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Synthesis and Stability of 1,1-Diphenyl-1*H*-azulenium Cation

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Abstract In three steps by aldol condensation with benzaldehyde, conjugate addition of lithium diphenylcuprate and subsequent oxidation, 1-acetylcyclohepta-1,3,5-triene (**10**) was transformed into 1-(3,3-diphenylacryloly)-cyclohepta-1,3,5-triene (**11**). The title cation **9** was synthesized from **11** by a sequence involving Nazarov cyclization, Shapiro reaction and final hydride abstraction with trityl perchlorate. The pK_R+ value was determined to be 6.4, which is less than that of the analogous fluorenyl cation **8**. Upon heating **9** rearranges to yield 1,2-diphenylazulene (**22**), quantitatively.

Keywords Azulene, Carbocation, Nazarov cyclization, Shapiro reaction, pK_R+ value

1. Introduction

We have investigated synthesis and stability of various 1,1-disubstituted 1H-azulenium cations, 1–8, in order to evaluate an electronic effect of the substituent at the C–1 position of the azulenyl skeleton on its stability (Fig. 1). [1-6] It has been found that cations **1**–**7** with alkyl and cycloalkyl groups at the position showed a range of pK_R+ values, 8.6–10.4, indicating that the cations are stabilized effectively by electron-donating nature of those groups. On the other hand, the pK_R+ value of cation **8**, having a fluorenyl moiety at the position, was found to be 7.8. The relative instablilty of **8** compared with those of **1**–**7** can be ascribed to weak electron-withdrawing nature of sp^2-hybridized carbon atoms of the fluorenyl group. Noteworthily, cation **8** shows an intramolecular charge-transfer (CT) excitation from the fluorenyl part to the azulenium ion part in its UV-vis absorption spectrum. [6] This phenomenon surprised us, since the planes of the two parts are expected to be perpendicular to each other based on the structure optimized by DFT calculations. In order to evaluate further an effect of a simple phenyl group on stability of the azulenium cation and an intramolecular CT, synthesis of the title ion, 1,1-diphenyl-1*H*-azulenium perchlorate (**9**), was contrived. Herein, we disclose a result of its synthesis, stability and spectroscopic properties.

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2. Results and Discussion

An original synthetic plan for **9** from 1-acetylcyclohepta-1,3,5-triene (**10**) is shown in Scheme 1, which is based on our previous syntheses, [7–9] involving aldol condensation of **10** with benzophenone, Nazarov cyclization [10] of **11**, transformation from **12** to **13**, and final hydride abstraction.

For the first step from **10** to **11**, silylenol ether **14** [9], prepared from **10**, was subjected to the Mukaiyama aldol reaction [11] with benzophenone in the presence of $TiCl_4$ and also to the Noyori-Mukaiyama aldol reaction [12–13] with benzophenone dimethylacetal in the presence of trimethylsilyl trifrate (TMSOTf). (Scheme 2) However, desired compound **15** was not obtained at all and only **10** was recovered. These results are contrasted to the successful aldol reactions of **14** with various ketones, such as acetone, 2-pentanone, 4-heptanone, fluorenone, and their dimethylacetals. The difficulty in these aldol reactions of **11** against benzophenone and its dimethylacetal may be ascribed to specific steric hindrance and/or generation of the relatively stable, therefore less reactive, cationic intermediates. Then, apart from the beginning synthetic plan based on the aldol reactions, alternative routes from **10** to **11** along Scheme 3 were examined. First, synthesis of **11** was examined by nucleophilic substitution of the methylthio groups of **16** with phenyl groups. Compound **10** was transformed into **16** in 80% yield by reaction with carbon disulfide in the presence of potassium *t*-butoxide, followed by quenching with iodomethane. However, subsequent reaction of **16** with two equivalents of lithium diphenylcuprate in ether resulted in only poor yield (3%

yield) of **11**, accompanied with several unidentified by-products. Next, we examined step-wise introduction of two phenyl groups. Compound **17** was obtained by aldol condensation of **10** with benzaldehyde [14], and, then, was employed in conjugate addition reaction with lithium diphenylcuprate. Trapping the reaction mixture with trimethylsilyl chloride resulted in formation of a mixture of *E*- and Z-stereoisomers of the enol ether 18 in 50% yield.

