Stereomutation of 7-Tropylionorbornane, 2-Tropyliobicyclo[2.2.2]octane, and 2-Tropylioadamantane: Evidence for the Intermediacy of Heptafulvenes

Keizo Ikai, Ken'ichi Takeuchi,* Tomomi Kinoshita, Ken'ichi Haga, Koichi Komatsu, and Kunio Okamoto†

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received July 17, 1990

The perchlorates of 7-tropylionorbornane (**3**), 2-tropyliobicyclo[2.2.2]octane (**4**), and 2-tropylioadamantane (**5**) were found to undergo stereomutation in acetonitrile at 25–85 °C, as evidenced by following the change in the ^{13}C NMR spectra of their deuterium-labeled compounds in acetonitrile-d_3. Addition of tetracyanoethylene to their solutions in acetonitrile gave the [8 + 2] cycloaddition products of the corresponding heptafulvenes, indicating the intermediacy of the heptafulvenes. This stereomutation was too slow to detect in dichloromethane at the same temperature. Therefore, it is concluded that the stereomutation proceeds through the abstraction of the α-hydrogen by acetonitrile as a base followed by the protonation of the heptafulvene intermediate from the rear side. The entropies of activation which are significantly negative and large indicate abstraction of the α-hydrogen is the rate-determining step. The enthalpy of activation for the norbornane system (22.1 ± 1.1 kcal/mol) is about 8 kcal/mol greater than that for the bicyclo[2.2.2]octane system (15.4 ± 1.1 kcal/mol) and that for the adamantane system (13.1 ± 1.3 kcal/mol). Molecular mechanics calculations (MMPI, MM2′) for the three heptafulvenes and the corresponding phenyl derivatives (instead of the tropylium ions) indicated that the angle strain at the 8-position of the heptafulvenes controls the rate of the stereomutation.

Introduction

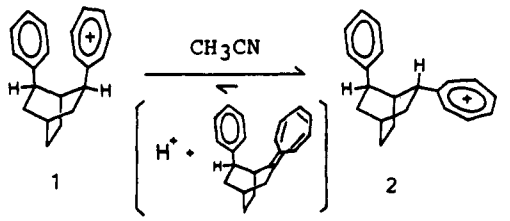
It is well known that tropylium ions which have a substituent containing α-hydrogen are converted into heptafulvenes by α-hydrogen abstraction with a strong base such as triethylamine or hydroxylic solvent.[1] The heptafulvenes return to the tropylium ions when treated with a strong acid.

On the other hand, the behavior of alkyltropylium ions in weakly basic organic solvents had not been reported until we recently reported the rearrangement of *endo*-2-phenyl-*endo*-6-tropyliobicyclo[2.2.2]octane (**1**) into the *endo*-2-phenyl-*exo*-6-tropylio isomer **2** (Scheme I) in acetonitrile at 25 °C.[2a] This stereomutation was too slow to detect at the same temperature in a less basic solvent dichloromethane. Also, we found that the racemization rate of optically active alkyltropylium ions depends on the solvent basicity.[2b] Thus, the stereomutation seemed to proceed through abstraction of the α-hydrogen by the solvent molecule as a base followed by protonation of the heptafulvene intermediate from the opposite side.[2]

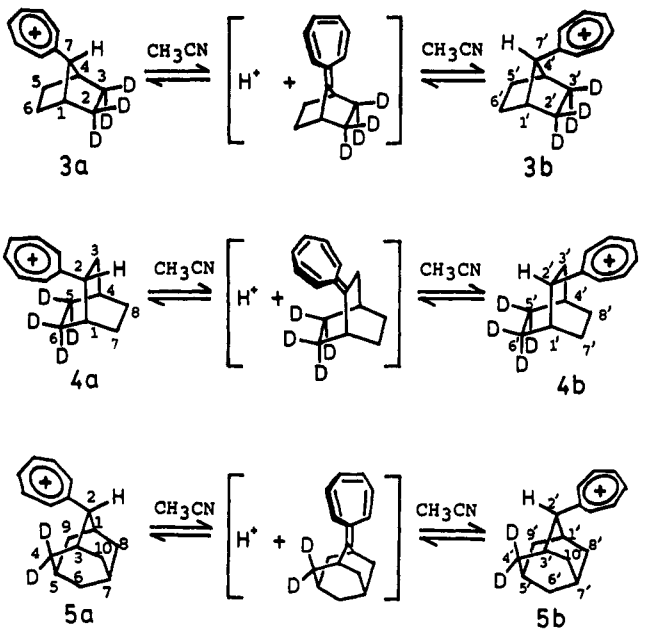
In the present work, deuterium-labeled salts of 7-tropylionorbornane (**3a** and **3b**), 2-tropyliobicyclo[2.2.2]octane (**4a** and **4b**), and 2-tropylioadamantane (**5a** and **5b**) were synthesized (Scheme II), and their stereomutation in acetonitrile was demonstrated by following the changes in their ^{13}C NMR spectra.

In order to prove the intermediacy of the heptafulvene, trapping experiments were conducted using tetracyanoethylene in the stereomutations of **3c**, **4c**, and **5c**. The relation between the thermodynamic stabilities of the heptafulvenes and the energy barriers for the stereomutations were also investigated for these three systems.

Scheme I



Scheme II



Results

Syntheses of the Tropylium Ions. Tropylium ions **3**, **4**, and **5** containing the 7-norbornyl, bicyclo[2.2.2]oct-2-yl, and 2-adamantyl substituent, respectively, were derived from the corresponding benzenes via ring expansion with diazomethane followed by hydride abstraction with trityl perchlorate. Deuterium was introduced before the ring expansion by Clemmensen reduction of appropriate ketones in DCl–CH_3COOD.[3] As an example, the preparation of 2-tropylio[5,5,6,6-$^2H_4$]bicyclo[2.2.2]octane perchlorates (**4a** and **4b**) is outlined in Scheme III. The *endo*-

† Present address: Meisei Chemical Works, Ltd., 1 Nakazawacho, Ukyo-ku, Kyoto 615, Japan.

(1) Nozoe, T.; Takahashi, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3277.
(2) (a) Ikai, K.; Takeuchi, K.; Komatsu, K.; Tsuji, R.; Kinoshita, T.; Okamoto, K. *Tetrahedron Lett.* **1989**, *30*, 99. (b) Kinoshita, T.; Haga, K.; Ikai, K.; Takeuchi, K.; Okamoto, K. *Ibid.* **1990**, *31*, 4057.
(3) Enzell, C. R. *Ibid.* **1966**, 1285.

0022-3263/91/1956-1052$02.50/0

Table I. 25 MHz ^{13}C NMR Data of the Unlabeled Tropylium Perchlorates 3c, 4c, and 5c[a]

	δ, ppm[b]									
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	tropylium ring
3c	42.0	30.9	30.9	42.0	27.4	27.4	60.5				154.1, 153.7, 155.6, 176.3
4c	33.1	49.3	33.0	25.2	25.7	20.2	28.0	25.4			153.5, 155.3, 181.0
5c	33.7	53.8	33.7	32.6	28.3	37.5	27.9	39.5	32.6	39.5	153.3, 153.7, 155.1, 179.8

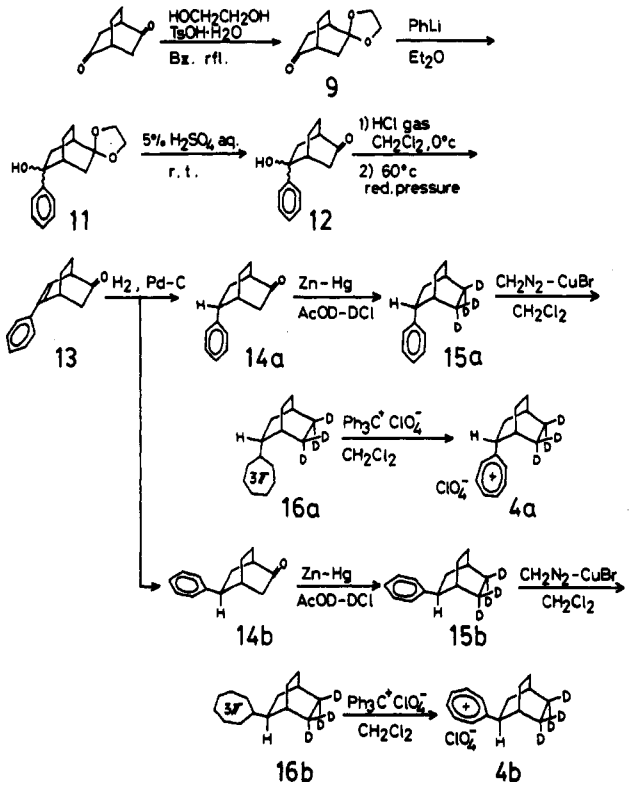
[a] In CD_3CN at room temperature. [b] δ values calculated based on δ = 1.35 ppm for CD_3CN.

