A ^{13}C NMR Study of 7-Norbornadienyl Cation by Modified Hammett-Brown Equation

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A series of the *para*-substituted 7-aryl-norbornadienyl cation (3) was prepared in FSO$_3$H/SO$_2$ClF solution at -100 °C and their ^{13}C NMR shifts were measured at -80 °C. The plots of the chemical shifts (changes in chemical shifts) of cationic carbon, $\Delta\delta^{C+}$, against our calculated new substituent constant, σ^{c+}s, gave an excellent correlation (r = 0.994), with a ρ^{c+} value of 12.63. These results indicate that the new substituent constants, σ^{c+}s, can be successfully employed to compare the relative charge demand of the carbonium ion by π- and $\pi\sigma$-participation.

Introduction

Norbornyl systems have been investigated extensively in the study of carbonium ion structure and reactivity. As shown in Table 1, 7-norbornenyl *p*-benzoate and 7-norbornadienyl *p*-benzoate are more reactive in solvolysis than 7-norbornyl analog by the respective factors of 10^{11} and 10^{14}. They are the classical examples of π-participation of the neighboring double bond(s).[1]

Also, solvolysis of the *Coates* cation 4 proceeds at an exceptionally large rate (10^{12}) compared with the 7-norbornyl system. This major rate enhancement is attributed to the $\pi\sigma$-participation of the remote cyclopropyl groups, which form a trishomocyclopropyl cation.[2]

One of the classical ways to estimate the stabilization of the developed charge in the carbon center is by the comparison of the slopes in the Hammett plot (plot of rate constant vs. σ). The solvolytic behavior of 7-norbornenyl systems is, however, far less dependent on the electronic contributions from the substituents Z because stabilization of the cationic center by π-participation of the double bond outweighs the contribution of aryl substitution, which was originally suggested by Bartlett.[3]

The ^{13}C chemical shift shows good sensitivity to the electron demand of the cation center and may be taken as a measure of the charge density in the corresponding carbon of the carbocations. If ^{13}C chemical shifts were linearly proportional to charge density, substituent constant, σ^{c+}, can be correlated with ^{13}C chemical shifts of the fully formed carbocation in super acids. G. Olah and co-workers attempted to correlate the ^{13}C chemical shifts of the cationic carbons with Hammett-Brown σ^+ constants.[4] It was shown, however, that the use of the σ^+ constants was inappropriate for this purpose.

Later Brown and co-workers[5] developed the following modified Hammett-Brown equation:

$$\Delta\delta^{c+} = \rho^{c+} \cdot \sigma^{c+},$$

where $\Delta\delta^{c+}$ is the difference between the chemical shifts of cationic carbon for the unsubstituted cation and those for the substituted cation species, *e.g.*, $\Delta\delta^{c+} = [\delta^{C+}(X=H) - \delta^{C+}(X=Z)]$. A plot of σ^{c+} values (modified Hammett-Brown constants) against $\Delta\delta^{c+}$ values of the 1-aryl-cyclopentyl cations gave an excellent correlation with a correlation coefficient r = 0.999.[6] Therefore, a set of new substituent constants, σ^{c+}, has been widely used for investigation of structure-reactivity relationships in acyclic, cyclic, and polycyclic cationic systems.[7]

These σ^{c+} constants, however, show only a fair fit in cation systems with neighboring π- or $\pi\sigma$-participating groups[8]. We previously calculated the new substituent constants, σ^{c+}s, and examined their ability to correlate $\Delta\delta^{c+}$ values for $\pi\sigma$-participating cations such as 9-aryl-pentacyclo [4.3.0. $0^{2,4}.0^{3,8}.0^{5,7}$] cation (**4**).[8] It was shown that the use of the new substituent constants, σ^{c+}s, gave a better fit.

In this paper, we present the results of correlation of the new subsitutent constants, σ^{c+}s with $\Delta\delta^{c+}$ values in π-participating cation species such as 7-arylnorbornadienyl cation (**3**) and 7-arylnorbornenyl cation (**2**) and discuss the electronic demand on the carbocation centers.

