Pergamon

Tetrahedron 55 (1999) 6081–6096

TETRAHEDRON

1,1-Ethylene-1*H*-azulenium Ion and Its Alkyl Substituted Derivatives: Synthesis, Characterization, and Some Reactions Thereof

Mitsunori Oda,* Takanori Kajioka, Takuya Uchiyama, Kohki Nagara, Tetsuo Okujima,† Shunji Ito,† Noboru Morita,*† Toshio Sato,†† Ryuta Miyatake, and Shigeyasu Kuroda*

Department of Applied Chemistry, Faculty of Engineering, Toyama University, Gofuku 3190, Toyama 930-8555 Japan,
†Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980-8578 Japan,
†† Instrumental Analytical Center for Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980-8578 Japan.

Received 17 February 1999; accepted 25 March 1999

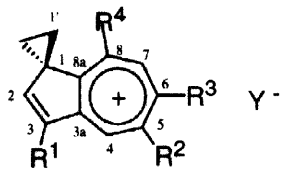
Keywords: carbocations; spiro compounds; tropylium ions; azulenium ions

Abstract. *1,1-Ethylene-1H-azulenium tetrafluoroborate (**1b**) and its alkyl substituted derivatives, 6-t-butyl (**1c**) and 4-isopropyl-3,8-dimethyl ones (**1d**), were synthesized starting from their corresponding azulenes by a three-step sequence which includes reduction, cyclopropanation and hydride abstraction reactions. The cation **1b** and its 6-t-butyl derivative **1c**, generated in deuterated acetonitrile at −20 °C, were characterized by low-temperature NMR spectroscopy. On the other hand, the cation **1d** was isolated as slightly unstable, greenish-yellow crystals. While the cation **1b** in solution underwent expansion of the cyclopropane ring at elevated temperatures, **1c** and **1d** just decomposed. All the cations were found to react easily with nucleophiles to give thermodynamically controlled, stable addition products at their cyclopropane methylene carbons.*

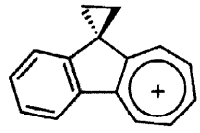
The solvolytic behavior of β-arylalkyl systems has been a widely studied and most controversial topic in modern physical and organic chemistry.[1] Solvolytic studies of a wide variety of benzenoid arylalkyl derivatives have been documented to prove the anchimeric assistance of the aromatic p-orbital.[2] On the other hand, McDonald *et al.* had reported that the 1-azulyl substituent, a typical nonbenzenoid group, was a super-participator in β-azulylethyl *p*-toluenesulfonate solvolysis, and the displacement of the leaving group by the solvent occurred via

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00280-X

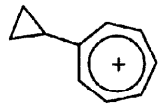
the intermediary 1,1-ethylene-1*H*-azulenium tosylate (**1a**).[3,4] Athough the cationic intermediates in benzenoid aryalkyl systems were elucidated in detail by the extensive works of Olah's group,[5] alternative generation and characterization of those in the azulene system have not been studied except the benzannelated cation **2**,[6] and a full account of the chemistry of **2** has not appeared yet. Meantime, the cation **1** embodies the structure of cyclopropyltropylium cation (**3**)[7] and is a more suitable candidate than **3** to evaluate σ–π interaction between a cyclopropane ring and an electron-defficient p-orbital[8] because of its structural rigidity and appropriate bisected geometry. Herein we report in full detail the synthesis, characterization, and some reactions of 1,1-ethylene-1*H*-azulenium tetrafluoroborate (**1b**) and its alkyl substituted derivatives **1c** and **1d**.[9]



1a ; Y = OTs, R^1, R^2, R^3, R^4 = H
1b ; Y = BF_4, R^1, R^2, R^3, R^4 = H
1c ; Y = BF_4, R^1, R^2, R^4 = H, R^3 = *t*-Bu
1d ; Y = BF_4, R^1, R^4 = Me, R^2 = *i*-Pr, R^3 = H



2

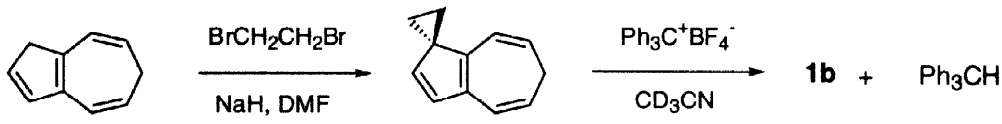


3

RESULTS AND DISCUSSION

Synthesis of 1,1-Ethylene-1H-azulenium Tetrafluoroborate and Its Alkyl Substituted Derivatives

The synthesis of **1b** was accomplished in a few steps starting from readily available azulene as follows (Scheme 1). Reaction of 1,6-dihydroazulene (**4**), prepared from azulene by the Birch reduction in good yield,[10] with 1,2-dibromoethane and sodium hydride as a base in DMF gave 1,1-ethylene-1,6-dihydroazulene (**5**),[11] the precursor for the title cation, as a slightly air-sensitive oil in 77% yield. Yields of **5** in THF or liquid ammonia as the solvent were far less than that in DMF. Addition of a molar equivalent of trityl tetrafluoroborate to a deuterated acetonitrile solution of **5** at -20 °C resulted in a slightly greenish solution. ^{1}H and ^{13}C NMR spectra measured at the same temperature are shown in Figure 1, which indicates complete disappearance of **5** and formation of the title cation **1b** along with triphenylmethane (**6**); the ^{1}H NMR spectrum of this reaction mixture showed a 4H singlet at δ = 2.75 ppm for the cyclopropane methylene protons, two doublets at δ = 7.69 and 7.82 ppm for the



4 **5** **6**

Scheme 1.

five-membered ring protons, and finely split 5H signals at δ = 8.51–9.02 ppm for the seven-membered ring protons. The ^{13}C NMR exhibited two aliphatic signals at δ = 24.1 and 44.7 ppm and nine olefinic signals between δ = 133.0 and 172.9 ppm for **1b**, besides signals for **6**. On the other hand, hydride abstraction of **5** with other reagents, such as nitrosonium tetrafluoroborate,[12] fluorosulfonic acid,[13] and dichlorodicyano-

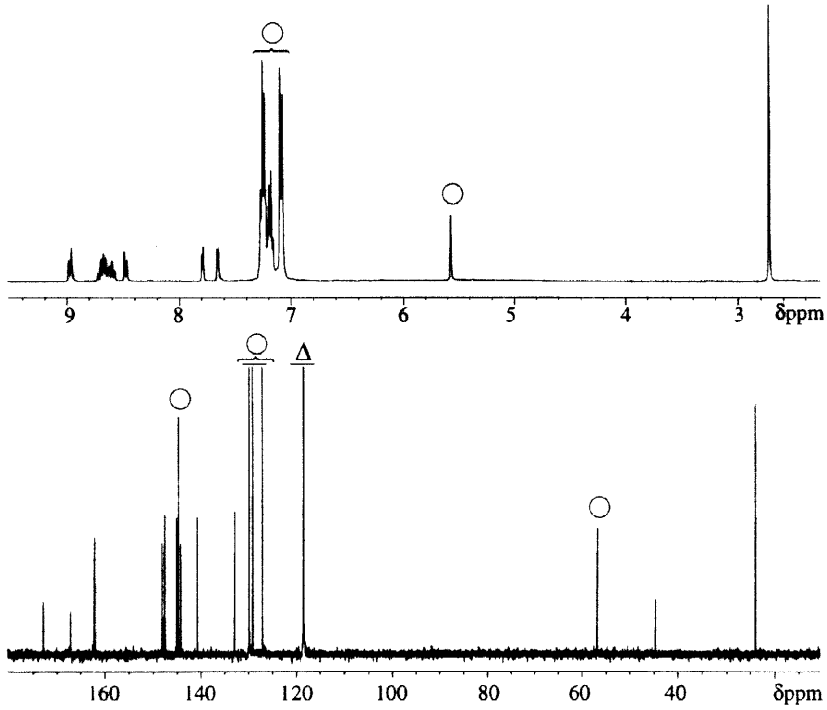
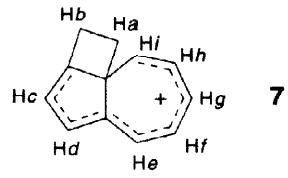


Fig. 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1b** in a CD_3CN solution at -20 °C. Δ ; solvent, ○ ; Ph_3CH.

benzoquinone,[14] gave only intractable spectra. Addition of Et_2O to the reaction mixture of **1b** at -20 °C gave greenish solids. However, several efforts for purification of these solids by filtration and recrystallization at low temperature under inert atmosphere met with little success, probably because of both its labile nature and nucleophile sensitivity (vide infra).

