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Formation, Characterization, and Some Reactions of Spiro[cyclobutane-1,1'-1'*H*-azulenium] Ion

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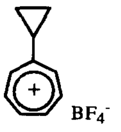
Abstract. *Direct cyclobutylation of 1,6-dihydroazulene gave the spiro hydrocarbon **6**, which was subjected to hydride abstraction with a molar equivalent of trityl salt to lead to the title cation **4**. Its hexafluorophosphate salt was obtained as crystals. The cation **4** in deuterated acetonitrile was stable at 0 °C; however, it underwent expansion of the cyclobutane ring at elevated temperatures to give 2,3-trimethylene-1H-azulenium cation **7**. On the other hand, treatment of **6** with an excess of trityl salt gave 1-(4,4,4-triphenylbutylidene)-1H-azulenium ion (**11**). The cation **4** reacted with pyrrolidine to give the adducts at their seven-membered ring carbons, which gradually rearranged to the adduct at the 2 position under the reaction conditions. Cycloaddition of the latter adduct with dimethyl acetylenedicarboxylate is also described. The cation **4** showed distinctive chemical behavior compared with its three-membered ring homolog.*

Cyclopropyltropylium salt (**1**)[1] is known to show greater thermodynamic stability than the cyclobutyltropylium salt (**2**),[2] indicating more significant interaction between the Walsh component and the p-orbital of the tropylium cation part in the former, though the valence orbital of cyclobutane can be also considered to be built up from four methylene groups oriented in the same way as in cyclopropane.[3] An increase in the number of cyclopropyl substitution around the tropylium ring resulted in a clear increase of the pK_{R^+} value and resistance to one-electron reduction,[1] also indicating the remarkable ability of the cyclopropane ring to stabilize the tropylium ion. We have reported generation of spiro[cyclopropane-1,1'-1'*H*-azulenium] ion (**3**),[4] which had been thought to be



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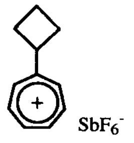

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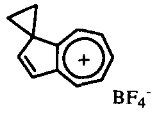

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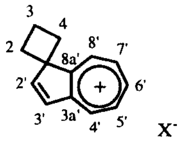

4a; X = BF_4
4b; X = PF_6

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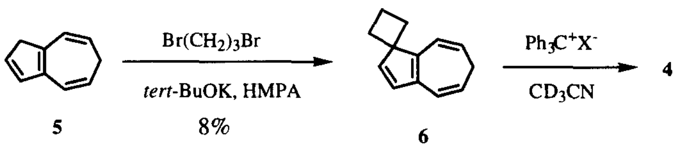
an intermediate in solvolysis of 2-(1-azulyl)ethyl tosylate.[5] This azulenium cation **3** embodies the structure of **1** and is a more suitable candidate than **1** to evaluate σ-π interaction between a cyclopropane ring σ-bond and an electron-deficient p-orbital at the tropylium part because of its structural rigidity and appropriate bisected geometry. However, **3** was found to undergo facile expansion of the three-membered ring at 0 °C and to react instantaneously with nucleophiles to give the adducts.[4] In order to gain insight into the structural effect on the stability of this type of azulenium ion, we directed our study to the homologous ions. Herein we describe full details of the synthesis and characterization of the cation **4** and its distinctive chemical behavior compared with **3**.[6]

RESULTS AND DISCUSSION

Synthesis and Characterization of Spiro[cyclobutane-1,1'-1'H-azulenium] Ion (4).

The synthesis of **4** was accomplished in two steps starting from 1,6-dihydroazulene (**5**)[4,7] under similar reaction conditions to those of **3**. Spirobutylation of **5** with 1,3-dibromopropane and potassium *tert*-butoxide in hexamethylphosphoric triamide (HMPA) gave **6** as an air-sensitive colorless oil in 8% yield. This yield was still superior to those obtained under conditions using other strong base, such as sodium hydride, lithium ethoxide, and sodium amide, and other solvents such as dimethyl sulfoxide, dimethylformamide, dioxane, dimethoxyethane, tetrahydrofuran, and liquid ammonia. The reaction conditions with a phase-transfer catalyst and sodium hydroxide as a base gave none of **6**.[8] Addition of a molar equivalent of either trityl tetrafluoroborate or hexafluorophosphate to a deuterated acetonitrile solution of **5** at 0 °C resulted in a dull-green solution. NMR spectra measured at the same temperature revealed formation of the title cation **4** and triphenylmethane.



Scheme 1.

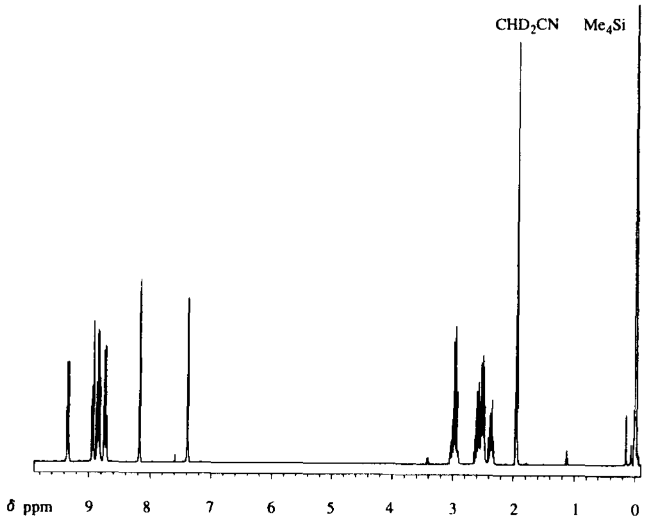


Fig. 1. The 400 MHz ^1H NMR spectrum of **4b** in a CD_3CN solution.

