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.

(12) (a) Yano, K. *J. Org. Chem.* **1975**, *40*, 414. (b) Coates, R. M.; Yano, K. *J. Am. Chem. Soc.* **1973**, *95*, 2203.

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,

(1) Stable Carbocations. 252. For part 251, see: Olah, G. A.; Singh, B. P. *J. Org. Chem.*, in press.

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

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

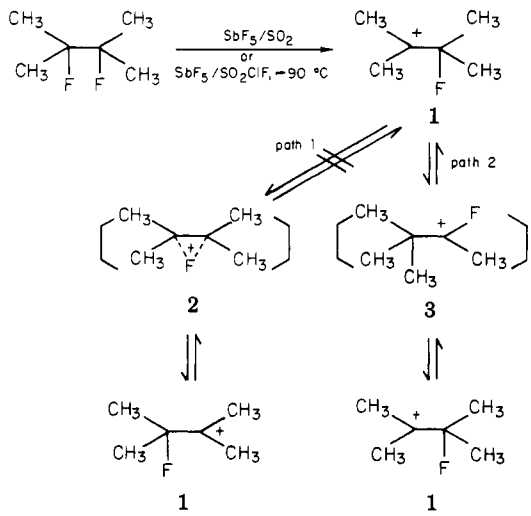
(4) Peterson has proposed a cyclic fluoronium ion as either an intermediate or a transition state in 1,4-fluorine migration reactions: Peterson, P. E.; Bopp, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1283.

(5) Beauchamp, J. L.; Holtz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798.

(6) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 4744.

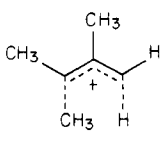
0022-3263/83/1948-5116$01.50/0

Scheme I



such a structure has been proposed by Clark, based on theoretical calculations.[7] If the exchange involves only rapid 1,2-methyl migration, then the 3,3-dimethyl-2-fluoro-2-butyl cation ((1-fluoro-1-*tert*-butyl)ethyl cation) **3** should be involved. These two possibilities, however, could not be distinguished on the basis of ^1H and ^{19}F NMR studies.[6]

We now report a ^{13}C NMR spectroscopic study of ion **1** in SbF_5/SO_2ClF solution that clearly rules out equilibration through rapid intramolecular fluorine exchange. The proton-decoupled 20-MHz ^{13}C NMR spectrum of ion **1** at −80 °C shows absorptions at δ 324.3 (C^+, broad <20 Hz), 115.2 (β CF, doublet, J = 208.8 Hz) and 36.3 (av CH_3, doublet, J = 13.2 Hz). The observation of three signals as opposed to two clearly supports the methyl migration pathway (path 2) through 1-fluoro-1-*tert*-butylethyl cation **3**. Further support comes from the observation of a highly deshielded carbocationic center, as well as a strongly coupled β-fluoro carbon. Attempts to freeze out the rapid methyl migration, even at −120 °C, were unsuccessful. There is no appreciable change in the NMR spectrum between −60 and −120 °C, except for some viscosity-induced line broadening, indicating that ion **3** is only a noncontributing higher lying intermediate. Below −120 °C, ion **1** tends to precipitate out of the acid solution, hindering further lower temperature studies. One can estimate an upper limit of 5 kcal/mol for the barrier of equilibration. Ion **1** at −40 °C irreversibly rearranges to the 2,3-dimethylbutenyl cation **4**. The ^{13}C chemical shifts of **4** are δ 272.4 (singlet), 170.8 (triplet), 154.8 (singlet), 37.3, 34.3, and 17.8 (quartets). The formation of **4** can be readily rationalized by a deprotonation–ionization mechanism.



4

The present study shows that there is no evidence for a fluorine shift, and consequently involvement of bridged tetramethylethylenefluoronium ion either as an intermediate or a transition state is clearly ruled out in the equilibration of the 2,3-dimethyl-3-fluoro-2-butyl cation **1** in superacid solution.

We know of no evidence for fluoronium ions in solution chemistry. Attempted acid-catalyzed isomerization of fluoroaromatics, including *o*-difluorobenzene, was unsuccessful,[8] again indicating the resistance of fluorine to participate in bridging with adjacent electrophilic centers, which would place partial positive charge on the fluorine. This is in contrast to electrophilic fluorination[9] with polarized or complexed elementary fluorine, where the weak F–F bond is sufficiently polarizable to allow electrophilic character on fluorine but certainly not formation of a positive fluorine ion.

Experimental Section

2,3-Difluoro-2,3-dimethylbutane was prepared from 2,3-dimethyl-2-butene as described.[6,10]

Preparation of the Ion. The difluoro precursor, dissolved in SO_2ClF precooled at −78 °C (dry ice/acetone bath), was slowly added with vigorous stirring to a freshly prepared solution of SbF_5/SO_2ClF at −90 °C (ethanol/liquid N_2 slush) in a 10-mm NMR tube so as to obtain an approximately 10–15% solution of the ion.

The ^{13}C NMR spectra were obtained on a Varian Associates Model FT-80 spectrometer equipped with a variable-temperature broad-band probe. The ^{13}C NMR chemical shifts are in part per million from external capillary tetramethylsilane.

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Registry No. **1**, 53172-48-8; **2**, 53172-53-5; **3**, 53172-41-1; **4**, 71983-43-2; 2,3-difluoro-2,3-dimethylbutane, 17603-29-1.

(7) Clark, D. T. In "Special Lectures of the 23rd International Congress of Pure and Applied Chemistry", Boston, 1971; Butterworth: London, Vol. 1, p 31.

(8) Olah, G. A., Schleyer, P. v. R., Eds. In "Carbonium Ions"; Wiley Interscience: New York, 1976; Vol. V, p 2207.

(9) (a) Barton, D. H. R.; Hesse, R. H.; Markwell, R. E.; Pechet, M. M.; Toh, H. T. *J. Am. Chem. Soc.* **1976**, *98*, 3034. (b) Lerman, O.; Rozen, S. *J. Org. Chem.* **1983**, *48*, 724 and references cited therein. (c) Rozen, S., unpublished results.

(10) Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872.

"Anti-Hammond" Transition-State Structural Variation in the Context of Marcus' Rate Theory

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Marcus' rate equation has been shown to be quite useful in the description of atom-transfer and group-transfer reactions,[1] even though it originally[2] was derived from a model for outer-sphere electron transfer. For example, it has been applied extensively to analyses of substituent and isotope effects on proton transfer[3] and has been used to correlate rates of methyl transfers in aqueous solution.[4]

Such general applicability is to be expected, since the form of Marcus' rate equation results from the widely valid

(1) For a critical review of applications of Marcus' rate theory, see: Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227–263.

(2) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679–701, and earlier papers cited therein.

(3) For example: (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891–899. (b) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475–503. (c) Kresge, A. J. In "Isotope Effects on Enzyme-Catalyzed Reactions"; Cleland, W. W., O'Leary, M. H., Northrup, D. B., Eds.; University Park Press: Baltimore, 1977; pp 37–63. (d) Kreevoy, M. M. In "Isotopes in Organic Chemistry"; Buncel, E., Lee, C. C., Eds.; Elsvier: Amsterdam, 1976; Vol. 2; pp 1–31.

(4) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87–157.

0022-3263/83/1948-5117$01.50/0