Results and Discussion

7-Aryl-norbornadien-7-ol derivatives were prepared by the addition of ketone to the Grignard reagents prepared from the corresponding 4-substituted bromobenzenes. The

Table 1. Summary of relative Solvolysis Rates

Cation	**1**	**2**	**3**	**4**
k, sec^{-1}	1	10^{11}	10^{14}	10^{12}
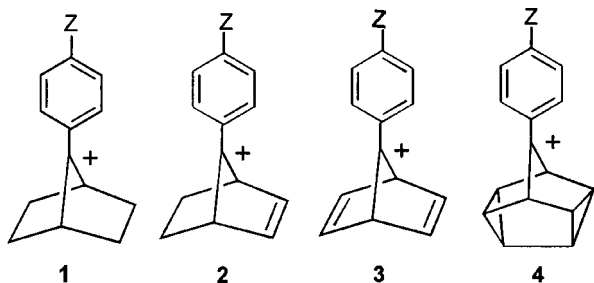
Table 2. ^{13}C chemical shifts[a] of substituted 7-aryl norbornadin-7-yl cations[b] at -80 °C

Substituent (Z)	C_7^+	$C_{1,4}$	$C_{2,3,5,6}$	C_8	$C_{9,13}$	$C_{10,12}$	C_{11}	X
H	80.087	60.600	128.741	119.973	130.166	130.007	133.885	
p-F	82.168	60.433	129.239	116.035	133.046	116.035	167.365	
				115.993	133.915	115.993	163.975	
p-Cl	78.688	60.778	128.771	118.789	131.427	130.276	139.753	
p-CH$_3$	89.783	59.414	129.970	116.191	130.921	130.730	146.563	21.211
p-CF3[c]	71.838	61.747	127.744	124.632	131.175	126.881		

[a]Referenced to the internal CD$_2$Cl$_2$. [b]These ions were prepared in FSO$_3$H/SO$_2$ClF and the spectra were measured at -80 °C. [c]CF$_3$ and aromatic C$_{11}$ carbon signals were too weak to assign.

cations were prepared by adding a measured quantity of the corresponding alcohols to the FSO$_3$H/SO$_2$ClF solution at -110 °C, and the ^{13}C NMR spectra of the cations were recorded at -80 °C. The ^{13}C chemical shifts of these cations are summarized in Table 2.

Since the rate enhancement by the substituent Z was not pronounced in 7-norbornadienyl cation **3** and 7-norbornenyl cation **2**, as mentioned before, we were interested determining if the ^{13}C chemical shifts would still reflect the delocalized charge density in the cation.

First, $\Delta\delta^{c+}$ values of the *p*-substituted 7-arylnorbornenyl cation (**2**) and 7-arylnorbornadienyl cations (**3**) were plotted against the substituent constant, σ^{c+}. The resulting plot has slope ρ^{c+} of 51.66 and correlation coefficient r of 0.904 for cation (**2**) and slope ρ^{c+} of 10.74 and correlation coefficient r of 0.923 for cation (**3**) as shown in Figure 1.

The slope of the plot reflects the charge demand of the generated cation center. A steeper slope means that more positive charge is distributed into the phenyl ring. Plots in Figure 1 indicate that cation **2** has more charge-stabilization contribution from the phenyl ring than cation **3**. Although plots in Figure 1 show the general trend of charge distribution, the correlation is rather poor.