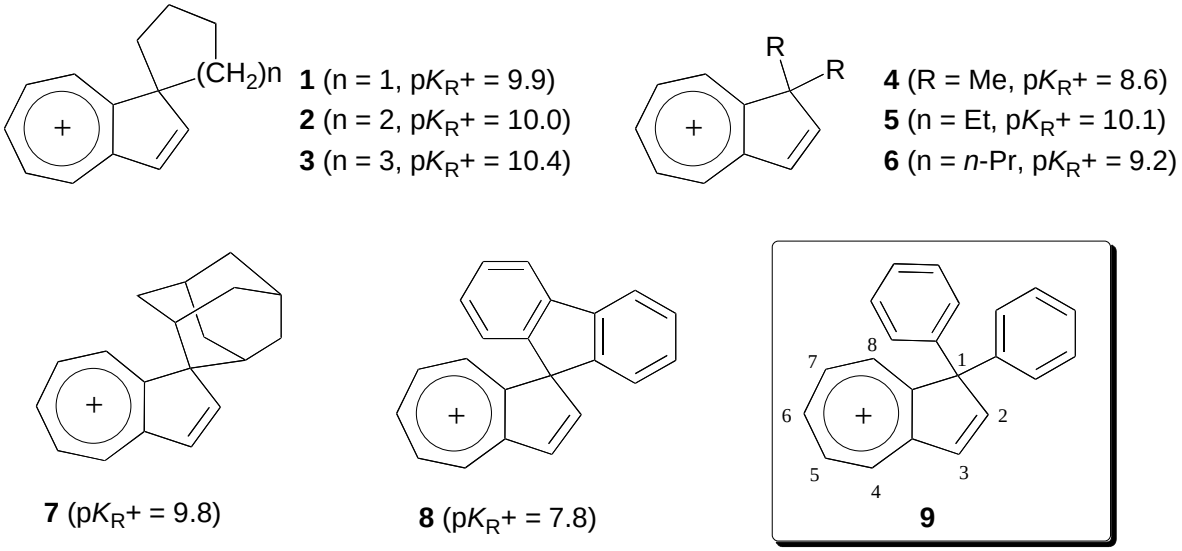
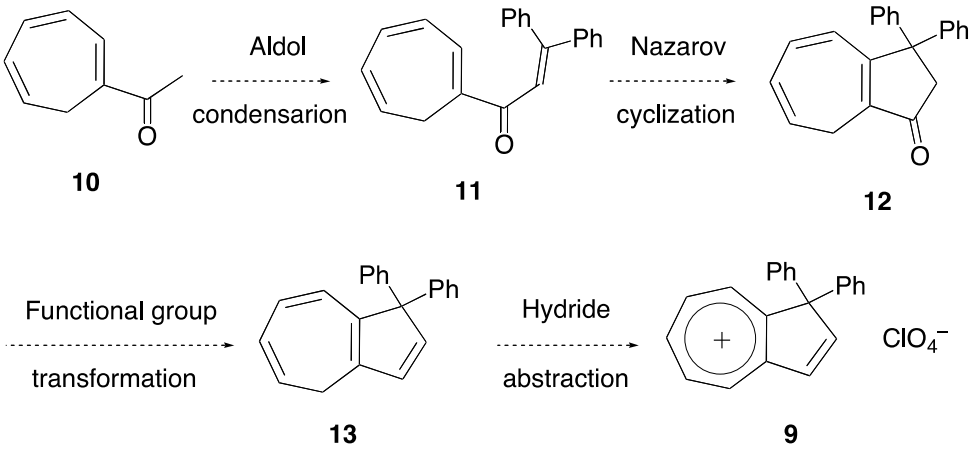
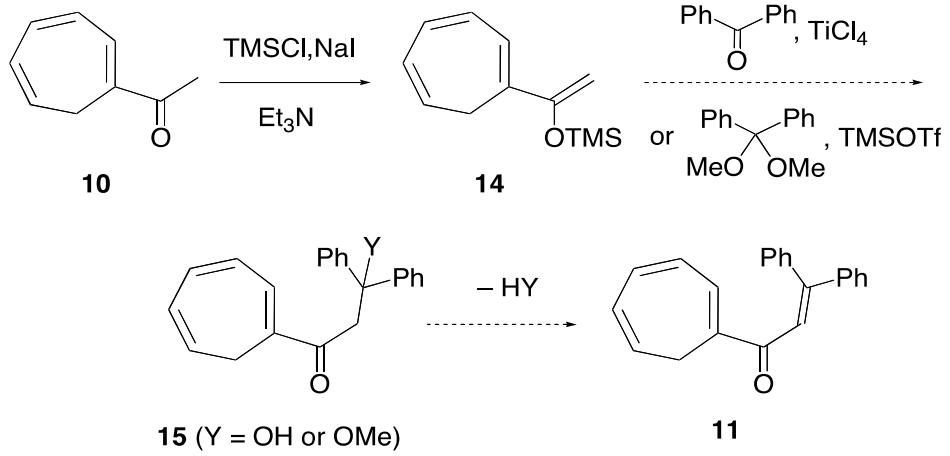


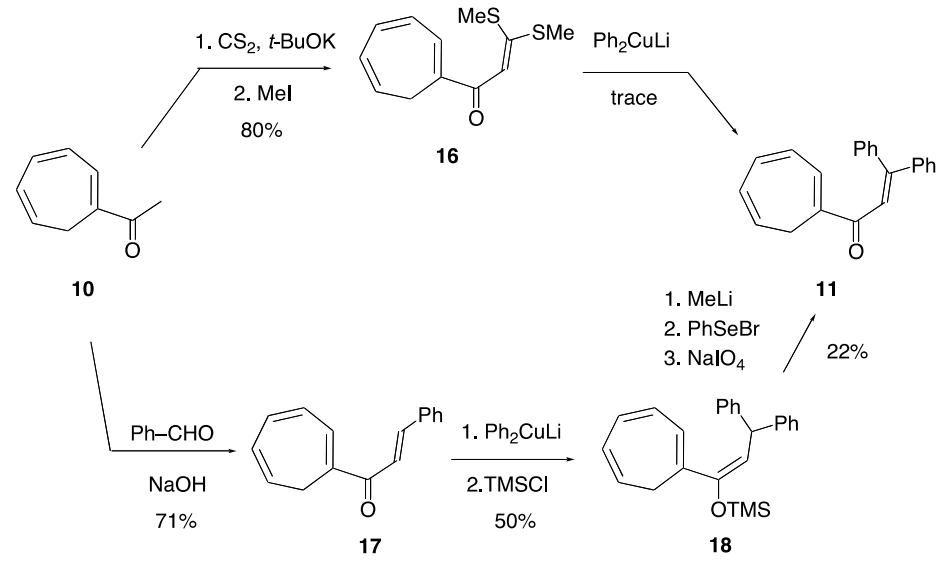
Figure 1. Various 1,1-disubstituted 1*H*-azulenium cations and their pK_R+ values



