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Synthesis and Reactions of 1,1-Trimethylene-1*H*-azulenium Ion

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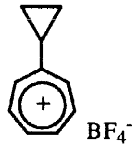
Abstract. Direct cyclobutylation of 1,6-dihydroazulene gave the spiro hydrocarbon **6**, which was subjected to hydride abstraction to lead to the title cation **4**. Its hexafluorophosphate salt was isolated as crystals. The cation **4** showed distinctive chemical behavior compared with its three-membered ring homolog.

Keywords: carbocations; rearrangements; spiro compounds; tropylium ions.

The remarkable ability of a cyclopropane ring to stabilize the tropylium ion has been demonstrated in a series of investigations by Komatsu and Takeuchi.1) Although saturation of the effect was observed, an increase in the number of cyclopropyl substitution around the tropylium ring resulted in clear increase of the pK_{R+} value and resistance to one-electron reduction. Additionally, cyclopropyltropylium salt (**1**) was known to show greater thermodynamic stability than the cyclobutyl 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) Meanwhile, we have reported generation of 1,1-ethylene-1*H*-azulenium cation (**3**),4) which had been thought to be 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 and an electron-defficient 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 addition product.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 synthesis of the title cation **4**, a higher homolog of **3**, and its distinctive chemical behavior compared with **3**.6)



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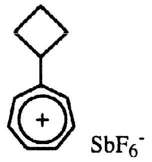

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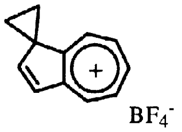

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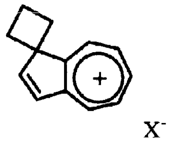

4a; $X = BF_4$
4b; $X = PF_6$

The synthesis of **4** was accomplished in a few steps starting from 1,6-dihydroazulene (**5**) under similar reaction conditions to those for **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.7) This yield

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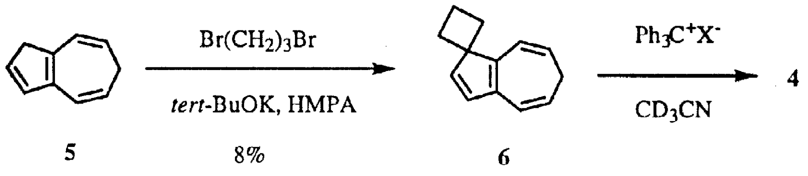
was still superior to that obtained under conditions using other strong bases, such as sodium hydride and sodium amide, and other solvents, such as dimethyl sulfoxide, dimethylformamide, tetrahydrofuran and liquid ammonia. Though the yield was not satisfactory, it should be emphasized that this reaction condition can be applied to direct spirobutylation of cyclopentadiene,[8] indene and fluorene.[9] 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. ^{1}H and ^{13}C NMR spectra measured at the same temperature revealed formation of the title cation **4** and triphenylmethane. 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 operation to the former gave a greenish oil. ^{1}H and ^{13}C NMR spectra of **4b** in CD_3CN are shown in Fig. 1 and the signal assignments are summarized in Fig. 2. The average chemical shift (δ_{av} = 8.93 ppm) of the protons at the seven-membered ring of **4** is greater than that (δ_{av} = 8.72 ppm) of **3**, indicating less delocalization of the positive charge in **4** than in **3**. The cation **4** in CD_3CN solution was stable at 0 °C; however, it was found to rearrange at elevated temperature to afford the ring expansion product, 2,3-trimethylene-1*H*-azulenium ion (**7**),[10] in a nearly quantitative yield. The half-life of **4** ($\tau_{1/2}$ = 10 min at 23 °C) in CD_3CN was longer than that of **3** ($\tau_{1/2}$ = 27 min at 0 °C). This rearrangement probably proceeds through an intermediate, 1,2-trimethylene-2*H*-azulenium ion (**8**), formed by 1,5-shift. This result is in contrast to the case of **3** which gave the ring expansion product shifted to the 8a position.[4] AM1 calculations[11] of heats of formation for **4**, **7**, **8** and **9** which would be formed by the shift to the 8a position predict down stream of the energy levels along the pathway from **4** to **7** through **8** and an endothermic reaction for conversion of **4** into **9**.[12]



Scheme 1.