Table II. The Rates of the Stereomutation[a]

systm	T, °C	k_1, s^{-1}	ΔH‡, kcal/mol	ΔS‡, eu
3a → 3b	25		22.1 ± 1.1	−19.3 ± 3.3
	65	$(2.39 \pm 0.12) \times 10^{-6}$		
	75	$(6.42 \pm 0.41) \times 10^{-6}$		
	85	$(1.57 \pm 0.07) \times 10^{-5}$		
4a → 4b	25		15.0 ± 1.2	−32.3 ± 3.6
	35	$(1.19 \pm 0.13) \times 10^{-5}$		
	50	$(3.90 \pm 0.57) \times 10^{-5}$		
	65	$(1.14 \pm 0.08) \times 10^{-4}$		
5a → 5b	25	$(2.85 \pm 0.45) \times 10^{-6}$	13.1 ± 1.3	−40.1 ± 3.9
	50	$(1.43 \pm 0.24) \times 10^{-5}$		
	75	$(7.81 \pm 1.11) \times 10^{-5}$		

[a] 0.6 M solution of the starting tropylium ion in CD_3CN.

Scheme III



and *exo*-5-phenylbicyclo[2.2.2]octan-2-ones (**14a** and **14b**, respectively) were synthesized from bicyclo[2.2.2]octane-2,5-dione[4] via five steps. 7-*anti*-Phenylnorbornan-2-one,[5] 7-*syn*-phenylnorbornan-2-one,[6] 4a-phenyladamantan-2-one,[7] and 4e-phenyladamantan-2-one[7] were prepared following reported methods. The ^{13}C NMR data of the unlabeled tropylium ions (**3c–5c**) are summarized in Table I. The ^{13}C NMR spectra of labeled tropylium ions were essentially identical with those of unlabeled ones, except

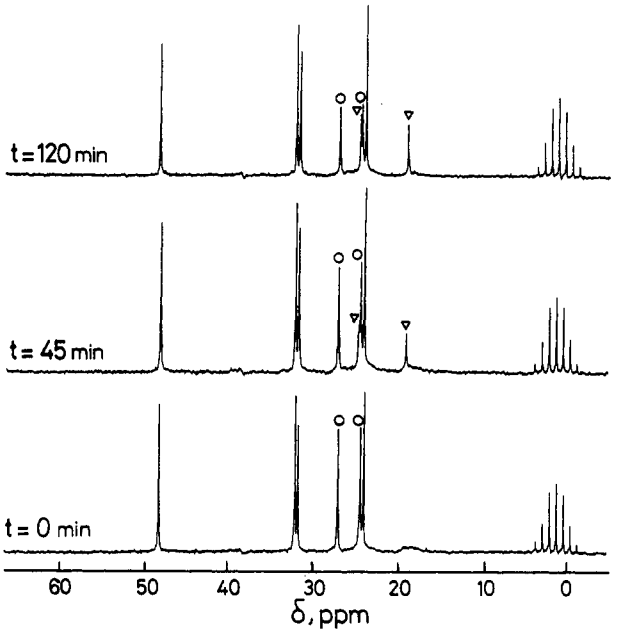


Figure 1. Monitoring of the stereomutation of *endo*-2-tropylio[5,5,6,6-$^2H_4$]bicyclo[2.2.2]octane perchlorate (**4a**) to the exo isomer (**4b**) in CD_3CN (0.6 M) at 65 °C by 25-MHz ^{13}C NMR. Spectral width, 2000 Hz; monitoring temperature, −50 °C; (○) denotes C_7 and C_8 of **4a**; (▽) denotes $C_{7'}$ and $C_{8'}$ of **4b**.

that the deuterated carbons were observed as multiplets.

Rates of Stereomutation of 3a, 4a, and 5a. The rates of conversion of **3a**, **4a**, and **5a** to respective stereoisomers **3b**, **4b**, and **5b** were determined in acetonitrile-d_3 under argon by following the change of the ^{13}C NMR signal intensities at three different temperatures. A typical example of the spectral change is shown for **4a** in Figure 1. The signals of the exo site carbons (C_7, C_8) appear at 24.7 and 27.3 ppm, whereas the endo site carbons (C_5, C_6) are not observed under the measurement conditions because of the 90% deuterium labeling. As the stereomutation proceeded, the signals of C_7 and C_8 (24.7 and 27.3 ppm) decreased, and two new signals appeared at 19.3 and 24.9 ppm which were in agreement with the chemical shifts of the endo site carbons of **4b** ($C_{7'}$, $C_{8'}$). No other changes were observed in the spectra. The change of the signal intensities obeyed first-order equilibrium kinetics $[(x_e/a) \ln \{x_e/(x_e - x)\} = k_1 t]$. The first-order plot is shown in Figure 2.

(4) Hill, R. K.; Morton, G. H.; Peterson, J. R.; Walsh, J. A.; Paquette, L. A. *J. Org. Chem.* **1985**, *50*, 5528.
(5) Kleinfelter, D. C.; Trent, E. S.; Mallory, J. E.; Dye, T. E.; Long, J. H., Jr. *Ibid.* **1973**, *38*, 4127.
(6) Wilt, J. W.; Narutis, V. P. *Ibid.* **1979**, *44*, 4899.
(7) Hoffmann, G. G.; Klein, H. *Tetrahedron* **1984**, *40*, 199.

Table III. Spectral Data of the Cycloaddition Products 17, 18, and 19

compd	IR ν, cm^{-1} [a]	^{1}H NMR δ, ppm[b]	^{13}C NMR δ, ppm[c]					
			—CH_2—	>CH	>C<	—CN	=CH—	=C<
17	2980 m, 2900 m,	1.2–3.0 (m, 11 H),	27.8	45.5	48.0	110.6[d]	118.8	131.5
	2250 w, 1620 w,	5.67 (dd, 1 H, J = 9.3, 5.3 Hz),	28.4	45.6	49.2	111.4	123.2	
	1490 m, 1470 m,	6.3–6.7 (m, 2 H), 6.7–7.0 (m, 2 H)	30.6	48.9	71.6	112.1	127.7	
	1385 m, 1325 m,		31.0				130.8	
	720 s						132.9	
18	2960 m, 2875 m,	1.2–2.6 (m, 12 H), 2.80 (br d, 1 H, J = 5.2 Hz),	22.9	25.0	45.6	109.8	118.1	137.2
	2250 w, 1480 m,	5.66 (dd, 1 H, J = 9.5, 5.3 Hz),	23.3	35.0	55.6	110.8	121.9	
	1460 m, 1380 m,	6.3–6.6 (m, 2 H), 6.6–7.0 (m, 2 H)	23.6	51.1	58.2	111.2	127.4	
	780 s, 710 s		24.0			111.6	131.2	
			39.6				131.8	
19	2920 s, 2870 s,	1.5–3.2 (m, 15 H), 5.69 (dd, 1 H, J = 9.2, 5.3 Hz),	31.7	26.0	46.5	110.5	119.9	137.2
	2250 w, 1620 w,	6.3–6.66 (m, 1 H), 6.6–6.9 (m, 3 H)	33.5	35.1	52.7	110.7	124.5	
	1480 m, 1455 s,		34.5	38.5	64.7	111.9	127.0	
	1440 m, 1380 m,		34.9	49.4		112.8	130.9	
	1095 s, 710 s		38.3				132.8	

[a] KBr. [b] 90 MHz. In $CDCl_3$ at room temperature. [c] 25 MHz. In $CDCl_3$ at room temperature. δ values calculated based on δ = 76.95 ppm for $CDCl_3$. [d] 2 C.

