To probe the geometrical effects of cyclopropyl moiety on the stabilization of an adjacent cation center, $^{19}$F chemical shift of 2-p-fluorophenyl-8,9-dehydro-2-adamantyl cation (3) was compared with that of 5-p-fluorophenyl-2,4-dehydro-5-homoadamantyl cation (4). Difference between the $^{19}$F chemical shift of 8,9-dehydro-2-adamantyl cation 3 and that of 2,4-dehydro-5-adamantyl cation 4 is 5.1 ppm ($\Delta\delta$). We conclude, therefore, that ion 3 is about 3.32 kcal more stable than ion 4 of which rigid carbon skeleton requires significant distortion of the cyclopropane ring from the ideal bisected conformation. The energy difference between these cations can be calculated by Taft-relationship on the basis of $^{19}$F chemical shift.

**Introduction**

It is generally conceded that the bisected conformation of cyclopropylcarbinyl cations is the most stable. Molecular orbital calculations indicate that there is stabilization of 9.16 kcal/mol between the bisected (1) and perpendicular (2) conformations (Figure 1). It is in the bisected orientation that the cyclopropyl moiety exhibits the largest stabilizing effect on an adjacent positively charged center whereas it destabilizes a carbocation when fixed in a perpendicular orientation. In the case of secondary and tertiary cyclopropylcarbinyl cations, nmr studies have led to conclusion that these ions exist in the bisected arrangement. In previous $^{19}$F nmr study, we have shown that the electronic effects were very sensitive to the conformation of the cyclopropane ring toward the vacant $p$ orbital in rigid cyclopropylcarbinyl cations. We have reported our results of $^{19}$F nmr studies on cyclopropylcarbinyl cations. We here report our results of $^{19}$F nmr studies on 2-p-fluorophenyl-8,9-dehydro-2-adamantyl (3) and 5-p-fluorophenyl-2,4-dehydro-5-homoadamantyl cations (4) under stable ion condition.

8,9-Dehydro-2-adamantyl cation 3 is one of the most typical systems which geometrically constrained. Since its feature is the symmetrical bisected conformation, it may be most favored for the $\pi$-conjugative interaction between a strained cyclopropyl moiety and an adjacent cation center. In contrast, 2,4-dehydro-5-homoadamantyl cation 4 has a geometry in which rigid carbon skeleton requires slight distortion of the cyclopropane ring from the bisected conformation.

In view of these points, we were interested in examining the relative stability of 8,9-dehydro-2-adamantyl cation 3 and 2,4-dehydro-5-homoadamantyl cation 4 using $^{19}$F nmr parameters. Despite of similar nuclear properties of fluorine and proton, there is an essential difference in the nmr parameters of the two nuclei. Whereas proton chemical shifts are usually confined to a range of 13 ppm, the resonance of fluorine encompasses a much broader range of approximately 500 ppm. Therefore, $^{19}$F-nmr has a advantage of the great sensitivity compared to $^1$H-nmr, and the comparative insensitivity to magnetic anisotropies of solvent and molecule.

It has been known that the fluorine nuclear magnetic resonance shielding or $p$-fluorophenyl derivatives is predominantly determined by the MO theory $\pi$-electron charge density at the $p$-carbon atom since the former is apparently directly related to the latter.

Thus there is theoretical basis for both direct shielding-$\pi$-charge density and shielding-$\pi$-electronic energy relationship. The latter relationship, however, can be directly utilized in the understanding of correlation between substituent shielding and reactivity parameter. A linear correlation of fluorine nmr parameters with the stabilization energy for substituted triarylcations was observed by Taft.

Using the Taft's $^{19}$F chemical shifts correlation line (slope: 1 ppm/0.75 kcal), therefore, we were compared to the relative stability and calculated a difference of stabilization energy between ion 3 and 4, and these results are described in this paper.

**Experimental**

$^1$H nmr spectra were obtained in CDCl$_3$ at 100 MHz, using a Varian XL-100 instrument, and chemical shifts were referenced from internal TMS. Cation solutions were made up
to approximately 10% (v/v) concentration by adding the corresponding carbinal in CD$_2$Cl$_2$ to stirred FSO$_2$H-SO$_2$Cl solution at -120 °C using a cation generation apparatus. ¹⁹F nmr spectra were recorded using Varian XL-100 spectrometer. The chemical shift in ¹⁹F nmr spectra were measured in ppm relative to an external standard CFCl$_3$.

**Synthesis of Carbinals**

8,9-dehydro-2-adamantalone, 2,4-dehydro-5-homoadamantaneone and 4-homoadamantaneone were prepared by the literature procedures. Adamantalone is commercially available. The Carbinals were prepared by the Grignard reaction of the corresponding ketone with p-fluorobromobenzene in dried ether and were purified by column chromatography (Merck silica gel, Art. 7734).

