

Table 5. Tolerance limits in the determination of Sc³⁺ (5 mg/l)

Foreign ions	Amount added(mg/L)	ppt. wt obtained at 104°C (cm)	ppt. wt obtained at 900°C (cm)
Sc ³⁺ only	5.00(0.111 M)	76.9	19.5
Al ³⁺ added	100(3.70 M)	76.9	19.7
Mg ²⁺ added	100(4.11 M)	77.1	20.1
Ca ²⁺ added	100(2.49 M)	78.8	20.1
Fe ³⁺ added	10.0(0.179 M)	82.3	20.3
	50.0(0.899 M)	88.1	23.5
	100(1.79 M)	93.6	30.4

ratio between Sc and P is 1:2.

Effects of foreign ions. The effects of foreign ions co-existing in tin slag solution were investigated in the procedure of precipitation of scandium and DEHPA. The result is Table 5.

This data show that iron ion among the ions influence the gravimetric determination of scandium using Sc-DEHPA precipitation method and other ions have no interference.

Conclusion

(1) The gravimetric determination of scandium with DEHPA as a precipitant in ethanol medium has been investigated.

(2) The mole ratio of Sc-DEHPA precipitate is 1:2 in ethanol medium.

(3) The formula of precipitate ignited at 900°C is Sc₂O₃(PO₃)₂.

(4) The gravimetric determination of scandium dried at 105°C was better than the method ignited at 900°C.

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π -Participation in Bicyclo[3.2.1]oct-6-en-2-yl Cation. ¹⁹F NMR Spectroscopy as a Probe

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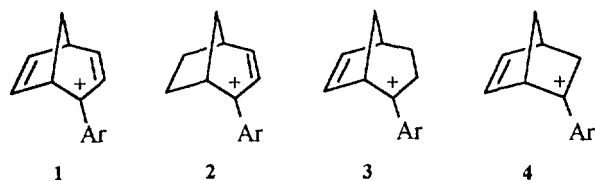
p-Fluorophenyl bicyclo[3.2.1]oct-6-en-2-yl cation (3) prepared in FSO₃H-SO₂-ClF solution at -90°C and examined by fluorine-19 nmr spectroscopy. The nmr data give a clear evidence for the formation of a stabilized π -bridging cation species in superacids. The degree of π delocalization in this cation is found to be inferior to the onset of nonclassical stabilization in 2-norbornenyl cation.

Introduction

Ever since the π -bridged formulation of the 2-arylnorbor-

nenyl 2-brosylate in solvolytic media by Brown¹, various approaches have been made by physical organic chemists to confirm the existence of such cationic species. Using the tool

of increasing electron demand, combined with ^{13}C -NMR spectroscopy as a probe, Farnum and co-workers² well demonstrated the nonclassical π -participation in 2-arylnorbornen-2-yl cation in superacids.



In an earlier paper³ we reported the ^{19}F -NMR study for 2-*p*-fluorophenylbicyclo[3.2.1]octa-3,6-diene-2-yl cation (1) and 2-*p*-fluorophenylbicyclo[3.2.1]oct-3-en-2-yl cation (2), in which ^{19}F chemical shift in cation (1) is considerably more downfield than that of cation (2). This result is in accordance with the corresponding solvolytic study on *p*-nitrobenzoate of bicyclo[3.2.1]octa-3,6-dienyl by Diaz.⁴ He suggested that the 6,7-double bond in diene-derivatives makes a four π -electrons antiaromatic cation species, and thus retards the reaction rate in contrast with monoene analog. During these investigations, it occurred to us that the relative stability of allylic cation *vs.* homoallylic cation species in these bicyclic systems might be interesting.

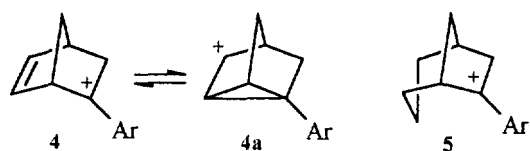
We now wish to report in this paper the ^{19}F -NMR study of 2-*p*-fluorophenyl bicyclo[3.2.1]oct-6-en-2-yl cation (3) and of its relative stability compared to the 2-*p*-fluorophenylbicyclo[3.2.1]oct-3-en-2-yl cation (2). The bicyclo[3.2.1]octa-3,6-dienyl cation (1) and the 2-*p*-fluorophenyl norbornen-2-yl cation (4) were also examined as to get more information on the degree of π delocalization and the trend of charge delocalization. These cations were generated from the corresponding carinols in $\text{FSO}_3\text{H}\text{-SO}_2\text{ClF}$ solution at low temperature.

