vestigations of the isomerase. Of immediate interest are the effects of site-directed mutagenesis on the individual steps of the reaction.

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(9) The effects of site-directed mutagenesis of some of the residues implicated in the catalytic mechanism on the overall rate of catalysis have been reported.[10].

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Photoinduced Electron-Transfer Reactions of 1,4-Dimethyl- and 1,2,3,4,5,6-Hexamethylbicyclo[2.2.0]hexanes. Evidence for Boat Cyclohexane-1,4-diyl Radical Cation and Its Stereospecific Cleavage

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Cyclohexane-1,4-diyl radical cation has recently attracted considerable interest as a radical cation counterpart of the elusive cyclohexane-1,4-diyl diradical and also as an intermediate associated with possible catalysis of the Cope rearrangement by electron transfer.[1] As for its structure, preferential formation in a chair form has been observed upon ionization of both 1,5-hexadienes and unsubstituted bicyclo[2.2.0]hexane.[1b,e] Its cleavage to 1,5-hexadiene radical cation is thought to be thermodynamically unfavorable,[1,2] and the feasibility of the process in the substituted derivatives has remained unsubstantiated. Herein we report studies of the title reactions that provide evidence for the intermediate formation of hitherto unobserved *boat* cyclohexane-1,4-diyl radical cations and their stereospecific cleavage.

Table I. Calculated ΔG for Electron Transfer, Fluorescence Quenching Rate Constants, and Quantum Yields in Acetonitrile

substrate	acceptor	ΔG,[a] kcal/mol	k_q, $M^{-1}\,s^{-1}$	ϕ[b]
1b	DCA	−7	1.8×10^9	
1c	DCN	−16	10.0×10^9	0.034[d]
	DCA	−12	7.2×10^9	0.014[e]
	TCB	−39	16.7×10^9	0.069[d]
	TCA	−21	13.8×10^9	0.048[e]
	TCNQ[c]	−29		
7c	DCN	−17	10.7×10^9	0.067[d]
	DCA	−13	5.8×10^9	0.029[e]
	TCB	−40	16.2×10^9	0.12[d]
	TCA	−22	13.5×10^9	0.14[e]
	TCNQ[c]	−30		

[a] Calculated for ET from substrate to singlet excited acceptor by using the Weller equation.[6] [b] For the consumption of substrate. [c] The lowest excited singlet energy was estimated from the absorption spectrum. [d] At 313 nm. [e] At 366 nm.

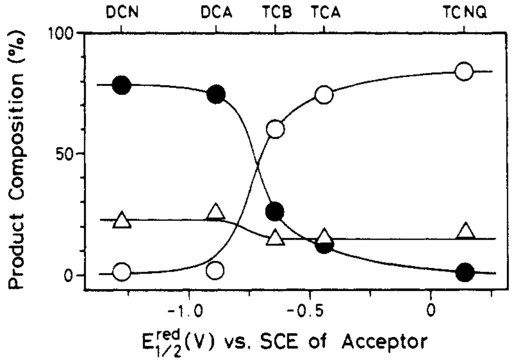

Figure 1. Correlation of product composition with the reduction potential of electron acceptor in the reaction of **7c**: (●) **1c**; (○) **6c**; (△) **11c**.

Photoinduced electron-transfer (ET) reactions of bicyclohexanes **1b**,[3] **1c**, and **7c**[4] (Scheme I) were investigated by irradiation of their solutions in acetonitrile in the presence of various acceptors.[5] Prerequisite initial ET from the bicyclohexanes to the excited singlet acceptors is supported by the exothermicity of the processes[6] and quenching of acceptor fluorescence by the former at near-diffusion-controlled rates (Table I).[7] The sensitized photolysis of **1c** was practically acceptor-independent and led to the stereospecific formation of *erythro*-(*E*,*E*)-diene **4c**[8,9] together with a small amount of hexamethylcyclohexene (**6c**) in 50–85% total yield (**4c**:**6c** = 86:14–93:7). DCA-sensitized photolysis of **1b** (*exo*-D:*endo*-D = ≥98:≤2) in acetonitrile afforded **4b** [*E*-D:*Z*-D = (83 ± 4):(17 ± 4)] in more than 80% yield.[10] On the other hand, the reaction of **7c** was strongly acceptor-dependent and the product compositions were found to be correlated with the reduction potentials ($E_{1/2}^{\text{red}}$) of acceptors (Figure 1).[12] Thus, **7c** was isomerized predominantly to **1c** by the acceptors whose $E_{1/2}^{\text{red}}$ is more negative than −0.8 V vs SCE,[13] while it afforded mainly **6c** when sensitized by the more readily reducible acceptors. In addition to **1c** and/or **6c**, *erythro*-(*E*,*Z*)-diene **11c**[9] was invariably obtained as the minor product, but *erythro*-*Z*,*Z* isomer **15c**[9] was not detected.

