

탄소-13 핵자기공명 화학적 이동을 이용한 9-바바라릴 양이온의 구조에 관한 연구

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Study on Structure of 9-Barbaralyl Cation by ¹³C NMR Chemical Shift

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요 약. 9-바바라릴 양이온의 구조를 탄소-13 핵자기공명을 이용한 Hammett-Brown 식을 이용해서 조사하였다. 이를 위하여 9-아릴트리시클로(3.3.1.0^{2,8})노난 (5) 및 9-아릴트리시클로(3.3.1.0^{2,8})노나-3,6-디엔 (6)계 양이온을 영하 120 °C에서 해당 알코올과 불화황산과의 반응에서 얻었고 양하진 탄소에 대한 화학적 이동이 측정되었다. 양이온 5와 6에 대한 Hammett-Brown 식의 기울기, 즉 ρ^{C^+} 값은 각각 -5.01과 -7.52였다. 이들 값의 결과로만 보면 이중결합의 영향이 있는 것처럼 보인다. 그러나, 9-바바라릴과 8,9-데히드로아다만틸 양이온들의 ρ^{C^+} 와 $\rho^{C_{\alpha^+}}$ 값들을 비교한 결과에서 9-바바라릴 양이온은 도표 1에서의 4의 구조를 가져야 된다는 결론을 얻어냈다.

ABSTRACT. The structure of 9-barbaralyl cation was examined by Hammett-Brown plot using ¹³C NMR chemical shifts. 9-Aryltricyclo(3.3.1.0^{2,8})nonan-9-yl cation (5) and 9-aryltricyclo(3.3.1.0^{2,8})nona-3,6-dien-9-yl cation (6) were prepared from the corresponding carbinols in FSO₃H-SO₂ClF solution at -120°C, and their chemical shifts of cation centers were measured. The slopes, ρ^{C^+} values, of the Hammett-Brown plot of (5) and (6) were -5.01 and -7.52, respectively. From these values themselves, it seemed that the double bonds participated in the delocalization of the positive charge. However, comparing ρ^{C^+} value and $\rho^{C_{\alpha^+}}$ value in 9-barbaralyl cation (6) and those in 8,9-dehydroadamantyl cation (7), we concluded that 9-barbaralyl should be represented by the structure 4 shown in Scheme I.

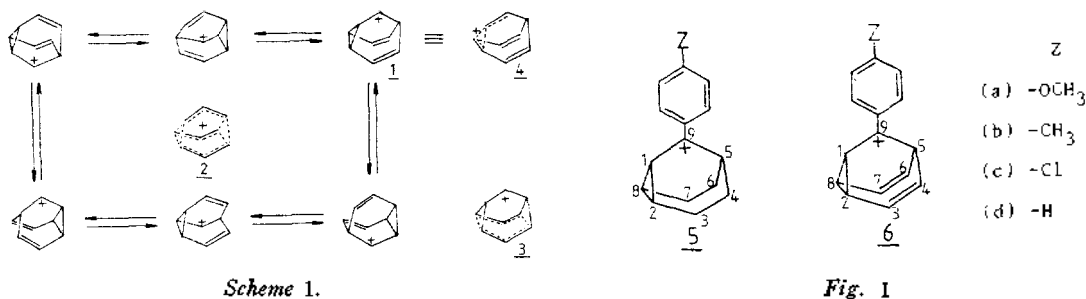
INTRODUCTION

The 9-barbaralyl (tricyclo(3.3.1.0^{2,8})nona-3,6-dien-9-yl) (1) contains as structural elements the cyclopropylcarbiny cation and two double bonds adjacent to the cyclopropane ring. The cation 1 has been studied under solvolytic conditions by Schleyer and coworkers¹, and by Grutzner and Winstein² using deuterium-labelled nitrobenzoates and dinitrobenzoates of 9-bar-

baralol. The results indicated the intermediacy of a cation which can be partially or totally degenerate or have D_{3h} symmetrical structure 2³.

