Generation, Characterization and Some Reactions of 1,1-Ethylene-1*H*-azulenium Ion

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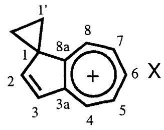
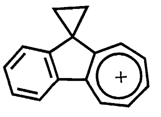
The title carbocation, generated from 1,1-ethylene-1,6-dihydroazulene and trityl tetrafluoroborate in deuterated acetonitrile at - 20 °C, was characterized by means of low temperature NMR spectroscopy, and was found to undergo expansion of the cyclopropane ring at elevated temperature and to react with nucleophiles to give the addition products at the cyclopropane methylene carbon.

The solvolytic behavior of β-arylalkyl systems has been one of the most studied and most controversial topic of modern physical and organic chemistry.[1] While solvolytic studies of a wide variety of benzenoid arylalkyl derivatives have been documented to prove the anchimeric assistance of aromatic π-orbital,[2] McDonald *et al.* had reported that the 1-azulyl substituent, one of typical nonbenzenoid groups, was a super-participator in β-azulylethyl *p*-toluenesulfonate solvolysis and the displacement of the leaving group by solvent occured *via* the intermediary 1,1-ethylene-1*H*-azulenium tosylate (**1a**).[3] However, alternative generation and characterization of the cationic intermediates in the azulene system have not been studied except the benzannelated cation **2**,[4] while those in benzenoid arylalkyl systems were elucidated in detail by extensive works of Olah's group.[5] Herein we report generation, characterization and some reactions of the title carbocation, 1,1-ethylene-1*H*-azulenium tetrafluoroborate (**1b**), whose chemistry has been veiled for a long time.

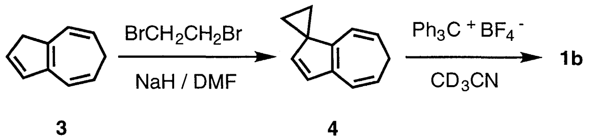


X^- X = TsO **1a**
BF_4 **1b**



BF_4^- **2**

Synthesis of **1b** was accomplished in a few steps starting from readily available azulene as follows. Reaction of 1,6-dihydroazulene (**3**), prepared from azulene by Birch reduction in good yield,[6] with 1,2-dibromoethane and sodium hydride as base in DMF gave 1,1-ethylene-1,6-dihydroazulene (**4**),[7,8] the precursor for the title cation, as a slightly air-sensitive colorless oil in 77% yield. Yields of **4** in THF or liquid ammonia as solvent were far less than that in DMF. Addition of a molar equivalent of trityl tetrafluoroborate to a deuterated acetonitrile solution of **4** at -20 °C resulted in a slightly greenish solution. ^1H and ^{13}C NMR spectra measured at the same temperature after the addition are shown in Figure 1, which indicates complete disappearance of **4** and formation of the title cation **1b** along with triphenylmethane (**5**); the proton NMR spectrum of this reaction mixture showed a 4H singlet at 2.75 ppm for the cyclopropane methylene protons, two doublets at 7.69 and 7.82 ppm for the five-membered ring protons, and finely split 5H signals for the seven-membered ring protons at 8.63 - 9.02 ppm, and the carbon NMR exhibited two aliphatic signals and nine olefinic signals between 133.0 and 172.9 ppm for **1b**, besides signals for triphenylmethane. Full assignment of these new signals for **1b** in both ^1H 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).[9] It is noteworthy that correlations observed between the three-membered methylene signal and both proton signals at 7.82 and 8.51 ppm in the NOESY spectrum were quite helpfull to make the definite assignment of ring protons on the azulene skeleton. Also correlations between the C-8a carbon and the H-4 and H-1' 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** and phenonium ion (**6**)[5] are summarized in Figure 2. The higher field shift of cyclopropane methylene proton signals in **1b** than those of **6** indicates less delocalization of positive charge to the three-membered ring part in **1b** than in the case of **6**. This might be attributed to difference of stability of the cationic parts between **1b** and **6**, the former of which has the stabilized tropylium cation



3 **4**

Scheme 1.

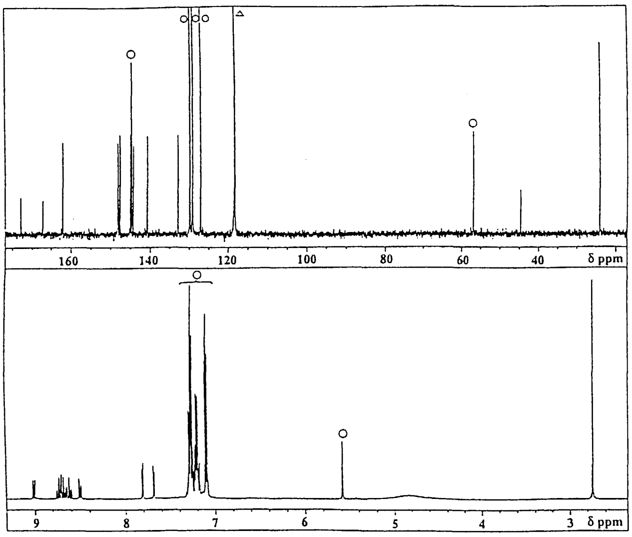
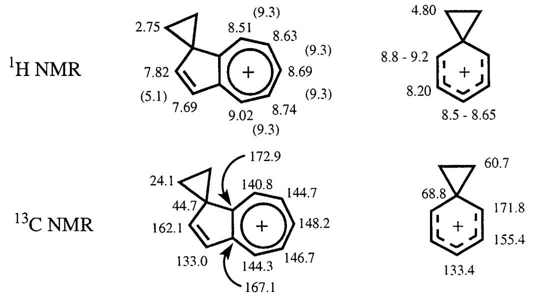


Figure 1. ^1H (bottom) and ^{13}C (top) NMR spectra of a mixture of **1b** and **5** in CD_3CN at -20 °C. Δ ; solvent, ○ ; 5.

