 m; D, Apiezone Grease L (APL) 15%, 2 m; E, APL 20%, 4 m; F, APL 15% on Celite 545 treated with KOH (3%), 2 m; and G, silicone XE-60 15%, 1.5 m. Elemental analyses were performed by the Center for Instrumental analysis of Hokkaido University.

exo- and *endo*-1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexanes,[7] 1,4-bis(hydroxymethyl)bicyclo[2.2.0]hexane,[11] 1,4-dimethylbicyclo[2.2.0]hexa-1,5-diene,[8] TCB,[55] and TCA[56] were prepared following the known procedures. TCNQ was a gift from Osaka Organic Chemicals Co. and was purified by recrystallization from acetonitrile. DCB, DCN, CA, and DCA were purchased from commercial sources and recrystallized prior to use. The solvents used in the photoreactions were spectrograde; they were dried with 4-Å molecular sieves and distilled prior to use.

Electrochemical Measurements. Oxidation potentials were determined by cyclic voltammetry with use of a three-electrode cell equipped with a platinum disk as working electrode, a platinum plate as counter electrode, and a silver/silver nitrate 0.1 M solution as reference electrode. Tetraethylammonium perchlorate was used as electrolyte. Solutions were typically prepared by dissolving substrates (1–3 mM) in 0.1 M acetonitrile solutions of electrolyte which were purged with argon for 5 min prior to measurement. The peak potentials were measured with a 200 mV/s sweep rate. No cathodic wave was detected following the anodic sweep.

Quantum Yield Determinations. Quantum yield measurements were carried out on an optical bench, and light intensities were determined with benzophenone/benzhydrol actinometry.[57] A Halos 500-W high-pressure mercury lamp (Eiko-sha, Japan) fitted with Corning glass filters 7-54 and 7-60 was employed as the 365-nm light source. A combination of a Corning glass filter 7-54 and a 1.4×10^{-3} M K_2CrO_4 solution in 1% aqueous K_2CO_3 (1 cm) was used to isolate 313-nm light. Fluorescence quenching experiments were done with a 2×10^{-5} to 5×10^{-4} M acetonitrile solution of a light-absorbing electron acceptor. Concentrations of donor were in the range 1×10^{-3} to 2×10^{-2} M. Argon was bubbled through the samples for 5 min before measurements were taken.

Irradiation Procedure. The photosensitized reactions were carried out in acetonitrile or dichloromethane solution. The solutions were placed in Pyrex tubes sealed with a rubber septum and purged with dry nitrogen or argon gas for 5 min prior to irradiation. A Halos 500-W high-pressure mercury lamp was used as the irradiation source. The lamp was equipped with a quartz cooling jacket with nests for irradiation tubes. The temperature of the samples was controlled at about 12 °C by water circulation. Photochemical reaction progress was monitored by capillary gas chromatography.