The cation **1b** in the reaction solution was stable at -20 °C, but it rearranged at 0 °C with a half-life time of 27 min ($k = 4.24 \times 10^{-4}$ sec^{-1} at 0 °C). After completion of the rearrangement, the color of the solution turned dark brown. New signals, displacing those of **1b**, in ^{1}H (Figure 2) and ^{13}C NMR spectra at 0 °C were best interpreted to be those of the cation **7** which was formed by expansion of the cyclopropane ring of **1b**. Further NMR studies such as the proton decoupling experiments, and DEPT, HMQC, and HMBC (Figure 3) spectra strongly suggested the structure of **7**. Proton spin-decoupling spectra of **7** showed an AB quartet at δ = 4.58 ppm with a coupling constant of 15.0 Hz under irradiation at δ = 2.88 ppm and also an AB quartet at δ = 2.88 ppm with a coupling constant of 14.4 Hz under that at δ = 4.58



7

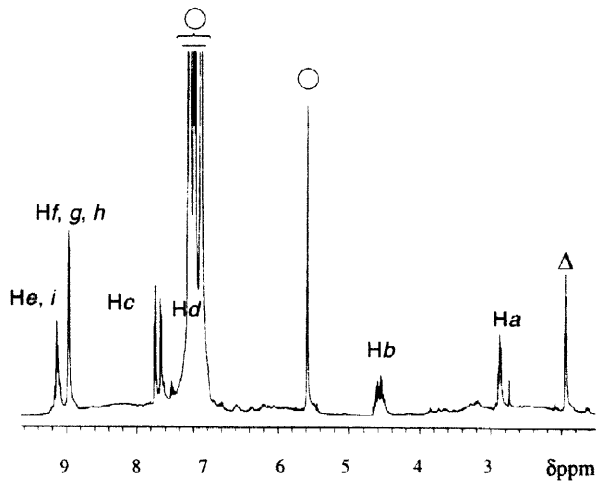


Fig. 2. The ^{1}H NMR spectrum of **7** in a CD_3CN solution at 0 °C. Δ ; solvent, ○ ; Ph_3CH.

ppm.The differences in both the geminal coupling constants and the vicinal coupling manner indicate that the cyclobutane ring of **7** was fairly strained in its congested ring system. Many efforts to trap the cation **7** with various nucleophiles, such as alcohols, water, and amines, were unsuccessful.

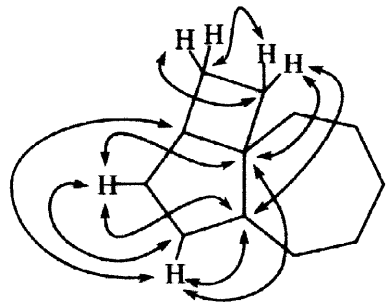
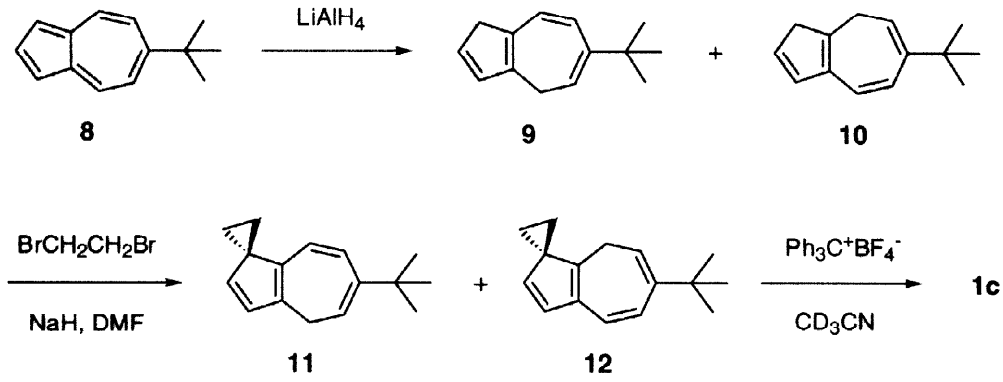


Fig. 3. Correlations in the HMBC spectrum of the cation **7**.

The 6-*t*-butyl substituted cation **1c** was synthesized from 6-*t*-butylazulene (**8**)[15] in a similar manner except for the reduction step (Scheme 2). We envisioned either 6-*t*-butyl-1,4- or 6-*t*-butyl-1,8-dihydroazulene (**9** or **10**) as an appropriate synthetic intermediate for **1c** instead of 6-*t*-butyl-1,6-one, because the hydride abstraction reaction of 7-substituted cycloheptatrienes with trityl salt has been known to suffer from steric hindrance.[7,16] Therefore, an alternative method was chosen for reduction of **8**; with lithium aluminium hydride in refluxing Et_2O, **8** gave a mixture of **9** and **10** in the ratio of 4 to 1 in 85% yield. This mixture was cyclopropanated with sodium hydride and 1,2-dibromoethane in DMF and then was subjected to hydride abstraction with trityl tetrafluoroborate in deuterated acetonitrile at -20 °C to give the cation **1c** and triphenylmethane; these products were detected by low-temperature NMR spectroscopy (Figure 4). This cation **1c** was found to be stable at -20 °C; however, contrary to the case of **1b**, at elevated temperatures its signals decreased without any detectable displacing signals. The half-life time ($t_{1/2}$ = 154 min, k = 7.47 x 10^{-5} sec^{-1} at 0 °C) in the decomposition was longer than that of the rearrangenment of **1b**.



Scheme 2.

The 5-isopropyl-3,8-dimethyl substituted cation **1d** was synthesized starting from guaiazulene (**13**) through the dihydroazulene **14** and its cyclopropanated precursor **15** in a completely similar manner to that of **1b**. Reaction of **15** with trityl tetrafluoroborate in acetonitrile at - 20 °C resulted in a greenish reaction solution from which **1d** was obtained as unstable greenish-yellow crystals in 58% yield by adding ether and subsequent filtration. Triphenylmethane **6** was isolated from the filtrate in a quantitative yield. This cation was characterized by IR, UV, MS, and NMR (Figure 5) spectroscopic methods. Notably, in the ^1H NMR spectrum of **1d** the methylene protons at the cyclopropane ring appear separately at δ = 2.37 and 2.94 ppm as a multiplet, while those of **1b** and **1c** combine as a singlet. The cation **1d** in a deuterated acetonitrile solution was stable at 0 °C, but gradually decomposed at room temperature without any detectable formation of product. Its half-life time was 230 min at 23 °C (k = 5.02 x 10^{-5} sec^{-1}), showing that **1d** is kinetically more stable than **1b** and **1c**. A solid sample of **1d** could be stored in a freezer over a year without any appreciable decomposition.

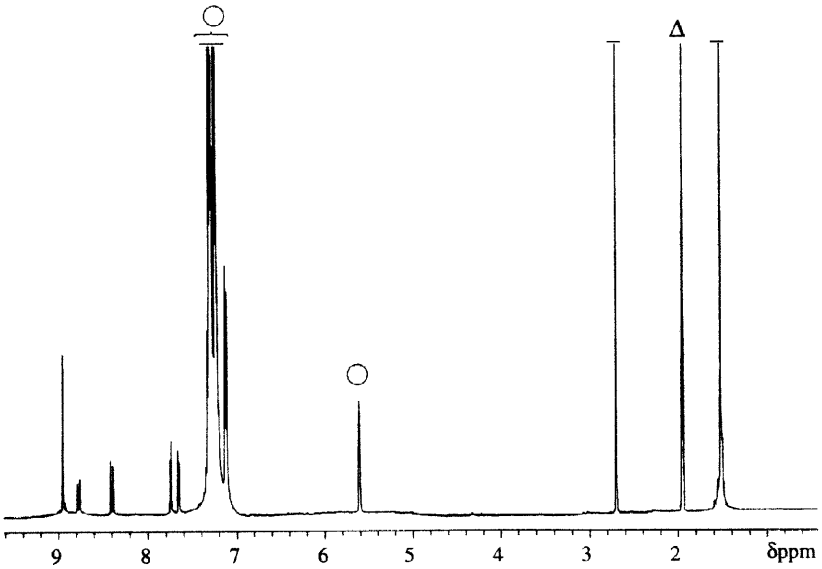


Fig. 4. The ^{1}H NMR spectrum of **1c** in a CD_3CN solution at -20 °C. Δ ; solvent, ○ ; Ph_3CH.

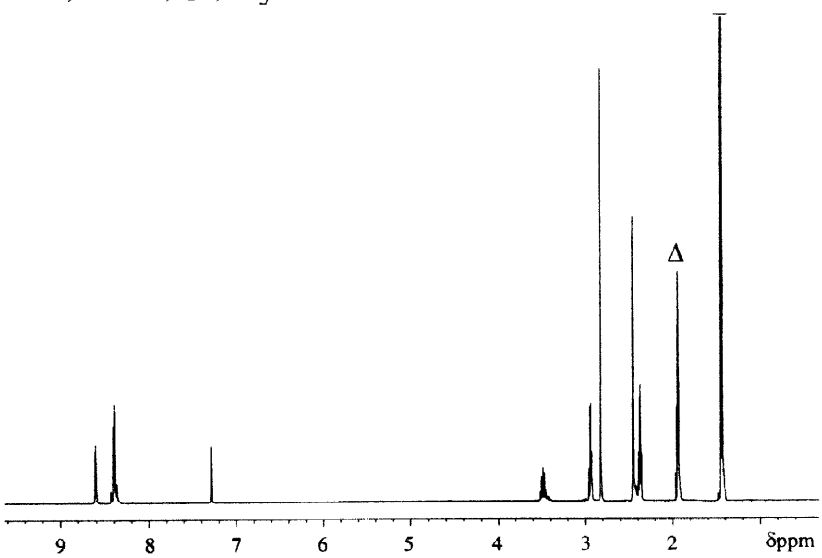
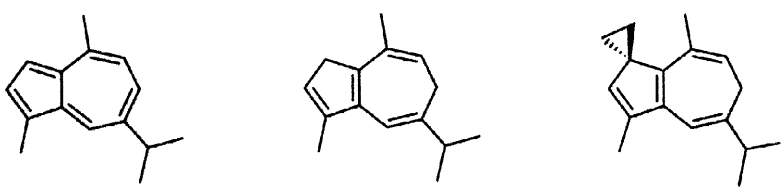


Fig. 5. The ^{1}H NMR spectrum of **1d** in a CD_3CN solution at 0 °C. Δ ; solvent.