An orbital correlation study by Hoffmann *et al.*⁴ and calculations(CNDO/2) by Yoneda *et al.*⁵ have suggested structure 3, which undergoes 3-fold degenerate rearrangement mechanism.

If the 9-barbaralyl cation has structure 1, it undergoes a 6-fold partially degenerate rearrangement mechanism, as shown in Scheme I.

Table 1. ¹³C chemical shifts of cation 5 and 6 in ppm from TMS

system	Z	C ₉	C ₁	C _{2,8}	C _{3,7}	C _{4,6}	C ₅
5	4-OCH ₃	234.6	57.9	70.8	41.8	18.7	42.8
	4-CH ₃	242.4	60.3	80.2	41.3	19.4	43.1
	4-Cl	242.8	60.3	87.1	42.3	19.9	43.8
	H	245.1	59.5	85.8	42.2	19.8	43.9
6	4-OCH ₃	219.6	47.4	58.2	127.3	117.3	45.0
	4-CH ₃	231.7	54.4	68.2	128.2	118.1	50.6
	4-Cl	232.3	60.9	67.4	129.9	118.8	53.0
	H	235.1	61.2	68.4	130.0	118.9	53.1

The study by Bouman and Trindle concluded that if the cation has structure 1, then 2 can be neither a transition state nor intermediate in rearrangement⁶. McIver's rules also exclude 2 as a transition state in the rearrangement of 1⁷.

However, the studies by Ahlberg *et al.* using ¹H-nmr⁸, ¹³C-spin transfer⁹, and isotopic perturbation experiment¹⁰, indicated the cationic structure 4 with the positive charge delocalized in to the cyclopropane ring.

In view of these observation, we were interested in the examining the structure of the 9-barbaralyl cation using Hammett-Brown type correlation, $\Delta\delta^{C^+} = \rho^{C^+} \cdot \sigma^{C^+11}$. To examine the structure of the cation, 9-aryltricyclo(3.3.1.0^{2,8})nonan-9-yl (5) and 9-aryltricyclo(3.3.1.0^{2,8})nona-3,6-dien-9-yl cation (6) were generated in super acid medium at -120 °C and their chemical shifts were measured. By comparing the ρ^{C^+} values, calculated from the plot of the substituent constant, σ^{C^+} , and the chemical shifts

of cationic centers of corresponding cations, we studied the effect of the double bonds on the stabilization of positive charge.

RESULTS AND DISCUSSION

The carbinols, (5-ol) and (6-ol), were prepared from the reaction of corresponding ketone with Grignard reagents prepared from the corresponding bromobenzene in absolute ether. Carbonium ions were prepared from carbinols according to the following general procedure; a solution of a pure carbinol in deuterated methylene chloride was added dropwise to the mixture of fluorosulfonic acid and sulfuryl chloride fluoride (SO₂ClF) (1 : 5 v/v) at -120 °C using a specially designed cation generating apparatus. The NMR spectra were recorded at -75 °C and -105 °C for the cation 5 and 6, respectively.

The ¹³C-nmr chemical shifts of the resulting solutions of 5 and 6 are summarized in Table 1.

A plot of the $\Delta\delta^{C^+}$ values for 9-aryltricyclo

[3.3.1.0^{2,8}]nonan-9-yl cation (5) against the Hammett-Brown σ^{C^+} constants gives a good correlation; with $r = -0.988$ and $\rho^{C^+} = -5.01$ (Table 2, Fig. 2). Similar treatment of the data for the 9-aryltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl cation (6) yields also a good correlation with $r = -0.987$ and $\rho^{C^+} = -7.52$ (Table 2, Fig. 3). And plots of the $\Delta\delta^{C_i}$, $\Delta\delta^{C_{i,s}}$, and $\Delta\delta^{C_i}$ for the cation 5 and 6 against the Hammett-Brown σ^{C^+} constants give correlations and are summarized in Table 2.

