

플루오르 19-NMR 을 이용한 구조적으로 고정된 사이크로프로필카르비닐 양이온의 상대적 안정도의 비교

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Study on Relative Stability of Geometrically Constrained Cyclopropylcarbinyl Cation by ¹⁹F-NMR Spectroscopy

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요 약. 고정된 사이크로 프로판환을 가진 양이온계에서 구조적 변화에 따른 상대적 안정도를 플루오르 19-핵자기공명분광기로 분석 검토했다. 이를 위해 8-파라-플루오벤젠트리사이크로 옥탄 양이온과 9-파라플루오벤젠 트리사이크로 노난 및 10-파라플루오벤젠 트리사이크로데칸 양이온을 해당알코올과 불화 황산과의 반응에서 얻었다. 플루오르 19-NMR 스펙트럼에서 얻어진 결론은 사이크로프로판환이 양이온 탄소의 궤도와 σ 컨쥬게이션을 위해 대칭적이며 바이섹트 구조의 유지가 하전의 안정화에 매우 중요한 요인인 반면, 사이크로 프로판환의 면과 양하전을 띤 탄소와 연결되는 결합각도(θ)의 변화는 하전의 안정화에 영향을 없음을 보여주었다.

ABSTRACT. The relative stability as a function of geometry in rigid cyclopropylcarbinyl cations was examined by ¹⁹F-nmr spectroscopy. 8-*p*-Fluorophenyl-tricyclo[3.3.1.0^{2,7}]octane-8-yl- (I), 9-*p*-fluorophenyl-tricyclo [3.3.1.0^{2,8}]nonane-9-yl- (II), and 10-*p*-fluorophenyl-tricyclo[4.3.1.0^{2,9}]decane-10-yl cation(III) were prepared from the corresponding carbinols in FSO₃H-SO₂ClF solution at -120°C. ¹⁹F-nmr data indicate that the symmetrical bisected geometry of cyclopropane ring for σ -conjugation is a very important factor in charge delocalization. However, varied orientation of the bond angle θ within the bisected conformation does not affect the charge delocalization into the cyclopropane ring.

1. INTRODUCTION

The renowned conjugative interaction of cyclopropane ring with cationic center continues to be demonstrated impressively. Cyclopropyl-carbonium ions are unusually stable^{1,2}. The fast rate of solvolysis of cyclopropylcarbinyl derivatives was originally attributed to the stabilization accompanying the formation of a through space σ -conjugation with one or both of the far

carbon atoms of the cyclopropane ring³.

Rhodes suggested that the angle of the orientation of the cyclopropane ring to the developing cation center exerted a larger influence on rates of solvolysis in the rigid cyclopropylcarbinyl systems⁴.

From results of many experimental studies and theoretical calculations, it is clear that the bisected conformation of a cyclopropyl carbinyl cations is energetically favored over the perpen-

dicular conformation⁵. For example, the rigid geometry of 3-nortricycyl derivatives forces them to exist in the bisected arrangement. Comparing the rate of solvolysis⁶ and results of nmr studies for 3-nortricycyl cation⁷ with 7-norbornyl derivatives, 3-nortricycyl systems are known to be enormously more reactive than the 7-norbornyl systems.

In view of these observations, we were interested in examining the relative stability of rigid cyclopropyl-carbinyl cations with varied bond angle (θ) between the plane of cyclopropane ring and the bond connecting cyclopropane ring to the cationic carbon. In order to examine the structural effect on relative stability, we prepared and studied 8-*p*-fluorophenyl-tricyclo [3.2.1.0^{2,7}] octan-8-yl-(I), 9-*p*-fluorophenyl-tricyclo [3.3.1.0^{2,8}] nonan-9-yl(II), and 10-*p*-fluorophenyl-tricyclo [4.3.1.0^{2,9}] decan-10-yl cation(III) by using ¹⁹F-nmr spectrometer in FSO₃H-SO₂ClF in temperature range -125°C to -60°C.

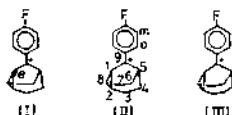


Fig. 1.

