Tetrahedron Letters,Vol.24,No.1,pp 69-70,1983 0040-4039/83/010069-02$03.00/0
Printed in Great Britain

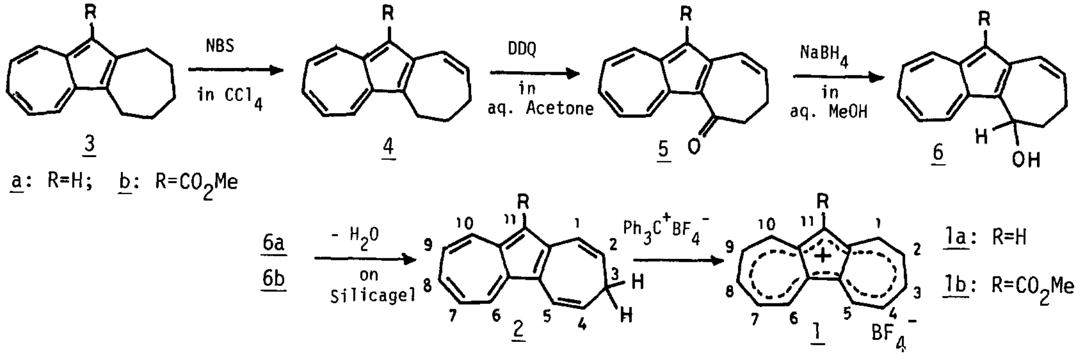
# THE SYNTHESIS OF CYCLOHEPT[a]AZULENYLIUM ION: A NEW 14π ELECTRON SYSTEM

Masafumi YASUNAMI,* Tamio AMEMIYA, and Kahei TAKASE
Department of Chemistry, Faculty of Science, Tohoku University
Aramaki-aza-Aoba, Sendai 980, Japan

Summary: Cyclohept[a]azulenylium ion and its 11-methoxycarbonyl derivative were synthesized as very stable crystalline tetrafluoroborates by the hydride abstraction of 3H-cyclohept[a]azulenes.

Cyclohept[a]azulenylium ion (1a) has been attracted interest in its properties as a new type of fully unsaturated nonbenzenoid aromatic compounds having a tricyclic carbon skeleton of 7,5,7-ring system and suggested to be a stable cation with 14π electrons on the basis of an HMO calculation.1) As the compounds having such a ring system, 3H-cyclohept[a]azulen-3-one and its derivative have been synthesized.2) This communication describes the synthesis of the parent cation (1a) and its 11-methoxycarbonyl derivative (1b).

As potential precursors for the synthesis of 1a and 1b, 3H-cyclohept[a]azulene (2a) and its 11-methoxycarbonyl derivative (2b) were synthesized as follows. A 1,2-pentamethyleneazulene derivative (3b)[violet prisms, mp 72-73 °C; IR(KBr): $\nu_{C=O}$ 1685 $cm^{-1}$] which was derived from 3a,3) was treated with 1.2 equivalents of NBS in dry carbontetrachloride under reflux giving an olefinic compound (4b)[blue oil; mass: m/e 252($M^+$, 100%); $^1$H-NMR($CDCl_3$): 6.19 ppm (dt, J=12.5, 5.0 Hz, H-2)] in 85% yield. Demethoxycarbonylation of 4b by heating with 100% phosphoric acid gave 4,5-dihydro-3H-cyclohept[a]azulene (4a). The oxidation of 4a with 2.2 equivalents of DDQ in 90% aq. acetone4) gave a carbonyl compound (5a)[reddish violet oil; IR($CHCl_3$): $\nu_{C=O}$ 1620 $cm^{-1}$] in 88% yield. The treatment of 4b with DDQ in a similar manner gave 5b [reddish violet needles, mp 93.5-95°C; IR(KBr): $\nu_{C=O}$ 1705, 1632 $cm^{-1}$] in 91% yield.