Table 2. ρ^{C^+} value of each carbon of cation 5 and 6 ($-r$ values in parentheses)

system	ρ^{C_i}	C_i	$C_{i,s}$	C_i
(5)	-5.01 (0.988)	-2.10 (0.951)	-11.64 (0.999)	-0.85 (0.938)
(6)	-7.52 (0.987)	-10.90 (0.991)	-7.74 (0.999)	-6.62 (0.999)

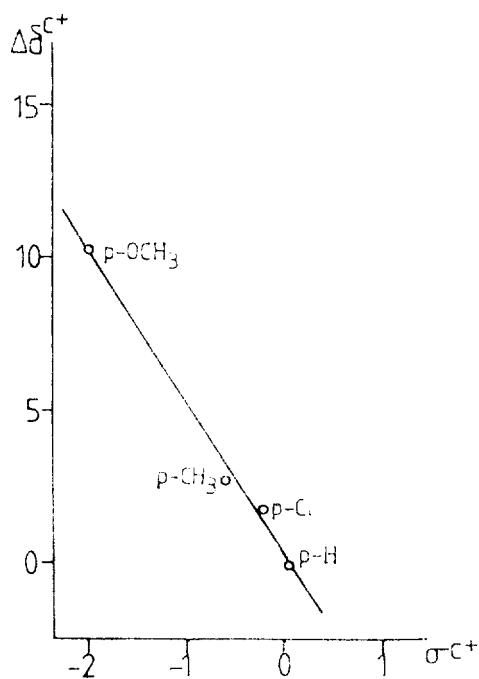


Fig. 2. Plot of $\Delta\delta^{C^+}$ against σ^{C^+} values for 9-aryltricyclo[3.3.1.0^{2,8}]nonan-9-yl cation (5).

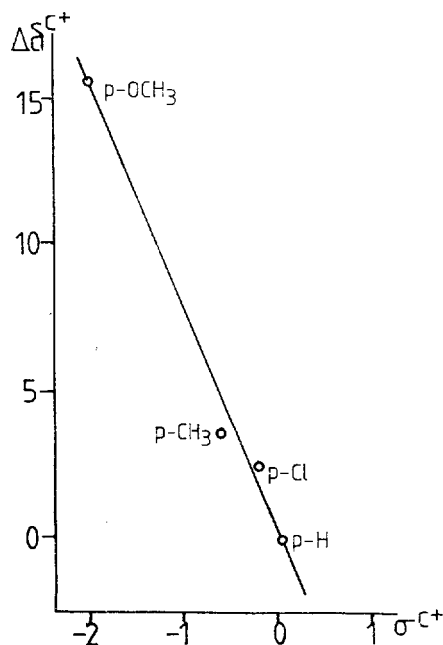


Fig. 3. Plot of $\Delta\delta^{C^+}$ against σ^{C^+} values for 9-aryltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl cation (6).

The slopes for the cationic center, ρ^{C^+} values, indicate that the cation 5 is less sensitive to the variation of electron supply from the substituent than the cation 6. This is because the cyclopropane ring of the cation 5 participates more strongly in the delocalization of positive charge than that of the cation 6. In the cation 6, as the effect of the cyclopropane ring is reduced by two double bonds, the smaller ρ^{C^+} is obtained. The ρ^{C^+} values (Table 2) of C-2,8 of the cation 5 and 6 show that these carbons are more sensitive to the variation of electron supply from the substituent than other carbons, however C-2,8 of the cation 6 are less sensitive than those of the cation 5. Therefore, these results suggest large positive charge delocalization into cyclopropane ring of cations 5 and 6. Furthermore, charge is distributed over C-1,2

and 8 in cations **5** and **6**, but the olefinic carbons ($C_{2,8}, C_{3,7}$) are essentially unperturbed as concluded from the constancy of the chemical shifts of those carbons in cations **6** (Table 1). In view of these results, the structure **2** or **3** can be eliminated.