**2-P-Fluorophenyl-8,9-dehydro-2-adamantyl-2-ol.**

$^1$H nmr(CDCl$_3$): 1.2-1.7(m, 4H), 1.7-2.6(m, 5H), 7.0(t, 2H), $^1$⁹F nmr(CDCl$_3$): -113.5 ppm.

**2-P-Fluorophenyl-2-adamantyl-2-ol.**

$^1$H nmr(CDCl$_3$): 1.6(s, 1H), 1.8-2.4(m, 1H), 2.4(s, 3H), 7.1(t, 2H), 7.6(q, 2H), $^1$⁹F nmr(CDCl$_3$): -114.4 ppm.

**5-P-Fluorophenyl-2,4-dehydro-5-homoadamantyl-2-ol.**

$^1$H nmr(CDCl$_3$): 1.2-2.6(m, 15H), 7.3(d, 2H), 7.8(q, 2H), $^1$⁹F nmr(CDCl$_3$): -116.1 ppm.

**4-P-Fluorophenyl-4-homo adamantyl-4-ol.**

$^1$H nmr (CDCl$_3$): 1.2-2.4(m, 14H), 2.8(m, 3H), $^1$⁹F nmr(CDCl$_3$): -115.6 ppm.

**Results and Discussion**

2-p-Fluorophenyl-8,9-dehydro-2-adamantyl(3) and 5-p-fluorophenyl-2,4-dehydro-5-homoadamantyl(4) cations were prepared from the corresponding carbinals in FSO$_2$H-SO$_2$Cl solution at -120 °C. The $^1$⁹F nmr spectra were recorded at -70 °C, and their chemical shift shown in Table 1.

The chemical shifts of the fluorine atom, 3 and 4, are -81.41 ppm and -77.02 ppm, respectively. The absorption signal of the fluorine atom in ion 3 appears upfield ($\Delta \delta$ = 3.38 ppm) compared to that of ion 4. This result reveals that the magnitudes of charge density delocalized into phenyl ring in ion 3 is considerably smaller than that in ion 4. In other words, it may suggest that the extent of positive charge being delocalized into cyclopropylmoeity in 8,9-dehydro-2-adamantyl cation 3 is a larger than that of 2,4-dehydro-5-homoadamantyl cation 4.

An examination of molecular model shows that substantially different representations of dehydro-5-homoadamantyl cation 4 the dihedral angle $\phi$ between the axis of the vacant p-orbital at C-5 and the adjacent cyclopropane ring should be about 30°-40°. Thus it is anticipated that the cone formation of cyclopropyl moiety situated for overlap with vacant p-orbital at cation center in contrast to the 8,9-dehydro-2-adamantyl cation 3. Indeed, the relative stability between ion 3 and ion 4 cannot be directly compared using $^1$⁹F chemical shifts because ring size and steric effects in cyclic hydrocarbon systems may influence the $^1$⁹F chemical shifts. Therefore, we have prepared 2-p-fluorophenyl-2-adamantyl cation 5 and 4-p-fluorophenyl-4-homoadamantyl cation 6, and $^1$⁹F nmr spectra of these cations also were recorded at -70 °C. The chemical shift of fluorine atom in ions, 5 and 6, are -63.23 and -63.96 ppm, respectively.

There is 18.18 ppm difference between the $^1$⁹F chemical shift of 8,9-dehydro-2-adamantyl cation 3 and that of 2-adamantyl cation 5 with the identical ring size but devoid of cyclopropyl moiety, and the corresponding value in the homologous series 2,4-dehydro-5-homoadamantyl cation 4 and 4-homoadamantyl cation 6 is 13.08 ppm. Thus the difference in $^1$⁹F chemical shift between 8,9-dehydro-2-adamantyl cation 3 and 2,4-dehydro-5-homoadamantyl cation 4 can be corrected to be 5.1 ppm ($\Delta \delta$, Table 1).

From this results, it suggests that ion 3 is more stable than ion 4. This remarkable difference in charge stabilizing power of cyclopropyl moiety must be attributed to the structural difference between 8,9-dehydro-2-adamantyl cation 3 and 2,4-dehydro-5-homoadamantyl cation 4, i.e., the difference in the dehedral angle $\phi$ between the axis of the vacant p-orbital at cation center and the adjacent cyclopropyl moiety. According to the Taft's $^1$⁹F chemical shift correlation, it can be calculated that 5.1 ppm corresponds roughly to 3.82 kcal.

We conclude, therefore, that 8,9-dehydro-2-adamantyl cation 3 is about 3.82 kcal more stable than 2,4-dehydro-5-homoadamantyl cation 4 of which rigid carbon skeleton requires significant distortion of the cyclopropyl moiety from ideal bisected conformation (Figure 1).

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**References**