13 **14** **15**

NMR Spectral Properties of the Cations

Full assignment of signals for **1b** in both ^{1}H and ^{13}C NMR spectra was made through experiments of the pulsed field gradient method of 2D spectra (H-H COSY, HMQC, HMBC and NOESY).[17] It should be noted that

correlations observed between the three-membered ring methylene signal and both proton signals at $\delta = 7.82$ and 8.51 in the NOESY spectrum were quite helpful to make the definite assignment of the ring protons on the azulene skeleton. Also, correlations between the C-8a carbon and the H-4 and cyclopropane methylene protons and between the C-3a carbon and the H-8 proton in the HMBC spectrum were essential to assign those quarternary olefinic carbons. Spectral data of **1b**, **1c**, **1d**, and phenonium ion (**16**)[2,5] are summarized in Figure 6. The higher field shift of the cyclopropane carbon and methylene proton signals in **1b** compared with those of **16** indicates less delocalization of the positive charge to the three-membered ring part in **1b** than in the case of **16**. This might be attributed to the difference in stability of the cationic parts between **1b** and **16**, the former of which has a part of a typically aromatic tropylium cation. An equivalent coupling constant between the vicinal protons on the seven-membered ring of **1b** testifies to the least bond alternation around the ring as a consequence of its aromatic nature. The average chemical shifts of the azulene ring and cyclopropane methylene protons of **1c** and **1d** are

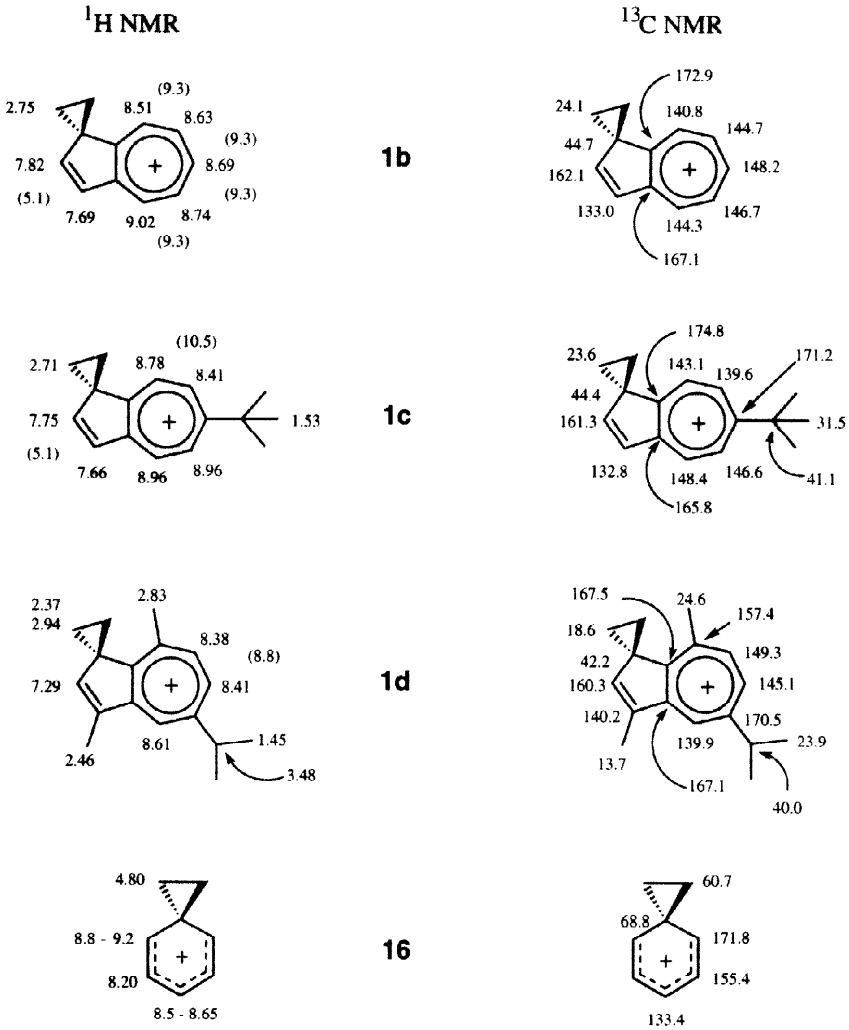


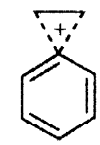
Fig. 6. NMR assignment for **1** and **16**. Coupling constants are given in parentheses.

apparantly shifted slightly to higher field than that of **1b**, showing the efficient inductive effect of the alkyl substituents. Although the thermodynamic stability of these cations has not been evaluated, the effect of alkyl substituents is consistent with their approximate kinetic stability in the order of **1d** > **1c** > **1b**.[18]

Schleyer *et al.*[19] reported that the phenonium ion was nonclassical with appreciable 6π-aromatic character and was most clearly represented by the structure **16'** based on the optimized geometry calculated by the *ab initio* MP2/6-31G* method. However, Olah *et al.* [20] lately concluded that the phenonium ion is predominantly classical in nature, judging from the total chemical shift difference (TCSD),[21] the difference in the sum of all ^{13}C shifts of the carbocation and its corresponding neutral hydrocarbon. In the meantime, it is of substantial interest to apply the TCSD approach to **1** to see whether the classical or nonclassical structure is ascendant in the nature of **1**. The TCSD between **1b** and **5** is 323 ppm which applies to borderline cases but is rather close to the lowest limit of values (350 ppm) for classical ions.[22] In view of both facts of this TCSD value and the degree of positive charge delocalization in **1b**, its structure is suggested to be classical. TCSD values for **1c** and **1d** (Table 1) are quite similar to that for **1b**, indicating that **1c** and **1d** have also the classical structure.

Table 1. The total chemical shift difference of phenonium and the azulenium cations (ppm).

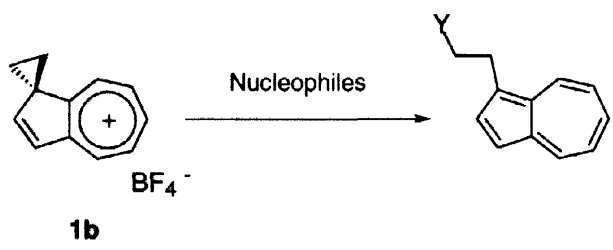
Cation	Total chemical shift of the cation	Total chemical shift of the corresponding hydrocarbon	Difference
16	958	582	376
1b	1454	1131	323
1c	1606	1277	329
1d	1603	1275	328



16'

Addition Reactions to the Cations

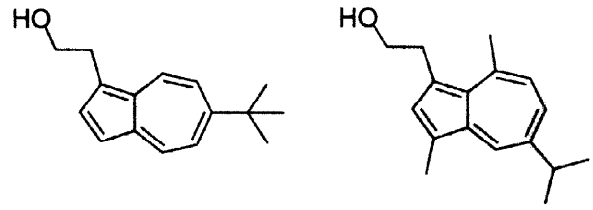
Addition of an excess of water to an acetonitrile solution of **1b** at -20 °C resulted in a blue reaction solution, from which the alcohol product **17**[4,23] was obtained in 83% yield as a blue oil after silica gel chromatography (Scheme 3). Cations **1c** and **1d** also reacted with water to give the alcohol products **18** and **19** in 31 and 21 % yields, respectively. Methanol, sodium acetate and diethylamine also added to the cation **1b** to yield the



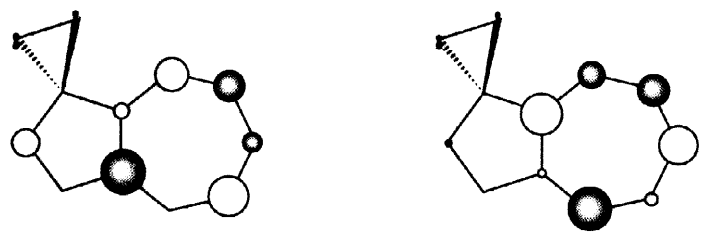
Scheme 3.