And the cation **5** and **6** are compared with 2-aryl-8, 9-dehydro-2-adamantyl cation (**7**), whose ρ^{C^+} value is -7.19^{12} . The ρ^{C^+} values of the cations **6** and **7** show similar, even though the cation **7** has not any double bond or other functional group which can affect the charge delocalization. The structure of the cation **7** is supposed to have the same one with that of the cation **5**.

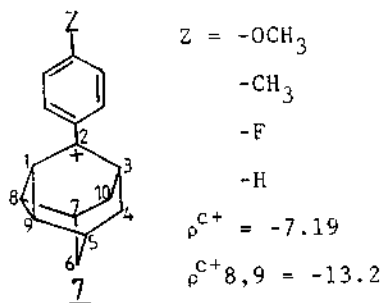


Fig. 4

Furthermore, the ^{19}F -NMR chemical shifts of the cations **5**, **6** and **7** for the 4-fluorophenyl substituent show similar values; -84.2^{13} , -83.2^{14} and -81.4^{15} for **5**, **6** and **7**, respectively. Strikingly, ^{19}F -chemical shifts of those cations show similar values. Consequently, it can be concluded that these cations have similar structures in terms of charge delocalization.

And the differences of the ρ^{C^+} values of the cations **5** and **7**, which have the similar structure, seem to be due to the methylene bridge. The similar values of ρ^{C^+} s of the cations **6** and **7** are supposed to be due to the rigidity of the cation **6** by the double bonds as in the cation **7** by the methylene bridge.

In conclusion, the results of ^{13}C -nmr studies

strongly suggest that 9-barbaralyl cation should be represented as the structure **4**, which contains a cyclopropylcarbinyl cationic structural element (Scheme I).

EXPERIMENTAL

All carbonium ion precursors were characterized by IR, ^1H - and ^{13}C -nmr. Infrared spectroscopic data were determined on an Analect Instruments FX-6160 IR spectrophotometer. NMR spectra were recorded on a Bruker WP-SY 80 and AM 250 spectrometers, TMS as an internal standard, and CDCl_3 as a solvent and locking material. Cation solutions were made up to approximately 10% concentration by addition of the carbinol in CD_2Cl_2 to stirred $\text{FSO}_3\text{H}/\text{SO}_2$ ClF at -120°C using cation generation apparatus. The chemical shifts in ^{13}C NMR spectra of the cations were referenced from internal CD_2Cl_2 (53.8 ppm from TMS).

(I) Synthesis of Ketones

(A) Tricyclo(3.3.1.0^{2,8})nonan-9-one

1-Pyrrolidino-1-cyclopentane (A-1): A mixture of 50g (0.49 mole) of cyclopentanone and 55g (0.77 mole) of pyrrolidine in 150 ml of benzene was refluxed to remove water by use of Dean-Stark apparatus for 5 hrs. After removal of benzene, the product was obtained by vacuum distillation ($88-92^\circ\text{C}/15\text{ mmHg}$), yield; 56.1g (83.6%).

1-Pyrrolidinobicyclo(3.2.1)octan-8-one (A-2): A solution of 56.1g (0.41 mole) of (A-1) in 400ml of dry dioxane was cooled to -5°C and 24g (0.43 mole) of acrolein was added over 45 min with stirring. The reaction mixture was then allowed to stir at r.t. overnight. After removal of dioxane, the residue was distilled to produce the ketone (A-2). bp; $110-115^\circ\text{C}/0.5\text{ mmHg}$, yield; 36.1g (45.6%), ^1H -nmr(CCl_4); 1.5~1.9(m, 12H), 2.0~2.2(m, 2H), 2.2~2.7(m, 5H).

