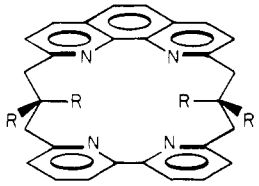

Figure 1. Perspective drawing of cyclophane **11** (R = CO_2CH_3).

corrected. ^1H and ^{13}C NMR spectra were determined on a Bruker WP-200 NMR spectrometer with $CDCl_3$ as solvent and Me_4Si as the internal standard. IR spectra were recorded on a Perkin-Elmer 621 grating-infrared spectrophotometer. Mass spectral (MS) data (70 eV) [reported as assignment, relative intensity] were determined by D. Patterson on a Hewlett-Packard HP 5985 GC/mass spectrometer. Reported R_f values were ascertained by a standardized thin-layer chromatographic (TLC) procedure: Baker-flex silica gel IB2-F plates by eluting with the stipulated solvent system. For preparative thick-layer chromatography (ThLC), 2-mm silica gel PF-254-366 plates were used. Elemental analyses were performed by R. Seab in these laboratories.

2,9-Bis(trichloromethyl)-1,10-phenanthroline (5). A stirred suspension of **4** (10 g, 50 mmol), NCS (39 g, 300 mmol), and benzoyl peroxide (50 mg) in CCl_4 (400 mL) was refluxed for 6 h. The mixture was cooled, filtered, and concentrated in vacuo to give a solid, which was dissolved in $CHCl_3$. The organic fraction was washed with a saturated aqueous Na_2CO_3 solution, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give **5**, as a pale yellow solid: 19.9 g (100%); mp 212–214 °C (lit.[5] mp 212–214 °C).

2,9-Bis(methoxycarbonyl)-1,10-phenanthroline (6). A stirred mixture of **5** (59 g, 140 mmol) and concentrated H_2SO_4 (27 mL) was heated to 90 °C for 2 h.[6] [*HCl gas was liberated*!] After cooling of the mixture, MeOH (65 mL) was *cautiously* added with rapid stirring, and then the solution was refluxed for 1 h. The mixture was cooled and neutralized *cautiously* with a saturated aqueous Na_2CO_3 solution and filtered to give (100%) **6**, as a light tan solid: mp 190–200 °C. The product was purified by sublimation to give (95%) the pure ester as colorless microcrystals: mp 210–212 °C (lit.[5] mp 213–214 °C).

2,9-Bis(hydroxymethyl)-1,10-phenanthroline (7). Solid $NaBH_4$ (3 g, 80 mmol) was slowly added to a solution of **6** (5 g, 20 mmol) in absolute EtOH (500 mL).[7] The solution was refluxed for 3 h, cooled, and concentrated to give a solid, which was dissolved in H_2O (200 mL) and continuously extracted with $CHCl_3$ for 6 h. The organic extract was concentrated in vacuo to give diol **7**, as light yellow microcrystals: 3.9 g (95%); mp 195–197 °C (lit.[5] mp 197–198 °C).

2,9-Bis(chloromethyl)-1,10-phenanthroline (8). To a solution of diol **7** (3 g, 12.5 mmol) in $CHCl_3$ (200 mL) was slowly added PCl_3 (12 mL) in $CHCl_3$ (20 mL) with constant stirring.[8] After addition was completed, the mixture was refluxed for 1 h and then concentrated in vacuo to give a viscous oil, which was neutralized with a saturated aqueous Na_2CO_3 solution. After filtration and washing with cold water, the bis chloride was isolated as a light yellow solid (which was further purified by passing through a short silica gel column eluting with CH_2Cl_2): 2.5 g (72%); mp 178–180 °C dec; ^1H NMR δ 5.11 (s, CH_2, 4 H), 7.83 (s, 5,6-phen H, 2 H), 7.95 (d, 3,8-phen H, J = 8.5 Hz, 2 H), 8.32 (d, 4,7-phen H, J = 8.5 Hz, 2 H); ^{13}C NMR δ 47.41 (CH_2Cl), 122.50 (C-3), 126.58 (C-5), 128.28 (C-4A), 137.35 (C-4), 144.77 (C-10B), 157.43 (C-2); IR (CsI) 1620, 1590, 1360, 1270, 1140, 850 cm^{-1}; MS, m/e 276 (M^+, 100), 241 (36.1), 205 (42.9). Anal. Calcd for $C_{14}H_{10}N_2Cl_2$: C, 60.69; H, 3.61; N, 10.11. Found: C, 60.32; H, 3.94; N, 9.88.

