CHEMISTRY LETTERS, pp. 1925-1928, 1986.

The Synthesis and Properties of 3-Arylcyclohepta[d]isoxazolylium Ions

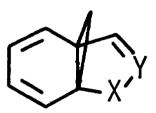
Makoto NITTA* and Nobuhiro KANOMATA
Department of Chemistry, School of Science and Engineering,
Waseda University, Shinjuku-ku, Tokyo 160

3-Arylcyclohepta[d]isoxazolylium tetrafluoroborates were synthesized by the cycloaddition of tricarbonyl(2-5-η-2,4,6-cycloheptatrienone)iron with aromatic nitrile oxides followed by several reactions. The pK_{R^+} values of these ions are less than +1.0 showing that the stability of the tropylium ions is much decreased by the fusion of the isoxazole ring.

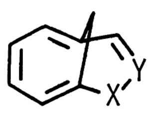
Tropylium cations annelated with heteroaromatic ring are interested because of their stabilities and properties.[1-10] The fusion of thiophene[2] or furan ring[9] with its b-side onto the tropylium ion increases the stability (1a: $pK_{R^+} = +6.0$; 1b: $pK_{R^+} = +6.9$), while isoelectronic benzoannelation decreases the stability ($pK_{R^+} = +1.6$),[12] compared to that of the tropylium ion ($pK_{R^+} = +4.7$).[13] Several factors for the increased stabilization of 1a,b as compared to benzoannelation are postulated:[11] i) the π-excessive five membered heterocyclic ring stabilizes a positive charge of benzylic type more effectively than the benzene ring,[2] ii) due to the heteroatom, peri interaction of hydrogens is deminished, iii) less angular strain upon annelation of thiophene or furan ring onto the tropylium ion (the ideal angle of the seven-membered ring is 129°) might be expected as compared to that of benzoannelation. Recently, 9-thiatricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (2a) has been shown to exist in equilibrium with its valence isomer, 2,7-methanothia[9]annulene (3a) (10π electron system).[14] On the other hand, we have previously shown that 7-oxa-8-azatricyclo[4.3.1.0^{1,6}]deca-2,4,8-triene derivative exists as the closed norcaradiene structure (2b) rather than the bridged oxazonine (3b).[15] These facts then raise the question as to whether cyclohepta[d]isoxazolylium ion might be more destabilized than the tropylium cation or not.

We report here the synthesis and properties of novel 3-arylcyclohepta[d]isoxazolylium tetrafluoroborates. The cycloaddition[16] of aromatic nitrile oxides (4a), (4b), and (4c) with tricarbonyl(2-5-η-2,4,6-cycloheptatrienone)iron (5) afforded the adducts 6a, 6b, and 6c in 88, 92, and 93% yields, respectively.[17,18] The