2. RESULTS AND DISCUSSIONS

The carbinols were synthesized by the reaction of the Grignard reagent, *p*-fluorophenyl-magnesiumbromide, with corresponding ketones in absolute ether. Preparation and identification of carbinols are described in the Experimental Section. Carbonium ions were prepared from related carbinols using the following general procedure; a solution of a pure carbinol in deuterated methylene chloride was added dropwise into the mixture of fluorosulfonic acid and sulfur chloride fluoride(SO₂ClF) (1:5, V/V) at -120°C using a special cation genera-

tion apparatus. The nmr spectra of carbonium ions did not change from -120°C to -30°C and were recorded at -60°C.

At -60°C the ¹H-nmr spectrum of ion I shows different groups of protons with chemical shift at δ 2.4(H₃, H₄) as double singlet, 2.8(H₆) as multiplet, 4.2(H₁, H₅) as multiplet, 4.4(H₂) as broad singlet, 4.7(H₇) as multiplet, 7.8(H_m) as triplet and 8.4(H_o) as broad multiplet. The signals for protons of the ion shifted downfield compared with those of the corresponding carbinol. Particularly, a considerably downfield shift of H₁, H₂ and H₇ in cyclopropane ring means that more positive charge is distributed over cyclopropane moiety in cation I.

The ¹H-nmr spectrum of ion II was recorded at -60°C. The nmr signals of the different groups of protons appear at δ 2.4(H₃, H₄, H₆, H₇) as broad singlet, 3.8(H₈) as singlet, 4.2(H₁) as triplet, 4.7(H₂, H₈) as doublet, 7.5(m_o) as triplet and 8.3(H_o) as double doublet. Protons (H₁, H₂, H₈) in cyclopropane ring in ion II shifted also considerably downfield relative to the corresponding carbinol, and this may be attributed to an effective charge delocalization into adjacent cyclopropane ring.

The ¹H-nmr spectrum of ion III was also recorded at -60°C. The nmr signals of H₃, H₄, H₅, H₇ and H₈ appear at δ 2.3 as complex multiplet. Protons H₁, H₂ and H₈ in cyclopropane ring give rise to signals at δ 4.4 and 4.9 as broad multiplet, also shifted downfield compared to those of other protons. Comparing ¹H-chemical shifts of cyclopropylcarbinyl cation with each other, it is strongly suggested that these cations have similar electronical structure in terms of charge delocalization over cyclopropane ring. However, it was difficult to correlate the degree of charge delocalization with different bond angle (θ) by ¹H-nmr spe-

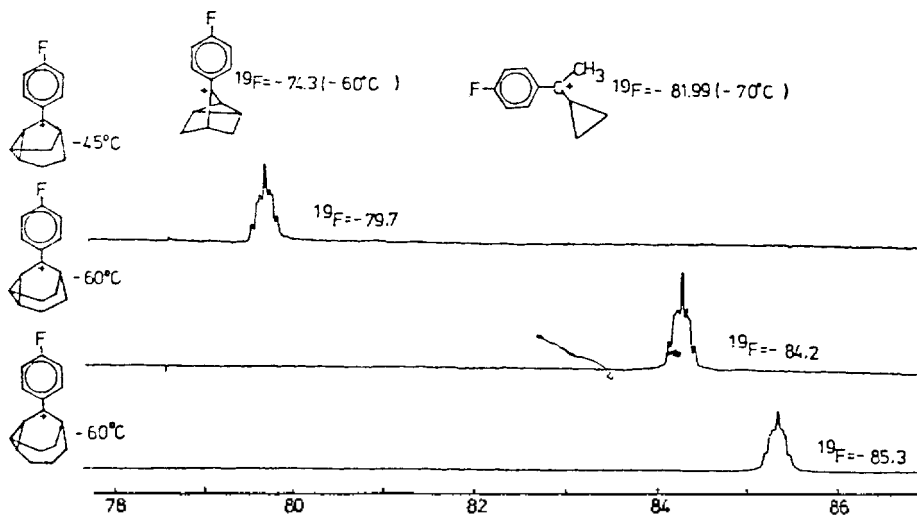


Fig. 2.

ctroscopy.