products **20**, **21**[24] and **22** in 31, 83, and 67% yields, respectively. The reaction of **1b** with sodium phenylsulfinate, a typical ambident nucleophile, afforded two products, the phenyl sulfone **23** and the phenylsulfinate **24**, in 28 and 19% yields, respectively. Independent of the nature of nucleophiles used, all

products obtained after silica gel chromatography are the ones derived from addition at the cyclopropane methylene carbons of the cations, though the tropylium ion is known to capture the nucleophile readily at their seven-membered ring carbons.[25,26] Since the coefficients of LUMO and nearly lying next LUMO calculated by semiempirical molecular orbital calculations–the AM1 method[27]–for **1b** predict higher reactivity at the seven-membered ring compared withthat of the cyclopropane ring (Figure 7), it seems possible that adducts at the azulene skeleton



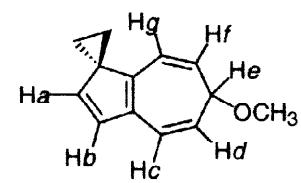
18 **19**



LUMO (– 6.190 eV) next LUMO (– 5.941 eV)

Fig. 7. LUMO and next LUMO orbitals for **1** calculated by the AM1 method.

carbons are formed. In order to gain insight into the mechanism of these reactions, the methoxy group addition reaction was carried out under several reaction conditions. Reaction of **1b** with a methanol solution of an excess sodium methoxide and subsequent purification of the crude product only by distillation gave a mixture of the methoxy ether products[28] in 48% yield. The ^{1}H NMR spectrum of this mixture revealed that it consists of several addition products at the seven-membered ring[29] and none of **20**. Although the signals in the spectrum were not fully characterized, the major component was deduced as 1,1-ethylene-6-methoxy-1,6-dihydroazulene (**25**); signals as a doublet at δ = 6.64 ppm (J = 5.2 Hz) for H*b*, a doublet of a doublet at δ = 6.45 ppm (J = 10.0, 1.2 Hz) for H*c*, a doublet at δ = 6.19 ppm (J = 5.2 Hz) for H*a*, a doublet of a doublet at δ = 6.00 ppm (J = 10.0, 1.2 Hz) for H*g*, a multiplet (2H) at δ = 5.39 ppm for H*d* and H*f*, a triplet of a triplet at δ = 3.44 ppm (J = 4.8, 1.2 Hz) for H*e*, a singlet (3H) at δ = 3.33 ppm for the methoxy group, and a multiplet (4H) at δ = 1.41-1.78 ppm for the cyclopropane methylene protons, were observed in the spectrum. Thus, addition at the seven-membered ring carbons was indeed found to proceed under basic conditions. This mixture was sensitive to acids so that it decomposed quickly on silica gel and rearranged to **20** in 83% yield under the acidic methanol conditions. Furthermore, by using 2% trifluoroacetic acid–methanol as a nucleophilic substrate for the addition reaction of **1b** the yield of **20** was improved to 77 %. Therefore, in nucleophilic reactions, the adducts at the seven-membered ring carbons are likely to be kinetically controlled ones as predicted by the molecular orbital calculations and those at the cyclopropane ring carbons are thermodynamically controlled ones.



25

SUMMARY

We have demonstrated the synthesis of 1,1-ethylene-1*H*-azulenium tetrafluoroborate and its alkyl substituted derivatives in short steps from azulene and the corresponging azulene derivatives, respectively. Although we were unable to evaluate their thermodynamic stability with respect to the σ–π conjugation, alkyl substituion on this cationic azulene skeleton was found to be effective to stabilize the π-electron system. Nucleophilic addition to these cations gave mainly the thermodynamically controlled, stable products, which are derived from addition at their cyclopropane methylene carbons.

EXPERIMENTAL

Melting points were measured on an Yanaco MP–3 and are uncorrected. IR spectra were recorded on a JASCO IR-810 spectrometer. UV spectra were measured on a Shimadzu UV-256FS spectrometer. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 Hz) were recorded with tetramethylsilane as an internal standard on a JEOL α400. Mass spectra were measured on a JEOL JMS-D-300 mass spectrometer. Column chromatography was done with Merck Kieselgel 60 Art 7734. Acetonitrile-d_3 (isotopic purity 99.5%) was purchased from Aldrich Chem. Co. and purified by distillation from calcium hydride. Azulene was prepared by Hafner's method[30] and 6-*t*-butylazulene was prepared by its modified method reported by Asao *et al.*[15] Guaiazulene was purchased from Tokyo Kasei Kogyo Co. Trityl tetrafluoroborate was prepared by the reported method.[31] 1,2-Dibromoethane was purchased from Wako Pure Chem. Ind. and purified by distillation from phosphorous pentaoxide. THF and Et_2O were purified just before use by distillation from sodium diphenylketyl under nitrogen atmosphere. DMF was purchased from Tokyo Kasei Kogyo Co. and purified by distillation from calcium hydride. Semiemperical moleclar orbital calculations were conducted on an IBM RS / 6800-580 computer by using the MOPAC program (ver. 6.02) with full geometrical optimization.

Birch Reduction of Azulene and Guaiazulene.

1,6-Dihydroazulene (**4**): A 1-l three-necked flask, fitted with a low-temperature condenser and an inlet tube connected to an ammonia source, was cooled by a dry ice-*i*-PrOH bath. The flask was charged with approximately 250 ml of liquid ammonia, and a solution of 5.00 g (39.1 mmol) of azulene in 60 ml of Et_2O was added. To this solution was added 2.50 g (0.109 atom) of sodium in small portions over 10 min. After this mixture was stirred for 30 min at -78 °C, 10 ml of MeOH, 50 ml of a saturated NH_4Cl solution and 100 ml of Et_2O were slowly added in that order and then the cooling bath was removed to evaporate the ammonia. The resulted reaction mixture was poured into 300 ml of 2 M hydrochloric acid and extracted with Et_2O (3 x 100 ml). The combined organic layer was washed with a saturated $NaHCO_3$ solution and brine, and then dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual oil was purified by chromatography (SiO_2, pentane) to give 4.72 g (93%) of **4** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ = 2.32 (t, *J* = 6.8 Hz, 2 H), 3.26 (brs, 2 H), 5.20 (dt, *J* = 8.8, 6.8 Hz, 1 H), 5.32 (dt, *J* = 8.8, 6.8 Hz, 1 H), 6.35 (d, *J* = 5.4 Hz, 1 H), 6.46 (d, *J* = 8.8 Hz, 1 H), 6.48 (d, *J* = 8.8 Hz, 1 H), 6.59 (d, *J* = 5.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 27.7 (t), 44.0 (t), 115.6 (d), 117.7 (d), 124.5 (d),125.7 (d), 131.7 (d), 135.0 (d), 143.7 (s), 144.1 (s); IR (film) 3010 (w), 2950 (w), 2860 (w), 1430 (w), 1375 (w), 645 (w), 895 (w), 840 (w), 790 (m), 690 (s) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 130 (M^+, 100), 129 (69), 128 (53), 127 (24), 115 (60), 93 (17), 91 (20), 69 (25), 51 (22). Found: *m/z* 130.0784. Calcd. for $C_{10}H_{10}$: M, 130.0782.

5-Isopropyl-3,8-dimethyl-1,6-dihydroazulene (**14**): In the same manner as described above, 2.00 g (10.1 mmol) of guaiazulene (**13**) was transformed to **14** (1.78 g, 88%). A pale yellow oil. ^{1}H NMR ($CDCl_3$) δ = 1.13 (d, *J* = 6.8 Hz, 6 H), 1.97 (s, 3 H), 2.03 (s, 3 H), 2.24 (d, *J* = 6.9 Hz, 2 H), 2.56 (hept, *J* = 6.8 Hz, 1 H), 3.13 (brs, 2H), 5.01 (t, *J* = 6.9 Hz, 1 H), 6.01 (brs, 1 H), 6.14 (s, 1 H); ^{13}C NMR ($CDCl_3$): δ = 14.1 (q), 21.1 (q), 22.6 (q), 30.3 (t), 35.6 (d), 40.7 (t), 113.8 (d), 114.6 (d), 125.5 (d), 132.8 (s), 142.9 (s), 143.3 (s), 143.5 (s), 144.0 (s); IR (film) 2995 (s), 2860 (m), 1630 (w), 1460 (w), 1450 (m), 1380 (m), 1305 (w), 1200 (w), 1010 (w), 860 (w), 790 (w), 740 (w) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 200 (M^+, 27), 198 (22), 185 (19), 183 (34), 158 (20), 157 (100), 143 (19), 142 (35), 141 (14), 128 (10), 68 (20), 28 (18); UV λmax (hexane) 220 nm(log ε = 4.14), 231 (4.16), 291 (3.49), 304 (3.48). Found: *m/z* 200.1528. Calcd for $C_{15}H_{20}$: M, 200.1564.

Lithium Aluminium Hydride Reduction of 6-t-Butylazulene (**8**).