Preparation of 1,4-Dimethylbicyclo[2.2.0]hexane (3a) and Its Deuterated Derivative (3b). To a magnetically stirred solution of *t*-BuOK (8.57 g, 76 mmol) in dry DMSO (150 mL) was added 1,1′-dimethyl-2,2′-dibromobicyclopropyl (4.24 g, 15.8 mmol) in pentane (150 mL) under N_2 at room temperature. After being stirred for 3.5 h, the reaction mixture was poured onto ice water and the aqueous layer was separated off and extracted with pentane (3 × 100 mL). The pentane layer and the extracts were combined, washed successively with water (2 × 100 mL) and brine (100 mL), and dried with $MgSO_4$. A small amount of hydroquinone was added to the pentane solution, from which the pentane was distilled off. Volatile components in the residue was condensed in vacuo (15 mmHg) in a flask cooled in liquid N_2 to separate 1,1′-dimethylbicyclopropenyl from higher boiling impurities. The condensate was dissolved in dry CH_3CN (40 mL) and added to a solution of $AgClO_4$ (104 mg, 0.5 mmol) in CH_3CN (20 mL) under N_2 at 0 °C to allow the product to be rearranged to dimethyl Dewar benzenes.[8] After the reaction mixture was stirred for 3 h at 0 °C, dipotassium azodicarboxylate (5.81 g, 30 mmol) and CH_3OD (40 mL) were added and CH_3CO_2D (6 mL, 104 mmol) in CH_3CN (40 mL) was injected over 3 h using a motor-driven syringe.[9] After an additional 3 h, the mixture was treated with water (150 mL) and extracted with pentane (3 × 100 mL). The extracts were combined, washed with aqueous $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated. The residual oil was subjected to preparative GLC (column E, 60 °C) to afford 324 mg of **3b** (2.84 mmol, 18%) and 279 mg of deuterated 1,2-dimethylbicyclo[2.2.0]hexane (2.45 mmol, 15%). **3b**: ^{1}H NMR (500 MHz) δ 0.97 (s, 6 H), 1.81–1.88 (m, 0.6 H), 1.96–2.05 (m, 4 H); IR (neat) 2936, 2858, 2184, 1450, 1376 cm^{-1}; MS (23 eV) *m/z* 114 (4.3), 113 (2.7), 112 (0.8), 111 (0.3), 99 (100), 98 (42), 84 (22), 71 (46), 70 (54), 69 (39), 57 (55).

Reduction of the Dewar benzene mixture with dipotassium azodicarboxylate/CH_3CO_2H in CH_3CN/CH_3OH provided a mixture of **3a** and 1,2-dimethylbicyclo[2.2.0]hexane, from which **3a** was isolated by preparative GLC: ^{1}H NMR (100 MHz) δ 0.98 (s, 6 H), 1.70–2.20 (AA′BB′ m, 8 H); IR (neat) 2940, 2852, 1450, 1436, 1376, 1290 cm^{-1};[58] MS (25 eV) *m/z* 110 (3.3), 96 (10), 95 (100), 81 (22), 68 (44), 67 (28), 55 (39). Upon irradiation of the methyl protons at δ 0.98, the half of the multiplet signal on the upper field side was enhanced and accordingly assigned to the exo protons. In the 500-MHz ^{1}H NMR, the methylene proton signal was resolved into two well-separated multiplets at δ 1.75–1.90 and 1.95–2.10, which were thus assigned to the exo and endo protons, respectively.

Preparation of the Methylene Acetal 4a. A solution of 1,4-bis(hydroxymethyl)bicyclo[2.2.0]hexane (1.35 g, 9.51 mmol), dimethoxymethane (1.51 g, 19.8 mmol), and *p*-TsOH·H_2O (0.10 g, 0.53 mmol) in benzene (50 mL) was heated to boiling, and the condensate was returned to the mixture through a column packed with 5-Å molecular sieves to remove methanol formed. After the diol was consumed, the solution was washed successively with water, aqueous $NaHCO_3$, and water and dried with $MgSO_4$. After removal of the solvent, the residue was distilled to give **4a** (0.45 g, 30%) as a colorless oil which soon solidified: bp 70–72 °C (15 mmHg); mp 51–52 °C; ^{1}H NMR (100 MHz) δ 1.85–2.35 (AA′BB′ m, 8 H), 3.64 (s, 4 H), 4.85 (s, 2 H); IR (neat) 2928, 2844, 1264, 1168, 1132, 1090, 1034, 956, 912 cm^{-1}; MS *m/z* 124 (19), 109 (85), 95 (43), 93 (64), 91 (60), 81 (58), 80 (60), 79 (77), 67 (72), 55 (72), 39 (100). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.25; H, 8.98.