An important evidence for relative stability as a function of bond angle (θ) in rigid cyclopropylcarbiny cations can be obtained from ^{19}F -nmr data. The ^{19}F -nmr spectroscopy is advantageous due to its greater sensitivity to electron demands of the cationic center and immediate surroundings. The ^{19}F -nmr spectra for ions shows in Fig. 2, and spectra was recorded at -60°C

The chemical shift of the fluorine atom in ion I appear at $\delta -79.7$, in ion II at $\delta -84.2$ and in ion III at $\delta -85.3$. The signal of the fluorine atom in ion III appear considerably upfield (5.6ppm) compared to that of ion I, suggesting more effective charge delocalization by adjacent cyclopropane ring. In other words, the value of ^{19}F -chemical shifts in *p*-fluorophenyl substituted carbonium ions provides the information about degree of charge delocalization into phenyl ring.

Although both the ion II and 3-nortricyclyl cation (IV) possess the same symmetrical bisected conformation, the nmr signal of the fluorine atom in ion II shifted considerably upfield

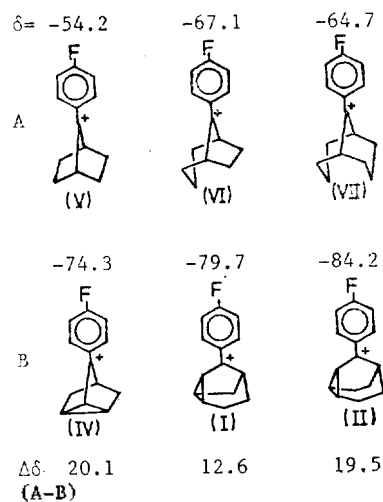


Fig. 3. Cation was prepared in $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ solution, and chemical shifts give in part per million from external CCl_3F or computer analyzed data.

(approximately 10 ppm) compared to that of 3-nortricyclyl cation. This result may suggest larger charge delocalization into cyclopropane ring in ion II than that of ion IV but the difference in ring sizes should also be considered.

Thus, they should be compared with model

cations with essentially identical ring sizes, and their ^{19}F -nmr data as well as $\Delta\delta$ -value are shown in Fig. 3.

^{19}F -nmr data for ion V, VI and VII had been reported by Volz and co-Workers⁸.

Surprisingly, the $\Delta\delta$ -value in case of the ion II is very similar to that of ion IV, in spite of the difference in ring size of the two cation species. Although the bond angle(θ) in ion II was varied by insertion of methylene in rigid 3-nortricycyl framework, structure of ion II must assume a symmetrically bisected conformation in the same manner as in the 3-nortricycyl cation (IV). Thus, the large $\Delta\delta$ -value (19.4 ppm) in case of the ion II compared to that of the ion I (12.6 ppm) is assumed to be due to the considerably charge delocalization from cationic center into cyclopropane ring.

Recently, it has been demonstrated that the bisected geometry has been shown to be the most favored for the interaction (σ -conjugation) between exocyclic cyclopropane orbital and the vacant p-orbital in cationic carbon.

In conclusion, the result of ^{19}F -nmr studies on relative stability in closely related series of rigid cyclopropylcarbinyl cations confirm that the symmetrically bisected geometry of the cyclopropane ring is a very important factor to stabilization of the cyclopropylcarbinyl cations through σ -conjugation. The bond angle(θ) between the plane of cyclopropane ring and the bond connecting cyclopropane ring to the cationic center appears to exert little influence on the degree of charge delocalization into cyclopropane ring.

3. EXPERIMENTAL

General Procedures. All carbonium ion precursors were characterized by IR, ^1H -, ^{19}F -, and ^{13}C -nmr, and mass spectra. Spectroscopic data were determined on Perkin-Elmer 283 infrared

spectrophotometer and Schmidaz GC-MS LKB 9000 mass spectrometer. Nmr spectra were recorded on a Varian EM-360 or XL-100 spectrometer, TMS being used as internal standard, and in CDCl_3 as lock. Cation solution were made up to approximately 10% concentration by addition of the corresponding carbinol in CD_2Cl_2 to stirred fluorosulfonic acid and SO_2ClF at -120°C using ion generation apparatus. The chemical shift in ^1H -nmr spectrum of cations were determined from referenced internal CD_2Cl_2 (δ 5.4) and ^{19}F -chemical shift were taken up from computer analyzed data.