In the present reactions of **1b**,**c** and **7c**, the initial generation of cyclohexane-1,4-diyl radical cations is reasonably assumed. It should be noted that the ring strain inherent in this system is largely relieved by stretching of the central bond. The ionization of the parent **1a** (=**7a**) has, in fact, been shown to give **9a**.[1c] The

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(1) (a) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1988**, *110*, 1974. (b) Miyashi, T.; Konno, A.; Takahashi, Y. *Ibid.* **1988**, *110*, 3676. (c) Adam, W.; Grabowski, S.; Miranda, M. A.; Rubenacker, M. *J. Chem. Soc., Chem. Commun.* **1988**, 142. (d) Hasegawa, E.; Mukai, T.; Yanagi, K. *J. Org. Chem.* **1989**, *54*, 2053. (e) Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B. K. *J. Am. Chem. Soc.* **1989**, *111*, 4133. (f) Dai, S.; Pappas, R. S.; Chen, G.-F.; Guo, Q.-X.; Wang, J. T.; Williams, F. *Ibid.* **1989**, *111*, 8759.

(2) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(3) The labeled **1b** was prepared by reducing 1,4-dimethyl(Dewar benzene) with diimine-d_2.

(4) Van Bekkum, H.; van Rantwijk, F.; van Minnen-Pathuis, G.; Remijnse, J. D.; van Veen, A. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 911.

(5) The electron acceptors ($E_{1/2}^{\text{red}}$ vs SCE) employed are 1,4-dicyanonaphthalene (DCN, −1.28 V), 9,10-dicyanoanthracene (DCA, −0.89 V), 1,2,4,5-tetracyanobenzene (TCB, −0.65 V), 2,6,9,10-tetracyanoanthracene (TCA, −0.45 V), and tetracyanoquinodimethane (TCNQ, 0.13 V).

(6) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834; *Isr. J. Chem.* **1970**, *8*, 259. The $E_{p/2}^{\text{ox}}$ values vs SCE of **1b**, **1c**, **7c**, and **11c** in acetonitrile are 1.74, 1.50, 1.54, and 1.73 V, respectively. Irreversible anodic waves were observed in all cases.

(7) Emission ascribable to an exciplex was not observed.

(8) *E* denotes that the terminal substituent ($R^1 = CH_3$ 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. The stereospecificity of the ring cleavage of **1c** was higher than 98%.

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

(10) Deuteriums in the recovered bicyclohexane had largely been retained in the exo positions even after 80% conversion. We suspect that the incomplete stereospecificity of the cleavage reaction of **1b** might be due to the configurational instability of **3b** rather than to the partial leakage of **2b** to **9b** prior to the cleavage.[11]

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

(12) The combined yields of the reaction products of **7c** were 50–85%.

(13) The secondary reaction of **1c** led to the formation of **4c**. The initial relative yield of **4c** was negligible.

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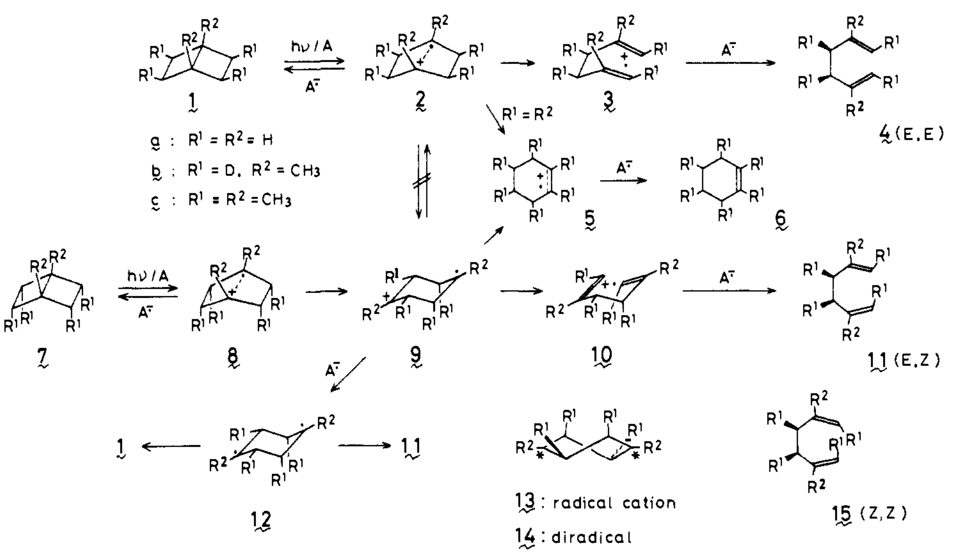
Scheme I



stereospecific production of **4c** from **1c** thus indicates the generation of boat **2c** which underwent $[2_s + 1_s]$ cleavage while retaining its configuration. Resultant **3c** could be reduced to **4c** without loss of its stereochemical integrity via back ET from an acceptor radical anion. Closely related 2-methyl-2-butene radical cation has been shown to prefer a planar geometry and to be configurationally relatively stable.[11] The cleavage of **1b** with relatively high stereospecificity reinforces the above mechanism.