Preparation of the Monomethyl Acetal 4b. A solution of 1,4-bis(hydroxymethyl)bicyclo[2.2.0]hexane (530 mg, 3.7 mmol), 1,1-diethoxyethane (910 mg, 7.7 mmol), and *p*-TsOH·H_2O (54 mg, 0.28 mmol) in benzene (50 mL) was refluxed, and the EtOH formed was distilled out as the benzene azeotrope through a column (30 cm) packed with glass helices. After the diol was consumed, the residual solution was washed successively with water, aqueous $NaHCO_3$, and water and dried with $MgSO_4$. After removal of the solvent, the residual oil was subjected to preparative GLC (column F, 120 °C) to give **4b** (420 mg, 67%): ^{1}H NMR (100 MHz) δ 1.41 (d, $J = 5.1$ Hz, 3 H), 1.8–2.3 (m, 6 H), 2.7–3.2 (m, 2 H), 3.62 (AB q, $J = 12.7$ Hz, 4 H), 4.56 (q, $J = 5.1$ Hz, 1 H); IR (neat) 2932, 2844, 1394, 1130, 1100, 1038, 878 cm^{-1}; MS *m/z* 153 (11), 124 (32), 109 (75), 95 (46), 91 (51), 81 (60), 80 (54), 79 (78), 67 (81), 59 (60), 55 (63), 43 (100). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.40; H, 9.62.

Preparation of the Dimethyl Acetal 4c and Its Deuterated Derivative 4d. A solution of 1,4-bis(hydroxymethyl)bicyclo[2.2.0]hexane (2.70 g, 19 mmol), 2,2-dimethoxypropane (3.12 g, 30 mmol), and *p*-TsOH·H_2O (20 mg, 0.11 mmol) in benzene (80 mL) was heated, and the methanol formed was distilled out as the benzene azeotrope through a column (30 cm) packed with glass helices. After the diol was consumed, the residual solution was washed with aqueous $NaHCO_3$ and dried with Na_2SO_4. After removal of the solvent, the residual oil was distilled to give **4c** (3.0 g, 87%) as a colorless oil: bp 80.5–82 °C (14 mmHg); ^{1}H NMR (90 MHz) δ 1.41 (s, 6 H), 1.8–2.3 (AA′BB′ m, 8 H), 3.56 (s, 4 H); IR (neat) 2992, 2928, 2860, 1382, 1214, 1072, 1030 cm^{-1}; MS *m/z* 167 (12), 124 (45), 109 (64), 107 (46), 95 (46), 91 (48), 81 (54), 79 (90), 67 (73), 43 (100). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.40; H, 10.06.

The deuterated derivative **4d** was prepared by treating 1,4-bis(methoxycarbonyl)bicyclo[2.2.0]hexane[11a] with $LiAlD_4$ and acetalizing the resultant diol as described above: ^{1}H NMR (90 MHz) δ 1.41 (s, 6 H),

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1.8–2.3 (AA′BB′ m, 8 H). Absorption ascribable to *O*-methylene hydrogens was not detected: IR (neat) 2980, 2964, 2920, 2208, 2084, 1380, 1372, 1218, 1106, 1006 cm^{-1}.

Preparation of the Bis(chloromethyl) Acetal 4e. Dry HCl was bubbled through a mixture of 1,4-bis(hydroxymethyl)bicyclo[2.2.0]hexane (1.05 g, 7.4 mmol), 1,3-dichloroacetone (4.58 g, 36 mmol), and pulverized 4-Å molecular sieves (0.5 g) in benzene (25 mL) for 1.5 h at room temperature. The diol was largely consumed to give a single major product while the resulting mixture was stirred overnight. The mixture was washed successively with water, aqueous $NaHCO_3$, and water and dried with $MgSO_4$. After removal of the solvent, the residue was subjected to preparative GLC (column C, 160 °C) to give analytically pure **4e** (520 mg, 28%) as colorless crystals: mp 64.5–65.5 °C; ^{1}H NMR (100 MHz) δ 1.85–2.3 (AA′BB′ m, 8 H), 3.66 (s, 4 H), 3.78 (s, 4 H); IR (KBr) 2964, 2932, 1448, 1220, 1104, 1038, 774 cm^{-1}; MS *m/z* 201 (4), 185 (4), 124 (30), 109 (65), 107 (100), 91 (55), 81 (49), 79 (84), 67 (59). Anal. Calcd for $C_{11}H_{16}O_2Cl_2$: C, 52.61; H, 6.42; Cl, 28.23. Found: C, 52.61; H, 6.46; Cl, 28.06.