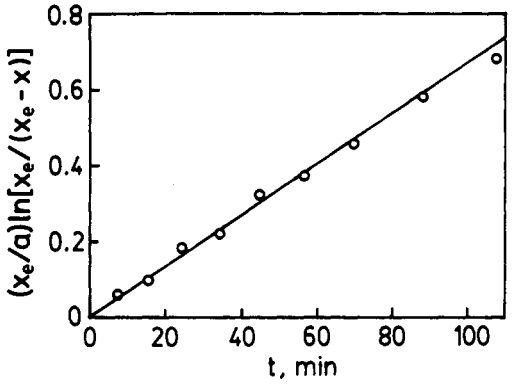


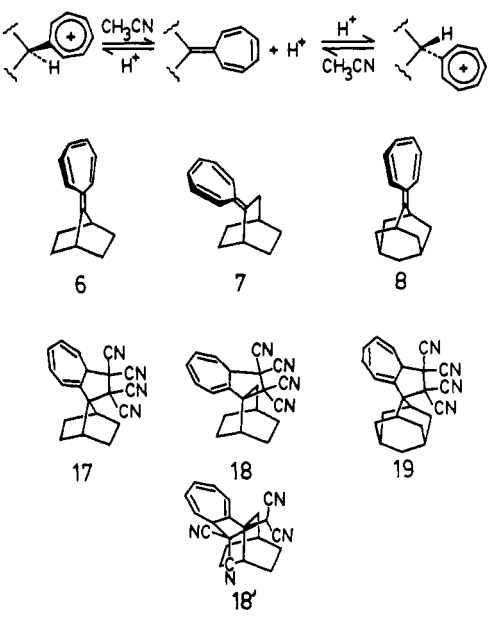
Figure 2. The first-order plot of the stereomutation of *endo*-2-tropylio[5,5,6,6-$^2H_4$]bicyclo[2.2.2]octane perchlorate (**4a**) in CD_3CN (0.6 M) at 65 °C.

Similarly, the rates of stereomutation of **3a** and **5a** were determined. In all cases, the equilibrium composition of two isomers was nearly 1:1 as measured by ^{13}C NMR spectroscopy. The first-order rate constants and activation parameters are summarized in Table II.

Evidence for the Intermediacy of Heptafulvene in the Stereomutation. The stereomutation of **3a**, **4a**, and **5a** which was observed in acetonitrile at 25–85 °C was too slow to detect in dichloromethane at same temperatures. Therefore, it was predicted that the stereomutation proceeded through the abstraction of the α-hydrogen by acetonitrile as a base followed by the protonation of the heptafulvene intermediate from the rear side (Scheme IV).[2b] Existence of the heptafulvene intermediate was proved by carrying out the stereomutation reaction of **3c**, **4c**, and **5c** in the presence of added tetracyanoethylene and isolating the [8 + 2] cycloaddition products **17**, **18**, and **19** of their corresponding heptafulvenes **6**, **7**, and **8** in 10–14% yields. Their formation was supported by the spectral data (Table III). The IR absorption at 2250 cm^{-1} and four ^{13}C NMR signals at 110–113 ppm show the presence of the cyano groups. The ^{1}H NMR signals in the olefinic region are very similar to those of cycloheptatrienes. As for the reaction of **4**, there is a possibility for the formation of another isomer **18′**. However, the ^{13}C NMR spectrum indicated the exclusive formation of the only one isomer. Investigation of molecular models indicated that the major product would be the isomer **18** which is produced by the attack of tetracyanoethylene from the less hindered side.

The three heptafulvenes **6**, **7**, and **8** were prepared also by directly deprotonating the corresponding tropylium ions

Scheme IV



with triethylamine in dichloromethane-d_2 in an NMR tube. The heptafulvenes **7** and **8** were stable at 40 °C, whereas **6** polymerized rapidly even at −78 °C in dichloromethane-d_2. Furthermore, **7** and **8** were isolated by medium-pressure liquid chromatography over silica gel under argon at room temperatue as deep red oils in 91–92% yields. The spectral data are listed in Table IV. Reaction of **7** and **8** with tetracyanoethylene gave the corresponding [8 + 2] cycloaddition products **18** and **19**, respectively, in 70% yields. The IR, ^{1}H NMR, and ^{13}C NMR spectra of these products were identical with those of the cycloaddition products obtained from the trapping experiments described above. Hydrogenation of **7** and **8** using 10% Pd/C catalyst gave 2-cycloheptylbicyclo[2.2.2]octane (**20**) and 2-cycloheptyladamantane (**21**), respectively. These products also support the structures of **7** and **8** chemically.

Discussion

Comparison of the Energy Barriers for the Stereomutation of 3, 4, and 5. The activation parameters for the stereomutation are summarized in Table II. The entropies of activation are significantly negative and large, being consistent with a bimolecular process of the stereomutation involving the tropylium ion and the solvent which was previously found by us.[2b] For a similar example,

Table IV. Spectral Data of the Heptafulvenes 7 and 8[a]

compd	IR ν, cm^{-1}[b]	^{1}H NMR δ, ppm[c]	^{13}C NMR δ, ppm[d] —CH_2—	>CH	=CH—	=CH<
7	3030 s, 2950 s, 2870 s, 1550 w, 1450 m, 1430 m, 1350 m, 930 m, 725 s	1.2–1.7 (m, 8 H), 1.82 (br 1 H), 2.07 (br d, 2 H, J = 2.9 Hz), 2.57 (br 1 H), 5.5–5.9 (m, 5 H), 6.02 (br d, 1 H, J = 11 Hz)	25.5[e] 25.6[e] 34.2	26.2 27.8	125.0 125.1 130.2 130.7 132.6 132.9	127.1 139.1
8	3020 m, 2910 s, 2850 s, 1550 w, 1450 m, 1100 m, 725 m, 700 s	1.4–2.1 (m, 12 H), 2.90 (br 2, H), 5.6–6.1 (m, 6 H)	36.9 38.7[f]	28.2[e] 32.0[e]	125.9[e] 130.6[e] 130.9[e]	122.5 144.2

[a] At room temperature. [b] CCl_4 solution. [c] 90 MHz. [d] 25 MHz. In $CDCl_3$. δ values calculated based on δ = 76.95 ppm for $CDCl_3$. [e] 2 C. [f] 4 C.

Table V. Calculated Steric Energies and Angle Strain

system	SE, kcal/mol phenyl[a] deriv	SE, kcal/mol hepta-fulvene[b]	ΔSE, kcal/mol	θ,[c] deg	EB,[d] kcal/mol
3	16.8	49.9	33.1	97.1	3.55
4	14.9	45.3	30.4	109.6	0.43
5	11.6	42.4	30.8	109.8	0.40

[a] Calculated by MM2′. [b] Calculated by MMPI. [c] Angle at the 8-position of the heptafulvene. [d] Bending energy.

the anion inversion of (7-phenylnorbornyl)lithium in THF-d_8 also has a negative and large entropy (−13 eu at −84 °C), and it has been concluded that solvation of the cation is the rate-determining step and not anion inversion per se.[8]

The enthalpy of activation for the norbornane system (22.1 ± 1.1 kcal/mol) is 7 and 8 kcal/mol greater than those for the bicyclo[2.2.2]octane system (15.4 ± 1.1 kcal/mol) and the adamantane system (13.1 ± 1.3 kcal/mol), respectively. This remarkably higher barrier for the interconversion in the norbornane system is most probably ascribed to the angle strain at the 8-position of the heptafulvene intermediate.