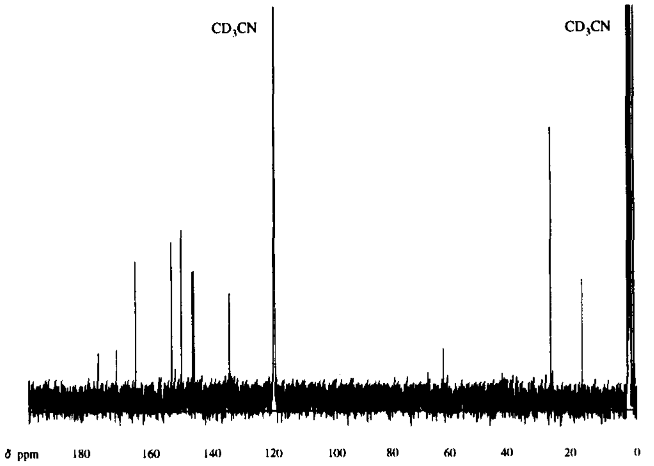


Fig. 2. The 100 MHz ^{13}C NMR spectrum of **4b** in a CD$_3$CN solution.

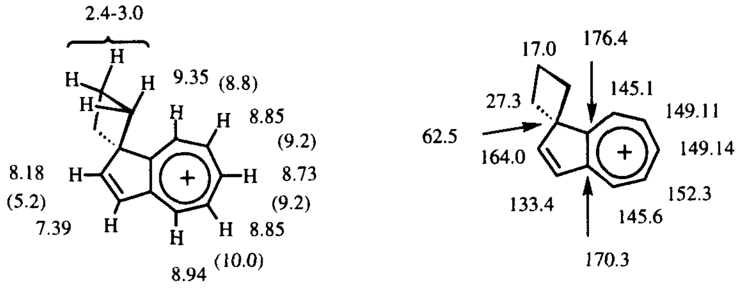
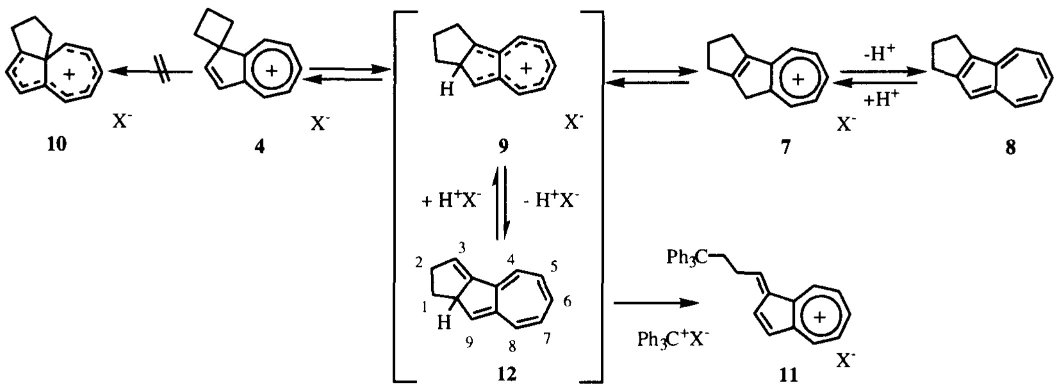


Fig. 3. Proton (left) and carbon (right) shift values (δppm) assigned for **4b**. Coupling constants are given in parentheses

Addition of dry ether to the latter reaction mixture at 0 °C resulted in separation of gray microcrystals which were isolated by filtration in 29% yield, while the same procedure using trityl tetrafluoroborate gave a greenish oil. ^{1}H and ^{13}C spectra of **4b** in CD$_3$CN are shown in Figures 1 and 2 and the signal assignments are summarized in Fig. 3. Since no clear NOE correlation between the cyclobutane methylene carbons and the neighboring methine protons was observed in the NOESY spectrum,[9] the assignments were based on that in the HMBC spectrum;[9] correlations between the C-1 (C-1') carbon and the H-8' proton, between the C-3a' carbon and the H-2' proton, and between the C-8a' carbon and the H-3' proton were essential to assign the azulene skeleton carbons and protons. The average chemical shift (δ_{av} = 8.94 ppm) of the protons at the seven-membered ring of **4** is greater than that (δ_{av} = 8.72 ppm) of **3** and that at the five-membered ring of **4** (7.79 ppm) is comparable to that (7.76 ppm) of **3**. Since the shielding effect of a cyclopropane ring is significant,[10] evaluation of the magnitude of the effect is requisite for assessment of the positive charge delocalization in both cations based on these shift values. According to McConnell's equation[11] with the anisotropy value of a cyclopropane ring C–C bond $\Delta\chi = -20 \times 10^{-30}$ cm^3/mol, that of a cyclobutane ring (an ordinary) C–C bond $\Delta\chi = -5.5 \times 10^{-30}$ cm^3/mol,[10] and the optimized geometry by the PM3 method, the average chemical shifts, disregarding the shielding effect of the cycloalkane rings, of the protons at the seven- and five-membered rings of **4** were calculated to be 8.99 and 7.88 ppm, and those of **3** are 8.89 and 7.72 ppm, respectively. Additionally, the average chemical shift of the methine carbons of **4** (147.7 ppm) is slightly greater than that (145.7 ppm) of **3** and is close to the value (148.5 ppm) obtained by the empirical equation of O'Brien *et al.* ($\delta_{av} = 289.5\text{-}156.3\rho_{av}$)[12] with the calculated average π-electron density (ρ_{av} = 0.902 by the PM3 method). These results indicate slightly less delocalization of the positive charge in **4** than in **3**, suggesting greater thermodynamic stability of **3** than that of **4**, as expected from the fact of the respective thermodynamic stability of **1** and **2**, though pK_{R^+} value of **4** could not been obtained because of its instability (*vide infra*).

Rearrangement of Spiro[cyclobutane-1,1'-1'H-azulenium] Ion (4) and Its Reaction with Trityl Salt.

The cation **4** in CD_3CN solution was stable at 0 °C; however, it was found to rearrange at elevated temperatures to afford the ring expansion product, 2,3-trimethylene-1*H*-azulenium ion (**7**), in a nearly quantitative yield. The



Scheme 2.