1-Pyrrolidinobicyclo [3. 2. 1] octan-8-one methiodide (A-3): To a solution of 36.1 g (0.187 mole) of (A-2) in 90 ml of dry ether was added 82 g (0.58 mole) of methyl iodide in one portion. The reaction mixture was allowed to stand for 18 hrs at r.t., then the solid product (A-3) was filtered from the mixture, the filtrate was re-reacted with 17g (0.12mole) of methyl iodide, and solid was again collected. yield; 53.2g (85.5%).

4-Cycloheptene-1-carboxylic acid (A-4): A mixture of 53.2g (0.16 mole) of (A-3) and 300 ml of 20% KOH solution was heated at 125°C for 5 hrs. The cooled mixture was diluted with water, washed twice with ether, acidified with HCl to pH 2, and then extracted with ether. The extract was washed with 10% Na₂S₂O₄ solution and dried over anhydrous MgSO₄. Removal of solvent afforded the product (A-4). yield; 17.1g (77.3%). ¹H-nmr (CCl₄); 1.4~2.8(m, 9H), 5.7(t, 2H), 10.6(s, H). ¹³C-nmr; 182.6, 131.5, 47.1, 29.2, 26.7.

4-Cycloheptene-1-carboxylic acid chloride (A-5): To a solution of 7.1g (0.051 mole) of the acid (A-4) in 60ml of benzene, 7.2g(0.06 mole) of thionyl chloride was added dropwise. After complete addition of the thionyl chloride, the mixture was refluxed for 1.5 hrs. After removal of solvent, the residue was distilled under reduced pressure (38 °C/0.14 mmHg). yield; 6.6g (82.3%). ¹H-nmr (CCl₄); 1.5~2.4(m, 8H), 2.9(m, 1H), 5.7(m, 2H).

Tricyclo[3.3.1.0^{2,8}]nonan-9-one (A-one): Diazoketone prepared from 6.6g (0.042 mole) of (A-5) and diazomethane in dry ether was refluxed for 1 hr in dry *n*-hexane in the presence of anhydrous CuSO₄. After filtration of the sulfate and removal of solvent, the residue was eluted on column chromatography (silica gel/*n*-hexane). yield; 3.2g(55%). mp; 126~127°C. ¹H-nmr(CCl₄); 1.5~2.3 (m, 12 H), ¹³C-nmr;

187.7, 44.3, 31.5, 29.4, 26.3, 15.7. ir(cm⁻¹); 3050 (w), 2940 (s), 2865 (s), 1700 (s), 1450, 1360, 1340, 1240(w), 1070(w), 1025(w), 910.

(B) Tricyclo [3. 3. 1. 0^{2,8}] nona-3, 6-dien-9-one

Tropylium fluoroborate (B-1): To 600 ml of acetic anhydride was added in the order of 180 g (0.66 mole) of 32% HBF₄, 156 g (0.60 mole) of triphenylmethanol in ice bath, and 52.5g (0.57 mole) of cycloheptatrieneslowly at r.t. After adding 150ml of ether, the precipitated solid was filtered, washed with cold ether, and dried in a desiccator. yield; 67.8g(70%).

7-Cyanocycloheptatriene (B-2): To a solution of 67.8g (0.38 mole) of the salt (B-1) in 240 ml of water was added 60g(1.22 mole) of NaCN solution in 100 ml of water at r.t. The reaction mixture was extracted with ether, and the extract was washed with satd. NaHCO₃ solution, and dried over anhyd. MgSO₄. Removal of solvent gave orange oil. yield; 39 g (81.6%).

7-Carbamoylcycloheptatriene (B-3): To a mixture of 36 g (0.31 mole) of the nitrile(B-2), 300 ml of acetone and 180 ml of 30% hydrogen peroxide, was added dropwise 180 ml of 10% Na₂CO₃ solution. After complete addition, the reaction mixture was allowed to stand overnight. After evaporation of acetone by bubbling air, the mixture was extracted with ether. The extract was dried over anhyd. MgSO₄, and then removal of solvent gave the solid (B-3). yield; 27 g (64.5%).