The reduction of 5a and 5b with sodium borohydride gave unstable alcohols (6a, 6b), which, without isolation, were easily resulted in dehydration on passing over a silica gel column to give 3H-cyclohept[a]azulene (2a)[green oil; mass: m/e 192($M^+$, 100%)] and its 11-methoxycarbonyl derivative (2b)[blue oil; mass: 250($M^+$, 100%); IR($CHCl_3$): $\nu_{C=O}$ 1678 $cm^{-1}$].

Cyclohept[a]azulenylium ions, 1a and 1b, were obtained by hydride abstraction of 2a and 2b as follows. To a solution of 2a in chloroform, equimolecular amounts of trityl tetrafluoroborate was added and the mixture was stirred for 20 hr at room temperature. The resulting precipitates were collected, washed with dry benzene, and recrystallized from acetonitrile to give 1a as tetrafluoroborate [violet brown needles, mp over 300°C; $pK_R+$: 7.3(UV method); UV(MeCN): λmax 251 nm(log ε 4.10), 285(3.95)sh, 333(4.76), 356(3.90)sh, 380(2.80), 444(3.15)sh, 476(3.84), 506(4.43), 556(3.12), 611(2.93), 673(2.71); IR(KBr): 1608, 1573, 1441, 1363, 1242, 1205, 1050, 883, 837, 744, 660 $cm^{-1}$; $^1H$-NMR($CF_3CO_2D$), δ ppm, J in Hz, 100 MHz: 8.50(s, H-11), 8.60-8.85(6H, m, H-2,3,4, 7,8,9), 9.33(2H, dd, J=10, 2.0, H-1, 10), 10.10(2H, dd, J=9.0, 2.0, H-5,6)] in 33% yield. The treatment of 2b with 1.5 equivalents of trityl tetrafluoroborate in the same manner gave 1b as tetrafluoroborate [dark brown needles, mp over 300°C; $pK_R+$: 6.4(UV method): UV(MeCN): λmax 255 nm(log ε 4.35), 285(4.19) sh, 297(4.32)sh, 332.5(4.87), 348(4.57)sh, 460(3.77)sh, 490(4.38), 560(3.21), 612(2.96), 676(2.88); IR(KBr): 2940, 1690, 1600, 1574, 1442, 1384, 1345, 1298, 1275, 1223, 1192, 1070, 851, 790, 670 $cm^{-1}$; $^1H$-NMR($CF_3CO_2D$), δ ppm, J in Hz, 100 MHz: 4.41(s, OMe), 8.65-9.02(6H, m, H-2,3,4,7,8,9), 10.18(2H, dd, J=8.2, 2.0, H-5,6), 10.29(2H, dd, J=10.5, 2.0, H-1,6); $^{13}C$-NMR($CF_3CO_2H$), δ ppm, 10 MHz: 54.8(q, OMe), 119.9(s, C-11), 138.5(d), 142.1(d), 144.4(d), 145.1(d), 145.1(s), 150.2(d), 154.3(s), 168.7(s, $CO_2Me$)] in 93% yield. The UV spectra of 1a and 1b exhibit characteristic absorption maxima at 506 and 490 nm, respectively. The $^1H$-NMR spectra of 1a and 1b show the signals corresponding to all ring protons at a low field. The simplicity of the signals suggests the symmetrical structures of the cations, 1a and 1b. This is also substantiated by the $^{13}C$-NMR spectrum of 1b which exhibits only eight signals corresponding to the ring carbons. These facts indicate that the cationic charge in 1a and 1b is celocalized over all ring carbons. Detailed studies on the structures of these cations are now in progress. The results will be reported in the near future.

## [References and Note]

1) R. Fleischer, K. Hafner, J. Wildgruber, P. Hochmann, and R. Zahradnik, Tetrahedron, 24, 5943 (1968).
2) M. Saito, T. Morita, and K. Takase, Chemistry Lett., 1974, 955; 1975, 441.
3) P. W. Yang, M. Yasunami, and K. Takase, Tetrahedron Lett., 1971, 4275.
4) All new compounds gave satisfactory results on elemental analyses and spectral data in accord with the assigned structures.
5) A. Amemiya, M. Yasunami, and K. Takase, Chemistry Lett., 1977, 587.

(Received in Japan 6 September 1982)