In order to substantiate this premise, the molecular mechanics calculations were performed. Steric energies (SE) and geometries of the heptafulvenes were calculated by means of Allinger's MMPI program.[9] Since we were unable to calculate the SE and geometries of the tropylium ions by molecular mechanics, those of the phenyl derivatives were calculated instead by means of MM2′ program,[10] and the increases in the SE (ΔSE) on converting the phenyl derivatives to the heptafulvenes were compared among the three systems. Table V shows the SE and the angles (θ) at the 8-position of the heptafulvenes along with the bending energies (EB). The ΔSE for the norbornane system is about 2–3 kcal/mol greater than that for the other systems. The angle at the 8-position of the heptafulvene in norbornane system (97.1°) is about 13° smaller than that for the other heptafulvenes (109.6° and 109.8°), so that the bending energy at this position in the norbornane system is about 3 kcal/mol greater than that in the other systems. These results suggest that the higher barrier for the stereomutation, observed for the norbornane system is caused by the angle strain at the 8-position of the heptafulvene.

A similar correlation between activation barriers and bond angles is observed in the nitrogen inversion of 7-methyl-7-azanorbornene,[11] 2-methyl-2-azabicyclo[2.2.2]-octane,[12] and 2-methyl-2-azaadamantane.[13] In these cases, the activation free energy ($\Delta G^{\ddagger}$) of 7-methyl-7-azanorbornene (14.9 kcal/mol at 22 °C) is 7–9 kcal/mol higher than those of 2-methyl-2-azabicyclo[2.2.2]octane (5.7 kcal/mol at 25 °C) and 2-methyl-2-azaadamantane (7.8 kcal/mol at 25 °C). The smaller the C–N–C bond angles are, the higher the nitrogen inversion barrier. This resemblance between the stereomutation and the nitrogen inversion also supports that the angle strain at the 8-position of the heptafulvene controls the barrier of the stereomutation.

Experimental Section

Melting and boiling points are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University. IR spectra were taken with a Hitachi 215 spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz) or a JEOL FX90-Q (90 MHz) spectrometer. ^{13}C NMR spectra were taken with a JEOL FX100 (25 MHz) or a JEOL FX90-Q (22.5 MHz) operating in the Fourier transform mode.

Materials. Reagents were of reagent-grade quality except when otherwise noted. Acetonitrile and dichloromethane, which were used for the syntheses of the tropylium ions and the observation of the stereomutation, were refluxed over P_2O_5 and distilled. Bicyclo[2.2.2]octane-2,5-dione,[4] 7-*anti*-phenylnorbornan-2-one,[5] 7-*syn*-phenylnorbornan-2-one,[6] 4a-phenyladamantan-2-one,[7] and 4e-phenyladamantan-2-one[7] were prepared following reported methods. 2-Phenylbicyclo[2.2.2]octane[14] was synthesized from 2-phenylbicyclo[2.2.2]oct-2-ene.[15] 7-Phenylnorbornane[16] was prepared from 7-*anti*-phenylnorbornan-2-one.[5] 2-Phenyladamantane[17] was prepared following reported method.

5-(Ethylenedioxy)bicyclo[2.2.2]octan-2-one (9). Bicyclo[2.2.2]octane-2,5-dione (5.00 g, 36.2 mmol) in benzene (70 mL) was mixed with ethylene glycol (2.22 g, 35.8 mmol) and *p*-TsOH (353 mg). The mixture was heated under reflux for 1 h with continuous removal of water. After cooling, the benzene solution was washed with saturated aqueous $NaHCO_3$ (20 mL × 3) and saturated aqueous NaCl (30 mL) and dried ($MgSO_4$). Evaporation of the solvent afforded a pale yellow oil (6.02 g). A GLC analysis (SE-30, 2 m × 3 mm) of the crude product showed 5-(ethylenedioxy)bicyclo[2.2.2]octan-2-one (**9**), 2,5-bis(ethylenedioxy)bicyclo[2.2.2]octane (**10**) and bicyclo[2.2.2]octane-2,5-dione in a ratio 74:14:12 in this sequence. MPLC over SiO_2 (hexane–ether) of the crude product furnished **10** (1.28 g, 16%), **9** (3.47 g, 53%), and bicyclo[2.2.2]octane-2,5-dione (0.46 g, 9%) in this sequence. **9**: white crystals; mp 35.3–35.5 °C (from diisopropyl ether); IR (CCl_4) 2950 s, 2870 s, 1725 vs, 1400 m, 1360 m, 1120 s, 1025 s cm^{-1}; ^{1}H NMR (CCl_4) δ 1.16–2.73 (m, 10 H), 3.86 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.0, 21.7, 38.3, 39.9, 63.7, 64.1 (CH_2), 36.0, 43.9 (CH), 108.7 (C), 214.5 (C=O). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H,

(8) Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709.
(9) Allinger, N. L.; Yuh, Y. H. *QCPE* **1979**, *11*, 318.
(10) Kindly provided by Professor Eiji Osawa of Hokkaido University.
(11) Marchand, A. P.; Allen, R. W. *Tetrahedron Lett.* **1977**, 619.
(12) Nelsen, S. F.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 1842.
(13) Nelsen, S. F.; Weisman, G. R.; Clennan, E. L.; Peacock, V. E. *Ibid.* **1976**, *98*, 6893.
(14) Akopyan, A. N.; Aslamazyan, V. S.; Kon'kova, S. G. *Arm. Khim. Zh.* **1975**, *28*, 101.
(15) Kleinfelter, D. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1961**, *83*, 2329.
(16) Kleinfelter, D. C.; Sanzero, G. *J. Org. Chem.* **1977**, *42*, 1944.
(17) Beckwith, A. L. J.; Cross, R. T.; Gream, G. E. *Aust. J. Chem.* **1974**, *27*, 1693.

7.74. Found: C, 65.89; H, 7.91. **10**: white crystals; mp 55.5–55.7 °C; IR (CCl_4) 2955 s, 2940 s, 2875 s, 1370 m, 1035 m cm^{-1}; ^1H NMR (CCl_4) δ 1.16–2.20 (m, 10 H), 3.76 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 19.5, 36.6, 63.4 (CH_2) 34.2 (CH), 109.2 (C). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.70; H, 8.12.

5-(Ethylenedioxy)-2-phenylbicyclo[2.2.2]octan-2-ol (11). To a stirred solution of 2 M PhLi in cyclohexane–ether (50 mL, 99.0 mmol) was added a solution of **9** (5.96 g, 32.7 mmol) in dry ether (30 mL) at −78 °C under nitrogen atmosphere. After stirring for 2 h at −78 °C, the reaction mixture was warmed to room temperature, and saturated aqueous NH_4Cl (90 mL) was added slowly. The reaction mixture was extracted with $CHCl_3$ (100 mL × 4). The combined extracts were washed with saturated aqueous NaCl (100 mL × 2) and dried ($MgSO_4$). Evaporation of the solvent afforded a pale yellow semisolid (12.5 g). Recrystallization from diisopropyl ether gave one pure isomer of **11** (**11′**) (2.51 g, 29%) as white crystals. MPLC over SiO_2 (hexane–ether) of the recrystallization residue furnished the other isomer of **11** (**11″**) as white crystals (1.05 g, 12%), unreacted **9** (2.55 g, 43%), and **11′** (1.09 g, 13%) in this sequence. The total yield of **11′** was 42%. **11′**: mp 127.2–127.9 °C (from hexane–diisopropyl ether); IR ($CHCl_3$) 3600 m, 3450 br, 1365 m, 1000 m, 980 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33–2.16 (m, 9 H), 1.80 (s, 1 H, OH), 2.56 (m, 1 H), 2.80 (m, 1 H), 3.86 (m, 4 H), 7.20–7.73 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.6, 20.0, 37.5, 38.2, 63.5, 63.9 (CH_2), 34.1, 38.5 (CH), 74.1, 110.0 (C), 126.1, 126.7, 127.9, 147.4 (Ph). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.61; H, 7.77. **11″**: mp 128.1–131.0 °C (from hexane); IR ($CHCl_3$) 3500 br, 1365 m, 1020 s, 990 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.43 (m, 9 H), 2.57 (m, 1 H), 3.10 (br s, 1 H, OH), 3.96 (m, 4 H), 7.16–7.70 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 20.0, 20.8, 36.2, 38.5, 63.9 (CH_2), 34.3, 38.6 (CH), 73.6, 110.3 (C), 125.8, 126.7, 127.8, 146.1 (Ph). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.87; H, 7.84.