Sensitized Photolysis of Hexamethylbicyclohexanes 1 and 2. The photosensitized reactions of **1** and **2** were carried out in CH_3CN or CH_2Cl_2 (2–15 mL) at a substrate concentration of 20–30 mM and a photosensitizer concentration of 0.5–1 mM (DCA, TCA) or 5–20 mM (CA, DCB, DCN, TCB, TCNQ) unless otherwise noted. The photolysates in CH_3CN were poured into water, and the product mixtures were extracted with a few portions of pentane. The extracts were combined, washed with water, dried with $MgSO_4$, concentrated, and subjected to preparative GLC (column D, 80–150 °C). The photolysates in CH_2Cl_2 were concentrated, diluted with pentane, filtered to remove insoluble materials including the sensitizers, and concentrated again before being subjected to preparative GLC. The ring cleavage products **6** and **7** were characterized by comparison of their ^{1}H and ^{13}C NMR and IR spectra with those of authentic samples.[17] **9a**: ^{1}H NMR (100 MHz) δ 0.86 (d, *J* = 7.1 Hz, 6 H), 0.96 (d, *J* = 7.3 Hz, 6 H), 1.62 (d, *J* = 1 Hz, 6 H), 1.50–1.95 (m, 2 H), 1.95–2.30 (m, 2 H); ^{13}C NMR δ 13.60 (q), 15.59 (q), 17.17 (q), 37.53 (d), 40.01 (d), 128.35 (s); IR (neat) 2960, 2870, 2830, 1450, 1380, 1320, 1265, 1095, 1045 cm^{-1}; MS *m/z* 166 (M$^+$, 24), 151 (19), 110 (100), 109 (17), 95 (72), 83 (43), 55 (22).

Sensitized Photolysis of 1,4-Dimethylbicyclohexane 3a. A solution of CH_3CN or CH_2Cl_2 (5 mL) containing **3a** (5 mg, 0.05 mmol), sensitizer (1–5 × 10^{-2} mmol), and 1,2-dimethoxyethane (in CH_3CN) or octane (in CH_2Cl_2) as an internal standard was irradiated. The progress of photolysis was monitored by GLC (column E, 100 °C), which showed the formation of **11a** as a single major product. The yield of **11a** at about 50% conversion of **3a** was as follows (sensitizer, yield of **11a**/solvent): DCB, 78%/CH_3CN, 80%/CH_2Cl_2; DCA, 95%/CH_3CN, 92%/CH_2Cl_2; TCA, 70%/CH_3CN, 96%/CH_2Cl_2; TCNQ, 35%/CH_3CN, 63%/CH_2Cl_2.

Sensitized Photolysis of Deuterated 1,4-Dimethylbicyclohexane 3b. A solution containing **3b** (50–55 mg, 0.45–0.50 mmol) and sensitizer (1–5 × 10^{-2} mmol) in CH_3CN or CH_2Cl_2 (2–20 mL) was irradiated. The photolyzed mixture was worked up as described for the photolysis of **1** and **2**, and the unreacted **3b** and **11b** were isolated by preparative GLC (column E, 100 °C). The (*E*)/(*Z*) distribution of deuteriums in **11b** was determined on the basis of its 500-MHz ^{1}H NMR spectrum, as described in the text.

Sensitized Photolysis of the Parent Acetal 4a. An acetonitrile solution (2 mL) containing **4a** (10–15 mg, 0.06–0.1 mmol), sensitizer (0.01–0.03 mmol), and diglyme as an internal standard was irradiated. The progress of photolysis was monitored by GLC (column B, 130 °C), which showed the formation of **14a** as a single major product. The GLC yield of **14a** was as follows: 75% (DCB, at 12% conversion of **4a**); 81% (TCB, at 18% conversion); 69% (TCA, at 7% conversion).