(1) Synthesis of carbinols

① **8-p-Fluorophenyl-tricyclo [3. 2. 1. 0^{2,7}] octan-8-ol(I-A). Ethyl 3-cyclohexene-1-carboxylate(1).** To a rapidly stirred mixture of 6.8g (0.05mole) of anhydrous aluminium chloride and 50g(0.5mole) of ethyl acrylate in 250ml of dry benzene is bubbled butadiene for 5h. The reaction temperature was maintained at $55\sim 60^\circ\text{C}$ during bubbling of 1,3-butadiene. After 5h the reaction mixture was cooled, and then poured into ice water and extracted with benzene. The extract was washed once with water and dried over magnesium sulfate. Solvent was removed and residue was fractionated to yield 71.6g (93%) of **1**, bp $61^\circ\text{C}/6\text{mmHg}$, ^1H -nmr(CDCl_3); δ 1.2(*t*, 3H), 2.1(*m*, 7H), 4.0(*q*, 2H), 5.6(*s*, 2H)

3-Cyclohexene-1-yl diazomethylketone(2). 3-Cyclohexen-1-carboxylic acid was prepared by hydrolysis of carboxylate **1** with ethanolic potassium hydroxide. The reaction mixture was worked up by usual procedure. The crude product was obtained in 95% yield, bp $62^\circ\text{C}/10\text{mmHg}$; ^1H -nmr (CDCl_3); δ 1.9~2.4(*m*, 7H), 5.6(*s*, 2H), 12(*s*, 1H). To a stirred solution of 7g(0.05mole) of 3-cyclohexene-1-carboxylic acid in 70ml anhydrous benzene was added dropwise 10g of thionyl chloride. After addition

of thionyl chloride, the reaction mixture was heated to reflux for 2h. Removal of the benzene on a rotary evaporator gave 7g (86.5%) of acid chloride as oil: $^1\text{H-nmr}$ (CDCl_3); δ 2.2 (*m*, 6H), 2.8 (*m*, 1H), 5.6 (*s*, 2H). To a stirred ethereal solution of diazomethane, which was prepared from Diazald (Aldrich, D2, 800-0) and potassium hydroxide in diglyme, was added dropwise 7g of acid chloride in 20ml of absolute ether. The reaction mixture was chilled in an ice-bath prior to and during the addition of the acid chloride, and was stirred for 4h and allowed to stand overnight. Removal of solvent under reduced pressure gave crude diazomethylketone **2** as a yellow oil: $^1\text{H-nmr}$ (CDCl_3); δ 1.6~2.4 (*m*, 7H), 5.3 (*s*, 1H), 5.6 (*s*, 2H).

Tricyclo [3.2.1.0^{2,7}] octan-8-one (3). To a refluxed suspension of 10g activated copper powder in 200ml of *n*-hexane was added dropwise the solution of 7g acid chloride in 60ml *n*-hexane. After addition of acid chloride **2**, the reaction mixture was heated to reflux for 4h. copper powder was removed from the crude product and *n*-hexane distilled. The ketone **3** was purified by column chromatography on silica gel using methylene chloride as eluent. mp 41~42°C: $^1\text{H-nmr}$ (CDCl_3); δ 1.65, 1.75, 1.95, 2.07, 2.17.