6-t-Butyl-1,4- and 6-t-butyl-1,8-dihydroazulenes (**9** and **10**): To a solution of 1.00 g (5.34 mmol) of 6-*t*-butylazulene (**8**) in 50 ml of THF at 0 °C under nitrogen atmosphere was added 406 mg (10.7 mmol) of lithium aluminium hydride in several portions. After the addition, the ice bath was removed and the mixture was refluxed on an oil bath for 1 h. Then, the resulted reaction mixture was cooled to 0 °C and water (5 ml) was added carefully to this mixture, which was poured into a cold 9 M hydrochloric solution (200 ml) and extracted with hexane (3 x 50 ml). The combined organic layer was washed with brine and dried with anhydrous $MgSO_4$. Evaporation of the solvent gave 0.95 g of a brown oil which was purified by chromatography (SiO_2, hexane) to give 848 mg (85%) of a mixture of **9** and **10** (4:1) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ = 1.04 (s, 9 H x 0.2), 1.09 (s, 9 H x 0.8), 2.60 (d, *J* = 6.8 Hz, 2 H x 0.2), 2.62 (d, *J* = 6.8 Hz, 2 H x 0.8), 3.05 (brs, 2 H x 0.8), 3.08 (brs, 2 H x 0.2), 5.24 (t, *J* = 6.8 Hz, 1 H x 0.8), 5.26 (t, *J* = 6.8 Hz, 1 H x 0.2), 6.18 (d, *J* = 5.6 Hz, 1 H x 0.2), 6.37 (d, *J* = 5.6 Hz, 1 H x 0.8), 6.44 (d, *J* = 5.6 Hz, 1 H x 0.8), 6.50 (d, *J* = 5.6 Hz, 1 H x 0.2), 6.55 (d, *J* = 11.6 Hz, 1 H x 0.8), 6.66 (d, *J* = 11.6 Hz, 1 H x 0.2), 6.71 (d, *J* = 11.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 27.2, 27.7, 30.3, 35.0, 35.1, 43.6, 49.9, 114.0, 114.9, 126.5, 127.3, 127.6, 129.5, 129.6, 133.7, 135.2, 138.4, 139.0, 139.8, 140.6, 146.6, 147.1; IR (film) 2995 (s), 2860 (m), 1465 (w), 1365 (m), 950 (w), 840 (m), 770 (m) cm^{-1}. EIMS (70 eV) *m/z* (%): 186 (M^+, 33), 185 (20), 171 (15), 145 (13), 143 (12), 130 (43), 129 (100), 128 (32), 115 (22), 93 (26), 77 (18), 57 (85), 41 (43), 39 (19). Found: *m/z* 186.1392. Calcd for $C_{14}H_{18}$: M, 186.1408.

Cyclopropanation of 1,6-Dihydroazulene and its Derivatives.

General Procedure : To a solution of the dihydroazulene (15 mmol) in 50 ml of DMF at 0 °C was added 708 mg (29.5 mmol) of sodium hydride in one portion and 2.82 g (15 mmol) of 1,2-dibromoethane dropwise. After the addition, the ice bath was removed and the reaction mixture was stirred for 30 min at room temp. Then 10 ml of EtOH and a saturated NH_4Cl solution was slowly added to the mixture. The resulted reaction mixture was poured into water (200 ml) and extracted with hexane (3 x 50 ml). The combined organic layer was washed with brine, and then dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual oil was purified by chromatography (SiO_2, hexane) to give the title compound.

1,1-Ethylene-1,6-dihydroazulene (**5**): 79% yield. A colorless oil. ^{1}H NMR ($CDCl_3$) δ = 1.50 (q-like, *J* = 3.7 Hz, 2 H), 1.66 (q-like, *J* = 3.7 Hz, 2 H), 2.36 (t, *J* = 6.8 Hz, 2 H), 5.28 (dt, *J* = 9.3, 6.8 Hz, 1 H), 5.30 (dt, *J* = 9.3, 6.8 Hz, 1 H), 5.95 (d, *J* = 9.3 Hz, 1 H), 6.09 (d, *J* = 5.1 Hz, 1 H), 6.50 (d, *J* = 9.3 Hz, 1 H), 6.63 (d, *J* = 5.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 14.5 (t), 27.9 (t), 37.4 (s), 116.8 (d), 117.0 (d), 120.5 (d), 125.1 (d),

131.0 (d), 138.4 (d), 141.7 (s), 146.1 (s); IR (film) 3010 (s), 2945 (m), 2860 (w), 1610 (m), 1485 (m), 1430 (s), 1395 (s), 1280 (s), 1075 (s), 1040 (s), 955 (s), 820 (s), 785 (s), 720 (s), 695 (s), 645 (s) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 156 (M^+, 60), 155 (48), 141 (100), 129 (29), 128 (44), 115 (39), 102 (8), 89 (5), 7 (20), 77 (13), 64 (17), 51 (16), 39 (12). UV λmax (hexane) 236 nm (log ε = 4.36), 311 (3.67). Found: *m/z* 156.0945. Calcd for C12H12: M, 156.0938.

1,1-Ehylene-5-isopropyl-3,8-dimethyl-1,6-dihydroazulene (**15**): 38% yield. A colorless oil. ^{1}H NMR ($CDCl_3$) δ = 1.12 (d, *J* = 6.8 Hz, 6 H), 1.50 (m, 2 H), 1.77 (m, 2 H), 1.84 (s, 3 H), 2.03(s, 3 H), 2.17 (d, *J* = 7.3 Hz, 2 H), 2.53 (hept, *J* = 6.8 Hz, 1 H), 5.02 (t, *J* = 7.3 Hz, 1 H), 5.58 (s, 1 H), 6.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ = 12.8 (t), 14.0 (q), 20.6 (q), 22.5 (q), 30.0 (t), 35.2 (d), 36.5 (s), 115.1 (d), 117.8 (d), 130.3 (s), 134.4 (d), 137.9 (s), 143.4 (s), 144.5 (s), 145.1 (s); IR (film) 2960 (w), 2920 (s), 2825 (m), 1610 (w), 1440(m), 1430 (m), 1360 (m), 1305 (w), 1195 (w), 1160 (w), 1025 (w), 955 (m), 920 (w), 840 (w), 6700 (m), 755 (w) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 226 (M^+, 45), 221 (57), 183 (100), 168 (21), 153 (17), 141 (10), 128 (9), 115 (7), 41 (8), 39 (7). UV λmax (hexane) 209sh nm (log ε = 4.05), 231sh (4.20), 238 (4.20), 298 (3.56). Found: *m/z* 226.1721. Calcd for $C_{17}H_{22}$: M, 226.1720.

A Mixture of 1,1-Ethylene-6-t-butyl-1,4- and 1,1-ethylene-6-t-butyl-1,8-dihydroazulenes(**11** and **12**, 1:1): 45% yieled. A colorless oil. ^{1}H NMR ($CDCl_3$) δ = 1.09 (s, 9 H), 1.48 (q, *J* = 3.6 Hz, 2 H x 0.5), 1.51 (q, *J* = 4.0 Hz, 2 H x 0.5), 1.61 (q, *J* = 3.6 Hz, 2 H x 0.5), 1.64 (q, *J* = 3.6 Hz, 2 H x 0.5), 2.24 (d, *J* = 6.6 Hz, 2 H x 0.5), 2.68 (d, *J* = 6.8 Hz, 2 H x 0.5), 5.13 (t, *J* = 6.6 Hz, 1 H x 0.5), 5.30 (t, *J* = 6.8 Hz, 1 H x 0.5), 5.99 (d, *J* = 5.4 Hz, 1 H x 0.5), 6.19 (d, *J* = 12.0 Hz, 1 H x 0.5), 6.19 (d, *J* = 5.2 Hz, 1 H x 0.5), 6.40 (d, *J* = 5.2 Hz, 1 H x 0.5), 6.52 (d, *J* = 5.4 Hz, 1 H x 0.5), 6.57 (d, *J* = 12.0 Hz, 1 H x 0.5), 6.62 (dd, *J* = 11.2, 1.2 Hz, 1 H x 0.5), 6.76 (d, *J* = 11.2 Hz, 1 H x 0.5); ^{13}C NMR ($CDCl_3$) δ = 12.9, 13.2, 23.4, 27.8, 30.3, 35.1, 35.9, 36.2, 113.4, 114.7, 122.2, 127.1, 128.4, 128.7, 129.8, 130.9, 136.3, 136.4, 137.7, 141.1, 141.3, 143.5, 146.9, 147.3; IR (film) 3000 (w), 2950 (s), 2895 (m), 2860 (m), 1680 (w), 1580 (w), 1460 (w), 1390 (w), 1360 (m), 1320 (w), 1280 (w), 1250 (w), 1140 (w), 1070 (w), 1030 (w), 1000 (w), 955 (m), 835 (w), 810 (w), 780 (w), 710 (w) cm^{-1}. MS (70 eV) *m/z* (rel intensity): 212 (M^+, 64), 201 (19), 187 (38), 159 (22), 157 (16), 155 (21), 132 (22), 128 (23), 115 (33), 91 (32), 77 (24), 57 (100). UV/Vis λmax (hexane) 204 nm (log ε = 4.12), 240sh (4.36), 275sh (3.91), 281 (3.98), 286 (3.97), 290sh (3.91), 347sh (3.21), 360sh (2.62). Found: *m/z* 212.1566. Calcd for $C_{16}H_{20}$: M, 212.1564.