Table 1. Heats of formation (kcal/mol) by semiempirical calculations and total energies (a.u.) by *ab initio* ones for the cations **4**, **7**, **9**, and **10**.

	4	**7**	**9**	**10**
AM1	238.81	218.00	237.28	247.87
PM3	235.53	218.90	240.06	248.24
MB3LYP/6-31G*	-502.585158	-502.623752	-502.575917	-502.569591

formation of the cation **7** was confirmed by ^1H and ^{13}C NMR spectral data which were in good agreement with those obtained from 1,2-trimethyleneazulene **8**[13] in the presence of sulfuric acid. Furthermore, pouring the solution of **7** into aqueous acetone and extraction with ether gave **8** in a yield of 67% based on the cation **4**. The cation **4** ($t_{1/2}$ = 10 min, $k = 6.27 \times 10^{-2}$ sec^{-1} at 23 °C) in CD_3CN rearranges more slowly than **3** ($t_{1/2}$ = 27

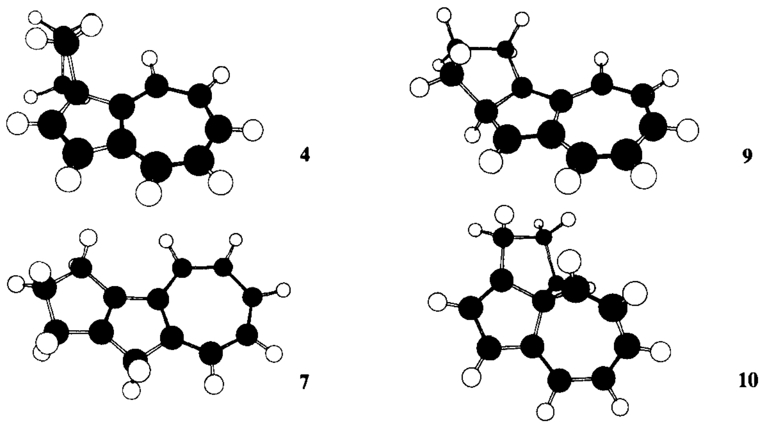


Fig. 4. MB3LYP/6-31G* optimized structures (Chem3D output) of the cations **4**, **7**, **9**, and **10**.

min, k = 4.24 x 10^{-4} sec^{-1} at 0 °C). Thus, under these conditions **4** was found to be kinetically more stable than **3**, contrary to their thermodynamic stability suggested above. This rearrangement probably proceeds through an intermediate, 1,2-trimethylene-2*H*-azulenium ion (**9**), formed by a 1,5-alkyl shift, and is in contrast to the case of **3** which gave the ring expansion product shifted to the 8a position.[4]

For these cations **4**, **7**, **9** and **10** which would be formed by the shift to the 8a position, their optimized structures were calculated by semiempirical molecular orbital and *ab initio* density functional methods (AM1, PM3, and MB3LYP/6-31G*). Although we reported in a preliminary account[6] that AM1 calculations (Table 1) predict the energy levels down along the pathway from **4** to **7** via **9** and an endothermic reaction for conversion of **4** into **10**, both PM3 and MB3LYP/6-31G* calculations, which are generally known to give more accurate energies than AM1 calculations, estimate a slightly higher energy level of **9** than that of **4**. Thus, a process from **4** to **9** seems to be a rate-determining step in the rearrangement of **4** leading to **7**. The structures of **4** optimized by these methods clearly show the bisected geometry between the cyclobutane and five-membered rings, though a bow of the cyclobutane ring is slightly bending (Fig. 4). Theses facile rearrangements in **3** and **4** are in contrast to the case of cations **1** and **2** which do not rearrange at least below room temperature,[1,2] that might be ascribed to the presence of the extra double bond at the 2 and 3 positions and to their greater ring strain in the sprio system.

On the other hand, reaction of **6** with two molar equivalents of trityl tetrafluoroborate at 0 °C also gave **4** as the first product; however, elevating the temperature of the reaction mixture resulted in formation of the cation **11**. The structure of the cation **11** was deduced by ^{1}H and ^{13}C NMR spectral data of this reaction mixture. NOE experiments confirmed the geometrical structure as depicted in Fig. 5. Reduction of **11** with sodium borohydride gave 1-(4,4,4-triphenylbutyl)azulene (**12**) as blue microcrystals. Since equilibration between the heptafulvene and substituted tropylium cation in acetonitrile is well known[14] and C–C bond cleavage forming a stable tropylium cation has also been reported by Komatsu *et al.*,[15] it is assumed that by the aid of acetonitrile, known as a weak base, **9** equilibrates with the hydrocarbon **12** which reacts with another trityl cation at the 1 position to lead to the cation **11**. Attempts to trap **12** with tetracyanoethylene (TCNE) were examined; however,

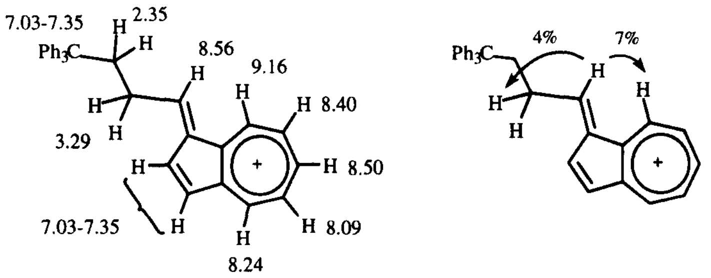
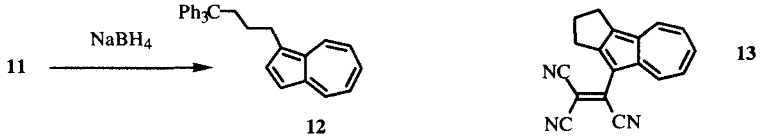


Fig. 5. ^{1}H NMR assignments (left) and results (right) of NOE experiments of **11**.

