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SYNTHESES OF 8-CYCLOHEPTATRIENYLHEPTAFULVENYLIUM ION AND ITS 8-METHYL DERIVATIVE[1]

Yasutaka KAYAMA, Masaji ODA, and Yoshio KITAHARA*
Department of Chemistry, Faculty of Science, Tohoku University,
Aramaki aza Aoba, Sendai 980

8-Cycloheptatrienylheptafulvenylium ion 2 and its 8-methyl derivative 3 are synthesized. The PK_{R^+} value of 2 is 7.49±0.05, the largest value so far known for hydrocarbon cations. The PK_{R^+} value of 3 is 5.89±0.05.

We have reported the synthesis of 8-cyano-8-cycloheptatrienylheptafulvenylium fluoroborate 1, a new stable carbonium ion[2]. In view of negative stabilization effect of a cyano group on carbonium ions, a higher electronic stability has been expected for the corresponding parent and alkylsubstituted cations. Fleming's recent report on the syntheses of parent cation 2 and its chloro and phenyl derivatives[3] prompted us to report our own results on 2 and its 8-methyl derivative 3. He obtained them only as solutions, but we could isolate 2 and 3 as pure crystals. We also here describe ^{13}C nmr data of 1, 2 and 3.

8-Cycloheptatrienylheptafulvenylium Ion 2

Heating of di(7-cycloheptatrienyl)acetic acid 4[4] at reflux in quinoline under the presence of copper powder as a catalyst for six minutes gave an isomeric mixture of dicycloheptatrienylmethanes 5 in 47% yield. Treatment of 5 with triphenylmethyl perchlorate (1.2 equiv.) in methylene chloride for one day gave ditropyliummethane diperchlorate 6 as off-white solids in 48% yield; nmr (CF_3COOH, TMS), δ 9.38 (s, 12H), and 5.65 ppm (s, 2H). In neutral solvents the dication 6 exists at equilibrium with the desired monocation 2a which exhibits deep blue color. Strikingly, when 6 was adsorbed on silica-gel column and then eluted with CH_3CN-CH_2Cl_2 (1;1), the deep blue color developed in the column and 2a, mp 120°C (decomp.), was isolated as dark blue crystals, although the yield was rather poor. These facts strongly suggest that 2 is a highly stabilized carbonium ion as was expected. A better preparation of 2a was accomplished by the following sequence. Reaction of 6 with sodium methoxide in methanol gave an isomeric mixture of di(methoxycycloheptatrienyl)methanes 7 in 96% yield. Addition of an ethereal solution of 7 into a solution of perchloric acid (slightly excess) in acetic anhydride immediately separated 2a out as almost pure dark blue crystals in 74% yield. By using hydrofluoroboric acid in place of perchloric acid the fluoroborate 2b, mp 105°C (decomp.), was also obtained in 85% yield. In crystal state 2a and 2b are fairly stable, but in neutral solutions they decompose gradually.

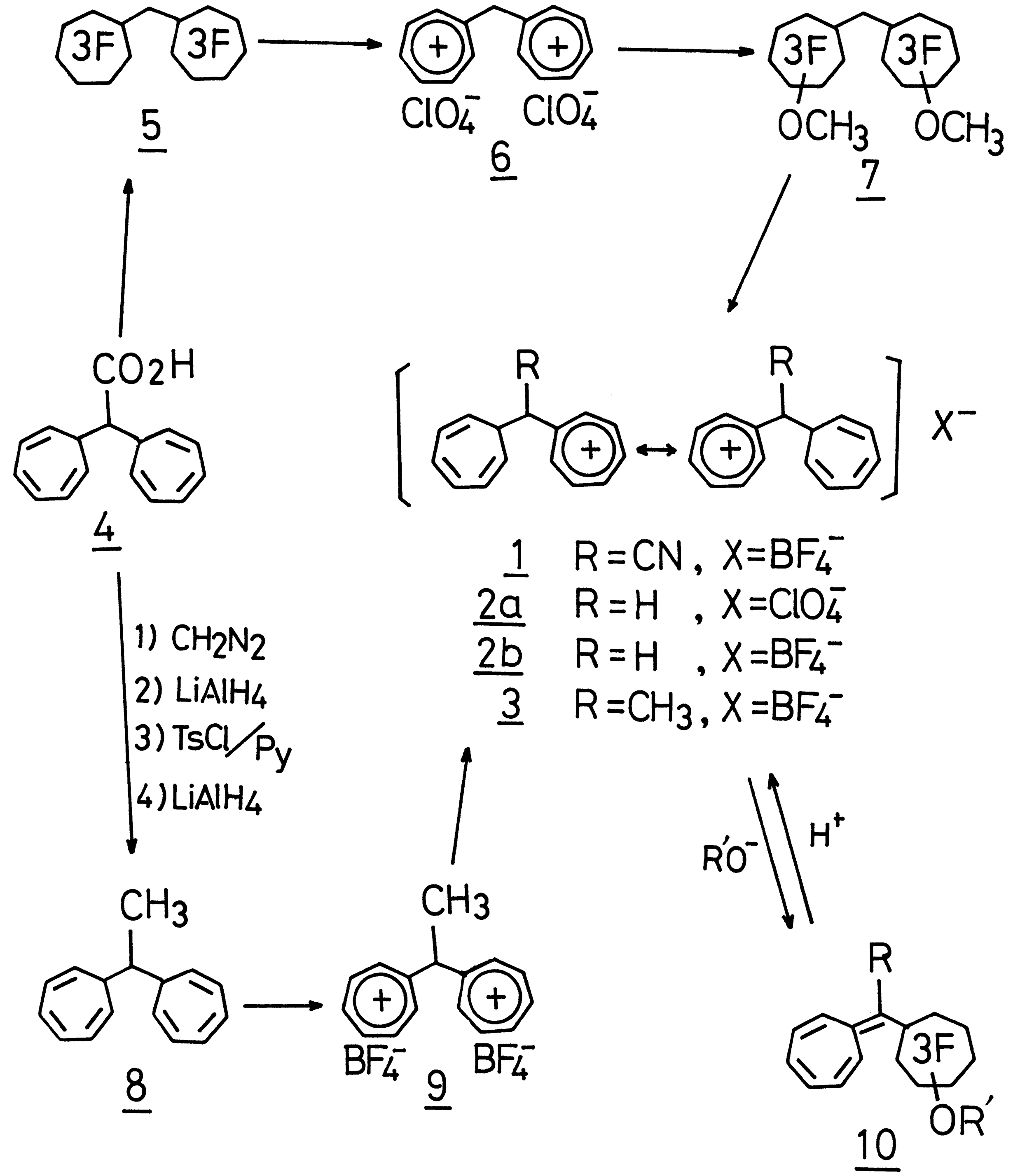
8-Cycloheptatrienyl-8-methylheptafulvenylium Ion 3