Generation of 1,1-Ethylene-1H-azulenium Ions.

The General Procedure for NMR Measurements : In an NMR tube was charged a solution of 1,1-ethylenedihydroazulene (30~60 mmol) in 0.7 ml of acetonitrile-d_3. This tube was cooled at -20 °C with a dry ice-carbontetrachloride bath. To this solution was added one equivalent of trityl tetrafluoroborate quickly in one portion and the tube was capped and shaken well. Spectra of cations were measured at the same temp. and decomposition and rearrangement of cations were also monitored by NMR analysis at elevated probe temperatures. For ^{1}H NMR and ^{13}C spectral data of 1,1-ethylene-1*H*-azulenium tetrafluoroborate (**1b**) and 6-*t*-butyl-1,1-ethylene-1*H*-azulenium tetrafluoroborate (**1c**), see Figure 6.

4-Tricyclo[5.5.0.0^{1,4}]dodeca-5,7,9,11-tetraenium Ion (**7**): An acetonitrile-d_3 solution of **1b** in an NMR tube was prepared as described above and allowed to stand in a refrigerator at 0 °C for 12 hr. Then, NMR spectra were

recorded at 0 °C. ^{1}H NMR (CD_3CN, 0 °C) δ = 2.88 (m, 2 H), 4.58 (m, 2 H), 7.66 (d, *J* = 5.6 Hz, 1 H), 7.74 (d, *J* = 5.6 Hz, 1 H), 8.98 (m, 3 H), 9.13 (m, 2 H); ^{13}C NMR (CD_3CN, 0 °C) δ = 28.0 (t), 55.1 (t), 74.2 (s), 140.9 (d), 147.6 (d), 148.0 (d), 152.0 (d), 152.7 (d), 154.2 (d), 155.9 (d), 168.0 (s), 171.8 (s).

1,1-Ethylene-5-isopropyl-3,8-dimethyl-1H-azulenium Tetrafluoroborate (**1d**); To a solution of 193 mg (854 mmol) of 16 in 6 ml of acetonitrile at -20 °C was added 282 mg (854 mmol) of trityl tetrafuloroborate in one prtion. After being stirred at -20 °C for 10 min, 30 ml of Et_2O was added to the reaction mixture. Greenish-yellow crystals formed were collected by quick suction filtration and washed well with Et_2O to give 155 mg (58% yield) of **1d**. M.p. 150 °C (dec.). ^{1}H NMR (CD_3CN) δ = 1.45 (d, *J*=6.8 Hz, 6 H), 2.38 (dd, *J*=8.8, 4.9 Hz, 2 H), 2.46 (s, 3 H), 2.83 (s, 3 H), 2.94 (dd, *J* = 8.8, 4.9 Hz, 2 H), 3.48 (hept, *J* = 6.8 Hz, 1 H), 7.29 (brs, 1 H), 8.39 (brs, 1 H), 8.41 (d, *J* = 1.9 Hz, 1 H), 8.61 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (CD_3CN) δ = 13.7, 18.6, 23.7, 24.6, 40.0, 42.2, 139.9, 140.2, 145.1, 149.3, 157.4, 160.3, 167.1, 167.5, 170.5; IR (KBr) 2943 (m), 2855 (w), 1595 (w), 1520 (m), 1440 (w), 1405 (w), 1300 (m), 1200 (w), 1050 (brs), 970 (m) cm^{-1}. UV λmax (CH_3CN) 246 nm (log ε = 4.48), 293 (4.56), 351sh (3.56), 370sh (3.83), 387 (3.98). FABMS *m/z* (rel intensity): 225 ($C_{17}H_{21}^+$, 100), 224 (6), 211 (14), 183 (4), 179 (5), 165 (7), 154 (4), 152 (4), 136 (4), 115 (3), 91 (5), 77 (4). EIMS *m/z* (rel intensity): 226 ($C_{17}H_{21}^+$+H, 67), 225 ($C_{17}H_{21}^+$, 5), 211 (100), 198 (14), 183 (10), 152 (7), 141 (3), 128 (3), 115 (3). Found: *m/z* 226.1719. Calcd for $C_{17}H_{22}$: M, 226.1722. Found: *m/z* 225.1661. Calcd for $C_{17}H_{21}$: M, 225.1643. It did not give the satisfactory result of combustion analysis probably because of its moisture sensitivity.

Reactions of 1,1-Ethylene-1H-azulenium Ions with Nucleophiles.

General Procedure : Trityl tetrafluoroborate (1.0 mmol) was added in one portion to a solution of 1,1-ethylenedihydroazulene (1.0 mmol) in 10 ml of acetonitrile at – 20 °C. After the mixture was stirred at the same temp. for 10 min, ten equivalents of a nucleophile either in solution with an appropriate solvent or without a solvent was added. After the addition, the bath was removed and the reaction mixture was gradually warmed to room temp. The resulted mixture was poured into water (50 ml) and extracted with dichloromethane (3 x 30 ml). The combined organic layer was washed with brine and dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual oil was purified by chromatography to give triphenylmethane (95~99%) as colorless crystals and the addition product.

2-(1-Azulyl)ethylalcohol (**17**)[24]: 83% yield. A blue oil. ^{1}H NMR ($CDCl_3$) δ = 1.49 (s, 1 H), 3.37 (t, *J* = 6.3 Hz, 2 H), 3.99 (t, *J* = 6.3 Hz, 2 H), 7.13 (t, *J* = 9.8 Hz, 1 H), 7.15 (t, *J* = 9.8 Hz, 1 H), 7.38 (d, *J* = 3.7 Hz, 1 H), 7.59 (t, *J* = 9.8 Hz, 1 H), 7.85 (d, *J* = 3.7 Hz, 1 H), 8.30 (d, *J* = 9.8 Hz, 1 H), 8.36 (d, *J* = 9.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 31.0, 63.9, 117.0, 121.9, 122.5, 126.5, 133.7, 136.6, 136.9, 137.4, 137.7, 140.9.

2-{1-(6-t-butyl)azulyl}ethanol (**18**): 31% yield. A blue oil. ^{1}H NMR ($CDCl_3$) δ = 1.45 (s, 9 H), 1.68 (bs, 1 H), 3.32 (t, *J* = 6.3 Hz, 2 H), 3.95 (t, *J* = 6.3 Hz, 2 H), 7.27 (d, *J* = 3.7 Hz, 1 H), 7.28 (dd, *J* = 10.2, 1.8 Hz, 1 H), 7.32 (dd, *J* = 10.2, 1.8 Hz, 1 H), 7.72 (d, *J* = 3.7 Hz, 1 H), 8.22 (d, *J* = 10.2 Hz, 1 H), 8.28 (d, *J* = 10.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 30.8, 31.9, 38.5, 63.9, 116.4, 120.2, 120.5, 128.5, 132.7, 135.6, 135.7, 136.4, 139.5, 161.5; IR (film) 3340 (br), 3055 (w), 3025 (w), 2950 (m), 2860 (w), 1580 (m), 1550 (w), 1400 (m), 1305 (w), 1240 (w), 1040 (m), 840 (m), 765 (w), 715 (w) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity) 228 (M^+, 5), 227 (24), 142 (24), 141 (26), 128 (19), 87 (99), 86 (100). UV/Vis λmax (hexane) 239 nm (log ε = 4.18),

272sh (4.61), 278 (4.67), 283sh (4.63), 298sh (3.66), 320sh (3.66), 320sh (3.31), 330sh (3.45), 346 (3.48), 345 (3.65), 361 (3.42), 534sh (2.16), 556sh (2.35), 583 (2.41), 606 (2.49), 632 (2.42), 663 (2.43), 695 (2.08), 735 (2.04). Found: *m/z* 227.1673. Calcd for $C_{16}H_{20}O$: M, 227.1724.

2-[1-(5-Isopropyl-3,8-dimethyl)azulyl]ethanol (**19**): 21% yield. A blue oil. ^{1}H NMR ($CDCl_3$) δ = 1.33 (d, *J* = 6.8 Hz, 6 H), 2.61 (s, 3 H), 2.97 (s, 3 H), 3.01 (t, *J* = 6.8 Hz, 2 H), 3.92 (t, *J* = 6.8 Hz, 2 H), 6.85 (d, *J* = 10.5 Hz, 1 H), 7.27 (d, *J* = 10.5 Hz, 1 H), 7.48 (s, 1 H), 8.07 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ = 12.8, 24.6, 27.1, 34.4, 37.6, 64.8, 123.5, 124.5, 126.5, 132.9, 133.4, 134.7, 137.9, 139.1, 140.0, 145.2; IR (film) 3320 (br), 2955 (m), 1700 (w), 1650 (m), 1540 (w), 1460 (m), 1360 (w), 1320 (w), 760 (w) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 242 (M^+, 17), 212 (15), 211 (100), 209 (16), 195 (12), 165 (25), 141 (7), 128 (5), 120 (6), 110 (16), 78 (13). UV/Vis λmax (hexane) 245 nm (log ε = 4.18), 287 (4.41), 305 (4.00), 352 (3.56), 369 (3.50), 619 (2.35), 676sh (2.23), 747 (1.73). Found: *m/z* 242.1676. Calcd for $C_{17}H_{22}O$: M, 242.1669.