1a: X = S
1b: X = O

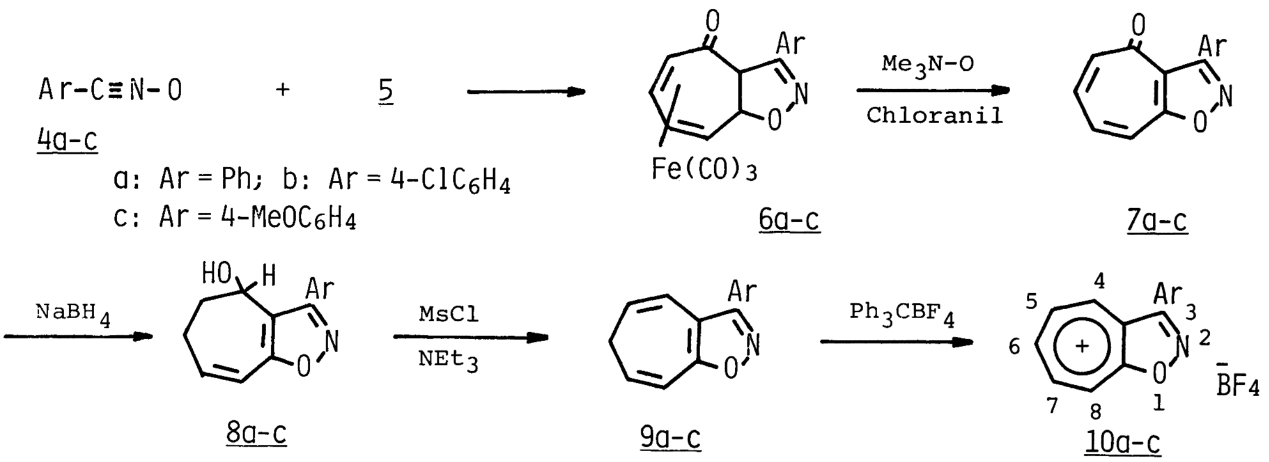


2



3

a: X = S; Y = CH
b: X = O; Y = N



compounds 6a-c could be decomplexed and dehydrogenated in a single step by oxidation with trimethylamine oxide19) (5.0 mol equiv.) in the presence of chloranil (1.0 mol equiv.) in dichloromethane at room temperature. From the crude reaction mixture, 3-aryl-4H-cyclohepta[d]isoxazol-4-ones (7a-c) were obtained in 62, 61, and 41% yields, respectively.20) Then, the reduction of 7a-c with sodium borohydride (4.0 mol equiv.) at room temperature resulted in the formation of alcohols 8a-c in 82, 73, and 76% yields, respectively.17) When the alcohols 8a-c and triethylamine (7.0 mol equiv.) dissolved in xylene were allowed to react under reflux with methanesulfonyl chloride (2.7 mol equiv.), desired 3-aryl-6H-cyclohepta[d]isoxazoles (9a-c) were obtained in 95, 81, and 80% yields, respectively, after chromatography on Florisil (hexane-AcOEt 5:1).21) The hydride abstraction of 9a-c was accomplished by the reaction with triphenylmethyl tetrafluoroborate (1.0 mol equiv.) in dichloromethane at room temperature to give 3-arylcyclohepta[d]isoxazolylium tetrafluoroborates (10a-c) in 80, 82, and 65% yields, respectively. The reduction of 10a with sodium borohydride gave 9a and a mixture (4H and 8H-isomers of 9a) in a ratio of 1:3 in 78% yield. The mixture could regenerate 10a in 60% yield by the reaction with triphenylmethyl tetrafluoroborate. These chemical transformations and the physical data22) support the structures of 10a-c.

The electronic spectra of 10a-c in ethanol [λ_{max} (log ε), 228 (sh, 4.54), 279 (4.10) for 10a; 237 (4.28), 278 (3.83) for 10b; 245 (4.23), 278 (sh, 3.99), 284 (sh, 3.97) for 10c] are quite different from those taken in acetonitrile.22) These spectra were changed to those in acetonitrile by adding sulfuric acid. The pK_R^+ values of 10a-c were measured and evaluated to be less than +1.0 in 23% aqueous acetonitrile solution.23) These facts clearly suggest that the cations 10a-c are much less stable than the benzotropylium ion.12)

The ^{13}C NMR spectral data of 9a-c and 10a-c are summarized in Table 1. The ^{13}C chemical shifts of the isoxazole moieties were assigned by comparison with those of several compounds.24) All the signals of the tropylium moiety were observed for 10a-c. Since it was difficult to assign each signals to the corresponding carbons in the tropylium moieties of 10a-c, we assigned them in the decreasing order of the calculated electron densities for five carbon atoms, C4-8. Fig. 1 shows the shifts for compound 10a plotted against the electron densities calculated by HMO method.25) The points fall on a straight line, except the one for oxy-

Table 1. ^{13}C NMR spectral data of 9a-c and 10a-c in CD_3CN[a)]

