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¹⁹F NMR Studies on 8,9-Dehydro-2-adamantyl and 2,4-Dehydro-5-homoadamantyl Cations

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To probe the geometrical effects of cyclopropyl moiety on the stabilization of an adjacent cation center, ¹⁹F 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 ¹⁹F chemical shift of 8,9-dehydro-2-adamantyl cation 3 and that of 2,4-dehydro-5-homoadamantyl cation 4 is 5.1 ppm ($\Delta\delta$). We conclude, therefore, that ion 3 is about 3.82 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-Relationship⁸ on the basis of ¹⁹F chemical shift.

Introduction

It is generally conceded that the bisected conformation of cyclopropylcarbinyl cations is the most stable¹. Molecular orbital calculations² 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 carbenium ion 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 arrangement³. In our previous ¹⁹F nmr study⁴, 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 here report our results of ¹⁹F 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 conformation⁵, it may be most favored for the σ -conjunctive 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 the examining the relative stability of 8,9-dehydro-2-adamantyl cation 3 and 2,4-dehydro-5-homoadamantyl cation 4 using ¹⁹F nmr parameters. Despite of similar nuclear properties of fluorine 19 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 broad range of approximately 500 ppm⁶. Therefore, ¹⁹F-nmr has an advantage of the great sensitivity compared to ¹H-nmr, and the com-

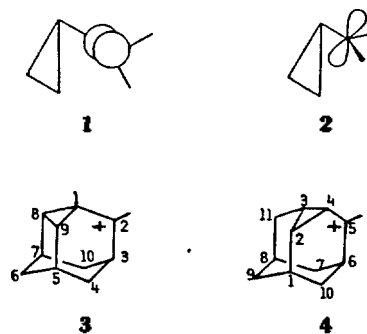


Figure 1.

parative 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 π -electron charge density at the p-carbon atom since the former is apparently directly related to the latter⁷.


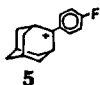

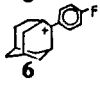
Thus there is theoretical basis for both direct shielding- π -charge density and shielding- π -electronic energy relationship. The latter relationship, however, can be directly utilized in the understanding of correlation between substituent shielding and reactivity parameter. A linear correlation of fluorine nmr parameters with the stabilization energy for substituted tritylcations was observed by Taft⁸.

Using the Taft's ¹⁹F chemical shifts correlation (line of 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

¹H nmr spectra were obtained in CDCl₃ at 100 MHz, using a Varian XL-100 instrument, and chemical shifts were referenced from internal TMS. Cation solutions were made up

Table 1. Comparison of ^{19}F NMR Chemical Shifts. Chemical Shifts are Referenced to External Standard CFCl_3 (δ , ppm)

Compound	δ ^{19}F	Compound	δ ^{19}F	$\Delta\delta_3$
	-81.41		-63.23	18.18
	-77.02		-63.96	13.08
	$\Delta\delta_1$ 4.327		$\Delta\delta_2$ 0.73	$\Delta\Delta\delta$ 5.1

to approximately 10% (v/v) concentration by adding the corresponding carbinol in CD_2Cl_2 to stirred $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ solution at -120°C using a cation generation apparatus. ^{19}F nmr spectra were recorded using Varian XL-100 spectrometer. The chemical shift in ^{19}F nmr spectra were measured in ppm relative to an external standard CFCl_3 .

Synthesis of Carbinols

8,9-Dehydro-2-adamantanone, 2,4-dehydro-5-homoadamantanone and 4-homoadamantanone were prepared by the literature procedures⁹. Adamantanone is commercially available. The Carbinols 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-adamantan-2-ol. ^1H nmr(CDCl_3); 1.2-1.7(m, 3H), 1.7-2.6(m, 9H), 7.0(t, 2H), ^{19}F nmr(CDCl_3); -115.3 ppm.

2-p-Fluorophenyl-2-adamantan-2-ol. ^1H nmr(CDCl_3); 1.6(s, 1H), 1.8(s, 10H), 2.4(s, 1H), 2.6(s, 3H), 7.1(t, 2H), 7.6(q, 2H). ^{19}F nmr(CDCl_3); -114.4 ppm.

5-p-Fluorophenyl-2,4-dehydro-5-homoadamantan-2-ol. ^1H nmr(CDCl_3); 1.1-2.0(m, 15H), 7.3(d, 2H), 7.8(q, 2H), ^{19}F nmr(CDCl_3); -116.1 ppm.

4-p-Fluorophenyl-4-homoadamantan-4-ol. ^1H nmr(CDCl_3); 1.2-2.4(m, 14H), 2.8(m, 3H), ^{19}F 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 carbinols in $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ solution at -120°C . The ^{19}F nmr spectra were recorded at -70°C , and their chemical shift shown in Table 1.

The chemical shifts of the fluorine atom in ion, 3 and 4, are -81.41 kppm and -77.02 ppm, respectively. The absorption signal of the fluorine atom in ion 3 appears upfield ($\Delta\delta$ 4.38 ppm) compared to that of ion 4. This result reveals that the magnitude of charge density delocalized into phenyl ring in ion 3 is considerably smaller than that in ion 4. In other word, it may suggest that the extend of positive charge being delocalized into cyclopropyl moiety 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 for such an idealized representation of dehydro-5-homoadamantyl cation 4 the dihedral angle ϕ between the axis of the vacant p-orbital at C-5 and the adjacent cyclopropane ring should be about 30° ¹⁰. Thus it is anticipated that the conformation 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 ^{19}F chemical shifts because ring size and steric effects in cyclic hydrocarbon systems may influence the ^{19}F chemical shifts. Therefore, we have prepared 2-p-fluorophenyl-2-adamantyl cation 5 and 4-p-fluorophenyl-4-homoadamantyl cation 6, and ^{19}F 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 ^{19}F 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 ^{19}F 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 ($\Delta\Delta\delta$, Table).

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 dihedral angle ϕ between the axis of the vacant p-orbital at cation center and the adjacent cyclopropyl moiety. According to the Taft's ^{19}F 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).

Acknowledgement. The authors gratefully acknowledge the financial support of Ministry of Education (Grant no. ED87-304).

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