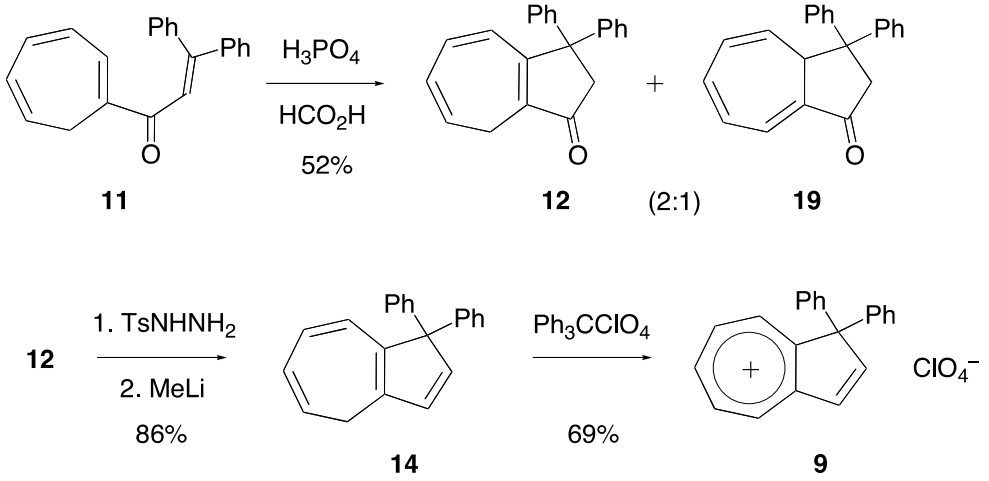
Scheme 1. A synthetic plan from **10** to **9** at the beginning



Scheme 2. An attempted synthetic approach from **10** toward **11**



Scheme 3. Synthetic routes from **10** to **11**



Scheme 4. Synthesis of **9** from **11**

Although direct oxidation of **17** either by $Pd(OAc)_2$/*p*-benzoquinone or by DDQ/pyridine was unsuccessful, the oxidation via an α-phenylselenyl intermediate provided **11** in 22% yield, accompanied with a trace amount of 1-(3,3-diphenylpropionyl)cyclohepta-1,3,5-triene, which may be derived from hydrolysis of 18. With compound **11** in our hands, its transformation into **9** was carried out by a previously reported three-step sequence (Scheme 4). It is worthy to note that the Nazarov cyclization of **11** gave not only **12** but also its regioisomer **19** as a by-product, as seen in previous results of structurally related substrates. [5, 7] The Shapiro reaction [15] of tosylhydrazone of **12** provided hydrocarbon **14** and the title cation **9** was obtained as a perchlorate salt by hydride abstraction of **14** with trityl perchlorate. Cation **9** was isolated as slightly greenish yellow crystals and its structure was supported by spectroscopic and combustion analyses. Selected assigned NMR signals of **9** with those of **8** [16] are shown in Fig. 2. The proton signals around the azulenyl ring in **9** were observed similar as seen in **4** and **5**. We reported that proton signals at the 2 and 8 positions in **8** were observed high-field shifted (δ_{ppm} 7.52 and 7.86) by a shielding effect of the fluorene moiety, supporting the perpendicular relationship between the azulenium ion part and the fluorene ring. The proton shift values of **9** indicate that the arrangement of the phenyl groups at the 1 position in **9** is different from that in **8**. [17] The optimized structure of **9** by DFT calculation at B3LYP/6-31G (d) level of theory [18] is shown in Fig. 3, which indeed shows two phenyl rings are connected to the azulenyl ring, not perpendicularly, with angles of 62.5 °and 76.0 °.

The UV-vis absorption spectra of **9** are shown Fig. 4. The spectrum of **9** in CH_2Cl_2 shows a shoulder absorption at 451 nm, which is longer than the expected wavelength (380~ 400 nm) for excitation based on π-conjugation of the azulenium ion part seen in the spectra of **1**–**7** and, therefore, is thought to be intramolecular CT absorption from the HOMO, whose π-orbital coefficients distribute almost at the phenyl group, to the LUMO, whose π-orbital coefficients distribute almost at the azulenium ion part. [19] However, its intensity

($\log\varepsilon = 1.91$) is smaller than that ($\log\varepsilon = 2.81$) of **8** in CH_2Cl_2, probably due to different arrangement between the phenyl and fluorenyl rings at the 1 position. The pK_R+ value of **9** was determined to be 6.4 by the UV method in 50% aqueous acetonitrile. Thus, the stability of **9** is greater than that of the tropylium ion (3.9), and less by about 1.4 pK_R+ units than that of **8**, suggesting that electron-withdrawing nature of the phenyl groups in **9** works more effectively than that of the fluorenyl group to destabilize the cationic part. The relative thermodynamical stability of **8** and **9** is reflected in their ability for thermal rearrangement. While **8** did not show any rearrangement at 100 ℃, **9** undergoes rearrangement above 80 ℃ in acetonitrile to yield 1,2-diphenylazulene (**22**) [20] quantitatively (Scheme 5).

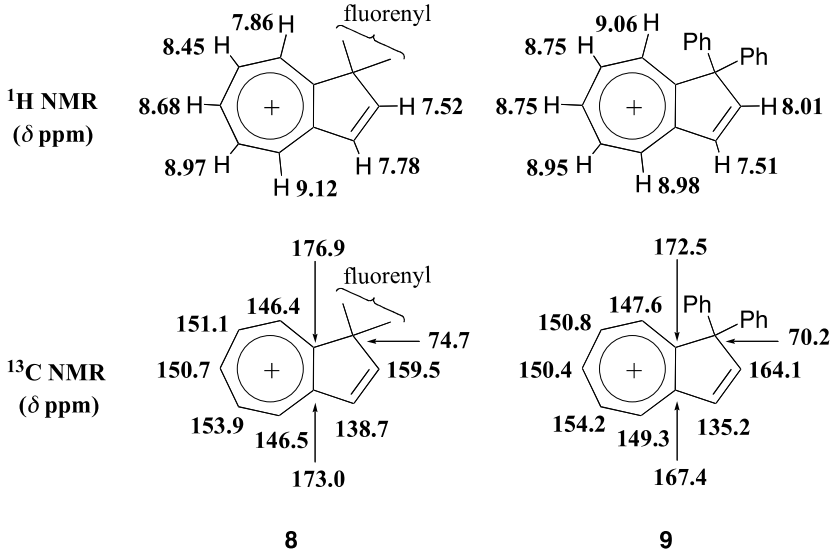


Figure 2. Assigned ^{1}H- and ^{13}C-NMR signals of the azulenium ion part of **8** an **9**

