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Synthesis and Stability of 1,1-Tetramethylene- and 1,1-Pentamethylene-1*H*-azulenium Ions

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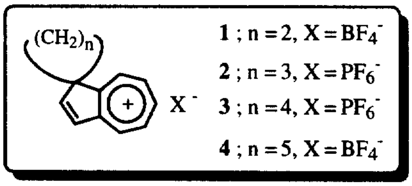
Abstract. Direct cycloalkylation of 1,6-dihydroazulene and subsequent hydride abstraction with trityl salt gave the title cations **3** and **4**. These cations showed greater kinetic stability than the three- and four-membered ring homologs, and their pK_{R^+} values indicated greater thermodynamic stability compared with the known disubstituted tropylium cations. © 1999 Elsevier Science Ltd. All rights reserved.

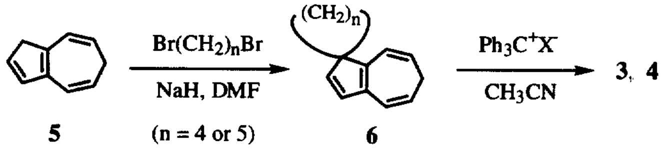
Keywords: carbocations; spiro compounds; tropylium ions; azulenium ions

We have recently reported synthesis and characterization of 1,1-ethylene- and 1,1-trimethylene-1*H*-azulenium ions **1**[1)] and **2**,[2)] the former of which had been postulated to be an intermediate in solvolysis of 2-(1-azulyl)ethyl tosylate.[3)] These cations were thought to be suitable candidates for evaluatation of the σ-π interaction[4)] between a σ-orbital of the spiro ring and an electron-deficient p-orbital at the tropylium part because of their structural rigidity and appropriate bisected geometry. However, both cations were found to undergo facile expansion of the cyclopropane and cyclobutane rings below room temperature or to react instantaneously with nucleophiles to give the addition products.[1,2)] Herein we describe the first synthesis of the title cations **3** and **4**, higher homologs of **1** and **2**, and evaluation of the stability of this type of cationic system.



The synthesis of **3** and **4** was accomplished in two steps starting from 1,6-dihydroazulene (**5**);[1)] spiroalkylation of **5** with 1,n-dibromoalkane (n = 4 or 5) in the presence of sodium hydride in dimethylformamide, and subsequent hydride abstraction with trityl salt in acetonitrile gave **3** and **4** as stable, greenish crystals in total yields of 51 and 31%, respectively (Scheme). Their structures were fully characterized by spectroscopic and elemental analysis.[5)] On heating in refluxing acetonitrile, **3** gradually rearranged to 2,3-tetramethylene-1*H*-azulenium ion while **4** did not show any appreciable change. The reluctance of **4** to rearrange indicates its greater kinetic stability compared with that of **1** and **2**. The pK_{R^+} values of **3** and **4** were determined by the UV method in buffered 50% aqueous acetonitrile solutions to be 9.9 and 10.0, respectively. Thus, the thermodynamic stability of these cations is comparable to that of the tris(cyclopropyl)cyclopropenium ion (pK_{R^+} =10.0)[6)] and is far greater than those of the known disubstitueted tropylium ions, such as 1,4-di-*t*-butyl one

Scheme



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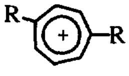
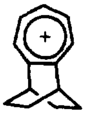
(**7**, 5.42),[7] 1,4-bis(cyclopropyl) one (**8**, 7.56),[7] 1,2-bicyclo[2.2.2]octeno one (**9**, 8.8)[8] and cyclohepta[*a*]-acenaphtalenylium ion (**10**, 8.7),[9] though less than that of the hexasubstituted derivative, 1,2:3,4:5,6-tris-(bicyclo[2.2.2]octeno)tropylium cation (**11**, 13.0).[4] Reduction peak potentials[10] for **3** and **4** measured by cyclic voltammetry were −0.41 and −0.46 V vs. SCE,[11] respectively, indicating increased reduction resistance of these cations compared with that of the tropylium cation (−0.12[12] or −0.16 V[13] vs. SCE). In the UV spectra of **3** and **4** in 50% H_2SO_4 the longest absorption maxima were observed at 364 and 367 nm, respectively, which are longer than that of the 1*H*-azulenium ion (**12**, at 352 nm).[14] These bathochromic shifts and stability of **3** and **4** might be attributed to the effective σ-π interaction in these title cations.



7 ; R = *t*-butyl
8 ; R = cyclopropyl



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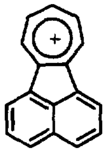

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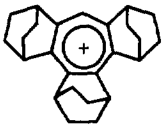

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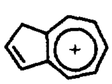

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5. Selected data for **3**: mp = 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$); δppm = 1.97 (m, 2H), 2.01 (m, 2H), 2.14 (m, 2H), 2.30 (m, 2H), 7.33 (d, *J* = 5.4 Hz, 1H), 7.72 (d, *J* = 5.4 Hz, 1H), 8.75 (tt, *J* = 8.8, 0.4 Hz, 1H), 8.87 (t, *J* = 8.8 Hz, 1H), 8.90 (t, *J* = 8.8 Hz, 1H), 8.96 (dd, *J* = 8.8, 0.4 Hz, 1H), 9.00 (dm, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$); δppm = 27.07, 34.24, 67.80, 132.13, 144.11, 145.45, 148.32, 148.73, 151.46, 164.16, 169.79, 179.05. MS (70 eV); *m/z* (rel intensity) 183 (M^+, 11), 154 (100). UV (50% H_2SO_4); λmax (log ε) = 231 (4.23), 272 (4.28), 364 (4.06) nm. For **4**: mp = 114–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$); δppm = 1.36 (dm, *J* = 12.4 Hz, 2H), 1.55-1.72 (m, 3H), 2.05 (m, 3H), 2.30 (td, *J* = 12.8, 3.6 Hz, 2H), 7.49 (d, *J* = 5.6 Hz, 1H), 8.13 (d, *J* = 5.6 Hz, 1H), 8.85 (tt, *J* = 9.6, 1.6 Hz, 1H), 9.00 (t-like, *J* = 9.8 Hz, 1H), 9.01 (t-like, *J* = 9.9 Hz, 1H), 9.10 (dd, *J* = 10.2, 1.6 Hz, 1H), 9.12 (dm, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$); δppm = 24.30, 25.05, 31.87, 62.07, 133.86, 144.84, 145.20, 149.04, 149.21, 152.08, 162.22, 169.09, 178.47. MS (70 eV); *m/z* (rel intensity) 197 (M^+, 100). UV (50% H_2SO_4); λmax (log ε) = 231 (4.27), 272 (4.38), 367 (3.98) nm.
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10. Cyclic voltammetry was measured in an acetonitrile solution with tetrabutylammonium tetrafluoroborate as a supporting electrolyte. Peaks of these title cations are irreversible.
11. These values are comparable to those of *p*-dimethyaminophenyltropylium ion (−0.40 V vs. SCE), **9** (−0.44 V vs. SCE), and *N*-methylcyclohepta[*b*][1,4]benzodiazinium ion (−0.47 V vs. SCE). See, ref 9 and 12.
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