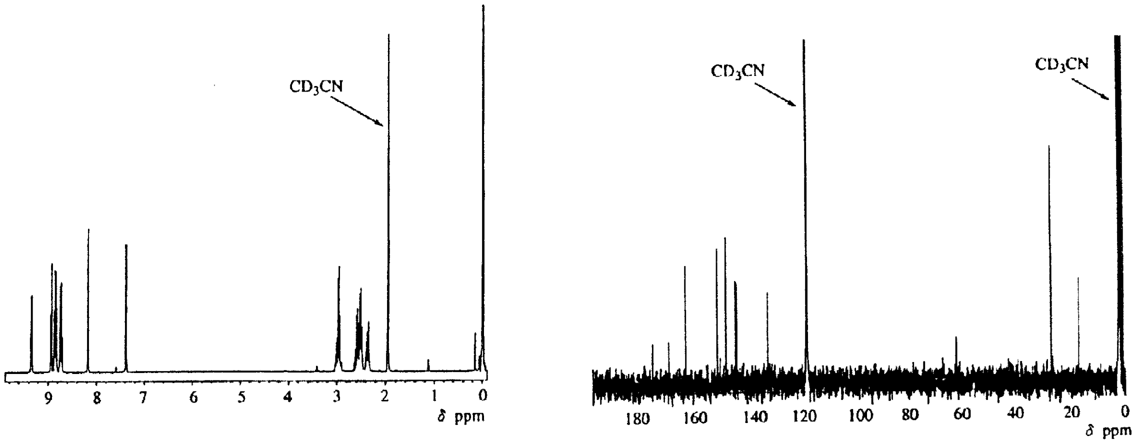


Figure 1. ^{1}H (400 MHz, left) and ^{13}C (100 MHz, right) NMR spectra of the cation **4b** in CD_3CN.

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 **10**. The structure of the cation **10** was deduced by ^{1}H and ^{13}C NMR spectral data of the reaction mixture.[13] NOE experiments confirmed the geometrical structure as depicted in Scheme 2. Since equilibration between the heptafluvene-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, **8** equilibrates with the hydrocarbon **11** which reacts with another trityl cation at the 1 position to lead to the cation **10**. Such a reaction has not been observed in **3**. Reactions of **4** with various nucleophiles, such as water, sodium hydroxide, methanol and sodium acetate, gave only an intractable mixture, also in contrast to the case of **3**.

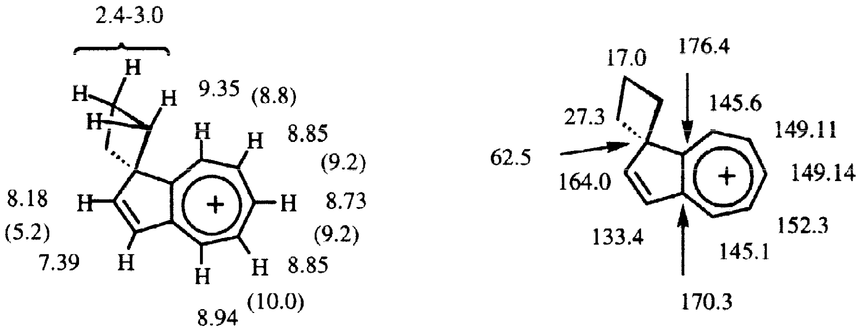
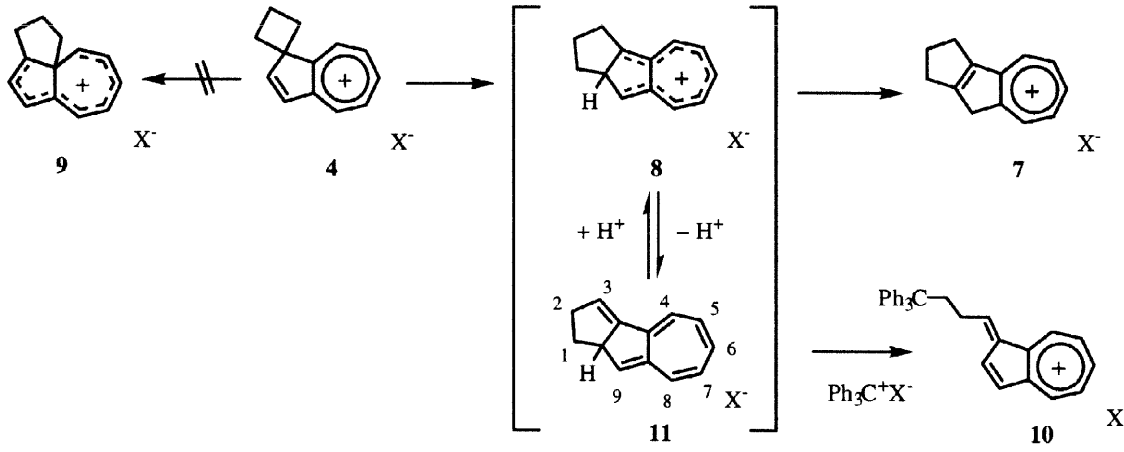


Figure 2. Proton (left) and carbon (right) shift values (δppm) assigned for **4b**. Coupling constants are given in parentheses



Scheme 2.