8-p-Fluorophenyl-tricyclo[3.2.1.0^{2,7}]octan-8-ol (I-A). To a stirred solution of the Grignard reagent prepared from 4-bromofluorobenzene (6.3g, 0.03mole) and magnesium turning (1.5g, 0.05mole) in absolute ether was added dropwise the ethereal solution of 3g (0.023 mole) of ketone **3**. After addition of ketone **3**, the reaction mixture was refluxed with stirring for 1h and cooled. The reaction mixture was poured into ice-water and worked up by usual procedure, and was obtained 6.5g (82%) of crude carbinol I. The carbinol I was purified by column chromatography on alumina. $^1\text{H-nmr}$ (CDCl_3); δ

1.1 (*m*, 1H), 1.6 (*m*, 6H), 2.01 (*t*, 2H), 6.89 (*t*, 2H), 7.4 (*q*, 2H): $^{19}\text{F-nmr}$ (CDCl_3); δ -115.4. IR (CCl_4) (cm^{-1}); 3600 (*s*), 2940 (*s*), 2870 (*s*), 1600 (*s*), 1500 (*s*), 1350 (*s*), 1300 (*m*), 1150 (*s*), 1020 (*s*), 920 (*w*), 830 (*s*).

② **9-p-Fluorophenyl-tricyclo[3.3.1.0^{2,8}]nonan-9-ol (II-A)**. A mixture of 50g (0.49 mole) of cyclopentanone and 55g (0.77mole) of pyrrolidine in 150ml benzene was placed in 250ml round bottom flask in Dean-Stark trap and the solution was heated to reflux for 4h. After the separation of water (theoretical amount 8.8ml) from reaction mixture, solvent was removed on rotary evaporator. Residue was fractionated to yield 56g (83%) of 1-pyrrolidino-1-cyclopentene, bp 88~90°C/15mmHg. A solution of 56g (0.41 mole) of 1-pyrrolidino-1-cyclopentene in 400ml of dry dioxane was cooled to -5°C in ice-salt bath. To the stirred chilled solution was added dropwise 24g (0.43 mole) of acrolein during 45 minute. The mixture was allowed to stand overnight at room temperature, and solvent was removed and residue was fractionated to give 36g (45%) of 1-pyrrolidino-bicyclo [3.2.1]octan-8-one, bp 110~115°C/0.5 mmHg: $^1\text{H-nmr}$ (CDCl_3); δ 1.5~1.9 (*m*, 12H), 2.0~2.2 (2H), 2.2~2.7 (5H). To a stirred solution of 36g (0.18 mole) of 1-pyrrolidino-bicyclo [3.2.1] octan-8-one in 90ml of dry ether was added 82g (0.63 mole) of methyl iodide in one portion. The reaction mixture was allowed to stand for 20h at room temperature. The solid product was filtered to give 53g (85%) of 1-pyrrolidino-bicyclo[3.2.1]octan-8-one-methiodide. The mixture of 53g (0.16 mole) of methiodide and 300ml of 20% aq. potassium hydroxide was refluxed for 5h. After cooling the reaction mixture was diluted with 50ml water and washed with ether. The aqueous layer was acidified with hydrochloric acid about pH 2. The ethereal extract was washed with 10% sodium

thiosulfate and dried over magnesium sulfate. Solvent was removed and residue was fractionated to give 17g (77.3%) of 4-cyclohepten-1-carboxylic acid, bp 137~139°C/12 mmHg: $^1\text{H-nmr}(\text{CDCl}_3)$; δ 1.4~2.8(*m*, 9H), 5.7(*t*, 2H), 10.6(*s*, 1H).

Tricyclo [3. 3. 1. 0^{2,8}] nonan-9-one (5). The ketone 5 was prepared from 4-cyclohepten-1-carboxylic acid according to methods of previous section. mp 126~128°C: $^1\text{H-nmr}(\text{CDCl}_3)$; δ 1.5~2.3(*m*, 12H): IR(CCl_4) (cm^{-1}); 3050(*w*), 2940(*s*), 2865(*s*), 1700(*s*), 1450(*m*), 1360(*m*), 1340(*m*), 1240(*w*), 910(*m*), 450(*m*).