Preparative irradiation was carried out in an CH_3CN solution (10 mL) containing **4a** (75 mg, 0.49 mmol) and DCB (28 mg, 0.22 mmol). After 65 h, 25% of **4a** had been consumed to produce **14a** in 60% yield. The resultant solution was poured into water (25 mL), and the product mixture was extracted with pentane (3 × 10 mL). The extracts were combined, washed with water, dried with $MgSO_4$, concentrated, and subjected to preparative GLC (column D, 100 °C) to isolate **14a**: ^{1}H NMR (100 MHz) δ 2.46 (s, 4 H), 4.12 (d, *J* = 1.0 Hz, 4 H), 4.82 (s, 2 H), 4.86 (m, 2 H), 4.99 (m, 2 H); IR (neat) 3076, 2928, 1646, 1450, 1158, 1110, 1048, 928, 898 cm^{-1}; MS *m/z* 124 (16), 109 (63), 93 (69), 91 (71), 80 (74), 79 (77), 67 (80), 55 (83), 41 (76), 39 (100).

DCB-Sensitized Photolysis of the Monomethyl Acetal 4b. A solution of **4b** (52 mg, 0.31 mmol) and DCB (23 mg, 0.18 mmol) in CH_3CN (10 mL) was irradiated. After 57 h, 26% of **4b** had been consumed to produce **14b** (42% by GLC) as a single major product. The photolyzed mixture was worked up as described above and then subjected to preparative GLC (column F, 110 °C) to isolate **14b**: ^{1}H NMR (500 MHz) δ 1.58 (d, *J* = 5.4 Hz, 3 H), 2.58–2.65 (m, 2 H), 2.73–2.81 (m, 2 H), 4.25 (d, *J* = 13.0 Hz, 2 H), 4.52 (d, *J* = 13.0 Hz, 2 H), 5.07 (q, *J* = 5.4 Hz, 1 H), 5.11 (s, 2 H), 5.17 (d, *J* = 1.0 Hz, 2 H); IR ($CHCl_3$) 3080, 2930, 1650, 1382, 1122, 1095, 1035, 908 cm^{-1}; MS *m/z* 124 (23), 109 (43), 93 (63), 91 (72), 80 (100), 79 (77), 67 (76), 55 (64), 41 (73), 39 (86).

Sensitized Photolysis of the Dimethyl Acetal 4c. An acetonitrile solution (20 mL) containing **4c** (103 mg, 0.57 mmol), DCB (31 mg, 0.24 mmol), and diglyme as an internal standard was irradiated. The progress of photolysis was monitored by GLC (column A, 100 °C), which showed the formation of two products in a ratio of ca. 1:2. When 52% of **4c** was consumed, irradiation was discontinued and the resultant mixture was worked up as described for the photolysis of **4a**. The minor product was isolated by preparative GLC (column F, 130 °C) and assigned the structure of **15a** (5 mg, 10%). The major product, however, had undergone decomposition during the workup. The TCA-sensitized photolysis of **4c** also afforded **15a** (10% at 14% conversion of **4c**; 3% at 57% conversion). When DCB, TCB, or TCNQ was used as the sensitizer, however, **15a** was not produced in an appreciable amount. **15a**: ^{1}H NMR (500 MHz) δ 0.84 (s, 3 H), 1.32–1.40 (m, 1 H), 1.48 (s, 3 H), 1.51 (s, 3 H), 2.36–2.51 (m, 2 H), 2.61–2.68 (m, 1 H), 3.61 (d, *J* = 12.0 Hz, 1 H), 3.80 (d, *J* = 12.0 Hz, 1 H), 4.00 (s, 1 H), 5.15 (s, 1 H), 5.29 (m, 1 H); IR (neat) 3075, 2980, 2950, 2860, 1660, 1380, 1368, 1255, 1200, 1104, 1072, 1030, 995, 935, 890, 835 cm^{-1}; MS *m/z* 167 (35), 124 (49), 109 (98), 107 (100), 95 (37), 91 (41), 81 (38), 79 (67), 43 (100). Upon irradiation of the methyl protons at δ 0.84, positive NOEs were induced in the signals at δ 2.36–2.51, 3.61, 3.80, and 4.00.