5-Hydroxy-5-phenylbicyclo[2.2.2]octan-2-one (12). To a solution of **11″** (1.27 g, 4.88 mmol) of CH_2Cl_2 (20 mL) was added 5% H_2SO_4 at room temperature. After stirring overnight at room temperature, the mixture was extracted with $CHCl_3$ (50 mL × 5). The combined extracts were washed with saturated aqueous NaCl (75 mL) and dried ($MgSO_4$). Evaporation of the solvent afforded crude **12″** as a pale yellow oil (1.17 g). **12″** was used without further purification. An analytical sample was obtained by MPLC over SiO_2 (hexane–ether) as a colorless oil: IR ($CHCl_3$) 3600 m, 3430 br, 1720 vs, 1060 m, 1000 m, 905 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06–2.76 (m, 10 H), 3.03 (s, 1 H, OH), 7.28 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.7, 21.8, 38.6, 40.5 (CH_2), 39.7, 43.6, (CH), 73.2 (C), 125.5, 126.9, 127.9, 145.2 (Ph), 216.8 (C=O). Because of the difficulty in complete removal of a trace amount of hexane, the elemental analysis data were not necessarily satisfactory. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 76.90; H, 8.06. Similarly, crude **12′** was obtained from **11′** (5.02 g, 19.3 mmol) as a pale yellow solid (4.22 g). **12′** was used without further purification. An analytical sample was obtained as white crystals by recrystallization from hexane: mp 97.6–98.5 °C (sealed tube); IR ($CHCl_3$) 3600 m, 3430 br, 1715 vs, 1075 m, 1060 m, 1000 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–3.20 (m, 10 H), 3.60 (s, 1 H, OH), 7.13–7.70 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.8, 21.0, 39.1, 39.5 (CH_2), 39.4, 42.8 (CH), 72.9 (C), 125.3, 126.5, 127.5, 145.7 (Ph), 217.2 (C=O). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.18; H, 7.41.

2-Phenylbicyclo[2.2.2]oct-2-en-5-one (13). A stirred solution of **12** (a mixture of **12′** and **12″**) (5.15 g, 24.0 mmol) in CH_2Cl_2 (20 mL) was treated at 0 °C for 35 min with HCl, which was generated by adding concentrated HCl (78 mL) to concentrated H_2SO_4 (100 mL). Pentane (20 mL) and $CaCl_2$ were added and then nitrogen gas was bubbled through the solution. After evaporating the solvent, the concentrate was heated at 60 °C under reduced pressure (30–100 mmHg) for 2 h by rotary evaporator. Column chromatography of the crude product (4.47 g) over SiO_2 (hexane–ether) furnished **13** (4.43 g, 94%) as a colorless oil: IR (CCl_4) 3050 m, 3020 m, 2950 s, 2900 s, 2870 s, 1725 vs, 1490 m, 1440 m, 1400 m, 690 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–1.93 (m, 4 H), 2.05–2.10 (d, 2 H), 3.15–3.43 (m, 2 H), 6.31 (dd, 1 H, J = 1.8, 7.2 Hz), 7.35 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 22.7, 24.1, 39.9 (CH_2), 31.8, 48.8 (CH), 121.5, 137.1 (olefin), 124.3, 127.2, 128.2, 147.4 (Ph), 211.4 (C=O). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.92; H, 7.04.

5-Phenylbicyclo[2.2.2]octan-2-one (14). A solution of **13** (4.30 g, 21.7 mmol) in ethanol (125 mL) was hydrogenated using 5% Pd/C catalyst (0.817 g) under atmospheric pressure at 0 °C until a theoretical amount of hydrogen was taken up. Filtration of the reaction mixture followed by evaporation of the solvent afforded a colorless oil. MPLC over SiO_2 (hexane–ether) furnished *endo*-5-phenylbicyclo[2.2.2]octan-2-one (**14a**) (1.91 g, 44%) as white crystals and *exo*-5-phenylbicyclo[2.2.2]octan-2-one (**14b**) (1.63 g, 37%) as a colorless oil in this sequence. **14a**: mp 68.9–69.8 °C (from hexane); IR (CCl_4) 3060 m, 3030 m, 2950 s, 2875 s, 1725 vs, 1600 m, 1500 m, 1465 m, 1450 m, 1400 m, 1225 m, 1100 m, 1050 m, 700 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (br s, 4 H), 2.00–2.63 (m, 6 H), 3.15 (br t, 1 H), 7.17 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 22.7, 26.4, 29.8, 39.8 (CH_2), 35.0, 40.5, 43.2 (CH), 126.1, 127.4, 128.4, 144.4 (Ph), 217.1 (C=O). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.17; H, 8.15. **14b**: IR (CCl_4) 3060 m, 3030 m, 2950 s, 2880 s, 1725 vs, 1715 vs, 1600 m, 1500 m, 1470 m, 1460 m, 1400 m, 1360 s, 1220 s, 700 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30–2.60 (m, 10 H), 3.07 (br t, 1 H), 7.31 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 18.4, 22.7, 28.7, 45.2 (CH_2), 34.5, 41.0, 42.3 (CH), 125.7, 126.9, 127.9, 143.5 (Ph), 215.9 (C=O). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.72; H, 8.26.

Deuterium-Labeled Phenyl Derivatives. *endo*-2-Phenyl[5,5,6,6-$^2H_4$]bicyclo[2.2.2]octane (15a). A mixture of deuterium chloride and deuterioacetic acid was prepared from acetyl chloride (38 mL) and deuterium oxide (19 mL) following the procedure of Enzell.[3] This mixture was added to a solution of **14a** (1.01 g, 5.04 mmol) in deuterioacetic acid (2 mL) containing dry amalgamated zinc filings (16 g), and the resulting mixture was refluxed for 2 h. The reaction mixture was poured into ice-cold water (200 mL) and extracted with ether (50 mL × 4). The extract was washed with saturated aqueous $NaHCO_3$ (50 mL × 4) and 10% aqueous NaCl (50 mL × 1) and dried ($MgSO_4$). Column chromatography of the crude product (860 mg) on silica gel (24 g) with hexane as eluent gave **15a** (820 mg, 86%) as an oil: IR (CCl_4) 3060 m, 3020 m, 2925 s, 2855 s, 2205 m, 2115 m, 1595 m, 1490 m, 1450 m, 695 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30–2.06 (m, 8 H), 2.92 (br t, 1 H, J = 9.0 Hz), 7.18 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.2, 27.4, 32.1 (CH_2), 19.5, 24.9 (CD_2, J = 19.5 Hz), 24.5, 30.7, 41.7 (CH), 125.4, 127.6, 128.0, 146.3 (Ph). The isotopic purity was 90% by ^1H NMR analysis.

***exo*-2-Phenyl[5,5,6,6-$^2H_4$]bicyclo[2.2.2]octane (15b).** From **14b** (1.55 g, 7.74 mmol), dry amalgamated zinc filings (27 g), acetyl chloride (62 mL), deuterium oxide (32 mL), and deuterioacetic acid (4 mL) was obtained 1.46 g of the crude product. Column chromatography on silica gel (47 g) with hexane as eluent gave **15b** (1.21 g, 82%) as an oil: IR (CCl_4) 3010 m, 2920 s, 2850 m, 2200 m, 2100 m, 1595 m, 1490 m, 1460 m, 695 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23–2.00 (m, 8 H), 2.92 (br t, 1 H, J = 9.0 Hz), 7.18 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.6, 25.9, 32.1 (CH_2), 24.3, 26.5 (CD_2, J = 19.5 Hz), 24.6, 30.8, 41.7 (CH), 125.4, 127.6, 128.0, 146.4 (Ph). The isotopic purity was 87% by ^1H NMR analysis.