[3.3]Cyclophane (11). To a refluxing mixture of anhydrous THF (200 mL) and NaH (216 mg, 50% dispersion in oil) were added simultaneously over 3 h tetraester **10**[11] (500 mg, 1.7 mmol) in THF (100 mL) and **8** (311 mg, 1.1 mmol) in THF (100 mL) under an inert atmosphere, using high-dilution conditions.[12] After an additional 12 h of reflux, the excess NaH was cautiously neutralized with MeOH and then the mixture was concentrated in vacuo to give a solid, which was continuously extracted with $CHCl_3$. After concentration in vacuo the crude product (>50% yield, 90% purity) was chromatographed (ThLC) on alumina, eluting with $CHCl_3$/EtOAc (5:4), to give (45%) pure **11** as white crystals: mp 200 °C; ^1H NMR δ 3.55, 3.84 (2 s, Py/phen CH_2, 4 H each), 3.67 (s, OCH_3, 12 H), 7.35 (d, 3,8-phen H, J = 8.0 Hz, 2 H), 7.72 (s, 5,6-phen H, 2 H), 7.88 (d, 5-Py H, J = 7.0 Hz, 2 H), 8.10 (dd, 4-Py H, J = 7.0, 7.0 Hz, 2 H), 8.11 (d, 3-Py H, J = 7.0 Hz, 2 H), 8.43 (d, 4,7-phen H, J = 8.0 Hz, 2 H); ^{13}C NMR δ 38.9 (Py CH_2), 40.7 (phen CH_2), 52.5 (OCH_3), 58.3 [$C(CO_2CH_3)_2$], 119.5 (Py C-3), 123.3 (phen C-3,8), 123.8 (Py C-5), 126.0 (phen C-5,6), 127.5 (phen C-4a,4b), 136.0 (Py C-4), 137.7 (phen C-4 and C-7), 146.1 (phen C-10a and 10b), 156.0 (Py C-6), 156.6 (Py C-2), 157.7 (phen C-2,9), 171.5 (C=O); IR (CsI) 1720, 1550, 1430, 1200, 790 cm^{-1}. Anal. Calcd for $C_{36}H_{32}N_4O_8 \cdot CH_3OH$ (methanol found to be incorporated by TGA—approximately 4% loss of mass between 150 and 200 °C): C, 65.29; H, 5.33; N, 8.23. Found: C, 65.28; H, 4.98; N, 8.11.

Acknowledgment. We thank the National Science Foundation for partial support of this work.

Registry No. **4**, 484-11-7; **5**, 78831-41-1; **6**, 78831-35-3; **7**, 78831-36-4; **8**, 87518-61-4; **10**, 87518-62-5; **11**, 87518-63-6; i, 87518-64-7.