9a	129.2, 129.9, 130.0, 130.9 (Ar), 27.9 (C6), 117.9, 120.3, 120.8 128.8 (C4,5,7,8), 132.9 (C3a), 161.2 (C3), 168.6 (C8a)	$\Delta\delta_A = -26.4$
10a	124.7, 130.5, 130.7, 133.1 (Ar), 136.4 (C5), 140.2 (C3a), 147.7 (C7), 149.3 (C8), 152.1 (C6), 156.3 (C4), 164.0 (C3), 175.1 (C8a)	$\Delta\delta_B = -2.8$
9b	128.6, 130.1, 130.7, 136.5 (Ar), 27.9 (C6), 117.9, 120.0, 121.1 129.1 (C4,5,7,8), 160.2 (C3), 168.8 (C8a), (one peak is overlapping)	$\Delta\delta_A = -26.4$
10b	123.5, 130.9, 132.1, 139.0 (Ar), 136.5 (C5), 140.0 (C3a), 147.7 (C7), 149.4 (C8), 152.0 (C6), 156.5 (C4), 163.2 (C3), 175.0 (C8a)	$\Delta\delta_B = -3.0$
9c	56.1, 115.3, 122.1, 130.5, 161.9 (Ar), 27.9 (C6), 117.9, 120.2, 120.4, 128.3 (C4,5,7,8), 130.8 (C3a), 160.6 (C3), 168.3 (C8a)	$\Delta\delta_A = -26.5$
10c	56.4, 116.3, 132.2, 163.7 (Ar), 136.3 (C5), 140.4 (C3a), 147.5 (C7), 149.2 (C8), 152.1 (C6), 156.1 (C4), 163.5 (C3), 175.2 (C8a), (one peak is overlapping)	$\Delta\delta_B = -3.1$

a) The spectra were recorded on a JMN-FX90Q spectrometer, and the chemical shifts are given in ppm (δ) relative to an internal Me_4Si standard.

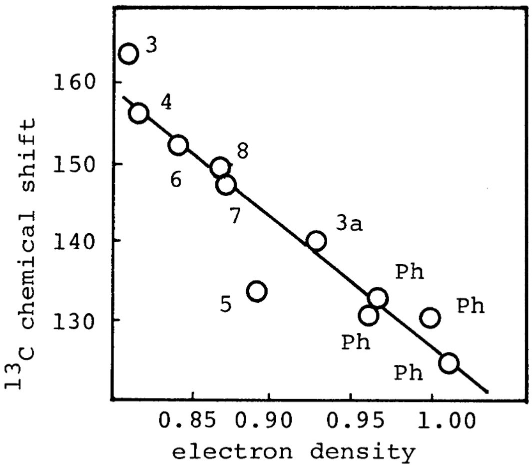
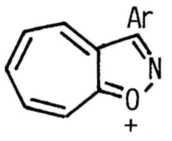
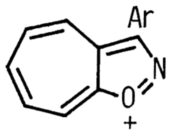


Fig. 1. ^{13}C chemical shifts vs. electron densities for 10a.



11a-c



12a-c

gen-bonded carbon (C8a) which is more deshielded (ca. 25 ppm) than that expected from the calculated value. The correlations similar to 10a were also obtained for 10b,c.

The difference of the mean values of the chemical shifts [$\Delta\delta_A = \delta^{\underline{9}}_{C4,5,7,8}$ (mean) - $\delta^{\underline{10}}_{C4-8}$ (mean)] and the deshielding effect at C3 [$\Delta\delta_B = \delta^{\underline{9}}_{C3} - \delta^{\underline{10}}_{C3}$] of tropylium ion for each pairs is also listed in Table 1. The appearance of ^{13}C signals for C4-8 of 10a-c at lower field compared with the corresponding olefinic signals of 9a-c (large $\Delta\delta_A$ values) suggests that the contribution of the structures 10a-c to the resonance hybrids must be important.[9)] The small values of $\Delta\delta_B$ seem also to suggest the minor importance of the contribution of structures 11a-c and 12a-c both of which might act as to increase the pK_R+ values of the cations 10a-c. The values of $\Delta\delta_A$ and $\Delta\delta_B$ for each pairs of 9a-c and 10a-c are very similar to each other, and no significant substituent effect of the Cl of 10b and the OMe of 10c was observed.

References

1) R. Guilard and P. Fournari, Bull. Soc. Chim. Fr., 1971, 1437.