7-*anti*-Phenyl[2,2,3,3-$^2H_4$]norbornane (22a). From 7-*anti*-phenylnorbornan-2-one[5] (1.30 g, 6.99 mmol), dry amalgamated zinc filings (16.3 g), acetyl chloride (50 mL) and deuterium oxide (25 mL) was obtained 1.21 g of the crude product. Column chromatography on silica gel (30 g) with hexane then hexane/ether (1:1) as eluents gave **22a** (904 mg, 74%) as an oil and unchanged ketone (250 mg, 19%) in this sequence. **22a** showed following spectral data: IR (CCl_4) 3020 m, 2950 s, 2870 s, 2220 m, 2170 m, 2120 m, 1600 m, 1500 m, 1465 m, 1448 m, 700 s cm^{-1}; ^1H NMR (CCl_4) δ 0.8–1.8 (m, 5.2 H), 2.50 (br s, 2 H), 2.82 (br s, 1 H), 7.10 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 27.2, 30.0 (CH_2), 29.6 (CDH, J = 19.8 Hz), 29.3 (CD_2, J = 19.7 Hz), 39.1, 39.2, 53.3 (CH), 125.3, 127.6, 127.9, 141.2 (Ph). The isotopic purity was 70% by ^1H NMR analysis.

7-*syn*-Phenyl[2,2,3,3-$^2H_4$]norbornane (22b). From 7-*syn*-phenylnorbornan-2-one[6] (570 mg, 3.06 mmol), dry amalgamated zinc filings (112 g), acetyl chloride (64 mL), and deuterium oxide (32 mL) was obtained 501 mg of the crude product. Column chromatography on silica gel (15 g) with hexane as eluent gave **22b** (350 mg, 65%) as an oil: IR (CCl_4) 3025 m, 2950 s, 2870 s, 2220 m, 2120 m, 1600 m, 1495 m, 1465 m, 1445 m, 700 s cm^{-1}; ^1H NMR (CCl_4) δ 1.0–2.0 (m, 5.3 H), 2.53 (br s, 2H), 2.86 (br s, 1H), 7.13 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 27.1, 30.1 (CH_2), 26.7 (CDH, J = 19.7 Hz), 26.4 (CD_2, J = 19.8 Hz), 39.1, 39.2, 39.3, 53.3 (CH),

125.3, 127.6, 127.9, 141.3 (Ph). The isotopic purity was 69% by ^{1}H NMR analysis.

2a-Phenyl[4,4-$^2H_2$]adamantane (23a). From 4a-phenyladamantan-2-one[7] (2.08 g, 9.19 mmol), dry amalgamated zinc filings (200 g), acetyl chloride (110 mL) and deuterium oxide (55 mL) was obtained 1.96 g of the crude product. Column chromatography on silica gel (55 g) with hexane then hexane–ether (1:1) as eluents gave **23a** (1.39 g, 71%) as an oil and unchanged ketone (425 mg, 20%) in this sequence. **23a** showed following spectral data: IR (CCl_4) 3090 m, 3060 m, 3020 m, 2900 s, 2850 s, 2200 m, 2100 m, 1600 m, 1500 m, 1445 m, 695 s cm^{-1}; ^{1}H NMR (CCl_4) δ 1.2–2.1 (m, 10 H), 2.43 (m, 2 H), 2.94 (m, 1 H), 7.20 (br s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 32.0, 37.9, 39.2 (CH_2), 27.9, 28.0, 30.9, 31.1, 46.8 (CH), 124.9, 126.6, 127.9, 144.1 (Ph), CD_2 was not observed. The isotopic purity was 100% by ^{1}H NMR analysis.

2e-Phenyl[4,4-$^2H_2$]adamantane (23b). From 4e-phenyladamantan-2-one[7] (1.52 g, 6.72 mmol), dry amalgamated zinc filings (77 g), acetyl chloride (50 mL), and deuterium oxide (25 mL) was obtained 1.40 g of the crude product. Column chromatography on silica gel (42 g) with hexane as eluent gave **23b** (1.16 g, 81%) as an oil: IR (CCl_4) 3090 m, 3060 m, 3020 m, 2910 s, 2850 s, 2200 m, 2100 m, 1600 m, 1500 m, 1450 m, 700 s cm^{-1}; ^{1}H NMR (CCl_4) δ 1.1–2.1 (m, 10 H), 2.46 (m, 2 H), 2.93 (m, 1 H), 7.13 (br s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.9, 37.8, 39.1 (CH_2), 38.2 (CD_2, J = 19.0 Hz), 27.6, 28.0, 30.8, 31.0, 46.7 (CH), 125.0, 126.7, 127.9, 144.1 (Ph). The isotopic purity was 100% by ^{1}H NMR analysis.

Deuterium-Labeled Tropylium Ions 3a, 3b, 4a, 4b, 5a, and 5b. A typical procedure follows. To a stirred solution of **15a** (1.49 g, 7.83 mmol) in CH_2Cl_2 (13 mL) in the presence of CuBr (743 mg, 5.18 mmol) was added dropwise a solution of diazomethane (8.00 mmol) in CH_2Cl_2 (48 mL), prepared from *N*-methyl-*N*-nitrosourea, at 40 °C over 1 h. After refluxing for 30 min, the mixture was filtered and concentrated to give 1.68 g of the crude product. Column chromatography on silica gel (25 g) with hexane as eluent gave a colorless oil (1.49 g), which was found to contain about 38 wt % of olefinic compounds (**16a**) by the ^{1}H NMR analysis. The hydride abstraction of this oil with trityl perchlorate (819 mg, 2.39 mmol) in CH_2Cl_2 (10 mL) at room temperature, followed by precipitation with dry ether and reprecipitation from acetonitrile/dry ether at 0 °C afforded **4a**·ClO_4^- (586 mg, 81% based on trityl perchlorate) as greenish yellow powder: mp 121–124 °C dec; IR (KBr) 3020 m, 2940 s, 2975 s, 2225 m, 2120 m, 2025 w, 1610 m, 1540 m, 1530 m, 1495 s, 1450 s, 1085 vs, 765 m, 750 m, 700 m cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.30–2.63 (m, 8 H), 3.70 (br t, 1 H, J = 9.0 Hz), 9.12 (br s, 6 H). **3a**, **3b**, **4b**, **5a**, and **5b** were prepared from **22a**, **22b**, **15b**, **23a**, and **23b**, respectively. **3a**·ClO_4^-: mp 151–155 °C dec; IR (KBr) 2960 s, 2875 s, 2240 m, 2180 m, 2125 m, 2025 m, 1530 s, 1490 s, 1445 s, 1095 vs, 700 s cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.41 (br s, 5.4 H), 2.87 (br s, 2 H), 3.55 (br s, 1 H), 9.13 (br s, 6 H). **3b**·ClO_4^-: pale yellow powder; mp 151–155 °C dec; IR (KBr) 3010 m, 2940 s, 2870 s, 2220 m, 2120 m, 2020 m, 1600 m, 1575 m, 1525 s, 1485 s, 1440 s, 1095 vs, 700 s cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.1–2.2 (m, 5.6 H), 2.86 (br s, 2 H), 3.54 (br s, 1 H), 9.10 (br s, 6 H). **4b**·ClO_4^-: greenish yellow powder; mp 117–122 °C dec; IR (KBr) 3020 m, 2950 s, 2910 s, 2870 s, 2220 m, 2110 m, 2020 w, 1605 m, 1560 m, 1520 m, 1490 s, 1445 s, 1090 vs, 760 m, 745 m, 695 m cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.13–2.60 (m, 8 H), 3.76 (br t, 1 H, J = 9.0 Hz), 9.12 (br s, 6 H). **5a**·ClO_4^-: pale yellow powder; mp 178–180 °C dec; IR (KBr) 3030 w, 2920 s, 2860 m, 2210 w, 2100 w, 1600 m, 1530 m, 1495 s, 1445 m, 1100 vs, 705 m cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.54–1.95 (m, 5 H), 1.95–2.22 (m, 5 H), 2.68 (m, 2 H), 3.67 (m, 1 H), 9.14 (br s, 6 H). **5b**·ClO_4^-: white powder; mp 179–181 °C dec; IR (KBr) 3050 w, 2925 s, 2860 m, 2210 w, 2100 w, 1605 m, 1535 m, 1495 s, 1450 s, 1100 vs, 705 m cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.60–2.00 (m, 7 H), 2.00–2.20 (m, 3 H), 2.70 (m, 2 H), 3.70 (m, 1 H), 9.16 (br s, 6 H).