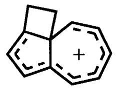


1b **6**

Figure 2. NMR assignment for **1b** and **6.** Coupling constants are given in parentheses.

part. 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.

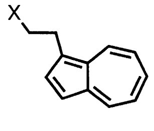
The cation **1b** in the reaction solution was stable at -20 °C, but it gradually rearranged at 0 °C with a half life of 27 min.[10] New signals, displacing those of **1b**, in ^1H and ^{13}C NMR spectra were interpreted best for those of the cation **7** which was formed



BF_4^- **7**

by expansion of the cyclopropane ring of **1b**.[7] The cation which would be formed by the cyclopropyl bond shift to the C-2 position was not observed. Many efforts to trap the cation **7** with various nucleophiles, such as alcohols and water, have been unsuccessful. So far we have not succeeded in isolation of **1b** probably because of both the labile nature and its moisture sensitibity (*vide infra*).[11]

Addition of a large excess of water to the solution of **1b** resulted in a blue reaction mixture, from which the alcohol product **8**[3,12] was obtained in 83% yield after chromatography. Similarly the reactions of **1b** with methanol and sodium acetate gave the addition products **9** and **10**[13] in 77% and 83% yields,



X = OH **8**
OCH_3 **9**
O_2CCH_3 **10**

respectively. All products found are derived from formal addition of nucleophiles at the cyclopropane methylene carbons, and any other isolable product was not observed in these reactions. Since tropylium ions are known to capture nucleophiles readily at their seven-membered ring carbons,[14] the reversible formation of the cation *via* the addition product at the tropylium ion part may proceed under the conditions to lead the final product. While the mechanistic details of the addition step remain to be established, the present reaction provides an alternative synthetic pathway to 2-(1-azulylethyl) derivatives. Further investigation of the chemistry of **1b** and related derivatives is proceeding.

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7 All new compounds were characterized by the spectroscopic methods and by high resolution mass spectroscopy except cations **1b** and **7**. *Spectral data* for **4**: IR ν_{max} 3010s, 2945m, 2860w, 2820w, 1610m, 1486m, 1430s, 1395s, 1278s, 1135m, 1073s, 1040s, 982m, 955s, 900w, 822s, 785s, 720s, 694s, 645s cm^{-1}; δ_H (400MHz, $CDCl_3$) 1.50 (q, J=3.7Hz, 2H), 1.66 (q, J=3.7Hz, 2H), 2.36 (t, J=6.8Hz, 2H), 5.28 (dt, J=, 9.3 and 6.8Hz, 1H), 5.30 (dt, J=9.3 and 6.8Hz, 1H), 5.95 (d, J=9.3Hz, 1H), 6.09 (d, J=5.1Hz, 1H), 6.50 (d, J=9.3Hz, 1H), 6.63 (d, J-5.2Hz, 1H); δ_C (100MHz, $CDCl_3$) 14.5, 27.9, 37.4, 116.8, 117.0, 120.5, 125.1, 131.0, 138.4, 141.7, 146.1; MS *m/z* (70eV) 156 (M^+, 60%), 155 (M^+-1, 48%), 141 (100%), 129 (29%), 128 (44%), 115 (39%), 77 (18%), 63 (17%), 51 (16%); HRMS calcd. for $C_{12}H_{12}$ 156.0938, obsd. 156.0945 ; UV (hexane) λ_{max} 236 nm (log ε=4.36), 311 (3.67). For **7**: δ_H (400MHz, CD_3CN, 0 °C) 2.88 (m, 2H), 4.58 (m, 2H), 7.66 (d, J=5.6Hz, 1H), 7.74 (d, J=5.6Hz, 1H), 8.98 (m, 3H), 9.13 (m, 2H); δ_C (100MHz, CD_3CN, 0 °C) 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). Spin-decoupling measurements in the ^1H NMR spectrum of **7** showed an AB quartet at 4.58 ppm with a coupling constant of 15.0 Hz under irradiation at δ 2.88 ppm and also an AB quartet at 2.88 ppm with a coupling constant of 14.4 Hz under that at 4.58 ppm. Both the difference of geminal coupling constants between these methylene protons and the vicinal coupling manner of them indicate that the cyclobutane ring of **7** is fairly disordered in its strained ring system.

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10 After completion of the rearrangement, the color of the solution turned dark brown.

11 Addition of ether to the solution of **1b** and **5** at -20 °C gave greenish solids. However, several efforts for purification of them by filtration and recrystalization at low temperature under inert atmosphere have met with little success so far.

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