But, when $\Delta\delta^{c+}$ values of cations **2** and **3** were plotted against σ^{c+}s, the new substituent constants, an excellent correlation was obtained, with r=0.999 for cation **2** and r=0.994
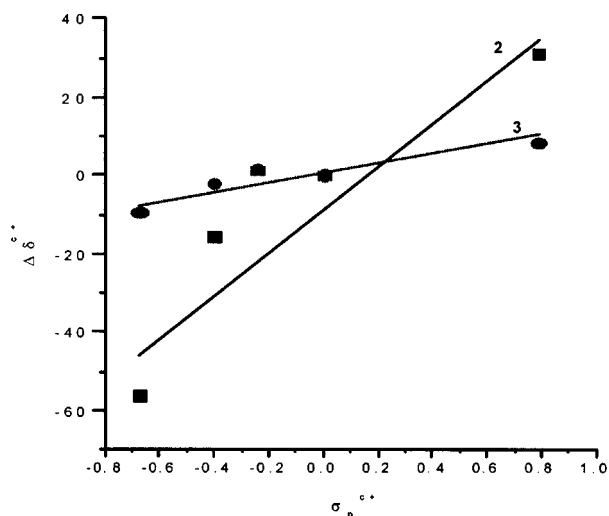
for cation **3** as shown in Figure 2. This indicated σ^{c+}s, the new substituent constants, can be used successfully to correlate ^{13}C chemical shifts for π-participating as well as $\pi\sigma$-participating systems. Table 3 summarizes the ρ^{c+} values along with the correlation coefficient of cation **2**, **3**, and **4** from the plots, using the new substituent constants, σ^{c+}s.

Cation **3** has the smallest ρ^{c+} value, which indicates that cation **3** is the least sensitive to the variation of electron supply from the substituent of phenyl ring. The Gassman-Fentiman[9] approach provides an alternative way to evaluate the electron deficiency of the developing cationic center in a system under ionization. The greater the electron deficiency on the developing cationic center, the more electronic demand on the substituted phenyl ring for electronic stabilization. *Coates* cation **4** has a larger ρ^{c+} value than cation **3**. It is clear that $\pi\sigma$-participation by the remote cyclopropyl group in cation **4** is superior to the π-participation by the
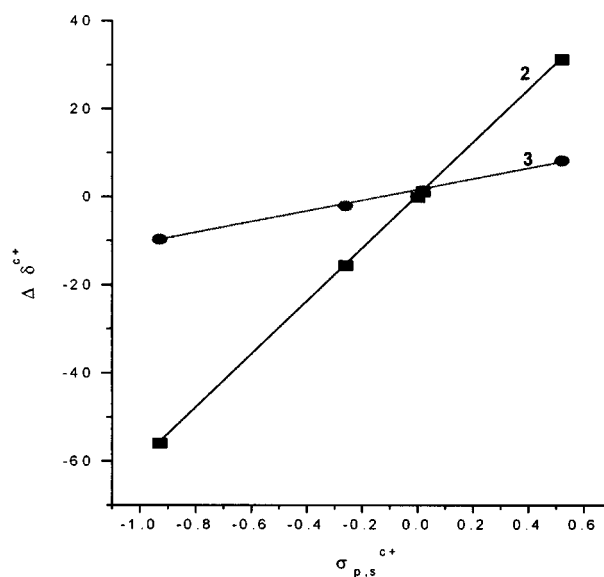
Figure 2. A plot of σ^{c+}s values against $\Delta\delta^{c+}$ for cation **2** (r = 0.999) and for cation **3** (r = 0.994).

Table 3. Comparison of ρ^{c+} values for cation **2**, **3**, and **4** correlation coefficient r in parentheses

Cation	2	3	4
ρ^{c+}	60.02	12.63	21.43
	(0.999)	(0.994)	(0.999)

Figure 1. A plot of σ^{c+} values against $\Delta\delta^{c+}$ for cation **2** (r = 0.904) and for cation **3** (r = 0.923).

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Table 4. Summary of ^{19}F Chemical Shifts[11]

Cation	**1**	**2**	**3**	**4**
δ (ppm)	-54.2	-95	-104.8	-99.8

double bond in cation **2** but inferior to the double π-participation in cation **3**.

These results clearly show that the new substituent constants, σ^{c+}s, give better correlation when π- or πσ-participation is involved. In other words, if good fit is obtained by using σ^{c+}s, it may be used as supporting evidence of π- or πσ-participation in the cationic systems.

^{19}F chemical shift is also known to have greater sensitivity to electron demand of the adjacent cation center.[10] 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 the shift of the uncharged species. Less efficient charge delocalization in the p-fluoropheny ring should result in greater charge dispersion by the neighboring substituent. Hence, the ^{19}F NMR data can provide important information on the degree of charge delocalization through neighboring group participation.

We reported previously the results of a ^{19}F NMR study on the *p*-fluorophenyl substitued *Coates* cation **4**,[12] and the ^{19}F NMR spectral data for cations are given in Table 4.