Results and Discussion

The use of ^{13}C -NMR rather than ^1H -NMR spectroscopy offered advantages as a probe into carbocation structures because of the large magnitude of the chemical shifts and of the opportunity to look directly at cationic carbons where the effect of a structural change would be maximized. However, it also presented recurring doubts about the reliability of the empirical charge-chemical shift correlation in cations.⁵ ^{13}C chemical shifts are also considerably sensitive to molecular geometry. It instead become a widely accepted practice to rationalize steric ^{13}C shifts effects in terms of the repulsive forces between closely spaced atoms.⁶ Whereas carbon chemical shifts are usually confined to a range of 250 ppm, the resonance of fluorine nuclei encompass a much larger range of approximately 500 ppm.⁷ Thus, for study of relative stability and substituent effects in cations, ^{19}F -NMR spectroscopy has the advantage of greater sensitivity to electron demand of the cation center.

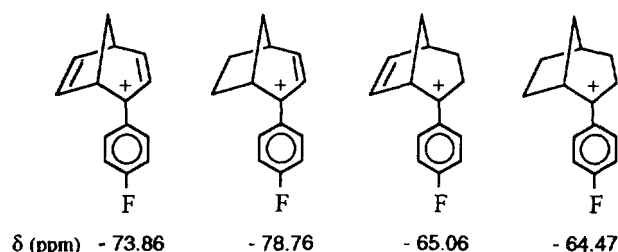
In solvolytic study of bicyclic systems, Brown¹ concluded that the 2-arylnorbornenyl-2-tosylates exhibit π -participation only when the aryl group was the very electron demanding 3,5-bis(trifluoromethyl)phenyl group. This conclusion was based on high *exo:endo* reaction rate and product ratio in the acetolysis of 2-norbornenyl brosylates.⁸

In the comparison of the ^{13}C chemical shifts of the cationic carbon, C (2), the chemical shift at the cationic carbon of cation 4, Ar=3,5-bis(trifluoromethyl)phenyl, is the same as that for the model cation 5 (282.2 ppm).²



If the cation 4 has π -participation in superacids, chemical shift of cationic carbon should appear at more upfields than that for the cation 5. Thus, Farnum and co-workers suggested that the cation 4 exists as the mobile equilibrium cation pair $4 \leftrightarrow 4a$, based on a reasonable linear free energy relationship for the equilibrium constants. The variation in the chemical shifts of the olefinic carbons, C-5 and C-6, can similarly be interpreted in term of an equilibrium between 4 and 4a. In spite of the easy accommodation of the data by the mobile equilibrium, they are emphasized that π bridging in the cation 4 or any combination of π bridging and equilibrating would not differ qualitatively in accommodating data. However, they suggested that the onset of π -bridging occurs with less electron demanding aryl groups in the 2-norbornenyl cation 4.

The fluorine atom in the *p*-fluorophenyl bicyclo[3.2.1]oct-6-en-2-yl cation appeared at δ -65.06 ppm. ^{19}F chemical shift in this cation is a bit upfields by 0.6 ppm compared with saturated bicyclo[3.2.1]oct-2-yl cation (δ -64.47 ppm). This result provides a clear evidence for π -electronic interaction with vacant *p*-orbital in cationic carbon.



When a positive charge is dispersed into an adjacent *p*-fluorophenyl ring, the chemical shift of the fluorine atom on the phenyl ring moves downfield compared with that of the uncharged species.⁹ Less efficient charge delocalization in the *p*-fluorophenyl ring should result in greater charge dispersion by the neighboring group. Thus, the chemical shift of fluorine atom can provide important information on the degree of charge delocalization through neighboring group participation.

The ^{19}F -chemical shift of the *p*-fluorophenyl bicyclo[3.2.1]oct-3-en-2-yl cation (2) (δ -78.76) appeared at considerably more upfields than that of the *p*-fluorophenyl bicyclo[3.2.1]oct-6-en-2-yl cation (3) (δ -65.06). It revealed that double bond in cation 3, C-6, is vastly inferior in the stabilization of positive charge through π participation (homoallylic conjugation) to that of the double bond (C-3) in cation 2. In other word, the allylic cation is extremely stable species³, we confirmed, the additional double bond (C-6) in bicyclo[3.2.1]octa-3,6-dienyl cation (1) exerted an unfavorable nonbonded interac-

tion between the vacant *p*-orbital at cationic carbon. However, the chemical shift of the fluorine atom in cation **1** indicated exceptionally upfield compared to that of cation **3**, even though the cation **1** was a four π -electrons *antiaromatic* cation species.