7-Carboxycycloheptatriene (B-4): A mixture of 27g (0.20 mole) of the amide and 600 ml of 2 N sulfuric acid was refluxed for 1.5 hrs. The mixture was cooled, brought to pH 2 with 6 N NaOH solution, extracted with ethyl acetate, and dried over anhyd. MgSO₄. Removal of solvent gave the product (B-4). yield; 15 g (55%).

7-Cycloheptatriene carboxylic acid chloride

(B-5): To a solution of 14 g (0.11 mole) of the acid in 200 ml of benzene, was added dropwise 17.8 g (0.15 mole) of SOCl_2 at r.t. After refluxing for 1.5 hrs, the solvent was removed. Vacuum distillation gave the acid chloride. bp; 41~44 °C/0.5 mmHg, yield; 15.4 g(90.9%).

Tricyclo (3. 3. 1. 0^{2.9}) nona-3, 6-dien-9-one (Barbaralone) (B-one): To a boiling suspension of 38 g(0.24 mole) of anhyd. CuSO_4 and 340 ml of *n*-hexane was added over 1 hr the diazoketone solution prepared from diazomethane and 15.4 g(0.10 mole) of the acid chloride. The mixture was refluxed for additional 2 hrs, and the slurry was filtered. Filtrate was concentrated, and eluted on column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/n$ -hexane = 1 : 1 v/v, R_f = 0.26). Further purification by sublimation gave pure solid (B-one). yield; 3.6g (20%).

(II) Synthesis of Carbinols

Carbinols were prepared from the Grignard reaction of 3.67 mmole of the corresponding ketone with 7.34 mmole of *p*-substitutedbromobenzenene and 8.08 mmole of Mg in dry ether. The crude product was purified by column chromatography (silica gel/ CH_2Cl_2), after work-up.

(5)-a; ^1H -nmr; 6.95 (*q*, 4 H), 3.7(*s*, 3 H), 2.0(*s*, 1 H), 1.8~2.0(*m*, 2H), 1.4~1.8(*m*, 4H), 0.8~1.4(*m*, 6H) ^{13}C -nmr; 158.6, 140.8, 127.2, 113.4, 72.5, 55.2, 40.8, 25.5, 22.8, 19.7, 17.1, 15.1, 14.7, 14.1 ir; 3454(*b*), 3004, 2935(*s*), 2863, 1683(*s*), 1608(*w*), 1551(*s*), 1457, 1364, 1298, 1247(*s*), 1178, 1064, 1031, 912, 836, 732, 432, 401.

(5)-b; ^1H -nmr; 7.20 (*q*, 4 H), 2.3 (*s*, 1 H), 1.9(*s*, 1 H), 1.9~2.1(*m*, 2H), 1.5~1.9(*m*, 4H), 0.9~1.5(*m*, 6H) ^{13}C -nmr; 145.6, 135.9, 128.5, 125.9, 72.7, 40.6, 31.6, 29.6, 25.4, 22.7, 19.4, 15.0, 14.6, 14.0 ir; 3432(*b*), 3005, 2937(*s*), 2863, 1682(*s*), 1551, 1452, 1413, 1366, 1272, 1142, 1183, 1114, 1062, 1028(*s*), 946, 910, 814, 757, 730, 599.

(5)-c; ^1H -nmr; 7.29 (*q*, 4 H), 2.1 (*s*, 1 H), 1.8~2.1 (*m*, 2 H), 1.4~1.8 (*m*, 4 H), 0.8~1.4 (*m*, 6H) ^{13}C -nmr; 146.9, 132.7, 128.0, 127.6, 72.7, 40.6, 25.3, 22.7, 19.5, 17.1, 14.9, 14.5, 14.1 ir; 3420(*b*), 3005(*s*), 2983, 2862, 1679(*s*), 1593, 1488(*s*), 1453, 1404, 1373, 1326, 1273, 1215, 1182, 1131, 1091(*s*), 1059, 1009(*s*), 946, 910, 834(*s*), 815, 757, 732, 599.