In summary, we have accomplished the synthesis of the title cation **4** by a route involving direct spirobutylation of dihydroazulene. In contrast to the greater thermodynamic stabilty of **1** than that of **2**, the analogous cation **4** was found to be kinetically more stable than **3**. Also, the chemical behavior of **4** was demonstrated to be quite distinctive compared with **3**.

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7. Selected data for **6**: ^{1}H NMR (400 MHz, CDCl3); δppm = 2.01–2.11 (m, 1H), 2.20–2.26 (m, 3H), 2.29 (t, J = 6.8 Hz, 2H), 2.33–2.38 (m, 2H), 5.29 (dt, J = 9.6, 6.8 Hz, 1H), 5.34 (dt, J = 9.6, 6.8 Hz, 1H), 6.37 (d, J = 9.2 Hz, 1H), 6.38 (d, J = 5.6 Hz, 1H), 6.65 (d, J = 9.6 Hz, 1H), 6.70 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$); δppm = 17.75, 28.31, 28.81, 59.63, 117.41, 118.52, 124.11, 125.24, 131.22, 141.79, 142.80, 150.04. MS (70 eV); *m/z* (relative intensity) 170 (M$^+$, 64), 168 (100), 158 (24), 155 (42), 153 (35), 145 (30), 142 (41), 129 (25), 128 (26). UV-vis (hexane); λmax (log ε) = 222(4.20), 268sh (3.45), 274sh (3.48), 279 (3.51), 308 (3.51) nm.
8. Chiurdoglu first reported that cyclopentadiene was converted to spiro[3.4]octa-5,7-diene (**13**) under the condition with sodium amide, 1,3-dibromopropane and liquid ammonia.$^{16)}$ However, both Miller$^{17)}$ and Wilcox$^{18)}$ independently claimed that they had been unable to reproduce the result of Chiurdoglu and the former author also indicated that the spectral data of **13**, prepared by an alternative route, do not correspond to those reported by Chiurdoglu. Thus, our results, details of which will be reported elsewhere, demonstrated for the first time that direct spirobutylation of cyclopentadiene is possible.
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10. The formation of the cation **7** was confirmed by ^{1}H and ^{13}C NMR spectral data which were in good agreement with those obtained for 1,2-trimethyleneazulene (**14**)$^{19)}$ in the presence of sulfuric acid. Furthermore, pouring the solution of **7** into aqueous acetone and subsequent extraction with ether gave **14** in a yield of 67% based on the cation **4**.
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12. Heats of formation (ΔH_f, kcal/mol) were calculated as follows. **4**: 238.68; **7**: 217.97; **8**: 237.24; and **9**: 247.83. Calculations were performed with the MOPAC program (ver. 6.02) installed on an IBM RS/6800-580 workstation.
13. Reduction of **10** with sodium borohydride gave 1-(4,4,4-triphenylbutyl)azulene (**15**) as blue microcrystals, further supporting the structure of **10**. Selected data for **15**: Mp 194–195 °C. ^{1}H NMR (400 MHz, CDCl3); δppm = 2.12 (t, J = 7.2 Hz, 2H), 2.24 (quin, J = 7.2 Hz, 2H), 3.02 (t, J = 7.2 Hz, 2H), 6.59 (t, J = 10.4 Hz, 1H), 6.92 (t, J = 9.6 Hz, 1H), 7.11–7.22 (m, 11H), 7.27–7.33 (m, 7H), 7.53 (d, J = 9.6 Hz, 1H), 7.96 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$); δppm = 25.25, 30.28, 31.22, 61.67, 121.21, 121.44, 125.60, 127.26, 127.56, 130.90, 131.06, 132.48, 135.42, 136.22, 136.89, 140.65, 147.40, 161.32. MS (70 eV); *m/z* (relative intensity) 412 (M$^+$, 3), 411 (17), 410 (47), 334 (29), 333 (100), 167 (27), 165 (61), 28 (89). UV-vis (hexane); λmax (log ε) = 218 (4.88), 289 (4.90), 374 (3.98), 3.63 (4.14), 381 (3.97), 563sh (2.66), 607 (2.76), 6.45sh (2.67), 633sh (2.65) nm.
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