When comparing the ^{19}F chemical shift of norbornadienyl cation **3** with that of norbornyl cation **1**, the absorption signal of the fluorine atom in ion **3** appeared considerably upfield (Δδ, 50.7). Consequently, the large Δδ ^{19}F value is assumed to be due to the greater charge delocalization from the adjacnent double bond. A similar tendency was also observed in the norbornenyl cation **2**, and the results of ^{19}F chemical shifts were in accord with results of solvolytic studies.

In the present ^{13}C NMR study, excellent correlations of ρ^{c+} value with σ^{c+}s were obtained for the cation **2**, **3**, and **4**. These results are consistent with the ^{19}F NMR study and solvolytic data. It was confirmed that the new substituent constants, σ^{c+}s, can be employed to compare the electronic charge distribution of carbonium ion in the presence of π- and πσ-participation.

Experimental Section

NMR Spectral. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX 300 MHz spectrometer. Spectra of alcohols were recorded at 300 °K in CDCl$_3$ solution referenced internal TMS. Assignments were based on DEPT, COSY, and CH-COSY experiments. Spectra of cations were recorded at -80 °C using 10 mm tubes containing a trace of CD$_2$Cl$_2$ for field stabilization. ^{13}C chemical shifts are reported in ppm relative to CD$_2$Cl$_2$ (internal reference). Data of cation spectra were accumulated by using 32768 data point, spectra widths of 5000 Hz.

Calculation of New Constant $_s$$^{c+}$. Because the data in the earlier studies were relatively few, we recently obtained the

^{13}C spectra of an extended range of both meta- and para-substiutted 7-arylnorbornenyl cations, When plotted against σ$_m$$^+$, the cation carbon chemical shifts (Δσ^{c+}) for the meta cations give correlation (X = H, F, Cl, CH$_3$).

$$\Delta\delta^+ = \rho^{c+}\cdot\sigma_m{}^+ \quad (r = 0.996, \rho^{c+} = 59.96)$$

Using the original approach of Brown and Okamoto[13], we used the slope of the line (59.96) for the meta substituents to calculate new constants, the values of which place the Δδ^{c+} values for the para derivatives on the line. The modified constant was derived from the equation σ$_s$$^{c+}$ = ρ^{c+}/Δδ^{c+} (ρ^{c+} = 59.96), where σ$_s$$^{c+}$ is the new substituent constant.

Preparation of Cations. Each cation was prepared by slow addition of a solution of the corresponding alcohols in dichloro-methane-d$_2$ to a rapidly stirred solution of FSO$_3$H/SO$_2$ClF at -110 °C using a cation generating apparatus. The concentration of the cation based on the precursor alcohol was in the range 0.3-0.5 M and the color of solution was generally yellow-brown.

(I) Synthesis of quadricyclanol. Quadricyclanol was synthesized by our modified literature route.[14]

7-*t*-Butoxynorbornadiene. To a mixture of bicyclo [2.2.1]heptadiene (149 g, 1.62 mol) and CuBr (0.325 g, 2.3 mmol) in 500 mL of benzene was added, in a N$_2$ atmosphere, a solution of *t*-butylperbenzoate (122.5 g, 0.63 mol) in 100 mL of benzene over a period of 1 hr. After refluxing for 30 min and cooling, the reaction mixture was extracted with 10% Na$_2$CO$_3$ to remove benzoic acid, washed with water and dried. Careful removal of benzene at reduced pressure and distillation of the crude product yielded 26.0 g (25%) of 7-*t*-butoxy norbornadiene: b.p. 70-72/14 mm; ^{1}H NMR (CDCl$_3$) δ: 1.12 (s, 9H), 3.37 (q, 2H), 3.77 (d, 1H), 6.56 (q, 2H), 6.65 (q, 2H); ^{13}C NMR (CDCl$_3$) δ: 28.3, 55.5, 104.3, 137.2, 139.8.