1-(2-Methoxyethyl)azulene (**20**): 31% yield. A blue oil. ^{1}H NMR ($CDCl_3$) δ = 3.33 (t, *J* = 7.4 Hz, 2 H), 3.35 (s, 3 H), 3.67 (td, *J* = 7.4, 1.5 Hz, 2 H), 7.01 (t, *J* = 9.8 Hz, 1 H), 7.04 (t, *J* = 9.8 Hz, 1 H), 7.30 (d, *J* = 3.9 Hz, 1 H), 7.47 (d, *J* = 9.8, Hz, 1 H), 7.79 (d, *J* = 3.9 Hz, 1 H), 8.19 (d, *J* = 9.8 Hz, 1 H), 8.26 (d, *J* = 9.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 27.9, 58.6, 73.6, 116.8, 121.5, 122.2, 127.0, 133.3, 136.2, 136.3, 137.2, 137.3, 140.6; IR (film) 3010 (w), 2915 (w), 1575 (s), 1430 (m), 1390 (s), 1295 (w), 1190 (s), 1110 (s), 960 (w), 940 (w), 770 (m), 740 (m) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 186 (M^+, 15), 142 (12), 141 (100), 139 (5), 115 (14), 102 (2), 92 (2), 88 (3), 69 (3), 64 (3). UV/Vis λmax (hexane) 210 nm (log ε = 4.26), 239 (4.38), 272sh (4.84), 277 (4.98), 281sh (3.97), 296sh (3.91), 319sh (3.41), 326sh (3.61), 334 (3.66), 343 (3.84), 360 (3.62), 533sh (2.36), 554sh (2.53), 578 (2.59), 602 (2.68), 627 (2.61), 692sh (2.27), 728 (2.24). Found: *m/z* 186.1027. Calcd for $C_{13}H_{14}O$: M, 186.1044. The yield was improved to 77% when addition of 10 equiv. of methanol with 2% of trifluoroacetic acid was used.

2-(1-Azulyl)ethyl acetate (**21**)[4,23]: 83% yield. A blue oil. ^{1}H NMR ($CDCl_3$) δ = 2.03 (s, 3 H), 3.40 (t, *J* = 7.3 Hz, 2 H), 4.37 (t, *J* = 7.3 Hz, 2 H), 7.08 (t, *J* = 9.8 Hz, 1 H), 7.12 (t, *J* = 9.8 Hz, 1 H), 7.33 (d, *J* = 3.9 Hz, 1 H), 7.54 (td, *J* = 9.8, 0.5 Hz, 1 H), 7.80 (d, *J* = 3.9 Hz, 1 H), 8.25 (dd, *J* = 9.3, 0.5 Hz, 1 H), 8.30 (d, *J* = 9.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 21.0, 26.9, 65.1, 116.8, 121.8, 122.5, 125.6, 133.3, 136.4, 136.5, 137.2, 137.5, 140.9, 171.1.

N, N-Diethyl-N-2-(1-azulyl)ethylamine (**22**): 67% yield. A blue oil. ^{1}H NMR ($CDCl_3$) δ = 0.99 (t, *J* = 7.1 Hz, 6 H), 2.58 (q, *J* = 7.1 Hz, 4 H), 2.74 (t, *J* = 7.6 Hz, 2 H), 3.15 (t, *J* = 7.6 Hz, 2 H), 7.07 (t, *J* = 9.8 Hz, 1 H), 7.10 (t, *J* = 9.8 Hz, 1 H), 7.31 (d, *J* = 3.7 Hz, 1 H), 7.55 (t, *J* = 9.8, Hz, 1 H), 7.80 (d, *J* = 3.7 Hz, 1 H), 8.25 (d, *J* = 9.8 Hz, 1 H), 8.32 (d, *J* = 9.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 12.6, 25.9, 47.7, 55.5, 117.7, 122.3, 123.0, 130.6, 134.5, 136.8, 137.2, 138.3, 138.4, 141.5; IR (film) 2960 (s), 2920 (m), 2780 (w), 1575 (m), 1450 (w), 1390 (m), 1295 (w), 1200 (w), 1065 (w), 770 (m), 735 (m), 770 (m) cm^{-1}. EIMS (70 eV) *m/z* (rel ntensity): 228 (M^+, 5), 227 (24), 142 (24), 141 (26), 128 (19), 87 (99), 86 (100). UV/Vis λmax (hexane) 239 nm (log ε = 4 .18), 272sh (4.61), 278 (4.67), 283sh (4.63), 298sh (3.66), 320sh (3.31), 330sh (3.45), 346 (3.48), 345 (3.65), 361 (3.42), 534sh (2.16), 556sh (2.35), 583 (2.41), 606 (2.49), 632 (2.42), 663 (2.43), 695 (2.08), 735 (2.04). Found: *m/z* 227.1673. Calcd for $C_{16}H_{21}N$: M, 227.1724. Hydrochloric acid salt; Blue leaflets, m.p. 140-142 °C. Found: C, 72.38; H, 8.30; N 5.52%. Calcd for $C_{16}H_{22}ClN \cdot 0.1H_2O$: C, 72.35; H,

8.42; N, 5.27%.

2-(1-Azulyl)ethyl phenyl sulfone (**23**): 28% yield. Blue leaflets, m.p. 92 – 94 °C. ^{1}H NMR ($CDCl_3$) δ = 3.50 (m, 4 H), 7.105 (t, *J* = 9.8 Hz, 1 H), 7.111 (t, *J* = 9.8 Hz, 1 H), 7.26 (d, *J* = 4.0 Hz, 1 H), 7.55 (m, 3 H), 7.65 (m, 2H), 7.95 (d, *J* = 7.6 Hz, 2 H), 8.13 (d, *J* = 9.6 Hz, 1 H), 8.24 (d, *J* = 9.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 20.6, 57.3, 116.9, 122.2, 122.9, 124.8, 128.0, 129.3, 133.0, 133.6, 135.7, 136.4, 136.8, 137.8, 139.1, 141.5; IR (film) 3000 (w), 1580 (s), 1450 (s), 1400 (s), 1300 (s), 1200 (w), 1150 (s), 1120 (s), 1085 (m), 1070 (m), 985 (w), 89 (w), 550 (s), 520 (s) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 296 (M^+, 11), 155 (26), 154 (100), 153 (63), 152 (18), 141 (25), 77 (26), 51 (10). UV/Vis λmax (MeOH) 213 nm (log ε = 4.25), 238 (4.18), 274sh (4.59), 278 (4.65), 282sh (4.61), 319sh (3.24), 333 (3.46), 343 (3.61), 358 (3.35), 553sh (2.34), 572sh (2.41), 593 (2.46), 614sh (2.42), 643 (2.29), 711 (1.34). Found: C, 72.73; H, 5.57%. Calcd for $C_{18}H_{16}O_2S$: C, 72.95; H, 5.44%.

2-(1-Azulyl)ethyl phenylsulfinate (**24**): 19% yield. A blue oil. ^{1}H NMR ($CDCl_3$) δ = 3.40 (m, 2 H), 3.92 (dt, *J* = 10.0, 7.2 Hz, 1 H), 3.42 (ddd, *J* = 10.0, 7.8, 6.6 Hz, 1 H), 7.06 (t, *J* = 10.0 Hz, 1 H), 7.09 (t, *J* = 10.0 Hz, 1 H), 7.31 (d, *J* = 3.6 Hz, 1 H), 7.43 (m, 4H), 7.54 (m, 2H), 7.72 (d, *J* = 3.6 Hz, 1 H), 8.14 (d, *J* = 10.0 Hz, 1 H), 8.25 (d, *J* = 9.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 28.2, 65.3, 116.8, 121.9, 122.5, 124.3, 125.2, 128.9, 131.9, 133.3, 136.4, 136.6, 137.3, 137.5, 140.7, 144.5; IR (film) 3050 (m), 2950 (m), 1735 (w), 1580 (s), 1535 (w), 1510 (m), 1445 (s), 1395 (s), 1370 (w), 1300 (m), 1245 (w), 1220 (w), 1130 (s), 1080 (m), 1065 (m), 1045 (w), 1020 (w), 940 (s), 860 (m), 775 (s), 750 (s), 740 (s), 700 (s) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 296 (M^+, 9), 155 (21), 154 (76), 153 (17), 142 (13), 139 (6), 125 (7), 115 (14), 104 (8), 77 (16), 76 (10), 64 (5), 51 (8). UV/Vis λmax (hexane) 239 nm (log ε = 4.21), 274sh (4.60), 278 (4.65), 282sh (4.61), 320sh (3.23), 334 (3.44), 330sh (3.45), 344 (3.60), 358 (3.30), 553sh (2.33), 573sh (2.40), 597 (2.46), 615 (2.42), 649 (2.38), 717 (1.93). Found: *m/z* 296.0894. Calcd for $C_{18}H_{16}O_2S$: M, 296.0871.