Unlabeled Tropylium Ions 3c, 4c, and 5c. These tropylium ions were prepared from the corresponding phenyl derivatives in 21–25% yields in the same manner described for **4a**·ClO_4^-. **3c**·ClO_4^- was obtained from 7-phenylnorbornane[16] prepared by Clemmensen reduction of 7-*anti*-phenylnorbornan-2-one[5] in HCl–CH_3COOH containing amalgamated zinc filings (vide supra). **4c**·ClO_4^- was synthesized from 2-phenylbicyclo[2.2.2]octane,[14] which in turn was synthesized by the hydrogenation of 2-phenylbicyclo[2.2.2]oct-2-ene[15] using Pd/C catalyst. **5c**·ClO_4^- was obtained from 2-phenyladamantane.[17] **3c**·ClO_4^-: white crystals; mp 155 °C dec; IR (KBr) 3010 m, 2950 s, 2870 s, 1600 m, 1575 m, 1525 s, 1485 s, 1440 s, 1095 vs, 700 s cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.1–2.2 (m, 8 H), 2.85 (br s, 2 H), 3.56 (br s, 1 H), 9.10 (br s, 6 H). Anal. Calcd for $C_{14}H_{17}ClO_4$: C, 59.06; H, 6.02. Found: C, 59.03; H, 6.00. **4c**·ClO_4^-: white powder; mp 123–126 °C dec; IR (KBr) 3020 m, 2940 s, 2860 s, 1600 m, 1535 m, 1520 m, 1490 s, 1445 m, 1095 vs, 755 m cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.3–2.4 (m, 12 H), 3.73 (br t, 1 H, J = 8.4 Hz), 9.07 (br s, 6 H). Anal. Calcd for $C_{15}H_{19}ClO_4$: C, 60.30; H, 6.41. Found: C, 59.35; H, 6.37. **5c**·ClO_4^-: pale yellow needle; mp 182 °C dec; IR (KBr) 3020 m, 2925 s, 2860 s, 1605 m, 1530 m, 1500 s, 1455 s, 1450 s, 1095 vs, 710 s cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.5–2.2 (m, 12 H), 2.70 (m, 2 H), 3.67 (m, 1 H), 9.13 (br s, 6 H). Anal. Calcd for $C_{17}H_{21}ClO_4$: C, 62.86; H, 6.52. Found: C, 62.71; H, 6.60. The ^{13}C NMR data are summarized in Table I.

Observation of the Stereomutation of 3a, 4a, and 5a. A 0.6 M solution of the tropylium ion in dry acetonitrile-d_3 was placed in an NMR sample tube. After the solution had been degassed at <10^{-3} mmHg, the sample tube was sealed under argon atmosphere. The changes of the spectra were followed at ten or more specified times by a 25-MHz ^{13}C NMR spectrometer (mode, complete decoupling; spectral width, 2000 Hz; data points, 8000; pulse interval, 1.0 s; pulse repetition, 2.5 s).

7-Tropylionorbornane System (3a ⇌ 3b). The stereomutation was observed at 65, 75, and 85 °C. The sample solution in an NMR tube was heated in the corresponding thermostats, and the ^{13}C NMR spectrum was observed at 24 °C. The rate constants from **3a** to **3b** were obtained from the changes of the peak intensities $I_{27.4}$ at 27.4 ppm and $I_{30.9}$ at 30.9 ppm, i.e., in the equation $[(x_e/a) \ln \{x_e/(x_e - x)\} = k_1 t]$, $a = 1$, $x = a - \{I_{27.4}/(I_{27.4} + I_{30.9})\}$. The x_e values at 65, 75, and 85 °C were 0.498, 0.504, and 0.497, respectively.

2-Tropyliobicyclo[2.2.2]octane System (4a ⇌ 4b). The stereomutation was observed at 35, 50, and 65 °C. The sample solution in an NMR tube was heated in the corresponding thermostats, and the ^{13}C NMR spectrum was observed at −50 °C. The rate constants from **4a** to **4b** were obtained from the changes of the peak intensities $I_{19.6}$ at 19.6 ppm and $I_{28.1}$ at 28.1 ppm, i.e., in the equation $[(x_e/a) \ln \{x_e/(x_e - x)\} = k_1 t]$, $a = 1$, $x = a - \{I_{28.1}/(I_{19.6} + I_{28.1})\}$. The x_e values at 35, 50, and 65 °C were 0.499, 0.504, and 0.501, respectively.

2-Tropylioadamantane System (5a ⇌ 5b). The stereomutation was observed at 25, 50, and 75 °C. The sample solution in an NMR tube was heated in the corresponding thermostats, and the ^{13}C NMR spectrum was observed at −50 °C. The rate constants from **5a** to **5b** were obtained from the changes of the peak intensities $I_{32.5}$ at 32.5 ppm and $I_{39.5}$ at 39.5 ppm, i.e., in the equation $[(x_e/a) \ln \{x_e/(x_e - x)\} = k_1 t]$, $a = (I_{39.5} - I_{32.5})/(I_{32.5} + I_{39.5})$, $x = \{I_{32.5}/(I_{32.5} + I_{39.5})\} - a$. The x_e values at 25, 50, and 75 °C were 0.500, 0.487, and 0.482, respectively. The rate data are summarized in Table II.

Trapping of the Heptafulvenes by Tetracyanoethylene. A typical procedure follows. A solution of **3c**·ClO_4^- (800 mg, 2.81 mmol) and tetracyanoethylene (716 mg, 5.59 mmol) in acetonitrile (4 mL) was placed in an ampoule and degassed at <10^{-3} mmHg. The ampoule was sealed under nitrogen atmosphere and then heated at 85 °C for 74 h. After cooling, the solution was diluted with CH_2Cl_2 (50 mL) and washed with saturated aqueous $NaHCO_3$ (40 mL × 3) and saturated aqueous NaCl (40 mL × 1) and dried ($MgSO_4$). Evaporation of the solvent afforded a brown solid (368 mg). MPLC over SiO_2 (hexane–ether, 3:1) and recrystallization from hexane gave the [8 + 2] cycloaddition product **17** as a white powder: mp 139–140 °C. Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.90; H, 5.16; N, 17.94. Found: C, 77.02; H, 5.05; N, 17.66. Similarly, the [8 + 2] cycloaddition products **18** and **19** were obtained from **4c**·ClO_4^- and **5c**·ClO_4^- as white powders in 10–12% yields. **18**: mp 151–154 °C (from hexane). Anal. Calcd for $C_{21}H_{18}N_4$: C, 77.28; H, 5.56; N, 17.17. Found: C, 77.02; H, 5.47; N, 16.91. **19**: mp 167–168 °C (from hexane). Anal. Calcd for $C_{23}H_{20}N_4$: C, 78.38; H, 5.72; N, 15.90. Found: C, 78.35; H, 5.48; N, 15.60. The spectral data are summarized in Table III.

Isolation of the Heptafulvenes. 7-(2-Bicyclo[2.2.2]-octylidene)-1,3,5-cycloheptatriene (7). To a stirred solution of **4c**·ClO_4^- (131 mg, 0.438 mmol) in dry CH_2Cl_2 (2 mL) was added triethylamine (49.4 mg, 0.488 mmol) at room temperature. The

solution turned red immediately. After the solution was stirred for 5 min at room temperature, hexane (10 mL) was added. The solution was washed with 10% aqueous NaCl (5 mL × 3), dried ($MgSO_4$), and concentrated to 5 mL under argon atmosphere. Hexane (30 mL) was added to the concentrate, and again this solution was concentrated to 5 mL under argon atmosphere. MPLC over SiO_2 (hexane) of the concentrate under argon atmosphere furnished **7** (79.2 mg, 91%) as a deep red oil.