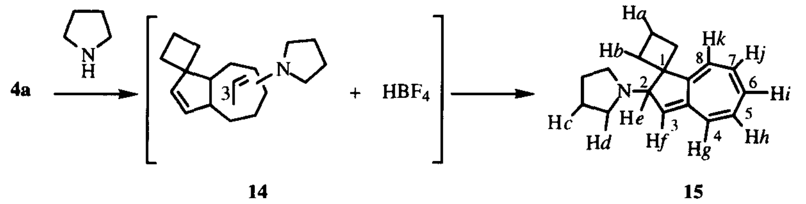
no adduct to **12** could be obtained and the tricyanovinylazulene **13** was given in 21% yield.[14] Since azulene itself reacts with TCNE to give a similar electrophilic substitution product,[16] the possibility exists that **13** arises from **8** under the conditions. Such a reaction of the cation **3** with another trityl salt was not observed under the similar conditions, showing manifest difference of reactivity between **3** and **4**.



Scheme 3.

Addition Reaction of Spiro[cyclobutane-1,1'-1'H-azulenium] Ion (4) with Pyrrolidine

While reactions of **4** with various oxygen nucleophiles such as water, sodium hydroxide, methanol and sodium acetate gave only an intractable mixture, the reaction with a nitrogen nucleophile produced the adducts.[17] To a CD_3CN solution of **4** in an NMR tube was added 10 molar equivalents of pyrrolidine and the reaction was monitored by ^{1}H NMR spectroscopy at 23 °C. Immediately upon the addition, the signals of **4** disappeared.



Scheme 4.

Concurrently, the color of the mixture turned dark-brown. New signals were deduced to be attributed to a mixture of several adducts **14** at the seven-membered ring. However, we could not define either their addition positions on the ring or the ratio because of their complexity and some unidentified signals. Furthermore, these siganals slowly decreased and were displaced completely by even newer ones after 20 h at the same temperature. During the time period the reaction mixture gradually turned dark-red. The final spectrum consists of signals of mainly one component which was ascribed to the adduct **15**; signals as five multiplets at δ = 5.44-5.99 ppm for H*g*, H*h*, H*i*, H*j*, and H*k*, a doublet of a doublet at δ = 5.24 ppm (J = 2.6, 1.6 Hz) for H*f*, a doublet at δ

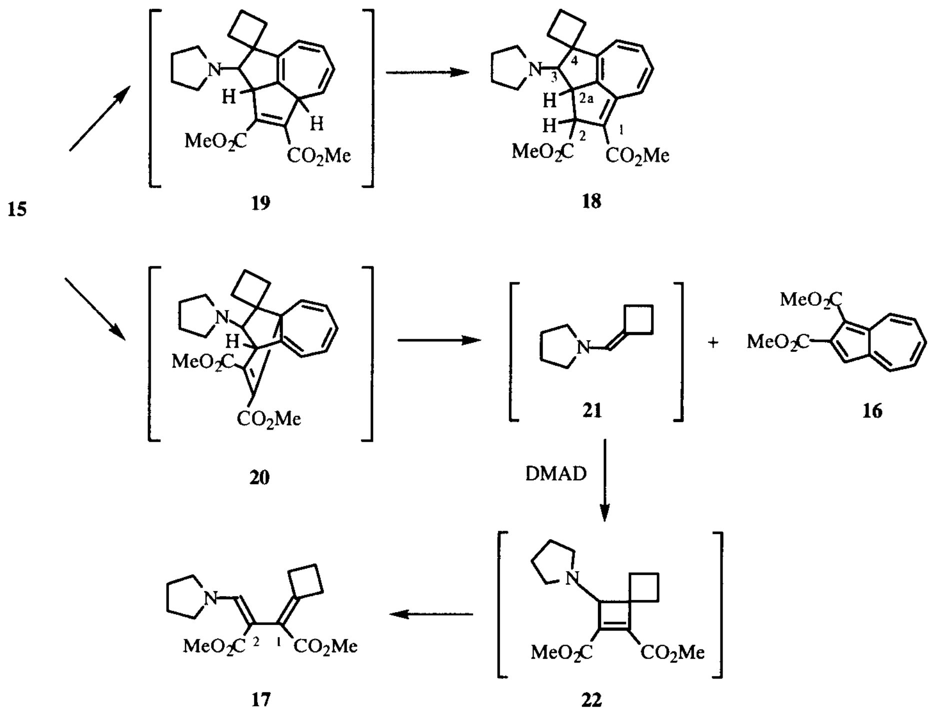
= 3.48 ppm (J = 2.6 Hz) for H*e*, a multiplet at δ = 2.31-2.55 ppm (4H) for H*d*, a multiplet at δ = 1.80-2.03 ppm (6H) for H*a* and H*b*, and a multiplet at δ = 1.64 ppm (4H) for H*c* were observed. The UV-VIS spectrum of this mixture showed absorption maxima at 278, 342^{sh}, 360^{sh}, 411, 432, 456^{sh}, and 512^{sh} nm, which are typical for heptafulvene,[18] also supporting the stucture of **15**.[19] From these findings, it is assumed that the adducts **14** are kinetically controlled ones which reproduce **4a** in the presence of hydrogen fluoroborate formed, leading to the thermodynamically controlled adduct **15**. Results of the PM3 calculations support the thermodynamic stability of **15**, *i.e.*, the calculated heats of formation of **15** and its simplified amino derivative are the lowest among the corresponding adducts at the azulene carbons (Table 2). We reported that the reaction of **3** with nucleophiles gave the thermodynamically controlled adduct by the cyclopropane ring cleavage.[4] The reluctant nature of the cyclobutane ring against ring cleavage seems to play a major role in the distinctive behavior of **4** towards a nucleophilic reaction in comparison with that of **3**.

Table 2. Calculated heats of formation (kcal/mol) of the possible pyrrolidine and amine adducts by the PM3 method.