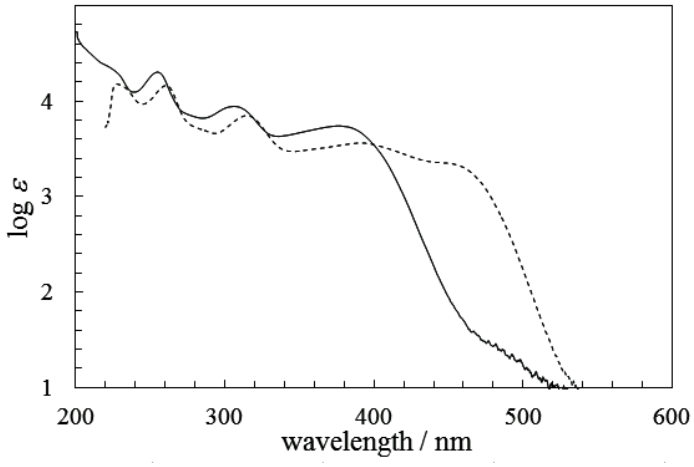


Figure 3. Optimized structure (Chem3D output) of **9** by DFT calculation at B3LYP/6-31G (d) level of theory

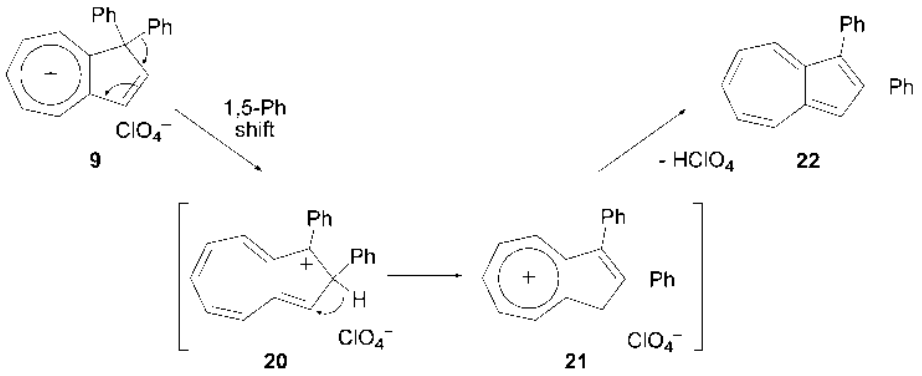
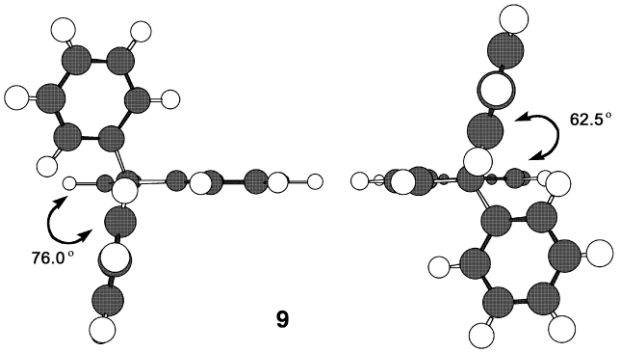


Figure 4. UV-Vis absorption spectra of cation **9** in acetonitrile (solid line), and dichloromethane (broken line)



Scheme 5. Thermal rearrangement of **9**

3. Experimental

3.1. General Remarks

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a PERKIN ELMER Spectrum RX-II spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL α400 spectrometer. Chemical shift values of tetramethylsilane (δ = 0 ppm) for ^{1}H-NMR spectra and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C-NMR spectra were used as internal standard. Mass spectra were measured on a JMS-700 mass spectrometer. Column chromatography was performed with Kiesel gel 60F from Merck Co. Benzaldehyde, cyclohepta-1,3,5-triene, acetyl chloride, and tosylhydrazine were purchased from Tokyo Chemical Ind. Chlorotrimethylsilane was purchased from Kanto Chem. and was distilled over CaH_2. Ether and tetrahydrofuran (THF) were distilled before use over sodium benzophene ketyl radical under nitrogen atomosphere. Acetonitrile was purchased from Kanto Chem. and was distilled over P_2O_5. A phenyllithium solution in ether was purchased from Tokyo Chemical Ind. A methyllithium solution in ether and phenylselenyl bromide were purchased from Aldrich Co. Compound **10** was obtained by acetylation of cyclohepta-1,3,5-triene with acetyl chloride and zinc chloride in dichloromethane. [21] Trityl perchlorate was prepared according to a method of Dauben *et al*. and was used after purification by recrystallization from dichloromethane-hexane. [22]

3.2. 1-Cinnamoylcyclohepta-1,3,5-Triene (17)

A solution of 10.1 g (7.54 mmol) of **10** in 60 mL of methanol was added slowly to a solution of benzaldehyde (6.06 g, 5.72 mmol) and sodium methoxide (12.3 g, 228 mmol) in 60 mL of methanol. The mixture was stirred at room temperature for 21 h, and then was poured into a 1M HCl solution and extracted with chloroform (50 mL x 4). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution and brine. The solvent was removed under vacuum and the residue was purified by silica gel chromatography (hexane/toluene = 3/7) to give 9.01 g (71% yield) of **17** as a pale yellow oil.