DCB-Sensitized Photolysis of the Deuterated Acetal 4d. An acetonitrile solution (15 mL) containing **4d** (150 mg, 0.81 mmol) and DCB (180 mg, 1.4 mmol) was irradiated. When 54% of **4d** was consumed, the irradiation was discontinued. The resultant mixture was worked up as described for the photolysis of **4a** and subjected to preparative GLC (column F, 130 °C) to isolate **17** (10 mg, 12%; 18% by GLC): ^{1}H NMR (500 MHz) δ 0.76 (t, *J* = 1.8 Hz, 2 H), 1.27–1.35 (m, 1 H), 1.40 (s, 3 H), 1.46 (s, 3 H), 2.30–2.43 (m, 2 H), 2.54–2.62 (m, 1 H), 5.08 (m, 1 H), 5.22 (m, 1 H), virtually no absorption signal in the range of δ 3.0–5.0; ^{2}H NMR ($CHCl_3$, 76.6 MHz) δ 0.78, 3.52, 3.73, 3.94.

Sensitized Photolysis of the Bis(chloromethyl) Acetal 4e. An acetonitrile solution (20 mL) containing **4e** (220 mg, 0.87 mmol) and DCB (270 mg, 2.1 mmol) was irradiated. The progress of photolysis was monitored by GLC (column A, 170 °C), which showed the formation of two products. When ca. 40% of **4e** was consumed, irradiation was discontinued and the photolysate was evaporated in vacuo. The residue was diluted with pentane (20 mL) and filtered. The filtrate was concentrated and subjected to preparative GLC (column F, 180 °C; column G, 120 °C) to yield **14e** (22 mg, 25%; 32% by GLC) and **15b** (5 mg, 6%; 8% by GLC). Prolonged irradiation induced secondary reactions and resulted in diminished yields of the products. Irradiation of an acetonitrile solution (10 mL) containing **4e** (56 mg, 0.22 mmol) and TCA (10 mg, 0.036 mmol) also afforded **14e** and **15b** in 17% and 14% yield, respectively (by GLC, at 21% conversion of **4e**). **14e**: ^{1}H NMR (100 MHz) δ 2.45 (s, 4 H), 3.73 (s, 4 H), 4.23 (d, *J* = 1 Hz, 4 H), 4.97 (m, 2 H), 5.03 (m, 2 H); IR ($CHCl_3$) 3080, 2945, 1650, 1465, 1440, 1302, 1142, 1095, 1050, 915 cm^{-1}; MS *m/z* 201 (2.5), 124 (41), 109 (80), 107 (86), 95 (42), 91 (68), 81 (51), 80 (58), 79 (93), 77 (100), 67 (71). **15b**: ^{1}H NMR (500 MHz) δ 0.88 (s, 3 H), 1.40 (ddd, *J* = 12.0, 8.5, 3.2 Hz, 1 H), 2.24–2.31 (m, 1 H), 2.34–2.42 (dtt, *J* = 17.1, 8.5, 2.2 Hz, 1 H), 2.55–2.63 (m, 1 H), 3.62 (d, *J* = 11.5 Hz, 1 H), 3.70 (AB q, *J* = 12.2 Hz, 2 H), 3.71 (d, *J* = 11.5 Hz, 1 H), 3.91 (s, 2 H), 3.96 (s, 1 H), 5.15 (t, *J* = 2.2 Hz, 1 H), 5.29 (t, *J* = 2.2 Hz, 1 H); IR ($CHCl_3$) 2960, 2870, 1386, 1112, 1095, 1052, 1022, 984, 916 cm^{-1}; MS *m/z* 203 (2.3), 201 (7.5), 109 (14), 107 (100), 91 (19), 79 (29), 77 (24), 55 (11).