Solvolysis of [4.2.2]Propellan-7-yl Derivatives

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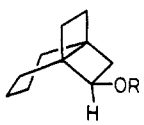
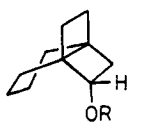
The solvolysis of constrained polycyclic cyclobutane derivatives has held considerable interest in recent years, because the geometry of the cyclobutane ring is of major importance in determining the solvolysis reactivity.[1] In this respect and in connection with the study on the carbocationic rearrangement of the propellanes involving a cyclobutane ring,[1f,2] we report here the solvolysis of tricyclic cyclobutane derivatives **1a** and **2a** having a highly strained [4.2.2]propellane framework.[3]





1a R = DNB **1b** R = H **1c** R = Ac

2a R = Ts **2b** R = H **2c** R = Ac

(1) (a) Wiberg, K. B.; Hess, B. A., Jr.; Ashe III, A. J. "Carbonium Ions"; Wiley-Interscience: New York, 1972; Vol III, Chapter 26, and references cited therein. (b) Dauben, W. G.; Reitman, L. N. *J. Org. Chem.* **1975**, *40*, 835. (c) Paquette, L. A.; Carmody, M. J. *Ibid.* **1978**, *43*, 1299. (d) Petty, R. L.; Ikeda, M.; Samuelson, G. E.; Boriack, C. J.; Onan, K. D.; McPhail, A. T.; Meinwald, J. *J. Am. Chem. Soc.* **1978**, *100*, 2464. (e) Diaz, A. F.; Miller, R. D. *Ibid.* **1978**, *100*, 5905. (f) Tobe, Y.; Hayauchi, Y.; Odaira, Y. *J. Org. Chem.* **1981**, *46*, 5219.

(2) (a) Tobe, Y.; Hayauchi, Y.; Sakai, Y.; Odaira, Y. *J. Org. Chem.* **1980**, *45*, 637. (b) Tobe, Y.; Terashima, K.; Sakai, Y.; Odaira, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2307. (c) Kakiuchi, K.; Hato, Y.; Tobe, Y.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 6. (d) Sakai, Y.; Toyotani, S.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1979**, 3855. (e) Sakai, Y.; Toyotani, S.; Ohtani, M.; Matsumoto, M.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1474. (f) Tobe, Y.; Yonezawa, T.; Kakiuchi, K.; Odaira, Y. *Ibid.* **1982**, *55*, 3262.

(3) Acid-catalyzed rearrangement of [4.2.2]propellan-2-yl derivatives has been shown by Eaton et al. to take place by way of 1,2-migration of the central propellane bond: Eaton, P. E.; Jobe, P. G.; Nyi, K. *J. Am. Chem. Soc.* **1980**, *102*, 6638.

0022-3263/83/1948-5114$01.50/0

Table I. Kinetic Data for the Solvolysis of 1a and 2a

compd	T, °C	k,[a] s⁻¹	ΔH‡, kcal/mol	ΔS‡, eu
1a[b]	30.0	(7.79 ± 0.08) × 10⁻⁵		
	50.0	(8.81 ± 0.06) × 10⁻⁴	22.9	−1.6
2a[c]	60.0	(5.32 ± 0.04) × 10⁻⁵	21.7	−13.1
	70.0	(1.52 ± 0.02) × 10⁻⁴		
	80.0	(3.68 ± 0.08) × 10⁻⁴		

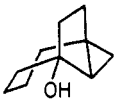
[a] Average of two runs; the standard errors in table indicate deviation from the average. [b] Hydrolysis in 80% aqueous acetone (v/v) without 2,6-lutidine. [c] Sodium acetate buffered acetolysis.

Table II. Relative Rates of [4.2.2]Propellan-7-yl and Bicyclo[2.2.0]hex-2-yl Derivatives

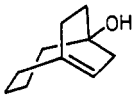
compd	k,[a] s⁻¹	k_{rel}
1a *exo*-[4.2.2]propellanyl	8.81 × 10⁻⁴	3.6 × 10⁹
2a *endo*-[4.2.2]propellanyl[b]	1.9 × 10⁻¹²	7.7
6 *endo*-bicyclo[2.2.0]hexyl[c]	1.9 × 10⁻⁵	8 × 10⁷
7 *exo*-bicyclo[2.2.0]hexyl[b]	2.4 × 10⁻¹³	1.0