The fluorine atom in 2-*p*-fluorophenyl-2-norbornenyl cation (**4**) appeared at δ -66.98 ppm and the 5-methyl-2-*p*-fluorophenyl norbornenyl cation in which double bond was activated by a methyl substituent gave a ^{19}F resonance at δ -68.83 ppm.⁹ The signal of the fluorine atom in this cation was shifted considerably upfields (1.92-3.77 ppm) relative to that of bicyclo[3.2.1]oct-6-en-2-yl cation **3**. This nmr data reveals the π -electronic interaction between the cationic center and the remote double bond in cation **3** is smaller than that of the 2-norbornenyl cation (**4**).

In the comparison of these results by ^{19}F -NMR data, therefore, we strongly suggests that the *p*-fluoropheny bicyclo[3.2.1]oct-6-en-2-yl cation (**3**) exists as π -bridging species in superacids. Moreover, the degree of π delocalization in this cation was found to be vastly inferior to that of the 2-norbornenyl cation (**4**).

Experimental Section

NMR Spectra. The proton and fluorine-19 nmr spectra were obtained on a Bruker AC-80 spectrometer. Spectra of neutral compounds were recorded at room temperature in CDCl_3 solution and chemical shifts were reported in ppm relative to tetramethylsilane and external CFCl_3 . Spectra of the cations were recorded at $-90^\circ\text{C} \sim -70^\circ\text{C}$ using 5 mm tubes containing a trace of CD_2Cl_2 for field stabilization. Chemical shifts were reported in ppm relative to CD_2Cl_2 (internal reference) and external CFCl_3 . Assignment of carbon-13 spectra was assisted by DEPT experiment.

Synthesis of Bicyclo[3.2.1]oct-6-en-2-one. Ketone was prepared 10: mp. $63\text{--}80^\circ\text{C}$ (Lit.: $65\text{--}81^\circ\text{C}$); mass spectrum m/e 122 (M^+); $^1\text{H-NMR}$ (CDCl_3) δ 6.26-5.94 (dq, 2H), 3.10-1.62 (m, 8H); $^{13}\text{C-NMR}$ (CDCl_3) δ 210.09, 137.66, 131.75, 55.80, 41.91, 38.62, 34.43, 25.14; IR (KBr) cm^{-1} : 3060, 2880, 2500, 1700, 1580, 1220, 1080, 720, 700.

9-*p*-Fluorophenyl bicyclo[3.2.1]oct-6-en-2-ol. The ketone (350 mg) was added in *p*-fluorophenyl magnesium bromide in anhydrous diethyl ether at room temperature, and the mixture was heated under reflux for 1 hr, hydrolyzed, and extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and the filtrate was eva-

porated in vacuo to give crude alcohol. The alcohol was purified by silica gel column using $\text{CH}_2\text{Cl}_2(\text{R}_f', 0.3)$ as the eluant to give 365 mg (69%) of alcohol as white solid: mass spectrum m/e 218 (6, m^+), 200 (8), 156 (1), 152 (11), 138 (19), 123 (31), 95 (12), 80 (18), 79 (12), 78 (9), 77 (7), 55 (9); $^1\text{H-NMR}$ (CDCl_3) δ 7.57 (t, 2H), 6.13 (dq, 2H), 2.66-1.42 (m, 9H); $^{13}\text{C-NMR}$ (CDCl_3) δ 152.06, 135.96, 132.93, 127.92, 114.38, 73.33, 51.60, 40.46, 38.90, 33.30, 24.32; $^{19}\text{F-NMR}$ (CDCl_3) δ 116.17; IR (KBr) cm^{-1} 34.27 (m), 3044 (w), 2953 (m), 2870 (w), 1605 (w), 1506 (s), 1225 (s), 1159 (m), 1051 (m), 1009 (m), 837 (s), 734 (s), 590 (s), 536 (m).

Preparation of *p*-fluorophenyl bicyclo[3.2.1]oct-6-en-2-yl Cations. The alcohol (20 mg) was dissolved in CD_2Cl_2 and the resulting solution slowly added dropwise to a vigorous stirring $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ solution (1.5 ml) at -120°C , in maintained under a blanked of nitrogen. The nmr spectra were recorded at -80°C ; $^1\text{H-NMR}$ (CD_2Cl_2) δ 8.79 (q, 2H), 7.59 (t, 2H), 7.11 (t, 2H), 6.14 (t, 1H), 5.26 (m, 1H), 3.66 (m, 2H), 2.4-1.50 (m, 5H); $^{19}\text{F-NMR}$ (CD_2Cl_2) δ 65.067.

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