17: IR (liq. film) ν_{max} = 1597 (s), 1575 (s), 1305 (s), 1200 (s), 1167 (s), 761 (s), 715 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.77 (d, *J* = 7.0 Hz, 2H), 5.62 (dt, *J* = 9.6, 7.0 Hz, 1H), 6.29 (dd, *J* = 9.6, 5.6 Hz ,1H), 6.73 (dd, *J* = 11.2, 5.6 Hz, 1H), 6.86 (dd, *J* = 11.2, 5.6 Hz, 1H), 7.19 (d, *J* = 5.6 Hz, 1H), 7.35 (*J* = 15.6 Hz, 1H), 7.40 (m, 3H), 7.57 (m, 2H), 7.65 (d, *J* = 15.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 26.2, 121.8, 125.6, 127.1, 128.2, 128.8, 129.2, 130.2, 132.2, 132.7, 135.0, 135.9, 143.3, 189.3 ppm; UV (CH_3OH) λ_{max} = 203 (logε = 4.43), 227 (4.09), 321 (4.26) nm; MS *m/z* (rel. int) 222 (M^+, 55 %), 221 (29), 207 (29), 131 (100), 103 (31), 77 (56). HRMS calcd for $C_{16}H_{14}O$ 222.1045, found 222.1050.

3.3. 1-(3,3-Diphenylacryloyl)Cyclohepta-1,3,5-Triene (11) from 17

A solution of 0.4 M phenyllithium solution in ether (50 mL, 20 mmol) was added slowly to a suspension of cupric iodide (1.90 g, 10.0 mmol) in 15 mL of ether at –20 ℃. To a resulted greenish solution of lithium diphenylcuprate was added a solution of **11** (2.23g, 10.0 mmol) in 30 mL of ether at the same temperature. After being stirred at room temperature for 1 h, the reaction mixture was quenched by adding 2.54 mL (20.0 mmol) of chlorotrimethylsilane and then stirred further for 4 h. The resulted reaction mixture was poured into water and solids were removed by passing through a Celite pad. The filtrate was extracted with ether (50mL x 3) and the combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was passed quickly through silica gel short column (hexane/ether = 95/5) to give 1.82 g (50% yield) of crude **18** as a pale yellow oil. Without further purification, this crude sample was used in a next step.

18: IR (liq. film) ν_{max} = 3025 (s), 1493 (s), 1252 (s), 1071 (s), 1041 (s), 1028 (s), 895 (s), 845 (s), 757 (s), 741 (s), 699 (s) cm^{-1}; ^{1}H NMR of the major isomer ($CDCl_3$, 400 MHz) δ = 0.07 (s, 9H), 2.55 (d, *J* = 7.2 Hz, 2H), 5.15 (d, *J* = 9.9 Hz, 1H), 5.40 (dt, *J* = 9.2, 7.2 Hz, 1H), 5.69 (d, *J* = 9.9 Hz, 1H), 6.19 (dd, *J* = 9.2, 5.3 Hz, 1H), 6.44 (d, *J* = 5.9 Hz, 1H), 6.54 (dd, *J* = 11.0, 5.3 Hz, 1H), 6.60 (dd, *J* = 11.0, 5.9 Hz, 1H), 7.15–7.30 (m, 10H) ppm; MS *m/z* (rel. int) 372 (M^+, 100), 371 (42), 357 (24), 295 (11), 282 (14), 281 (23), 205 (14), 191 (14), 179 (20), 178 (19), 167 (16), 165 (29), 152 (11), 115 (10). HRMS Calcd for $C_{25}H_{28}OSi$ 372.1884, found 372.1882.

To a solution of crude **18** (186 mg, 0.500 mmol) in 10 mL of THF at 0 ℃ was added a 1.25 M methyllithium solution in ether (0.44 mL, 0.55 mmol), followed by 118 mg (0.500 mmol) of phenylselenyl bromide with 5 mL of THF. The reaction mixture was stirred at room temperature for 4 h, and then was poured into water and extracted with ether (40 mL x 3). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution and brine. After being dried over $MgSO_4$, the solvent was removed under vacuum. The residue was dissolved in 5 mL of methanol. To this solution was added 107 mg (0.500 mmol) of $NaIO_4$ and 0.5 mL of water. The mixture was refluxed on an oil bath for 3 h, and then was poured into water and extracted

with chloroform (20 mL x 3). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution and brine. The solvent was removed under vacuum and the residue was purified by silica gel chromatography (AcOEt/hexane = 18/82) to give 33 mg (22% yield) of **11** as a pale yellow oil, accompanied with 4 mg (3% yield) of 1-(3,3-diphenylpropionyl)cyclohepta-1,3,5-triene as creamy white solids.

11: IR (liq. film) ν_{max} = 1644 (s), 1603 (s), 1265 (s), 1200 (s), 1167 (s), 774 (s), 715 (s), 698 (s) cm^{-1}.^{1}H NMR ($CDCl_3$, 400 MHz) *d* = 2.56 (d, *J* = 7.1 Hz, 2H), 5.48 (dt, *J* = 9.3, 7.1 Hz, 1H), 6.18 (dd, *J* = 9.3, 5.6 Hz, 1H), 6.57 (dd, *J* = 11.2, 6.1 Hz, 1H), 6.75 (dd, *J* = 11.1, 5.5 Hz, 1H), 6.83 (s, 1H), 7.08 (d, *J* = 5.9 Hz, 1H), 7.12–7.15 (m, 2H), 7.27–7.37 (m, 8H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 25.64, 124.90, 125.70, 127.01, 127.83, 128.11, 128.20, 128.37, 128.49, 129.02, 129.63 (2C), 132.96, 133.63, 135.55, 141.26, 152.49, 193.19 ppm; UV (CH_3OH) λ_{max} = 204 ($\log\varepsilon$ = 4.62), 226sh (4.30), 255sh (4.05), 321 (3.99) nm; MS *m/z* (rel. int) 298 (M^+, 100), 297 (21), 221 (11), 207 (51), 179 (42), 178 (90), 177 (12), 176 (12), 167 (14), 165 (12), 152 (14), 133 (11), 105 (20), 91 (20). HRMS Calcd for $C_{22}H_{18}O$ 298.1338, found 298.1335.