[a] Estimated rates of the corresponding 3,5-dinitrobenzoates in 80% aqueous acetone at 50 °C. [b] Estimated from the rate of acetolysis of the tosylate 2a or 7 (ref 6a) using an approximate factor of 10⁷ for the difference in the rate between a tosylate in acetic acid and a dinitrobenzoate in 80% acetone (ref 8). [c] Estimated from the reported k_{endo}/k_{exo} ratio (ref 6b) and the value for endo isomer.

exo-3,5-Dinitrobenzoate **1a** and *endo*-tosylate **2a** were prepared from the corresponding alcohols **1b** and **2b**, which were in turn obtained by lithium aluminum hydride reduction of the acetates **1c** and **2c**.[4,5] The product study on the solvolysis of **1a** was carried out in 80% aqueous acetone (v/v) containing 10 equiv of 2,6-lutidine to afford 6-hydroxytricyclo[4.2.2.0^{1,7}]decane (**3**) predominantly



3



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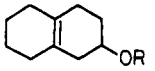


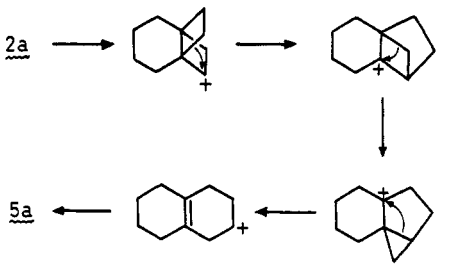
5a R = Ac

5b R = H

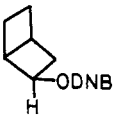
(86%), along with a small amount of 6-hydroxybicyclo[4.2.2]dec-1(8)-ene (**4**) (6%), which were identified with their authentic samples.[2e] On the other hand, sodium acetate buffered acetolysis of **2a** gave 3-acetoxybicyclo[4.4.0]dec-1(6)-ene (**5a**) as the major product (89%), together with 5% of the unrearranged acetate **2c** and a trace of unidentified olefins. The structure of **5a** was established by lithium aluminum hydride reduction to the alcohol **5b**, whose authentic sample was prepared independently.[7]

The kinetic data on the hydrolysis of **1a** and on the acetolysis of **2a** are listed in Table I. The relative rates of [4.2.2]propellanyl and bicyclo[2.2.0]hex-2-yl derivatives[6] are summarized in Table II. As shown in Table II, the

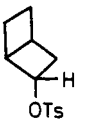
Scheme I



propellane derivatives are more reactive than the corresponding bicyclo[2.2.0] derivatives; *exo*-**1a** is more reactive than **6** by a factor of more than 40 times, and *endo*-**2a** solvolyzes 7.7 times faster than **7**.



6



7

The products from the solvolysis of **1a** and the very large exo/endo rate difference (k_{exo}/k_{endo} = 4.7 × 10⁸) indicate that the solvolysis of **1a** occurs with σ participation of the central propellane bond. The above observation represents a relatively rare example of the migration of the central bond in the carbocationic rearrangement of [*m.n.*2]propellanes[2c,3] and should be contrasted to the cases of the less strained [*m*.3.2]propellanes, which solvolyze by way of the migration of the external cyclobutane bond.[2a,b,9] More interestingly, it is deduced from the fact that the solvolysis rate of **1a** is greater than that of **6**, that the participation of the central cyclobutane bond of **1a** is greater than that in **6** due to the larger degree of strain, although the rearranged bridgehead cations, such as tricyclo[4.2.2.0^{1,7}]dec-6-yl and bicyclo[4.2.2]dec-1(8)-en-6-yl, seem to be considerably strained.[10]

On the other hand, in the case of *endo*-tosylate **2a**, the formation of **5a** is explained in terms of the migration of the external bond of the other cyclobutane component, a process well-known in the acid-catalyzed rearrangement of [*m.n.*2]propellanes,[2a,b,9] followed by further migrations as shown in Scheme I, on the basis of the mechanistic consideration of the acetolysis of *exo*-bicyclo[2.2.0]hex-2-yl tosylate (**7**).[6a,c] A slight enhancement in the solvolysis rate of **2a** compared to **7** may be due to steric acceleration associated with the steric crowding in the endo direction of **2a** by the conformationally mobile six-membered ring.

