Tetrahedron Letters Vol. 21, pp 3375 - 3376
0040-4039/80/0822-3375$02.00/0

SYNTHESIS OF FURO[b]TROPYLIUM TETRAFLUOROBORATE

Masahiko Kato*, Hisako Kobayashi, and Toshio Miwa
Faculty of Science, Osaka City University,
Sugimoto-cho, Sumiyoshi-ku, Osaka 558, Japan

Summary: The first synthesis and characterization of the title compound are described.

Tropylium cations annelated with heteroaromatic ring have been attracted interest in their stabilities and properties.[1-7]

We now wish to report the synthesis and characterization of furo[b]tropylium cation (**1**), as the stable tetrafluoroborate as follows.

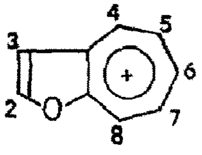
Benzylic bromination of 5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-one (**2**)[8] with NBS followed by dehydrobromination with calcium hydrogen phosphate in DMF gave 5,6-dihydro-4H-cyclohepta[b]furan-4-one (**3**) (yield; 72%). The tosylhydrazone, mp. 151-152°C, was treated with methyl lithium in ether[9] to give 6H-cyclohepta[b]furan (**4**) (78%). The triene **4** dissolved in dry ethyl acetate was allowed to react with triphenylmethyl fluoborate in acetonitrile to give furo[b]tropylium fluoborate (**1**), mp. 194-195°C (dec.) (34%).

The pK_R+ value (6.9 ± 0.3) could be determined by titrating the aqueous solution (1.01×10^{-4} Mol/L) with dilute aq. sodium hydroxide under nitrogen atmosphere.[10]

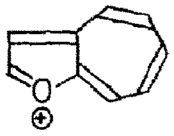
All the 9 signals of C-13 chemical shift were observed; $\delta(CD_3CN)$: 115.5, 137.0, 143.8, 145.1, 146.3, 150.5, 150.9, 160.1, 166.1 ppm. The Fig.1 shows the shifs for compound **1** and **4** ploted against the electron densities calculated by HMO (ω-method; $a_X=1.5$, $b_{CX}=0.7$ for oxygen; in the latter case, the electron densities calculated on 2,3-divinylfuran was used).[11] The plots fall on a straight line, except the ones for oxygen-bonded carbons (C_2 and C_{8a}) which were more deshielded (20-21 ppm) than those expected from the electron densities.

The appearance of the C-13 signals for C_4-C_8 of compound **1** in a narrow range and at lower field ($\delta^{(\mathbf{1})}_{C4-C8}$(mean) - $\delta^{(\mathbf{4})}_{C4,C5,C7,C8}$(mean) = -25.1 ppm) compared with the olefinic signals of **4**[12] suggest that the contribution of the structure **1a** to the resonance hybrid must be important. On the other hand, the deshielding effect of tropylium cation on C-2 ($\delta^{(\mathbf{1})}_{C2} - \delta^{(\mathbf{4})}_{C2} = -18.7$ ppm) is found to be larger than that on C-3 ($\delta^{(\mathbf{1})}_{C3} - \delta^{(\mathbf{4})}_{C3} = -4.6$ ppm). This indicates that there are some minor contribution of structures **1b** and **1c** which might act as to increase the pK_R+ of the tropylium cation.

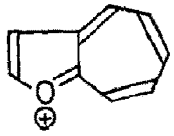
The PMR spectrum of **1** showed a complicated feature appeared in the rather lower field[13] [δ (CD_3CN): 9.70-9.48 (2H, m), 9.20-9.05 (4H, m), 8.08 ppm (1H, dd, H_3)]. The electronic spectrum of **1** in water showed absorption maxima, 254 (log ε; 4.52), 298 (3.42), and 359 nm (3.71), which gradually changed to new absorption maxima, 235 (4.33), 320 nm (3.86). The spetrum obtained in 96% sulfuric acid [λ_{max}: 253.5 (log ε; 4.68), 295 (3.44), 359 nm (3.79)] was similar to the original one in water.



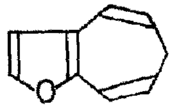
(**1a**)



(**1b**)



(**1c**)



(**4**)

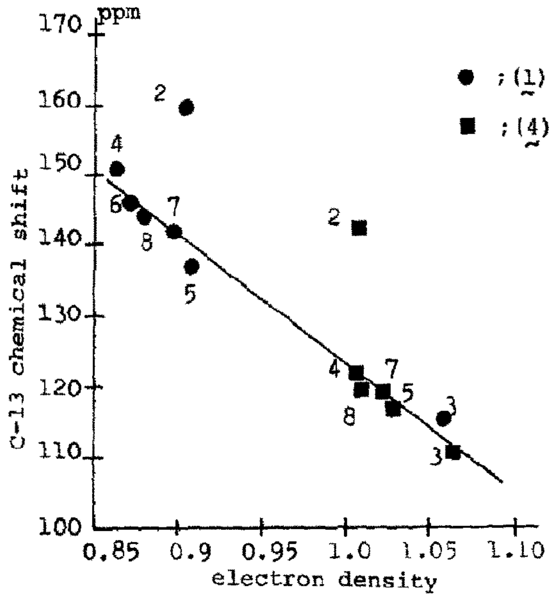


Figure 1. C-13 chemical shifts vs. electron densities for **1** and **4**.

References

1) R. Guilard and P. Fournari, Bull. Soc. Chim. Fr., 1437 (1971); Compt. Rend., 273 (1971).
2) R. Turnbo, D. L. Sullivan, and R. Pettit, J. Am. Chem. Soc., **86**, 5630 (1964).
3) D. N. Nicolaides and C. N. Coutrakis, Synthesis, 268 (1977).
4) S. Gronowitz, B. Yom-Tov, and U. Michael, Acta Chem. Scand., **27**, 2257 (1973).
5) S. Gronowitz and P. Pedaja, Tetrahedron, **34**, 587 (1978).
6) M. El Borai, R. Guilard, P. Fournari, Y. Dusausoy, and J. Protas, Bull. Soc. Chim. Fr., 75 (1977).
7) K. Komatsu, S. Tanaka, S. Saito, and K. Okamoto, Bull. Chem. Soc. Jpn., **50**, 3425 (1977); K. Okamoto, J. Synth. Org. Chem. Jpn., **37**, 405 (1979).
8) W. v. E. Doering and L. H. Knox, J. Am. Chem. Soc., **76**, 3203 (1954).
9) K. A. Burdett, F. L. Shenton, D. H. Yates, and J. S. Swenton, Tetrahedron, **30**, 2057 (1974).
10) The pH-value at a half neutralization equivalent was taken as pK_R+.[4]
11) Because it was difficult to assign each signal to the corresponding carbon in 7-membered ring of **1**, we arranged them in the decreasing order to make allot to the electron densities for five carbon atoms, C_4-C_8, arranged in the same way.
12) A. V. Kemp-Jones, A. J. Jones, M. Sakai, C. P. Beeman, and S. Masamune, Can. J. Chem., **51**, 767 (1973).
13) H. Gunther, A. Shyoukh, D. Cremer, and K.-H. Frisch, Ann. Chem., 150 (1978).

(Received in Japan 10 May 1980)