(5)-d; ^1H -nmr; 7.1~7.4 (*m*, 5 H), 2.0 (*s*, 1H), 1.8~2.0(*m*, 2 H), 1.4~1.8(*m*, 4 H), 0.8~1.4 (*m*, 6 H) ^{13}C -nmr; 148.4, 128.0, 126.9, 126.1, 72.9, 40.7, 25.5, 22.8, 19.6, 17.2, 15.0, 14.6, 14.1 ir; 3449(*b*), 3006, 2983(*s*), 2861, 1681(*s*), 1450, 1327(*s*), 1165, 1123(*s*), 1064(*s*), 1022(*s*), 949, 909, 846, 792, 702, 590, 552.

(6)-a; ^1H -nmr; 7.0(*q*, 4 H), 5.12(*t-t*, 2 H), 4.2(*t*, 2H), 3.75 (*s*, 3 H), 2.1 (*t*, 2 H), 1.95(*s*, 1H) ^{13}C -nmr; 158.6, 135.7, 127.5, 122.9, 120.7, 113.1, 77.0, 75.3, 68.3, 55.1, 38.0 ir; 3542(*b*), 3040(*s*), 2950, 2863, 1613(*s*), 1583, 1512(*s*), 1461, 1416, 1384, 1361, 1303, 1247(*s*) 1178(*s*), 1111, 1039(*s*), 1013, 970, 905, 833, 811, 748.

(6)-b; ^1H -nmr; 7.2 (*q*, 4 H), 5.7 (*t-t*, 2 H), 4.2(*t*, 2H), 2.56(*t*, 2 H), 2.3 (*s*, 3 H), 1.95 (*s*, 1H) ^{13}C -nmr; 140.5, 136.3, 128.3, 126.3, 122.8, 120.6, 77.5, 75.2, 68.4, 37.9, 20.9 ir; 3541(*b*), 3040(*s*), 2940, 1613, 1512(*s*), 1451, 1381, 1332, 1267, 1172(*s*), 1118, 1056, 1009, 967, 926, 903, 818, 746, 528.

(6)-c; ^1H -nmr; 7.25(*q*, 4 H), 5.7(*t-t*, 2 H), 4.2(*t*, 2H), 2.55(*t*, 2H), 1.99(*s*, 1H) ^{13}C -nmr; 142.1, 132.6, 127.9, 127.7, 123.0, 77.4, 75.1, 68.3, 37.9 ir; 3552, 3445(*b*), 3043(*s*), 2984, 1618, 1595, 1490(*s*), 1402(*s*), 1383, 1361, 1318, 1268, 1211, 1177(*s*), 1092(*s*), 1051, 1012(*s*), 969, 945, 925, 903, 831, 810, 738, 469.

(6)-d; ^1H -nmr; 7.1~7.45(*m*, 5H), 5.7(*t-t*,

2H), 4.2 (*t*, 2 H), 2.61 (*t*, 2 H), 1.99 (*s*, 1 H)
¹³C-nmr: 143.3, 127.6, 127.0, 126.4, 123.0,
 120.7, 77.6, 75.2, 68.6, 38.0 ir: 3552, 3457
 (*b*), 3040 (*s*), 2947, 1618, 1493 (*s*), 1446 (*s*),
 1363 (*s*), 1319, 1269, 1179 (*s*), 1121, 1064,
 1048(*s*), 1011 (*s*), 969, 935, 907, 813, 747,
 699, 651, 599.

(III) Synthesis of Carbonium Ions

The cation solutions were prepared from the corresponding carbinols according to the method described in the Results and Discussion section.

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