It is therefore concluded that the solvolysis behavior of [4.2.2]propellan-7-yl derivatives **1a** and **2a** are critically dominated by the exo/endo stereochemistry of the leaving group: *exo*-**1a** solvolyzes with participation of the central propellane bond, whereas *endo*-**2a** solvolyzes with assistance of the external bond of the other cyclobutane component. Moreover, **1a** and **2a** are more reactive than the corresponding bicyclo[2.2.0]hex-2-yl derivatives **6** and **7** because of increased σ participation of the central bond and steric acceleration, respectively.

(4) The acetates **1c** and **2c** were prepared by the Baeyer–Villiger oxidation of the corresponding methyl ketones (Tobe, Y.; Ohtani, M.; Kakiuchi, K.; Odaira, Y. *Tetrahedron Lett.*, **1983**, *24*, 3639), which were derived by reaction of the propellanecarboxylic acids[2d,e] with methyllithium.

(5) The solvolysis study of *exo*- and *endo*-[4.2.2]propellanyl systems was carried out with *exo*-3,5-dinitrobenzoate (**1a**) and *endo*-tosylate (**2a**) for the purpose of comparison with the corresponding bicyclo[2.2.0]hex-2-yl derivatives **6** and **7**.[6] However, the kinetic study on the solvolysis of **1a** was undertaken in 80% aqueous acetone instead of a 60% solvent system[6b] because of the limited solubility of **1a** in the latter solvent.

(6) (a) McDonald, R. N.; Reineke, C. E. *J. Org. Chem.* **1967**, *32*, 1878. (b) McDonald, R. N.; Davis, G. E. *J. Am. Chem. Soc.* **1972**, *94*, 5078. (c) McDonald, R. N.; Curi, C. A. *Ibid.* **1979**, *101*, 7116 and 7118.

(7) House, H. O.; Blankley, C. J. *J. Org. Chem.* **1968**, *33*, 53.

(8) Wiberg, K. B.; Williams, V. Z., Jr.; Friedrich, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 564.

(9) (a) Cargill, R. L.; Crawford, J. W. *J. Org. Chem.* **1970**, *35*, 356. (b) Cargill, R. L.; Beckham, M. E.; Damewood, J. R.; Pond, D. M.; Bundy, W. A. *Ibid.* **1972**, *37*, 78. (c) Peet, N. P.; Cargill, R. L.; Bushey, D. F. *Ibid.* **1973**, *38*, 1218. (d) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106.

(10) The cation center being formed in the rearrangement of **1a** is tertiary rather than secondary. This may also contribute to the greater solvolysis rate of **1a** than that of **6** in addition to the strain release factor.

Experimental Section[11]

***exo*-[4.2.2]Propellan-7-yl 3,5-Dinitrobenzoate (1a).** To a suspension of 31 mg (0.82 mmol) of lithium aluminum hydride in 10 mL of ether was added a solution of 132 mg (0.68 mmol) of acetate **1c**[4] in 5 mL of ether, and the mixture was stirred at room temperature for 1 h. Water was added, followed by 1 N hydrochloric acid, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined extracts were washed with sodium bicarbonate solution and water and then dried ($MgSO_4$). Evaporation of the solvent gave 105 mg (96%) of **1b** as a waxy solid. An analytical sample of **1b** was obtained by preparative GLC: mp 63–65 °C; IR (KBr) 3400, 1080, 1020 cm^{-1}; MS, *m/e* (relative intensity) 152 (M^+, 29), 111 (37), 110 (46), 95 (45), 91 (41), 79 (100), 57 (46), 41 (38); ^1H NMR (CCl_4) δ 1.0–2.8 (m, 15 H), 4.14 (t, J = 8 Hz, 1 H).