Reaction of 1,1-Ethylene-1H-azulenium Tetrafluoroborate with Sodium Methoxide: To a solution of 68.0 mg (436 mmol) of **5** in 7 ml of acetonitrile at - 20 °C was added 144 mg (436 mmol) of trityl tetrafluoroborate in one portion. After the mixture was stirred at the same temp. for 10 min, two equivalents (47.0 mg, 872 mmol) of sodium methoxide in 2.4 ml of methanol was added dropwise. After being stirred at - 20 °C for 30 min, at 0 °C for 1 h and then at room temp. for 30 min, the reaction mixture was poured into water (100 ml) and extracted with Et_2O (3 x 30 ml). The combined organic layer was washed brine and dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual oil was distilled with a Kugelrohr apparatus (45 °C, 0.05 Torr) to give 39.0 mg (48%) of a mixture of the addition product, which contained **25** as a major component, as a colorless oil. EIMS *m/z* (rel intensity): 186 (M^+, 17), 170 (7), 154 (5), 141 (100), 129 (31), 128 (13), 115 (16). UV/Vis λmax (hexane) 234 nm (log ε = 4.28), 268sh (3.84), 273sh (3.95), 279 (4.01), 283 (4.00), 290sh (3.84), 298 (3.64), 307sh (3.60), 344sh (3.23), 360 (2.82). Found: *m/z* 186.1052. Calcd for $C_{13}H_{14}O$: M, 186.1044.

Acid Catalyzed Rearrangement of **25**: To a solution 18.5 mg (99.5 mmol) of **25** in 5 ml of methanol was added 0.01 ml of trifluoroacetic acid. The reaction mixture immediately turned to blue. After being stirred at room temp. for 30 min, the mixture was poured into a saturated $NaHCO_3$ aqueous solution and extracted with Et_2O (3 x 10 ml). The combined organic layer was washed with brine and dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual oil was purified by chromatography (SiO_2, hexane : AcOEt = 8:2) to give 15.3 mg (83%)

of **20** as a blue oil.

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid Scientific Research (No. 09640631) from the Ministry of Education, Science, Culture, and Sports, Japan.

REFERENCE AND NOTES

1. For recent work on this topic: Okamura, M.; Hazama., K.; Ohta, M.; Katoh, K.; Horaguchi, T. *Chem. Lett.* **1997**, 973–974; Nagumo, S.; Furukawa, T.; Ono, M.; Akita, H. *Tetrahedron Lett.* **1997**, *38*, 2849–2852; Nagumo, S.; Hisano, T.; Kakimoto, Y.; Kawahara, N.; Ono, M.; Furukawa, T.; Takeda, S.; Akita, H. *Tetrahedron Lett.* **1998**, *39*, 8109–8112.
2. Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. "*Carbonium Ions* " (Ed.: Olah G. A.; Schleyer, P. v. R.), Wiley-Interscience, New York, 1972, Vol. III, ch 27, p. 1347.
3. IUPAC name for **2a**: spiro[cyclopropane-1,1'-(1'*H*-azulenium)] tetrafluoroborate.
4. McDonald R. N.; Curtis, J. R. *J. Am. Chem. Soc.* **1971**, *95*, 2530–2532; McDonald, R. N.; Wolfe, N. L.; Petty, H. P. *J. Org. Chem.* **1973**, *38*, 1106–1113; McDonald, R. N.; Richmond, J. M. *J. Org. Chem.* **1975**, *40*, 1689–1694.
5. Olah G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 7627–7629 and **1971**, *93*, 6877–6887; Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284–6289; Olah, G. A.; Singh, B. P.; Liang, G. *J. Org. Chem.* **1984**, *49*, 2922–2925; Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69–95.
6. Jason, M. E. *Tetrahedron Lett.* **1982**, *23*, 1635–1638.
7. Bauld, N. L.; McDermed, J. D.; Hudson, C. E.; Rim, Y. S.; Zoeller, Jr., J.; Gordon, R. D.; Hyde, J. S. *J. Am. Chem. Soc.* **1969**, *91*, 6666–6676; Okamoto, K.; Komatsu, K.; Murai, O.; Sakaguchi, O.; Matsui, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1785–1790; Takeuchi, K.; Yasuda, K.; Okamoto, K. *Chem. Lett.* **1976**, 715–716; Takeuchi, K.; Komatsu, K.; Yasuda, K.; Okamoto, K. *Tetrahedron Lett.* **1976**, 3467–3470; Takeuchi, K.; Komatsu, K.; Yasuda, K.; Mikuchi, F.; Okamoto, K. *J. Chem. Soc., Perkin Trans. II* **1979**, 1005–1010; Komatsu, K.; Takeuchi, K.; Arima, M.; Waki, Y.; Sirai, S.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3257–3261.
8. Schleyer, P. v. R.; Maerker, C.; Buzek, P.; Sieber, S. ch 2, "*Stable Carbocation Chemistry*" (Ed.: Prakash, G. K. S.; Schleyer, P. v. R.), Wiley-Interscience, New York, 1997, p. 19; Wiberg, K. B.; Hess, Jr., B. A.; Ashe, III, A. J. "*Carbonium Ions* " (Ed.: Olah, G. A.; Schleyer, P. v. R.), Wiley-Interscience, New York, 1972, Vol. III, ch 26, p. 1295.
9. A preliminary account of this work has appeared; Oda, M.; Kajioka, T.; Okujima, T.; Itoh, S.; Morita, N.; Miyatake, R.; Kuroda, S. *Chem. Lett.*, **1997**, 1011–1012. For a homologous cation see; Oda, M.; Sakamoto, A.; Miyatake, R.; Kuroda, S. *Tetrahedron Lett.* **1998**, *39*, 6195–6198.
10. Kuroda, S; Asao, T. *Tetrahedron Lett.* **1977**, 285–288.
11 For synthesis and chemical reactions of spiro[2,4]hepta-4,6-diene which is a part of the structure **5**, see; Menchikov, L. G.; Nefedov, O. M. *Russ. Chem. Rev.* **1994**, *63*, 449–469.
12. Yamashita, Y.; Hagiya, K.; Saito, G.; Mukai, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 271–279.

13. Pagni, R. M.; Bouis, P. A.; Easley, P. *Tetrahedron Lett.* **1975**, 2671–2674.
14. Muller, P.; Rocek, J. *J. Am. Chem. Soc.* **1972**, *94*, 2716–2719.
15. Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409–1436.
16. Heyd W. E.; Cupas, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 6086–6092.
17. For other examples of structural elucidation of an unstable cationic species by the pulsed field gradient method, see; Nozoe, T.; Shindo, K.; Wakabayashi, H.; Kurihara, T.; Uzawa, J. *Chem. Lett.* **1995**, 687–688.
18. For a theoretical study of the substituent effect on the structure of the phenonium ion, see; Yamabe, S.; Tanaka,T. *Nippon Kagaku Kaishi*, **1986**, 1388–1394.
19. Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987–6988.
20. Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 875–882.
21. Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683–691.
22. Olah *et al.* reported that TCSDs of 350 ppm or greater indicate a predominantly classical structure and values below 200 ppm imply structures with considerable nonclassical character.
23. Anderson, Jr., A. G.; Anderson, R. G.; Fujita, T. S. *J. Org. Chem.* **1962**, *27*, 4535–4539.
24. McDonald, R. N.; Richmond, J. M.; Curtis, J. R.; Petty, H. E.; Hopki, T. L. *J. Org. Chem.* **1976**, *41*, 1811–1821.
25. Asao, T.; Oda, M. "*Methoden Der Organischen Chemie*" (Houben-Weyl), Bd. 5, 2c ; "*Carbocyclische p-Elktronen-Systeme*" (Ed.: Kropf, H.), Georg Thieme Verlag, Stuttgart, 1986, p. 49.
26. Doering, W. v. E.; Knox, J. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203–3206; Doering, W. v. E.;Knox, J. H. *J. Am. Chem. Soc.* **1957**, *79*, 352–356; Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4963–4965; Kayama, Y.; Oda, M.; Kitahara,Y. *Chem. Lett.*, **1973**, 1169–1172.
27. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
28. Separation of the regioisomers by distillation or basic alumina chromatography was unsuccessful.
29. The UV–VIS spectrum of this mixture showed neither absorption maximum nor shoulder at longer wavelength than 400 nm, suggesting that it does not contain the addition product at the 2 position which has a heptafulvene structure and should have shoulder absorptions around 500 nm.
30. Hafner, K; Meinhardt, K.–P. "*Organic Syntheses*," (Ed.: Semmelhack, F.), John Wiley & Sons, New York, 1984, Vol. 62, p134–139.
31. Dauben, Jr., H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.*, **1960**, *25*, 1442–1445.