7-Norbornadienyl acetate. A mixture of 15 g (0.092 mol) *t*-butoxynorbornadien, 150 mL of glacial acetic acid and 30 mL of acetic anhydride was cooled in an ice bath and quickly added to 20.3 g (0.14 mol) of 70% perchloric acid previously cooled to 0 °C and placed in an ice bath. The red mixture was swirled and allowed to stand in the ice bath for exactly 1 min. Ice and water were added to dissipate the red color and the mixtures were extracted with dichloromethane. Distillation yielded 10.0 g (73%) of the desired product: b.p. 65 °C/8 mm; ^{1}H NMR (CDCl$_3$) δ: 1.90 (s, 3H), 4.50 (d, 1H),

Table 5. ^{13}C NMR chemical shifts of cations (**2**) and New substituent constant σ$_s$$^{c+}$

X	meta-^{a}	para-^{b}	σ$_{m,s}$$^{c+}$	σ$_{p,s}$$^{c+}$
H	111.47	111.47	0	0
F	90.67	127.10	0.35	-0.26
Cl	90.01	110.28	0.36	0.02
CH$_3$	117.85	167.44	-0.10	-0.93
CF$_3$	85.79	80.44	0.43	0.52
OCH$_3$	88.33	217.02	0.39	-1.76
3,5(Cl)$_2$		78.62		0.55

(^{a}at 178 K, ^{b}at 183 K)

5.53 (q, 2H), 6.51 (q, 2H), 6.63 (q, 2H); ^{13}C NMR (CDCl$_3$) δ: 21.3, 52.4, 99.3, 137.8, 140.2, 171.2.

3-Acetoxytetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane. In a quartz probe was placed 2.5 g (15.6 mmol) of norbornadienyl acetate and 500 mL of pentane. The solution was irradiated for 2 hr with 240 nm medium pressure arc. The pentane solvent was removed by a rotary evaporator and the residue was vacuum distilled to yield 2.375 g (95%) of the desired product: b.p. 72 °C/6 mm; m.p. 33-35; ^{1}H NMR (CDCl$_3$) δ: 1.48 (m, 2H), 1.57 (m, 2H), 1.79 (m, 2H), 2.08 (s, 3H) 5.59 (d, 1H); ^{13}C NMR (CDCl$_3$) δ: 14.6, 15.9, 21.4, 25.6, 82.2, 172.3.

3-Hydroxytetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane. To a cold stirred slurry of 1.27 g of LiAlH$_4$ in 100 mL of anhydrous ether was added 9.06 g of 3-acetoxytetracyclo [3.2.0.0^{2,7}.0^{4,6}]heptane dissolved in 30 mL of ether. The mixture was stirred at room temperature for 15 min and then cooled to 0 °C. Water (5.1 mL) was added dropwise with cooling. The precipitated inorganic salts were removed by filtration and the filtrate was concentrated by distillation. Vacuum distillation of the residue gave 5.99 g (92%) of the desired alcohol: b.p. 78 °C/10 mm; ^{1}H NMR (CDCl$_3$) δ: 1.30 (m, 2H), 1.47 (m, 2H), 1.68 (m, 2H) 4.81 (d, 1H); ^{13}C NMR (CDCl$_3$) δ: 14.7, 15.6, 28.8, 79.3.

3-Tosyloxytetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane. To a cold stirred solution of 12.04 g (0.1 mol) of the above alcohol dissolved in 100 mL of dry pyridine was added 31.8 g (1.06 mol) of tosylchloride over a 30 min period. The solution was let stand at -12 °C for 12 hr. The reaction mixture was poured into a slurry of 100mL of hydrochloric acid and 500 g of ice. The precipitate was collected by filtration and then dissolved in methylene chloride. The resulting solution was dried over MgSO$_4$ and concentrated. The oily residue was crystallized from a pentane/dichloromethane mixture. Recrystallization gave 21.06 g (72%) of tosylate as white crystal: m.p. 65-67 °C/14 mm; ^{1}H NMR (CDCl$_3$) δ: 1.43 (m, 2H), 1.57 (m, 2H), 1.82 (m, 2H), 5.47 (d, 1H), 7.34 (d, 2H), 7.87 (d, 2H); ^{13}C NMR (CDCl$_3$) δ: 14.9, 16.5, 21.6, 26.1, 89.8, 127.8, 129.7, 134.7, 144.4.