Sensitized Photolysis of 7. A CH_2Cl_2 solution (10 mL) containing **7** (25 mg, 0.15 mmol), DCB (8 mg, 0.06 mmol), and decane as an internal standard was irradiated. Capillary GLC (column A, 100–150 °C) showed the formation of three major products, two of which appeared at retention times corresponding to **1** and **6**. When 38% of **7** was consumed, irradiation was discontinued and the photolysate was subjected to preparative GLC (column D, 120 °C) to isolate **7** and the products as a mixture. The 500-MHz ^{1}H NMR spectrum of the mixture indicated the formation of **1** and **6** and also suggested that the third product was **18a**[7] (48% by GLC, **1**:**6**:**18a** = 1:8:1). Irradiation of a mixture of DCN and **7** in CH_2Cl_2 also led to the formation of those products (46% by GLC at 32% conversion of **7**, **1**:**6**:**18a** = 3:4:3).

DCB-Photosensitized Cyclization of 11a To Give 3a. A solution of **11a** (0.50 g, 4.5 mmol) and DCB (20 mg, 0.16 mmol) in acetonitrile (20 mL) was irradiated. After 72 h, 15% of **11b** had been consumed to produce a single major product. The photolyzed mixture was poured into water (50 mL), and the resultant solution was extracted with pentane (3 × 10 mL). The extracts were combined, washed with water (2 × 10 mL), dried with $MgSO_4$, concentrated, and subjected to preparative GLC (column D, 100 °C). The IR spectrum of the isolated product was superimposable to that of **3a** prepared in this study. The yield of **3a** was 20% by GLC.

DCB-Photosensitized (*E*)/(*Z*) Isomerization of 11b. A solution of **3b** (25 mg, 0.22 mmol) and DCA (12 mg, 0.05 mmol) in acetonitrile (10 mL) was irradiated until 80% of **3b** was consumed. The photolyzed mixture was worked up as described above, and **11b** produced was isolated by preparative GLC (column D, 100 °C). The ^{1}H NMR spectrum of **11b** thus obtained indicated that the ratio of **12a**:**12b** in it was 71:29.

An acetonitrile solution (2 mL) containing **11b** (7 mg, 0.06 mmol) obtained above and DCB (2 mg, 0.016 mmol) was irradiated until ca. 20% of **11b** was consumed. The photolysate was subjected to preparative GLC to recover the unreacted **11b**. The ratio of **12a**:**12b** in the recovered **11b** had decreased to 55:45.

DCB-Sensitized Photolysis of 14e. A solution of **14e** (9 mg, 0.036 mmol) and DCB (12 mg, 0.094 mmol) in acetonitrile (1 mL) was irradiated to examine the possible formation of **15b** via secondary photolysis of **14e**. The diene **14e** was consumed under the photolysis conditions, but no volatile product was detected by GLC (column A, 170 °C).

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The Fluorine Atom as a Cation-Stabilizing Auxiliary in Biomimetic Polyene Cyclizations. 1. Background and Exploratory Experiments[1]

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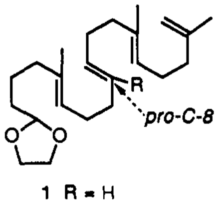
Abstract: With the aim of testing the fluorine atom as a potential cation-stabilizing (C-S) auxiliary for enhancing polyene cyclizations, new methodology has been developed for the stereoselective synthesis of polyenic cyclization substrates in which the vinyl H of an *E*-trisubstituted olefinic bond is replaced by F. Thus the substrate **5** was produced, as suggested by formulas **13–24**, the Claisen rearrangements **15** → **17** and **18** → **19** being the key steps for producing the vinyl fluoride moiety. $SnCl_4$-catalyzed cyclization of substrate **5** gave a relatively high yield of a complex mixture of tetracyclic materials indicating that, in principle, the fluorine atom can serve effectively as a C-S auxiliary. The major product of the cyclization was proved by X-ray crystallography to be **25**, resulting from dehydrofluorination of compound **6**. A fluorine-containing substance was isolated in low yield, and it most likely was the compound **6**, because when treated with the Ohsawa–Oishi reagent (Na/K, crown ether, toluene) it was converted into a product which appeared to be identical with compound **2**. That this reduction is synthetically useful and does, indeed, proceed stereoselectively with retention of configuration has been confirmed unequivocally in another example described in the next paper of this series.