Dinitrobenzoate **1a** was prepared in the usual manner,[12a] followed by aqueous workup in 85% yield, which was recrystallized from petroleum ether: mp 86–88 °C; IR (KBr) 3070, 1710, 1615, 1530, 1330, 1260, 1150, 700 cm^{-1}; ^1H NMR (CCl_4) δ 1.0–2.8 (m, 14 H), 5.24 (t, J = 8 Hz, 1 H), 9.0–9.2 (m, 3 H). Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 58.80; H, 5.23; N, 7.94. Found: C, 58.96; H, 5.24; N, 8.09.

***endo*-[4.2.2]Propellan-7-yl Tosylate (2a).** Alcohol **2b** was prepared from acetate **2c**[4] in a manner similar to that described for **1b** in 87% yield: mp 78–80 °C; IR (KBr) 3350, 1110, 1050 cm^{-1}; MS, *m/e* (relative intensity) 152 (M^+, 12), 119 (47), 109 (56), 95 (75), 93 (88), 91 (69), 81 (75), 79 (97), 67 (85), 55 (69), 41 (100); ^1H NMR (CCl_4) δ 1.0–2.2 (m, 13 H), 2.37 (dd, J = 6 and 12 Hz, 1 H), 2.73 (br s, 1 H), 4.22 (t, J = 6 Hz, 1 H). *p*-Nitrobenzoate:[12a] mp 104–106 °C. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.62; H, 6.30; N, 4.55.

Tosylate **2a** prepared in the usual fashion[12b] would not crystallize, though spectral and analytical data indicated that it was sufficiently pure. It was subsequently used in the kinetic and preparative runs without further purification: IR (neat) 3070, 1595, 1350, 1160, 1070, 650 cm^{-1}; ^1H NMR (CCl_4) δ 1.0–2.3 (m, 14 H), 2.41 (s, 3 H), 4.83 (t, J = 6 Hz, 1 H), 7.24 (d, J = 8 Hz, 2 H), 7.68 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.64; H, 7.24. Found: C, 66.20; H, 7.32.

Preparative Solvolysis of 1a. A solution of 80 mg (0.23 mmol) of **1a** and 246 mg (2.3 mmol) of 2,6-lutidine in 50 mL of 80% aqueous acetone (v/v) was heated under reflux for 24 h. Acetone was evaporated in vacuo, and the solution was extracted with ether. The extracts were combined, washed with 1 N hydrochloric acid, sodium bicarbonate solution, and water, and then dried ($MgSO_4$). Evaporation of the solvent gave 32 mg (92%) of a mixture of alcohols **3** and **4** in a ratio of 93:7 (GLC). The products were separated by preparative GLC and identified with their authentic samples[2e] by GLC, IR, and ^1H NMR spectra.

Preparative Acetolysis of 2a. A solution of 700 mg (2.29 mmol) of **2a** and 377 mg (4.60 mmol) of sodium acetate in 80 mL of acetic acid was heated at 80 °C for 48 h. The solution was diluted with water and extracted with ether. The combined extracts were washed with sodium bicarbonate solution and water and then dried ($MgSO_4$). Evaporation of the solvent gave 433 mg of pale yellow oil involving acetates **5a** (87%) and **2a** (5%) and a small amount of two unidentified olefins: MS, *m/e* 134. The products were isolated by column chromatography on silica gel, followed by preparative GLC. **5a**: IR (neat) 1730, 1240, 1030 cm^{-1}; MS, *m/e* (relative intensity) 194 (M^+, trace), 134 (100), 119 (65), 92 (70), 91 (76), 43 (61); ^1H NMR (CCl_4) δ 1.4–2.3 (m, 17 H), 4.75–5.04 (m, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.86; H, 9.50.