Possible adduct		Heat of formation	Possible adduct		Heat of formation
Position	Substituent		Position	Substituent	
2	pyrrolidino	65.163	6	pyrrolidino	68.042
	amino	69.404		amino	75.622
3a	pyrrolidino	70.527	7	pyrrolidino	65.279
	amino	72.337		amino	74.432
4	pyrrolidino	68.035	8	pyrrolidino	68.746
	amino	72.787		amino	75.494
5	pyrrolidino	66.722	8a	pyrrolidino	73.125
	amino	74.701		amino	74.418

Cycloaddition of the Pyrrolidine Adduct 15 with Dimethyl Acetylenedicarboxylate

We attempted to trap **15** by cycloaddition reaction with electron-deficient $_{\pi}2$-cycloaddends. Reactions of the crude reaction mixture of **15** with tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione in $CHCl_3$ at room temperature did not give any identifiable product, though **15** was completely consumed in these reactions. On the other hand, refluxing with dimethyl acetylenedicarboxylate (DMAD) in benzene for 2 h and subsequent purification on silica gel chromatography gave three products, 1,2-bis(methoxycarbonyl)azulene (**16**),[18,20] dimethyl (*Z*)-1-cyclobutylidene-2-(pyrrolidinylmethylene)ethane-1,2-dicarboxylate (**17**), and an unseparable mixture (in a ratio of 3:2) of the adducts **18** in 38, 25, and 13% yields, respectively. The structure of **16** was confirmed by comparison of its spectral data with the authentic ones. The gross structural features of **17** and **18** were well characterized by their spectral data. The geometrical relationship between the methoxycarbonyl at the 2 position and the pyrrolidiny groups in **17** was determined to be *cis* to each other by the results of NOE experiments, *i.e.*, the correlation (2% enhancement) between the the methoxycarbonyl methyl at the 2 position and pyrrolidine α-methylene hydrogens was observed but there was no correlation between the methyl and vinylic methine hydrogens. Although definite stereochemistry of **18** could not be determined by its spectral data, the carbon framework was confirmed by 2D H-H COSY and HMBC spectra. Plausible mechanisms for the formation of **16**, **17**, and **18** are shown in Scheme 5. Two modes of [8+2]cycloaddition[21] of **16** and DMAD leads to adducts **19** and **20**. In these additions DMAD probably approaches from the opposite side of the azulene skeletal plane to the pyrrolidinyl group of **15** because of steric reason and the stereochemistry between the two methine protons at the 2a and 3 positions in **18** is assumed to be *cis*. The adduct **18** is derived from **19** by a base-catalyzed proton shift. Therefore, **18** is suggested to consist of the two stereoisomers with the different configuration only at the 2 position. Another cycloadduct **20** undergoes cycloreversion[22] to produce **16** and the enamine **21** which reacts with another DMAD to give **17** via **22** by a sequence involving [2+2]cycloaddition and electrocyclic ring-opening steps.



Scheme 5.

SUMMARY

We have accomplished the synthesis of the title cation **4** by a route involving direct spirobutylation of dihydroazulene. The NMR spectral data indicate slightly less delocalization of the positive charge in **4** than in **3**, suggesting greater thermodynamic stability of **3** than that of **4**, as expected from the fact of the respective thermodynamic stability of **1** and **2**, though pK_{R^+} values of **3** and **4** remain undisclosed because of their instability. However, the rearrangements of these cations show that **4** is kinetically more stable than **3**. Additionally, the distinctive chemical behavior of **4** compared with **3** was demonstrated, *i.e.*, reaction of **4** with pyrrolidine gave the adducts at the azulene skeleton and none of a ring opened product was observed, whereas the reaction of **3** with nucleophiles gave the adduct derived from the cyclopropane ring cleavage as a thermodynamically controlled product. We have also revealed the cycloaddition reaction of the pyrrolidine adduct of **4** with dimethyl acetylenedicarboxylate.

EXPERIMENTAL

Melting points were measured on a 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 either Merck Kieselgel 60 Art 7734 or activated alumina from Wako Pure Chem. Ind. 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.[23] Trityl tetrafluoroborate and hexafluorophosphate prepared by the reported method.[24] 1,3-Dibromopropane was purchased from Wako Pure Chem. Ind. and purified by distillation from phosphorous pentaoxide. HMPA was purchased from Tokyo Kasei Kogyo Co. and purified by distillation from calcium hydride. The semiempirical molecular orbital calculations were conducted on an IBM RS / 6800-580 computer by using the MOPAC program (ver. 6.02) with full geometrical optimization, and the density fuctional calculations were done on an IBM RS / 6000-397 computer by using the MULLIKEN (ver. 2.0.0, 1995, IBM Co.) one. The MB3LYP (MBecke3LYP) functional in MULLIKEN uses the local correlation function of Perdew and Wang[25] instead of the Vosko, Wilk, and Nusair functional,[26] and is very similar to Becke3LPY density by Stephens *et al.*[27]

Spiro[cyclobutane-1,1'-1',6'-dihydroazulene] (**6**)

To a solution of 1,6-dihydroazulene[4] (**5**, 1.25g, 9.60 mmol) in 20 ml of HMPA at 0 °C was added 2.37 g (21.1 mmol) of potasium *tert*-butoxide in one portion and 1.07 ml (10.6 mmol) of 1,3-dibromopropane dropwise. After the addition, the ice bath was removed and the reaction mixture was stirred for 20 min at room temp. Then, the resulting reaction mixture was poured into 2M hydrochloric solution (100 ml) and extracted with hexane (70 ml x 3). 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 an unseperable trace amount of **5** and allylated dihydroazulenes, followed by 140 mg of **6** (8% yield) as an air-sensitive colorless oil. For the yields under other reaction conditions, see Table 3. ^{1}H NMR ($CDCl_3$) δ = 2.01-2.11 (m, 1 H), 2.20-2.26 (m, 3 H), 2.29 (t, J = 6.8 Hz, 2 H), 2.33-2.38 (m, 2H), 5.29 (dt, J = 9.6, 6.8 Hz, 1 H), 5.34 (dt, J = 9.6, 6.8 Hz, 1 H), 6.37 (d, J = 9.2 Hz, 1 H), 6.38 (d, J = 5.4 Hz, 1 H), 6.65 (d, J = 9.6 Hz, 1 H), 6.70 (d, J = 5.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 17.8, 28.3, 28.8, 59.6, 117.4, 118.5, 124.1, 125.2, 131.2, 141.8, 142.8, 150.0; IR (film) 3040 (w), 3010 (m), 2940 (m), 2860 (w), 1690 (w), 1655 (w), 1610 (w), 1505 (w), 1430 (w), 1395 (w), 1370 (s), 1370 (w), 790 (m), 690 (m) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 170 (M^+, 64), 168 (100), 167 (58), 158 (24), 155 (42), 153 (35), 145 (25), 144 (30), 142 (41), 129 (25), 128 (29), 105 (13), 72 (11), 55 (13). UV λmax (hexane) 222 nm ($\log\varepsilon$ = 4.20), 268sh (3.45), 274sh (3.48), 279 (3.51), 308 (3.51). Found: *m/z* 170.1078. Calcd for $C_{13}H_{14}$: M, 170.1096.