9-p-Fluorophenyl-tricyclo [3. 3. 1. 0^{2,8}] nonan-9-ol (III-A). The carbinol (II-4) was prepared from Grignard reagent and ketone 5 in absolute ether according to methods of previous section, and purified by column chromatography on alumina using methylene chloride as eluent. $^1\text{H-nmr}(\text{CDCl}_3)$; δ 1.1~1.5(*m*, 8H), 1.6(*s*, 1H), 1.8(*t*, 1H), 2.1(*m*, 1H), 6.9(*t*, 2H), 7.5(*q*, 2H): $^{19}\text{F-nmr}(\text{CDCl}_3)$; δ -115.3. IR(CCl_4) (cm^{-1}); 3600(*m*), 2940(*s*), 2860(*s*), 1600(*s*), 1500(*s*), 1410(*s*), 1220(*s*), 1150(*m*), 1005(*m*), 840(*s*).

③ **10-p-Fluorophenyl-tricyclo [4. 3. 1. 0^{2,9}] decan-10-ol (III-A):**

Tricyclo [4. 3. 1. 0^{2,9}] decan-10-one (6). The ketone 6 was prepared from cyclohexanone according to the methods of previous sections. $^1\text{H-nmr}(\text{CDCl}_3)$; δ 2.6(*m*, 1H), 1.0~2.3(*m*, 13H): IR(CCl_4) (cm^{-1}); 3000(*m*), 2920(*s*), 2850(*s*), 1680(*s*), 1460(*m*), 1445(*m*), 1360(*w*), 1250(*w*), 1150(*w*), 1040(*w*), 710(*w*),

10-p-Fluorophenyl-tricyclo [4. 3. 1. 0^{2,9}] decan-10-ol (III-A). The carbinol (III-A) was prepared from the Grignard reagent and 2.4g (0.01 mole) of ketone 6 in dry ether according to the method of the previous section. The purification of carbinol was performed by column chromatography on alumina, and gave 2.6g (75%). $^1\text{H-nmr}(\text{CDCl}_3)$; δ 0.9~1.4(*m*, 3H), 1.4~2.4

(*m*, 12H), 6.9~7.6(*t*, 2H), 7.6(*q*, 2H): $^{19}\text{F-nmr}(\text{CDCl}_3)$; δ -116.06. IR(CCl_4) (cm^{-1}); 3600(*m*), 2960(*s*), 1600(*s*), 1510(*s*), 1450(*s*), 1330(*w*), 1220(*s*), 1100(*s*), 990(*w*), 920(*w*).

(2) Synthesis of carbonium ions.

8-p-Fluorophenyl-tricyclo [3. 2. 1. 0^{2,7}] octan-8-yl cation (I). The cation (I) solution was prepared from corresponding carbinol (I-A) by a described method according to the general procedure in experimental section. The nmr spectra were recorded at -80°C. $^1\text{H-nmr}(\text{CD}_2\text{Cl}_2)$; δ 2.32(4H), 2.84(*m*, 2H), 4.2(*m*, 2H), 4.4(*m*, 1H), 4.7(*m*, 1H), 7.44(*t*, 2H), 8.4(2H): $^{19}\text{F-nmr}(\text{CD}_2\text{Cl}_2)$; δ -79.7.

9-p-Fluorophenyl-tricyclo [4. 3. 2. 0^{2,9}] nonan-9-yl cation (II). The cation (II) was prepared from carbinol (II-4), and the nmr spectra were recorded at -60°C. $^1\text{H-nmr}(\text{CD}_2\text{Cl}_2)$; δ 2.4(*m*, 8H), 3.8(*s*, 1H), 4.2(*t*, 1H), 4.7(*d*, 2H), 7.5(*t*, 2H), 8.3(*q*, 2H): $^{19}\text{F-nmr}(\text{CD}_2\text{Cl}_2)$; δ -84.2.

10-p-Fluorophenyl-tricyclo [4. 3. 1. 0^{2,9}] decan-10-yl cation (III). The cation (III) was prepared from carbinol (III-A), and the nmr spectra were recorded at -60°C. $^1\text{H-nmr}(\text{CD}_2\text{Cl}_2)$; δ 2.3(*m*, 10H), 34.4(*m*, 3H), 4.9(*m*, 1H), 7.4(*t*, 2H), 8. (d, d, 2H): $^{19}\text{F-nmr}(\text{CD}_2\text{Cl}_2)$; δ -85.3.

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