1-(3,3-Diphenylpropionyl)cyclohepta-1,3,5-triene: M.p. 70–72 ℃; IR (KBr) ν_{max} = 1656 (s), 720 (s), 703 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.57 (d, *J* = 7.1 Hz, 2H), 3.47 (d, *J* = 7.3 Hz, 2H), 4.70 (t, *J* = 7.3 Hz, 1H), 5.50 (dt, *J* = 9.0, 7.1 Hz, 1H), 6.23 (dd, *J* = 9.4, 5.7 Hz, 1H), 6.66 (dd, *J* = 11.2, 6.1 Hz, 1H), 6.83 (dd, *J* = 11.2, 5.6 Hz, 1H), 7.10 (d, *J* = 6.1 Hz, 1H), 7.16 (tt, *J* = 7.0, 1.8 Hz, 2H), 7.20–7.28 (m, 8H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 25.57, 44.28, 46.47, 125.70, 126.31, 127.05, 127.83, 128.49, 129.08, 131.51, 132.02, 135.93, 144.17, 197.49 ppm; UV (CH_3OH) λ_{max} = 204 ($\log\varepsilon$ = 4.54), 2.18sh (4.39), 271sh (3.70), 294 (3.73) nm; MS *m/z* (rel. int) 300 (M^+, 21), 181 (18), 179 (12), 178 (15), 168 (17), 167 (100), 166 (21), 165 (52), 152 (25), 134 (21), 133 (83), 119 (10), 105 (17), 103 (21), 91 (36). HRMS Calcd for $C_{22}H_{20}O$ 300.1514, found 300.1511. Elemantal analysis; calcd for $C_{22}H_{20}O$ C 87.96, H 6.71%, found C 87.68, H 6.77%.

3.4. 1-[3,3-Bis(Thiomethyl)Acryloyl]Cyclohepta-1,3,5-Triene (16)

A solution of 1.34 g (10.0 mmol) of **10** in 10 mL of THF was added to a suspension of 2.24 g (20.0 mmol) of *t*-BuOK in 20 mL of THF, followed by addition of carbon disulfide (0.60 mL, 10.0 mmol), and then iodomethane (1.34 mL, 22.0 mmol). After being stirred at room temperature for 2 hr, the reaction mixture was poured in water and extracted with dichloromehane (30 mL x 3). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (AcOEt/hexane = 4/1) to give 1.90 g (80%) of **16** as yellow needles.

16: M.p. 77–78 ℃; IR (KBr) ν_{max} = 1597 (s), 1483 (s), 1472 (s), 1170 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.46 (s, 6H), 2.70 (d, *J* = 7.2 Hz, 2H), 5.57 (dt, *J* = 9.4, 6.8 Hz, 1H), 6.26 (dd, *J* = 9.4, 5.6 Hz, 1H), 6.55 (s, 1H), 6.68 (dd, *J* = 11.2, 6.2 Hz, 1H), 6.81 (dd, *J* = 11.2, 5.6 Hz, 1H), 6.84 (d, *J* = 6.2 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 15.05, 17.27, 26.23, 110.07, 124.95, 126.91, 129.18, 129.24, 133.39, 134.87, 164.09, 185.27 ppm; UV (CH_3OH) λ_{max} = 218 ($\log\varepsilon$ = 3.91), 360 (4.27) nm; MS *m/z* (rel. int) 238 (M^+, 25), 208 (10), 191 (28), 175 (29), 161 (50), 144 (73), 133 (38), 118 (41), 91 (100), 77 (15), 75 (38), 65 (42). HRMS Calcd for $C_{12}H_{14}OS_2$ 238.0486, found 238.0490. Elemental analysis; calcd for $C_{12}H_{14}OS_2$ C 60.46, H 5.92%, found C 60.78, H 5.95%.

3.5. 1-(3,3-Diphenylacryloyl)Cyclohepta-1,3,5-Triene (11) from 16

A solution of 0.4 M phenyllithium solution in ether (20 mL, 10.0 mmol) was added slowly to a suspension of cupric iodide (952 mg, 5.00 mmol) in 10 mL of ether at –20 ℃. To a resulted greenish solution of lithium diphenylcuprate was added a solution of **16** (595 mg, 2.50 mmol) in 7 mL of ether at the same temperature. After the reaction mixture was stirred at room temperature for 10 h, the resulted reaction mixture was poured into 0.05M HCl (70 mL) and solids formed were removed by passing through a Celite pad. The filtrate was extracted with ether (50mL x 3) and the combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by silica gel chromatography (AcOEt/hexane = 18/82) to give 22 mg (3% yield) of **11** as a pale yellow oil.

3.6. Nazarov Cyclization of 1-(3,3-Diphenylacryloyl)-Cyclohepta-1,3,5-Triene (11)

A solution of **11** (2.37g, 7.95 mmol) in a mixture of phosphoric acid (50 mL) and formic acid (50 mL) was heated on an oil bath at 90 ℃ for 24 h. After being cooled to room temperature, the resulted reaction mixture was poured into water and extracted with ether (80 mL x 3). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution and brine. The solvent was removed under vacuum and the residue was purified by silica gel chromatography (AcOEt/hexane = 5/95) to give 903 mg (38% yield) of **12** as yellow solids and 448 mg (14% yield) of **19** as yellow microcrystals.