For more than 20 years, efforts to simulate the biological conversion of squalene to tetracyclic triterpenoids such as lanosterol have been abortive. At best, poor yields of tetracyclic products were obtained in model systems. Thus, the aim to effect such transformations efficiently, without the agency of the enzyme, was generally regarded as futile. Recently a new concept for improving such cyclizations was disclosed.[1a] This principle employs a polyene substrate with a cation-stabilizing (C-S) substituent appended to the carbon that is likely to become positively charged in the transition state, e.g., at the bicyclic stage, thus lowering the activation energy of the process. In the seminal work, the cyclization of the tetraenic acetal substrate **1**[2] was compared with that of the modified form **3**, in which the hydrogen atom at *pro*-C-8 (steroid numbering) was replaced by the cation-stabilizing isobutenyl group. The yields of tetracyclic products, consisting mainly of substances **2** and **4**, respectively, along with some isomers also having the all-trans configuration of the ring fusions, were 30% for the cyclization of **1**[2] and 77% for the cyclization of **3**.[1a] Thus, the effect of the C-S auxiliary at *pro*-C-8 was to more than double the yield of the tetracyclic product.



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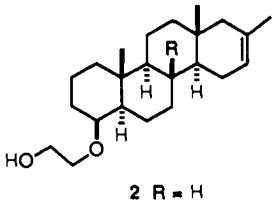
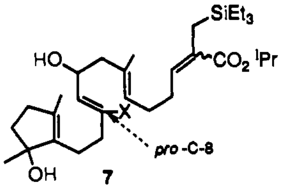
3 R = -CH=CMe$_2$
5 R = F

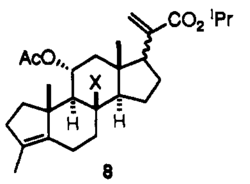


2 R = H
4 R = -CH=CMe$_2$
6 R = F

An even more dramatic effect of the C-S auxiliary was observed in the following case. The rate of TFA-catalyzed cyclization of the substrate **7** (X = H) is strongly attenuated by the OH at *pro*-C-11; therefore, side reactions become a significant factor, and the optimized yield of product **8** (X = H) was only 20% after a reaction time of 24 h. In striking contrast, the cyclization of the substrate **7** (X = CH=CMe$_2$), having the isobutenyl C-S auxiliary at *pro*-C-8, was complete in about 1 min, and the product **8** (X = CH=CMe$_2$) was isolated in 80–83% yield.[1b]



7



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† The X-ray crystallographic analyses reported herein were performed by F.S.T. and R.K.K. at the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180.

(1) This represents paper no. 4 on cation-stabilizing auxiliaries in polyene cyclizations. For the first three papers in the series, see: (a) Johnson, W. S.; Telfer, S. J.; Cheng, S.; Schubert, U. *J. Am. Chem. Soc.* **1987**, *109*, 2517–2518. (b) Johnson, W. S.; Lindell, S. D.; Steele, J. *J. Am. Chem. Soc.* **1987**, *109*, 5852–5853. (c) Guay, D.; Johnson, W. S.; Schubert, U. *J. Org. Chem.* **1989**, *54*, 4731–4732.

(2) Johnson, W. S.; Wiedhaup, K.; Brady, S. F.; Olson, G. L. *J. Am. Chem. Soc.* **1968**, *90*, 5277–5279. Johnson, W. S.; Wiedhaup, K.; Brady, S. F.; Olson, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 3979–3984.

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