This hydrocarbon **6** in neat liquid slowly reacted with atmospheric oxygen to form an intractable oxygen-cotaining product which exhibited a strong broad band at 3450 cm^{-1} in the IR spectrum. On the other hand, a diluted solution of **6** in hexane under nitrogen atmosphere was moderately stable and could be stored in a refrigerator for more than a month.

Table 3. Selected results of cyclobutylation of **5** under various reaction conditions.

entry	base[a]	alkylating reagent $[X(CH_2)_2X]$[b]	solvent[c]	temperature / time (min)	yield of **6** (%)
1	NaH	X = Br	DMF	rt / 30	0
2	NaH	X = Br	HMPA	rt / 20	4
3	NaH	X = Br	HMPA	rt / 15	6
4	*t*-BuOK	X = OTs	HMPA	rt / 15	1
5	*t*-BuOK	X = I	HMPA	rt / 15	0.4

[a] Base was 2.2 equiv with respect to **5**; [b] The reagent was 1.1 molar equiv with respect to **5**; [c] 20 Ml of solvent was used with respecet to 1 g of **5**.

Generation of Spiro[cyclobutane-1,1'-1'H-azulenium] Ion (**4**) *and 2,3-Trimethylene-1H-azulenium Ion* (**7**). *The General Procedure for NMR Measurements* : In an NMR tube was charged a solution of **6** (0.1-0.3 mmol) in 0.7 ml of acetonitrile-d_3. This tube was cooled to 0 °C with an ice bath. To this solution was added one equivalent of trityl salt quickly in one portion and the tube was capped and shaken well. Spectra of the cation were measured at the same temp. and the rearrangement of the cation was also monitored by NMR analysis at elevated probe temperatures. After being allowed to spin at 23 °C of the probe temperature for 3 hr, the following signals of **7** were observed; ^1H NMR (CD_3CN) δ = 2.56 (quin, *J* = 7.2 Hz, 2 H), 2.89 (tm, *J* = 7.6 Hz, 2 H), 3.03 (t, *J* = 7.6 Hz, 2 H), 4.06 (s, 2 H), 8.52-8.60 (m, 3 H), 8.70-8.76 (m, 2H); ^{13}C NMR (CD_3CN) δ = 26.7, 28.9, 32.9, 43.3, 141.1, 145.1, 146.9, 147.0, 151.3, 155.8, 167.8, 174.6, 184.2. The cation **7** was also generated from 1,2-trimethyleneazulene **8**[13] in sulfuric acid with CH_2Cl_2 as internal standard; ^1H NMR (H_2SO_4/CH_2Cl_2) δ = 2.69 (quin, *J* = 7.2 Hz, 2 H), 2.95 (m, 2 H), 3.10 (m, 2 H), 4.02 (s, 2 H), 8.51 (m, 3 H), 8.60-8.73 (m, 2 H); ^{13}C NMR (H_2SO_4/CH_2Cl_2) δ = 25.8, 28.1, 32.2, 42.2, 139.9, 143.6, 145.8, 145.9, 150.4, 155.9, 167.6, 173.5, 184.4.

Spiro[cyclobutane-1,1'-1'H-azulenium] Hexafluorophosphate (**4b**); To a solution of 115 mg (0.676 mmol) of **6** in 5 ml of acetonitrile at 0 °C was added 262 mg (0.676 mmol) of trityl hexafluorophosphate in one portion. After being stirred at 0 °C for 10 min, 100 ml of Et_2O was added to the reaction mixture. Gray crystals formed were quickly collected by suction filtration and washed with cold Et_2O to give 61 mg (29% yield) of **4b**. M.p. 110-111 °C (dec.). ^1H NMR (CD_3CN) δ = 2.32-2.41 (m, 1 H), 2.47-2.61 (m, 3 H), 2.93-3.01 (m, 2 H), 7.39

(d, J = 5.2 Hz, 1 H), 8.18 (d, J = 5.2 Hz, 1 H), 8.73 (tt. J = 9.2, 1.2 Hz, 1 H), 8.85 (m, 2 H), 8.94 (dd, J = 10.0, 1.2 Hz, 1 H), 9.35 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (CD_3CN) δ = 17.0, 27.3, 62.5, 133.4, 145.1, 145.6, 149.11, 149.14, 152.3, 164.0, 170.26, 176.4; UV λmax(CH_3CN) 234 nm, 278, 286sh, 305sh, 355sh, 352sh, 366. Found: *m/z* 169.1031. Calcd for $C_{13}H_{13}$: M, 169.1017. It did not give the satisfactory result of combustion analysis even after repeated purification. The analysis of other salts such as its perchlorate and hexafluoroantimonate gave the same results.