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-one. N$_2$ was bubbled through a mixture of 5 g of NaHCO$_3$ and 90 mL of dry DMSO and the solution was heated to 100 °C, and 4.0 g of tosylate dissolved in 10 mL of dry DMSO was added rapidly. After 4.5 min the reaction mixture was poured into 300 g of ice. The resulting aqueous solution was continuously extracted with hexane over 1 day period. Hexane was removed and the residue was vacuum distilled to give 1.37 g (85%) of the desired ketone: b.p. 46 °C/14 mm; ^{1}H NMR (CDCl$_3$) δ: 1.08 (t, 2H), 2.21 (d, 1H); ^{13}C NMR (CDCl$_3$) δ: 19.02. 20.49, 218.06.

7-Aryltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-7-ol. (**quadricyclanol**) A substituted 7-aryl tetracyclo-[3.2.0.0^{2,7}.0^{4,6}] heptan-7-ol was synthesized by reaction of the ketone with the Grignard reagent prepared from corresponding bromobenzene, and was purified by column chromatography.

7-Phenyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-7-ol. ^{1}H NMR δ: 1.56 (t, 2H), 1.90 (m, 4H), 2.21 (bs, 1H), 7.36 (m, 3H),

7.77 (d, 2H), ^{13}C NMR δ: 16.1, 17.8, 35.6, 88.6, 125.6, 127, 128.1, 143.2.

7-*p*-Fluorophenyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-7-ol. ^{1}H NMR δ: 1.53 (t, 2H), 1.89 (q, 4H), 2.19 (bs, 1H), 7.07 (t, 2H), 7.71 (q, 2H); ^{13}C NMR δ: 16.5, 18.2, 36.1, 88.8, 115.2, 115.4, 127.7, 127.8, 139.3, 160.8, 164.1.

7-p-Methylphenyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-7-ol. ^{1}H NMR δ: 1.51 (t, 2H), 1.86 (m, 4H), 2.05 (bs, 1H), 2.37 (s, 3H), 7.19 (d, 2H), 7.61 (d, 2H) ^{13}C NMR δ: 16.1, 17.7, 21.1, 35.6, 88.5, 125.5, 128.9, 136.7, 140.2.

7-*p*-Chlorophenyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-7-ol. ^{1}H NMR δ: 1.52 (t, 3H), 1.90 (m, 4H), 1.75 (d, 2H), 1.67 (d, 2H) ^{13}C NMR δ: 16.1, 17.8, 35.8, 88.2, 116.6, 127.1, 128.2, 129.3, 132.8, 141.7.

7-p-Trifluoromethylphenyltetracyclo[3.2.0.0^{2,7}.0^{4,6}] heptan-7-ol. ^{1}H NMR δ: 1.55 (t, 2H), 1.93 (m, 4H), 2.15 (bs, 17), 7.63 (d, 2H), 7.84 (d, 2H) ^{13}C NMR δ: 16.2, 17.9, 36.2, 88.2, 122.5, 125.0, 125.9, 128.9, 147.4.

(II) Synthesis of 7-arylnorbornadien-7-ol. A solution of 100 mg of quadricyclanol and 5 mg of (bicyclo[2.2.1]-2,5-diene)-palladium(II)chloride in dichloromethane (10 mL) was stirred for 2-4 hr at room temperature. Solvent was evaporated and column chromatography gave corresponding alcohols.

7-Phenylnorbornadien-7-ol. ^{1}H NMR δ: 3.97 (t, 2H), 6.45 (t, 2H), 6.70 (t, 2H), 7.21 (m, 1H), 7.28 (m, 4H). ^{13}C NMR δ: 58.49, 113.20, 126.88, 127.44, 127.77, 139.53, 140.6 3, 141.65; MS (CI) m/z 185 (MH$^+$).