7-Adamantylidene-1,3,5-cycloheptatriene (8).[18] The procedure was essentially similar to that described for **7**. From **5c**·ClO_4^- (215 mg, 0.662 mmol) in dry CH_2Cl_2 (2 mL) and triethylamine (73.3 mg, 0.724 mmol) was obtained **8** (136 mg, 92%) as a deep red oil. The spectral data are summarized in Table IV.

Reaction of the Heptafulvenes 7 and 8 with Tetracyanoethylene. To a stirred solution of **4c**·ClO_4^- (92.5 mg, 0.310 mmol) in dry CH_2Cl_2 (1 mL) was added triethylamine (62.4 mg, 0.617 mmol) at room temperature. The solution turned red. After stirring for 1 min at room temperature, a solution of tetracyanoethylene (79.0 mg, 0.617 mmol) in CH_2Cl_2 (11 mL) was added. The red color disappeared immediately. After stirring for 30 min, the solution was washed with 10% aqueous NaCl (10 mL × 3) and dried ($MgSO_4$). Evaporation of the solvent afforded a brown solid (132 mg). MPLC over SiO_2 (hexane–ether) and then recrystallization from hexane gave the [8 + 2] cycloaddition product **18** as a pale yellow powder (71.4 mg, 71% based on **4c**·ClO_4^-).

In the similar manner, the [8 + 2] cycloaddition product **19** was obtained from **5c**·ClO_4^- (111 mg, 0.342 mmol) in dry CH_2Cl_2 (1 mL), triethylamine (35 mg, 0.34 mmol), and tetracyanoethylene (86.2 mg, 0.673 mmol) in CH_2Cl_2 (12 mL) as a pale yellow powder (100 mg, 83% based on **5c**·ClO_4^-).

IR, ^1H NMR, and ^{13}C NMR spectra for **18** and **19** thus prepared were superimposable with those of the cycloaddition products obtained by trapping experiments of hetpafulvene intermediates (vide supra).

Hydrogenation of 7 and 8. A solution of **7** (279 mg, 1.41 mmol) in ethyl acetate (12 mL) was hydrogenated using 10% Pd/C catalyst (63 mg) under atmospheric pressure at room temperature for 20 h. Filtration of the reaction mixture followed by evaporation of the solvent afforded a colorless oil (245 mg). Distillation using Kugelrohr (145–160 °C/1.5 mmHg) gave **20** (226 mg, 78%): IR (CCl_4) 2930 s, 2860 s, 1460 m cm^{-1}; ^1H NMR (CCl_4) δ 0.7–2.2 (m, 26 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 25.3, 26.2, 26.4, 26.7, 27.6, 28.5, 31.2, 32.6, 33.9 (CH_2), 25.1, 25.4, 29.2, 41.4, 43.2 (CH). Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.56; H, 12.99.

Similarly, hydrogenation of **8** (229 mg, 1.02 mmol) with 10% Pd/C catalyst (47 mg) in ethyl acetate (9 mL) under atmospheric pressure at room temperature for 21 h followed by distillation using Kugelrohr (145–160 °C/2 mmHg) afforded **21** (235 mg, 99%) as a colorless oil: IR (CCl_4) 2925 s, 2860 s, 1470 m, 1455 m, cm^{-1}; ^1H NMR (CCl_4) δ 1.0–2.0 (m, 28 H); ^{13}C NMR ($CDCl_3$) δ 26.3, 29.0, 31.2, 32.0, 38.4, 39.6 (CH_2), 27.9, 28.2, 29.2, 37.5, 48.8 (CH). Anal. Calcd for $C_{17}H_{28}$: C, 87.86; H, 12.18. Found: C, 87.80; H, 12.18.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 01648002) from the Ministry of Education, Science and Culture, Japan.

(18) A paper describes the ^{13}C NMR data for **8**, but it reports one extra signal [Adam, W.; Peters, E.-M.; Peters, K.; Rebollo, H.; Rosenthal, R. J.; Schnering, H. G. v. *Chem. Ber.* **1984**, *117*, 2393].

Anodic Amide Oxidations in the Presence of Electron-Rich Phenyl Rings: Evidence for an Intramolecular Electron-Transfer Mechanism

Kevin D. Moeller,* Po W. Wang, Sharif Tarazi, Mohammad R. Marzabadi, and Poh Lee Wong

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received April 23, 1990

The anodic oxidations of amides in the presence of mono-, di-, and trialkoxyphenyl rings were examined. Although literature reduction potentials suggest that these oxidations would lead to either selective aromatic ring oxidation or mixtures, the chemoselectivity of the reactions was found to be dependent on the substitution pattern of the phenyl ring. For example, the anodic oxidations of ((3-methoxyphenyl)acetyl)pyrrolidine, ((2-methoxyphenyl)acetyl)pyrrolidine, ((3-methoxy-4-(pivaloyloxy)phenyl)acetyl)pyrrolidine, and ((3,5-dimethoxy-4-(pivaloyloxy)phenyl)acetyl)pyrrolidine all led to selective methoxylation of the pyrrolidine ring. The anodic oxidations of ((4-methoxyphenyl)acetyl)pyrrolidine and ((3,4-dimethoxyphenyl)acetyl)pyrrolidine led to selective methoxylation of the benzylic carbon. Mechanistic studies indicate that both amide and aryl oxidation processes compete under the reaction conditions, but that intramolecular electron transfer leads to the selective formation of products. Evidence for this mechanism was obtained by examining the cyclic voltammogram of ((3-methoxyphenyl)-acetyl)pyrrolidine, competition studies, and the preparative electrolysis of ((4-methoxyphenyl)dimethyl-acetyl)pyrrolidine. The methoxylated amides were cyclized to form tricyclic amides using titanium tetrachloride.

The electrochemical oxidation of amides is among the most developed of electrochemical synthetic methods. It has been shown to be a versatile method for the preparation of *N*-(α-alkoxyalkyl)amides and hence *N*-acyliminium ions.[1] The potential power of these reactions lies in the oxidative alternative they can provide to the more common methods of *N*-acyliminium ion formation,[2] and the possibility they afford for developing a general annulation procedure for amines and amides.[3] However, a variety of questions still exist about the overall synthetic utility of these reactions. For example, although the anodic ox-

(1) For pioneering work, see: (a) Ross, S. D.; Finkelstein, M.; Peterson, C. *J. Am. Chem. Soc.* **1964**, *86*, 4139. Ross, S. D.; Finkelstein, M.; Peterson, C. *J. Org. Chem.* **1966**, *31*, 128. Ross, S. D.; Finkelstein, M.; Peterson, C. *J. Am. Chem. Soc.* **1966**, *88*, 4657. For reviews, see: (b) Shono, T. *Tetrahedron* **1984**, *40*, 11. (c) Shono, T.; Matsumura, Y.; Tsubata, K. In *Organic Synthesis*; Saucy, G., Ed.; John Wiley and Sons: New York, 1984; Vol. 63, p 206 and references therein.

(2) For reviews, see: (a) Zaugg, H. E. *Synthesis* **1984**, *85*, 181. (b) Speckamp, W. N.; Hiemstra, H. *Tetrahedron* **1985**, *41*, 4367. (c) Speckamp, W. N. *Recl. Trav. Chem. Pays-Bas* **1981**, *100*, 345.

(3) For a variety of examples, see: (a) Ban, Y.; Okita, M.; Wakamatsu, T.; Mori, M. *Heterocycles* **1980**, *14*, 1089. (b) Ban, Y.; Irie, K. *Heterocycles* **1981**, *15*, 201. (c) Ban, Y.; Irie, K. *Heterocycles* **1982**, *18*, 255. (d) Ban, Y.; Okita, M.; Wakamatsu, T. *Heterocycles* **1983**, *20*, 401. (e) Shono, T.; Matsumura, Y.; Uchida, K.; Tsubata, K.; Makino, A. *J. Org. Chem.* **1984**, *49*, 300. (f) Shono, T.; Matsumura, Y.; Uchida, K.; Tagami, K. *Chem. Lett.* **1987**, 919. (g) Mori, M.; Kagechika, K.; Tohjima, K.; Shibasaki, M. *Tetrahedron Lett.* **1988**, *29*, 1409.

0022-3263/91/1956-1058$02.50/0