1-(4,4,4-Triphenylbutylidene)-1H-azulenium Ion (**11**) *and 1-(4,4,4-Triphenylbutyl)azulene* (**12**); In an NMR tube was charged a solution of **6** (51.1 mg, 0.300 mmol) in 1.5 ml of acetonitrile-d_3. This tube was cooled to 0 °C with an ice bath. To this solution was added two equivalents of trityl tetrafluoroborate (198 mg, 0.600 mmol) quickly in one portion and the tube was capped and shaken well. This mixture was allowed to stand at room temp. for 8 hr and then ^{1}H-NMR spectrum was recorded, showing the formation of **11**; δ = 2.35 (tm, J = 3.2 Hz, 2 H), 3.29 (q, J = 3.2 Hz, 2 H), 7.03-7.35 (m, 17 H), 8.09 (t, J = 9.2 Hz, 1 H), 8.24 (d, J = 10.8 Hz, 1 H), 8.40 (tm, J = 9.2 Hz, 1 H), 8.50 (tm, J = 9.2 Hz, 1 H), 8.56 (t, J = 3.2 Hz, 1 H), 9.16 (dd, J = 9.2, 1.6 Hz, 1 H). The mixture was diluted with THF (20 ml) and 11 mg of sodium borohydride was added to this solution. After being stirred at room temp. for 2 hr, the resulted dark-blue reaction mixture was poured into water and extracted with dichloromethane (50 ml x 2). 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 (Al_2O_3, hexane) to give 6.2 mg of **12** (5% yield based on **6**) as blue microcrystals. Mp = 194-195 °C. ^{1}H NMR ($CDCl_3$) δ = 2.14 (t, J = 7.2 Hz, 2 H), 2.24 (quin, J = 7.2 Hz, 2 H), 3.02 (t, J = 7.2 Hz, 2 H), 6.59 (t, J = 10.4 Hz, 1H), 6.92 (t, J = 9.6 Hz, 1 H), 7.11-7.22 (m, 11 H), 7.27-7.33 (m, 7H), 7.53 (d, J = 9.6 Hz, 1 H), 7.96 (d, J = 9.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 25.3, 30.3, 31.2, 61.7, 121.2, 121.4, 125.6, 127.3, 127.6, 130.9, 131.1, 132.5, 135.4, 136.2, 136.9, 140.7, 147.4, 161.3; IR (film) 3050 (m), 3010 (m), 2910 (s), 2840 (m), 1890 (w), 1800 (w), 1790 (w), 1680 (m), 1670 (w), 1590 (m), 1565 (m), 1530 (w), 1505 (w), 1490 (s), 1440 (s), 1390 (s), 1310 (w), 1300 (w), 1270 (m), 1180 (m), 1160 (m), 1030 (m), 1000 (m), 735 (s), 700 (s), 620 (m) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 412 (M^+, 3), 411 (17), 410 (47), 334 (29), 333 (100), 167 (27), 165 (61). UV λmax (hexane) 218 nm (logε = 4.88), 289 (4.90), 347 (3.98), 363 (4.14), 381 (3.97), 563sh (2.66), 607 (2.76), 645sh (2.67), 663sh (2.65). Found: *m/z* 412.2167. Calcd for $C_{32}H_{28}$: M, 412.2191. Found: C, 92.88; H, 7.16%. Calcd for $C_{32}H_{28}$: C, 93.16; H, 6.84%.

4-Tricyanovinyl-1,2,3-trihydrocyclopenta[a]azulene (**13**); To a solution of 100 mg (0.590 mmol) of **6** in 10 ml of acetonitrile at 0 °C was added 195 mg (0.590 mmol) of trityl tetrafluoroborate. After 10 min at the same temp., 75.5 mg (0.590 mmol) of TCNE was added in one portion. The reaction mixture was warmed up to room temp. and then stirred for 1 hr. The resulted mixture was poured into 50 ml of water and extracted with dichloromethane (30 ml x 3). The combined organic layer was washed with brine and dried with anhydrous $MgSO_4$. The solvent was evaporated and the residue was purified by chromatography (SiO_2, AcOEt : hexane = 1:1) to give 135 mg (94%) of triphenylmethane and 53 mg (21%) of **13** as red prisms. Similar conditions with two equivalents of trityl tetrafluoroborate gave 17% yield of **13**. Also, **13** was obtained by reaction of TCNE and 1,2,3-trihydrocyclopenta[a]azulene (acetonitrile, r.t., 20 hr) in 71% yield. Mp = 228-229 °C. ^{1}H NMR ($CDCl_3$) δ = 2.65 (quin, *J* = 7.6 Hz, 2 H), 3.10 (t, *J* = 7.6 Hz, 2 H), 3.33 (t, *J* = 7.6 Hz, 2 H), 7.65 (t, *J* = 9.6 Hz, 1H), 7.72 (t, *J* = 9.6 Hz, 1H), 7.90 (t, *J* = 9.6 Hz, 1 H), 8.23 (d, *J* = 9.6 Hz, 1 H), 8.38 (d, *J* = 9.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 25.8, 29.8, 30.9, 81.5, 113.4, 114.0, 114.5, 114.9, 130.3, 131.2, 132.7, 135.7, 136.2, 139.9, 140.5, 143.2, 145.6, 164.2; IR (film) 2940 (w), 2220 (m), 1540 (m), 1495 (m), 1460 (m), 1450 (w), 1440 (w), 1425 (m), 1410 (m), 1330w (m), 1310 (w), 1300 (w), 1280 (w), 1240 (w), 1230 (w), 1190 (w), 1140 (w), 1070 (w), 1050 (w), 760 (m) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 269 (M$^+$, 69), 268 (66), 242 (35), 241 (41), 215 (22), 214 (35), 165 (20), 119 (22), 69 (44), 44 (63), 28 (100). UV λmax (hexane) 232 nm (logε = 4.03), 262 (4.08), 296 (3.86), 405 (3.65), 512sh (3.75), 545 (3.78), 581sh (3.60). Found: C, 78.95; H, 4.37; N, 14.96%. Calcd for $C_{18}H_{11}N_3$: C, 78.70; H, 4.26; N, 15.30%.