7-*p*-Fluorophenylnorbornadien-7-ol. ^{1}H NMR δ: 3.99 (t, 2H), 4.10 (s, 1H) 6.49 (t, 2H), 6.94 (t, 2H), 6.98 (t, 2H), 7.29 (m, 2H). ^{13}C NMR δ: 58.69, 112.55, 114.50, 114.78, 129.11, 129.22, 137.36, 137.40, 139.54, 140.70, 160.02, 163.27; MS (CI) m/z 203 (MH$^+$).

7-*p*-Methylphenylnorbornadien-7-ol. ^{1}H NMR δ: 2.30 (s, 3H), 3.96 (t, 2H), 6.46 (t, 2H), 6.89 (t, 2H), 7.08 (d, 2H), 7.18 (d, 2H). ^{13}C NMR δ: 21.06, 58.53, 113.14, 127.28, 128.55, 136.55, 138.63, 139.61, 140.67; MS (CI) m/z 199 (MH$^+$).

7-*p*-Chlorophenylnorbornadien-7-ol. ^{1}H NMR δ: 3.97 (t, 2H), 4.07 (s, 1H), 6.48 (t, 2H), 6.9 3 (t, 2H), 7.25 (s, 4H). ^{13}C NMR δ: 58.56, 112.52, 127.30, 129.02, 132.70, 139.58, 140.18, 140.68; MS (CI) m/z 219 (MH$^+$).

7-*p*-Trifluoromethylphenylnorbornadien-7-ol. ^{1}H NMR δ: 4.00 (t, 2H), 4.09 (s, 1H), 6.49 (t, 2H), 6.47 (t, 2H), 6.94 (t, 2H), 7.41 (d, 2H), 7.53 (d, 2H). ^{13}C NMR δ: 58.40, 112.36, 124.80, 124.85, 127.99, 139.57, 140.62, 145.66; MS (CI) m/z 253 (MH$^+$).

(III) Preparation of cations. The cation solution were prepared from the corresponding alcohol according to the above described method.

7-Phenylnorbornadien-7-yl cation. ^{13}C NMR δ: 60.6, 80.1, 119.9, 128.7, 130.0, 130.1, 133.9.

7-p-Fluorophenylnorbornadien-7-yl cation. ^{13}C NMR δ: 60.4, 82.2, 115.9, 116.0, 129.2, 133.0, 133.9, 163.9, 167.4.

7-p-Chlorophenylnorbornadien-7-yl cation. ^{13}C NMR δ: 60.7, 78.7, 118.8, 128.7, 130.3, 131.4, 139.7.

7-p-Methylphenylnorbornadien-7-yl cation. ^{13}C NMR

δ: 21.2, 59.4, 89.8, 116.2, 130.0, 116.2, 130.7, 130.9, 146.5.

7-p-Trifluoromethylphenylnorbornadien-7-yl cation. ^{13}C NMR δ: 61.7, 71.8, 124.6, 126.8, 127.7, 131.2.

References

1. Winstein, S.; Shatavsky, M.; Norton, C. *J. Am. Chem. Soc.* **1955**, *77*(4), 4183.
2. Coates, R. M.; Kirkpatrick, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 2538.
3. Bartlett. P. D.; Gidding, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.
4. Olah, G. A.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3961.
5. Brown, H. C.; Kelly, D. P. *Natl. Acad. Soc. USA* **1980**, *77*, 6956.
6. Brown, H. C.; Kelly, D. P.; Perisamy, D. P. *J. Org. Chem.* **1981**, *46*, 1646.
7. Brown, H. C.; Perisamy, M.; Kelly, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 2359.
8. Cho, J. H.; Shin, J. H. *Bull. Korean Chem. Soc.* **1996**, *17*(4), 347
9. P. G. Gassman,; A. F. Fentiman, *J. Am. Chem. Soc.* **1981**, *92*, 2549,
10. Taft, R. W.; McKeever, L. D. *J. Am. Chem. Soc.* **1965**, *87*, 2489.
11. Volz, H.; Miess, R. *Terahedron Lett.* **1975**, *21*, 1665.
12. Ahn, Y. S.; Volz, H.; Shin, J. H. *J. Chem. Soc., Commun.* **1991**, *16*, 1094.
13. Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.
14. Story, P. R. *J. Org. Chem.* **1961**, *26*, 287.