The formation of **11c** but not of **15c** from **7c** suggests that radical cation **8c**, in contrast to **2b** and **2c**, underwent ring flipping to give **9c**[14] prior to the cleavage reaction. The conformational instability of **8c** may be attributable to repulsive interactions among the four *endo*-methyl groups.[15] The observed correlation between the product composition and the $E_{1/2}^{\mathrm{red}}$ of acceptor in the reaction of **7c** suggests the involvement of back ET in the product-determining stage. The oxidation potential ($E_{1/2}^{\mathrm{ox}}$) of *tert*-butyl radical has been reported to be 0.09 V vs SCE.[17] If the $E_{1/2}^{\mathrm{ox}}$ value of **12c** is assumed not to be greatly different from that value, free energy changes for the back ET from the radical anions of the acceptors here employed to **9c** [$\Delta G = E_{1/2}^{\mathrm{red}}$(acceptor) − $E_{1/2}^{\mathrm{ox}}$(**12c**)] should be in the range of −1.4–0.1 eV. In this range of ΔG, it is reasonable to assume that the higher the exothermicity of the back ET ($-\Delta G$), the faster the process tends to be.[18] Thus, the isomerization of **7c** to **1c** and **11c** via the back ET to **9c** would predominate when the $E_{1/2}^{\mathrm{red}}$ of acceptor was <-0.8 V vs SCE. As the exothermicity decreased, the back ET to **9c** would become slower and eventually overshadowed by the transformation of **9c** into **5c** and **10c**. The above scheme is supported by the reported formation of **1c** and **11c** upon thermolysis of **7c**[9] and the known tendency of **9a** to isomerize to **5a**.[1a,e] The invariably observed production of **11c** demonstrates that it derived from both the intermediates **9c** and **12c**.

The different stereospecificities of the ET-induced cleavage reactions of **1c** and **7c** clearly indicate that a concerted, one-step mechanism did not operate and that **2c** and **9c** did not interconvert to an appreciable extent within their lifetimes under the present conditions. Although the possibility that the acceptors might somehow influence the stereochemical course of the reactions of the radical cations is not rigorously ruled out, the stereochemical outcome of the observed rearrangements would most probably be due to their inherent properties. The boat structure of **2** would be held in its form by virtue of a single-electron 1,4-bond. The stereospecific reaction pathway from **1** to **3** via **2** seems in good accord with the energy profile calculated by Pabon and Bauld for [2 + 1] olefin cyclodimerization.[19]

Acknowledgment. We thank Professors K. Yagi and F. Morita for the use of their instrument for the measurement of fluorescence spectra.

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[14] Chair **9** and **12** cannot be distinguished from twist-boat forms **13** and **14**, respectively, in the present reactions. The parent species has been shown to possess a chair structure.[1e]

[15] According to molecular mechanics calculations (MM2),[16] **7c** is less stable by 8 kcal/mol than **1c** and a dihedral angle between the two rings in **7c** is significantly widened (by ca. 10°) compared to that in **1c**.

[16] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

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

[18] Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

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Highly Stereocontrolled Syntheses of Isomeric Pairs of Di- and Trisubstituted Olefins through [2,3] Sigmatropic Rearrangement of Allyldimethylammonium Methylides

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[2,3] and [3,3] sigmatropic rearrangements are often used for the stereoselective preparation of di- and trisubstituted olefins.[1] Herein we report an interesting [2,3] sigmatropic *N*-ylide rearrangement that provides *Z*- or *E*-homoallylic dimethylamines with ≥95% stereoselectivity as exemplified in Scheme I.

Quaternization of allylic amine **1a** with MeI (24 h, 25 °C) furnished trimethylammonium iodide **2a** quantitatively. Treatment of **2a** (1 mmol) with excess $NaNH_2$ (20 mmol) in NH_3 (100 mL) resulted in the formation of the ammonium ylide intermediate followed by spontaneous [2,3] sigmatropic rearrangement (30 min, −33 °C) to give homoallylic dimethylamine **3a** in 72% yield. Capillary GC analysis showed **3a** to be 100% one isomer. The examination of **3a**[2] by ^{1}H NMR after derivatization to the corresponding trimethylammonium salt [NMR (CD_3OD) δ 5.71 (=CH, dq, $J = 6.6, 10.6$ Hz), 5.35 (=CH, dt, $J = 7.0, 10.6$ Hz)] and the observation of 20% NOE between the C-5 methyl protons

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[2] **3a** and **3b** formed azeotropic mixtures with the extracting solvent (ether, pentane).

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