The Addition of Spiro[cyclobutane-1,1'-1'H-azulenium] Ion (**4**)*with Pyrrolidine and Cycloaddition of the Adduct with Dimethyl Acetylenedicarboxylate*; To a solution of 170 mg (1.00 mmol) of **6** in 10 ml of acetonitrile at 0 °C was added 330 mg (1.00 mmol) of trityl tetrafluoroborate in one portion. After the mixture was stirred at the same temp. for 10 min, 0.840 ml (10.0 mmol) of pyrrolidine was added. After the addition, the bath was removed, and the reaction mixture was gradually warmed to room temp. and was allowed to stand for 20 h. The resulted mixture was passed through a pad of alumina and was evaporated to give a dark-red oil, which was dissolved in 10 ml of benzene. To this solution was added 142 mg (1.00 mmol) of dimethyl acetylenedicarboxylate and the mixture was refluxed for 2 h. Then, the solvent was evaporated and the residue was repeatedly chromatographed on silica gel to give 237 mg (97%) of triphenylmethane, 84 mg (38%) of **16** as a purple oil, 102 mg (25%) of **17** as an yellow oil, and 49 mg (13%) of **18** as a red oil.

1,2-Bis(methoxycarbonyl)azulene (**16**);[20] ^{1}H NMR ($CDCl_3$) δ = 3.96 (s, 3 H), 3.99 (s, 3 H), 7.48 (t, *J* = 10.0 Hz, 1 H), 7.47 (s, 1 H), 7.56 (t, *J* = 10.0 Hz, 1 H), 7.85 (tm, *J* = 10.0 Hz, 1 H), 8.50 (d, *J* = 10.0 Hz, 1 H), 8.43 (d, *J* = 10.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ = 51.7, 52.4, 115.43, 117.8, 127.3, 128.1, 139.9, 140.0, 140.6, 140.8, 141.4, 142.4, 165.2, 167.7.

Dimethyl (Z)-2-cyclobutylidene-3-(pyrrolidinylmethylene)butane-1,4-dioate (**17**); ^{1}H NMR ($CDCl_3$) δ =1.87 (m, 4 H), 2.03 (m, 2 H), 2.44 (m, 1 H), 2.60 (m, 1 H), 3.10 (m, 1 H), 3.29 (m, 5 H), 3.64 (s, 3 H), 3.70 (s, 3 H), 7.61 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ = 16.7, 25.4, 32.0, 33.6, 51.0, 51.3, 92.8, 120.5, 146.4, 162.2, 167.9, 169.8; IR (film) 2960 (m), 2940 (m), 2860 (m), 1700 (vs), 1690 (s), 1670 (s), 1610 (s), 1600 (s), 1590 (s), 1460 (m), 1430 (m), 1390 (m), 1340 (w), 1330 (w), 1270 (s), 1240 (s), 1190 (m), 1140 (m), 1110 (m), 1040 (m), 920 (m), 870 (w), 800 (w), 780 (m), 730 (m) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 279 (M$^+$, 17), 251 (69), 236 (100), 160 (24), 91 (26), 77 (24), 70 (36), 44 (2), 41 (37), 31 (36). UV λmax (hexane) 226 nm (log ε = 3.98), 289 (4.25). Found: *m/z* 279.1461. Calcd for $C_{15}H_{21}NO_4$: M, 279.1468.

A 3:2 Mixture of 1,2-Bis(methoxycarbonyl)-3-pyrrolidinyl-4,4-trimethylene-2,2a,3,4-tetrahydroaceazulenes (**18**); ^{1}H NMR ($CDCl_3$) δ = 1.79 (m, 4 H), 1.88-2.36 (m, 6 H), 2.53 (m, 2 H + 1 H x 0.4), 2.65 (d, *J* = 10.0

Hz, 1 H x 0.6), 2.75 (m, 2 H), 3.47 (m, 1 H), 3.59 (d, *J* = 10.0 Hz, 1 H x 0.4), 3.65 (s, 3 H x 0.4), 3.67 (s, 3 H x 0.6), 3.68 (s, 3 H x 0.4), 3.72 (s, 3 H x 0.6), 3.73 (d, *J* = 11.2 Hz, 1 H x 0.6), 6.23 (m, 1 H), 6.32 (m, 1 H), 6.57 (d, *J* = 5.6 Hz, 1 H x 0.6), 6.59 (d, *J* = 6.0 Hz, 1 H x 0.4), 7.29 (d, *J* = 11.2 Hz, 1 H x 0.6), 7.36 (d, *J* = 11.6 Hz, 1 H x 0.4); ^{13}C NMR ($CDCl_3$) δ = 16.14, 16.16, 23.45, 23.53, 27.22, 27.33, 29.96, 30.31, 50.35, 50.90, 50.94, 51.51, 51.97, 53.30, 53.44, 53.84, 54.46, 55.19, 59.41, 59.87, 74.10, 78.16, 120.53, 120.93, 130.20, 130.28, 130.65, 130.92, 130.93, 130.97, 134.23, 134.44, 143.69, 143.99, 149.83, 150.82, 155.71, 156.08, 165.75, 166.01, 171.97, 176.75; IR (film) 2950 (s), 2870 (w), 2800 (w), 1740 (vs), 1695 (vs), 1690 (vs), 1640 (m), 1600 (m), 1540 (vs), 1540 (vs), 1480 (s), 1435 (s), 1420 (w), 1395 (w), 1350 (w), 1280 (s), 1260 (s), 1240 (s), 1200 (s), 1170 (m), 1120 (s), 1050 (m), 960 (w), 910 (m), 860 (w), 790 (m), 730 (m), 650 (w) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 381 (M^+, 4), 310 (55), 250 (66), 70 (51), 43 (51). UV λmax (hexane) 204 nm (logε = 4.46), 244 (4.26), 277sh (4.11), 286sh (4.05), 374 (4.31), 444sh (3.20), 471sh (3.05), 510sh (2.72). Found: *m/z* 381.1905. Calcd for $C_{23}H_{27}NO_4$: M, 381.1938.

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