12: M.p. 142–144 ℃; IR (KBr) ν_{max} = 1688 (s), 1655 (m), 703 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.80 (d, *J* = 6.5 Hz, 2H), 3.25 (s, 2H), 5.73 (dt, *J* = 9.9, 6.5 Hz, 1H), 6.20 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.44 (d, *J* = 11.5 Hz, 1H), 6.72 (dd, *J* = 11.5, 6.0 Hz, 1H), 7.11–7.32 ppm; UV (CH_3OH) λ_{max} = 204 ($\log\varepsilon$ = 4.54), 212sh (4.47), 273sh (3.64), 297 (3.72) nm; MS *m/z* (rel. int) 298 (M^+, 73), 256 (42), 255 (23), 239 (16), 221 (28), 220 (29), 219 (15), 207 (15), 193 (16), 192 (29), 191 (50), 189 (33), 179 (45), 178 (100), 176 (20), 165 (58), 152 (25), 118 (17), 115 (35). HRMS calcd for $C_{22}H_{18}O$ 298.1358, found 298.1348. Elemental analysis calcd for $C_{22}H_{18}O$ C, 88.56, H 6.08 %; found C, 88.76, H, 6.19 %.

19: M.p. 42–44 ℃; IR (KBr) ν_{max} = 1709 (s), 1617 (s), 699 (s) cm^{-1}; ^1H NMR ($CDCl_3$,400 MHz) δ = 2.97 (dm, *J* = 6.3 Hz, 1H), 2.99 (d, *J* = 16.4 Hz, 1H), 3.38 (d, *J* = 16.4 Hz, 1H), 5.12 (dd, *J* = 9.5, 6.3 Hz, 1H), 6.22 (m, 1H), 6.97 (m, 2H), 7.06 (m, 2H), 7.11–7.14 (m, 2H), 7.20 (tm, *J* = 7.3 Hz, 2H), 7.24–7.31 (m, 3H), 7.40 (tm, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 48.79, 50.76, 52.26, 123.31, 125.03, 125.45, 126.57, 126.78, 128.27, 128.62, 128.73 (2C), 129.83, 129.96, 135.95, 144.44, 147.89, 201.15 ppm; UV (CH_3OH) λ_{max} = 206 (logε = 4.56), 219sh (4.40), 233sh (4.13), 293 (3.78), 317sh (3.70), 361sh (2.99) nm; MS *m/z* (rel. int) 298 (M^+, 12), 256 (12), 192 (11), 191 (13), 179 (18), 178 (28), 167 (16), 165 (21), 118 (100), 115 (12), 105 (57), 91 (14), 90 (81), 89 (14). Elemental analysis calcd for $C_{22}H_{18}O$ C, 88.56, H 6.08 %; found C, 88.78, H, 6.34 %.

3.7. 1,1-Diphenyl-1,4-Dihydroazulene (14) via Tosyl-Hydrazone of 12

To a solution of **12** (900 mg, 3.02 mmol) in 45 mL of THF was added tosylhydrazine (560 mg, 3.00 mmol) was added. This mixture was stirred at room temperature under nitrogen for 4 days. Solids of tosylhydrazine gradually dissolved and the mixture became a clear solution after one day. Then after, the hydrazone product slowly crystallized and were collected by a suction filtration. After being washed with a trace amount of cold THF and well with ether to give 1.20 g (86% yield) of the tosylhydrazone of **12** as brownish microcrystals.

Tosylhydrazone of **12**: M.p. 173–176 ℃ (dec.); IR (KBr) ν_{max} = 1421 (m), 1334 (m), 1185 (m), 1170 (s), 701 (s), 667 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.44 (s, 3H), 2.87 (d, *J* = 6.4 Hz, 2H), 3.21 (s, 2H), 5.61 (dt, *J* = 10.0, 6.4 Hz, 1H), 6.12 (dd, *J* = 10.0, 6.0 Hz, 1H), 6.21 (d, *J* = 11.5 Hz, 1H), 6.50 (dd, *J* = 11.5, 5.9 Hz, 1H), 7.02–7.05 (m, 4H), 7.18–7.28 (m, 6H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm = 21.66, 23.03, 47.11, 59.23, 126.43, 126.65, 126.84, 127.87, 127.91, 128.03, 128.19, 128.22, 128.33, 128.45, 128.51, 129.57, 135.24, 144.20, 145.84 ppm; MS *m/z* (rel. int) 466 (M^+, 7), 312 (25), 311 (100), 256 (6), 203 (6), 191 (8), 91 (12). HRMS calcd for $C_{29}H_{26}N_2O_2S$ 466.1715; found, 466.1719.

To a suspension of 466 mg (1.00 mmol) of the tosylhydrazone in 5 mL of THF was added a 1M methyllithium solution in ether (10 mL, 10 mmol) at 0 ℃ under nitrogen atmosphere. The resulted orange solution was stirred at room temperature for 5 h and then was quenched by adding water. The mixture was extracted with ether (20 mL x 3) and the combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (AcOEt/hexane = 2/98) to give 195 mg (69%) of **14** as a pale yellow oil.