Lithium aluminum hydride reduction of **5a** was carried out as described above to afford **5b**, which was identical in GLC, IR, and ^1H NMR spectra with an authentic sample prepared independently by the method of House et al.[7]

Kinetic Measurements. Hydrolysis of 1a. Solutions of **1a** (0.05 M) in 80% aqueous acetone (v/v) were placed in a thermo-controlled bath, and 3.0-mL aliquots were removed at appropriate intervals and titrated with a 0.0040 M solution of sodium hydroxide in methanol by using Bromothymol blue indicator.

Acetolysis of 2a. The rates of the buffered acetolysis of **2a** were measured by the titrimetric method as previously described.[2a]

Registry No. **1a**, 87495-01-0; **1b**, 87554-09-4; **2a**, 87495-02-1; **2b**, 87554-10-7; **3**, 77871-22-8; **4**, 77871-16-0; **5a**, 31517-53-0.

(11) IR spectra were recorded on a Hitachi 260-10 spectrometer. ^1H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer. Mass spectra were measured on a Hitachi RMU-6E instrument. Analytical GLC was carried out on a Hitachi 163 gas chromatograph with 10% FFAP and 5% SE-30 columns, and preparative GLC separation was conducted on a Varian Aerograph 920 chromatograph.

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The 2,3-Dimethyl-3-fluoro-2-butyl Cation Revisited: Exclusive Methyl Exchange Ruling Out Fluorine Shift through Bridged Fluoronium Ion[1]

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The intermediacy of alkene halonium ions in electrophilic addition of halogens to olefins is well recognized. In fact, a wide variety of chloronium, bromonium, and iodonium ions have been prepared and studied.[2] Several studies on the fluorination of olefins have lead to the suggestion of trivalent fluorocarbenium ions as intermediates.[3] However, there is little evidence[4] for the bridged fluoronium ion formation in solution. On the other hand, in the gas phase, Beauchamp and co-workers[5] reported to have observed the $C_2H_6F^+$ ion in ion–molecule reactions using ion–cyclotron resonance spectrometry and referred to it as the dimethylfluoronium ion. By the very nature of the technique, however, no unequivocal structural proof could be obtained.

In an attempt to observe the tetramethylethylenefluoronium ion **2** in solution, Olah and Bollinger[6] ionized 2,3-difluoro-2,3-dimethylbutane in SbF_5/SO_2 at −90 °C. The ^1H NMR spectrum of the acid solution at −90 °C showed a deshielded doublet at δ 3.10 (J = 11.0 Hz), indicating the formation of an ionic species wherein all the methyl groups are equivalent with a long-range proton-fluorine coupling in between that of two and three bonds in magnitude. In the ^{19}F NMR spectrum the observed fluorine signal was deshielded by ca. 31.0 ppm from the difluoro progenitor. On the basis of these data, it was suggested[6] that the ion obtained was the 2,3-dimethyl-3-fluoro-2-butyl cation (α-fluorodimethylisopropylcarbenium ion) **1**, wherein the methyl groups become equivalent either by a fast intramolecular fluorine exchange or by methyl group shifts. The formation of a long-lived tetramethylethylenefluoronium ion **2** was ruled out on the basis of comparison with model compounds. If equilibration of ion **1** occurred through rapid intramolecular fluorine exchange, one could invoke **2** as a noncontributing high-lying intermediate or a transition state (Scheme I, path 1). Indeed,

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(2) Olah, G. A. "Halonium Ions"; Wiley-Interscience: New York, 1975.

(3) Merritt, R. F. *J. Am. Chem. Soc.* **1967**, *89*, 609.

(4) Peterson has proposed a cyclic fluoronium ion as either an intermediate or a transition state in 1,4-fluorine migration reactions: Peterson, P. E.; Bopp, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1283.

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