2) R. G. Turnbo, D. L. Sullivan, and R. Pettit, J. Am. Chem. Soc., 86, 5630 (1964).
3) D. N. Nicolaides and C. N. Coutrakis, Synthesis, 1977, 268.
4) B. Yom-Tov and S. Gronowitz, J. Heterocycl. Chem., 15, 285 (1978).
5) S. Gronowitz and P. Pedaja, Tetrahedron, 34, 587 (1978).
6) P. Pedaja and S. Gronowitz, Chemica Scripta, 22, 53 (1983).
7) M. El Borai, R. Guilard, P. Fournari, Y. Dusausoy, and J. Protas, Bull. Soc. Chim. Fr., 1977, 75.
8) K. Komatsu, S. Tanaka, S. Saito, and K. Okamoto, Bull. Chem. Soc. Jpn., 50, 3425 (1977).
9) M. Kato, H. Kobayashi, and T. Miwa, Tetrahedron Lett., 21, 3375 (1980).
10) G. Seitz and H. -S. The, Synthesis, 1984, 119.
11) S. Gronowitz, B. Yom-Tov, and U. Michael, Acta Chem. Scand., 27, 2257 (1973); and references cited therein.
12) D. Meuche, H. Straus, and E. Heilbronner, Helv. Chim. Acta, 41, 57 (1958).
13) W. von E. Doering and L. H. Knox, J. Am. Chem. Soc., 76, 3203 (1954).
14) R. Okazaki, T. Hasegawa, and Y. Shishido, J. Am. Chem. Soc., 106, 5271 (1984).
15) M. Nitta, S. Sogo, and T. Nakayama, Chem. Lett., 1979, 1431.
16) M. Bonadeo and R. Gandolfi, Gazz. Chim. Ital., 107, 577 (1977).
17) With exception of 6a and 7a, (Ref. 16), all compounds described in this paper are new and gave satisfactory elemental analyses and spectral data.
18) For 6b: mp 156-157 °C (decomp). For 6c: mp 159-162 °C (decomp).
19) Y. Shvo and E. Hazum, J. Chem. Soc., Chem. Commun., 1974, 336.
20) For 7b: mp 155-156 °C. For 7c: mp 153-154 °C.
21) For 9a: bp 120-122 °C/13.3 Pa; ^{1}H NMR (CD_3CN), δ=2.61 (2H, t, J=6.8 Hz), 5.51 (1H, dt, J=9.5, 6.8 Hz), 5.90 (1H, dt, J=9.8, 6.8 Hz), 6.69 (1H, d, J=9.5 Hz), 6.82 (1H, d, J=9.8 Hz), 7.37-7.90 (5H, m); λ_{max} (EtOH) (log ε), 226 (4.24), 282 (3.63). For 9b: mp 100-101 °C; λ_{max} (EtOH) (log ε), 237 (4.09), 281(3.50). For 9c: mp 60-61 °C; λ_{max} (EtOH) (log ε), 244 (4.29), 277 (sh, 3.91), 285 (sh, 3.88).
22) For 10a: green crystals; mp 139-143 °C (decomp); ^{1}H NMR (CD_3CN), δ=7.64-7.98 (5H, m), 9.03-9.69 (5H, m); λ_{max} (CH_3CN) (log ε), 235 (4.37), 280 (3.85), 302, (sh, 3.52), 353 (2.81). For 10b: green crystals; mp 119-121 °C (decomp); λ_{max} (CH_3CN) (log ε), 230 (sh, 4.56), 239 (4.63), 283 (3.98), 303 (sh, 3.77), 355 (3.28). For 10c: red crystals: mp 125-130 °C (decomp); λ_{max} (CH_3CN) (log ε), 233 (4.51), 246 (4.46), 294 (4.00), 416 (3.09).
23) The procedure adopted was to examine the ultraviolet spectra of solutions of 10a-c in various buffers and in aqueous H_2SO_4 (in the cases of pH $<$ 3), and to plot the extent of dissociation vs. pH: R. Breslow and H. W. Chang, J. Am. Chem. Soc., 83, 2367 (1961).
24) R. Faure, J. R. Llinas, E. J. Vincent, and M. Rajzmann, Can. J. Chem., 53, 1677 (1975); G. M. Buchan and A. B. Turner, J. Chem. Soc., Perkin Trans. 1, 1975, 2115.
25) Following parameters were used: $\alpha_{\ddot{O}} = 3.20$, $\alpha_{\dot{N}} = 1.00$, $\alpha_{C(-\ddot{O})} = 0.32$, $\alpha_{C(-\dot{N})} = 0.10$, $\beta_{C-N} = 1.20$, $\beta_{C-O} = 1.40$, $\beta_{N-O} = 0.60$; L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, Trans. Farady Soc., 47, 113 (1951).

(Received August 19, 1986)