14: IR (liq. film) ν_{max} = 3059m, 3021m, 1597m, 1489m, 786s, 761s, 731s, 699s cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.75 (d, *J* = 6.5 Hz, 2H), 5.43 (dt, *J* = 9.6, 6.5 Hz, 1H), 6.15 (dd, *J* = 9.8, 5.6 Hz, 1H), 6.26 (d, *J* = 5.3 Hz, 1H), 6.41 (dd, *J* = 11.2, 5.6 Hz, 1H), 6.48 (d, *J* = 11.2 Hz, 1H), 6.79 (d, *J* = 5.3 Hz, 1H), 7.09–7.12 (m, 4H), 7.17–7.25 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 27.8, 68.8, 121.1, 126.6, 127.6, 127.7, 128.0, 128.19, 128.23, 132.5, 136.1, 142.0, 147.0, 148.2 ppm; UV (CH_3OH) λ_{max} 204 (logε = 4.38), 243 (3.69), 328 (3.50) nm; MS *m/z* (rel. int) 282 (M^+, 100), 281 (34), 268 (65), 267 (86), 266 (20), 265 (42), 252 (29), 205 (25), 204 (29), 203 (38), 202 (39), 191 (65), 189 (29). HRMS calcd for $C_{22}H_{18}$ 282.1409, found, 282.1411.

3.8. 1,1-Diphenyl-1*H*-azulenium Perchlorate (9)

To a solution of 190 mg (0.674 mmol) of **14** in 2 mL of acetonitrile was added 231 mg (0.674 mmol) of trityl perchlorate. After being stirred at room temperature for 1 h, the reaction solution was concentrated to ca. 0.5 mL under vacuum. To this mixture was added 4 mL of ether. The solids formed were collected by a suction filtration and were recrystallized from dichloromethane-ether to give 155 mg (82% yield) of **9** as greenish yellow microcrystals.

9: M.p. 113–116 ℃; IR (KBr) ν_{max} = 1508 (m), 1491 (m), 1450 (s), 1092 (br, s), 804 (m), 756 (m), 700 (m), 623 (s) cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ = 7.24 (dm, *J* = 7.1 Hz, 4H), 7.37 (tm, *J* = 7.1 Hz, 4H), 7.42 (tm, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 5.4 Hz, 1H), 8.01 (d, *J* = 5.4 Hz, 1H), 8.75 (m, 2H), 8.95 (tm, *J* = 9.6 Hz, 1H), 8.98 (dm, *J* = 9.6 Hz, 1H), 9.06 (d, *J* = 9.6 Hz, 1H) ppm; ^{13}C NMR (CD_3CN) δ = 70.21, 128.94, 130.27, 130.47, 135.18, 137.55, 147.56, 149.31, 150.39, 150.75, 154.19, 164.15, 167.35, 172.54 ppm; UV-vis (CH_3CN) λ_{max} = 223sh (logε = 4.36), 255 (4.30), 306 (3.88), 378 (3.76) nm; UV-vis (CH_2Cl_2) λ_{max} = 233sh (logε = 4.74), 261 (4.67), 316 (3.98), 389 (3.76), 541sh (1.95) nm; MS *m/z* (rel. int) 281 ($C_{22}H_{17}^+$, 34), 280 (100), 279 (18), 278 (19), 277 (14), 276 (14), 252 (12), 202 (13). HRMS calcd for $C_{22}H_{17}^+$ 281.1325; found, 281.1327. Elemental analysis calcd for $C_{22}H_{17}ClO_4$ C, 69.39, H 4.50%; found C, 69.33, H, 4.82%.

3.9. Thermal Rearrangement of Cation 9

An NMR tube was sealed with a solution of **9** (19.0 mg, 50.0 mmol) in 1.0 mL of CD_3CN. The tube was spun and heated at 100 ℃ inside the NMR spectrometer and the rearrangement reaction was monitored by the ^1H NMR spectrum. After the reaction completed (210 min), the tube was cooled to room temperature and opened. The reaction mixture was poured into 20 mL of water and was extracted with chloroform (10 mL x 3). The combined organic layer was washed with a saturated $NaHCO_3$ solution and brine. After dryness over $MgSO_4$, the solvent was removed and the residue was purified by alumina chromatography to give 13.7 mg (98% yield) of **22** [20] as a greenish blue oil.

^1H NMR ($CDCl_3$, 400 MHz) δ = 7.11 (t, *J* = 9.8 Hz, 1H), 7.16 (t, *J* = 9.8 Hz, 1H), 7.23–7.45 (m, 10H), 7.53 (t, *J* = 9.8 Hz, 1H), 7.58 (s, 1H), 8.25 (d, *J* = 9.8 Hz, 1H), 8.34 (d, *J* = 9.8 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 116.9, 123.3, 123.6, 123.8, 126.5, 127.3, 128.2, 128.3, 128.4, 129.9, 131.4, 131.7, 135.5, 136.5, 136.7, 137.3, 139.5,

140.2 ppm; MS *m/z* (rel. int) 280 (M^+, 100), 279 (22), 268 (44), 267 (54), 266 (26), 252 (20), 205(46), 203 (60), 202 (68), 192 (17), 189 (36), 165 (27), 126 (30), 91 (25), 77 (34), 51 (39). HRMS calcd for $C_{22}H_{16}$ 280.1252; found, 280.1258.

3.10. Determination of pK_R+ Value of Cation 9

The UV spectra in various pH of 50% aqueous acetonitrile solutions were measured by exactly the same method of Komatsu *et al*. [23–24] Observed absorbance at the longest absorption maxima at 378 nm was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_R+.

4. Conclusions

We have accomplished the synthesis of the title compound, 1,1-diphenyl-1*H*-azulenium perchlorate (**9**), from 1-acetyl-1,3,5-cycloheptatriene (**10**). The compound **9** shows less stability than **8** compared with their pK_R+ values and upon heating **9** undergoes rearrangement to produce 1,2-diphenylazulene. Further studies on synthesis of 1,1-diphenyl-1*H*-azuleniums having substituents on the phenyl rings are in progress to evaluate an effect of the substituents on stability of the cationic system.

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