1,1-Di(7-cycloheptatrienyl)ethane 8 was prepared from 4 by the sequence shown in the Scheme in 82% overall yield. Compound 8 was then converted into the dication 9 through thermal isomerization (15 hrs reflux in xylene) followed by treatment with triphenylmethyl fluoroborate in 53% overall yield; nmr (CF_3COOH, TMS), δ 9.30 (s, 12H), 5.73 (q, J=7.0Hz, 1H), and 2.21 ppm (d, J=7.oHz, 3H). The fluoroborate 3, mp 173°C (decomp.), was obtained as dark blue crystals in 64% yield from 9 by a similar way employed for 2b.

The spectral data are summarized in the Table together with those of 1 for a comparison. Since the structure of 1 has been established without doubt by X-ray analysis[5], the resemblance of spectral data verifies the structures of 2 and 3 to be as shown. Both average chemical shifts of ^1H and ^{13}C of 2 (δ 7.7 to TMS and +51 ppm to CS_2, respectively) lie between those of benzene (7.27 and +65 ppm) and tropylium ion (9.38 and +39 ppm)[6], and are in good agreement with the calculated values (8.0 and +54 ppm)[6,7] based on the assumption that the positive charge delocalizes throughout the molecule (ca 1/15 positive charge on each carbon).

Our ^1H nmr data of 2 in acetonitril (δ 7.86, 7.50, and 6.57 ppm in the integral ratio of 4:8:1) are a little different from Fleming's ones (δ 8.2, 2.34, and 2.85 ppm in 1:1:1)[8] in aqueous trifluoroacetic acid. In our experiment 2 became colorless in 100% trifluoroacetic acid and its nmr spectrum was the same with that of the dication 6 in the same solvent, indicating that 2 undergoes protonation at 8-position in this solvent. Therefore, his nmr data of lower chemical shifts are probably of averaged ones of 2 and the protonated species rather than the solvent effect.

The PK_R+ value of 2 (UV method in 10% aqueous EtOH) is 7.49±0.05 (Fleming's value is 7.1). This value is ca 0.3 unit larger than that of tri-n-propylcyclopropenylium ion (PK_R+ 7.2)[9] which has been the most stable hydrocarbon carbonium ion. Compound 3 has a smaller PK_R+ value of 5.89±0.05 in spite of electron releasing character of a methyl group. The less stability of 3 may be due to a greater deviation of the molecule from planarity[5] because of steric interaction of the methyl group with the ortho protons on the seven membered rings, as argued by Fleming for 8-chloro and 8-phenyl cations. The greater deviation of 3 is also suggested by a notably small extinction coefficient of the absorption at the longest wavelength (ε=16,200) compared with that of 2 (ε=50,200). Although 2 and 3 are electronically more stabilized than 1 is, they are less stable in solutions at near PH of their PK_R+. This is probably due to less stability of the heptafulvene moiety of 10 (R=H, CH_3) compared with the 8-cyanoheptafulvene moiety (R=CN in 10).



1 R = CN, X = BF_4^-
2a R = H, X = ClO_4^-
2b R = H, X = BF_4^-
3 R = CH_3, X = BF_4^-

Table. Spectral Data of The Ions

Compound	UV visible[a] nm (logε)	^{1}H nmr[b] ppm	^{13}C nmr[c] ppm (average)
1	216 (4.56), 270 (3.95) 300 (3.53), 592 (4.41)	8.30 m 4H 7.80 m 8H	+47.08 +47.81 (+48.76) +51.39
2	226 (4.28), 288 (3.89) 596 (4.70)	7.86 m 4H 7.50 m 8H 6.57 S 1H	+50.36 +50.96 (+51.08) +51.93
3	220 (4.61), 290 (4.05) 612 (4.21)	7.80 m 4H 7.51 m 8H 2.18 S 3H	+51.02 +51.81 (+51.58) +51.93

a: in 0.01 N HCl

b: in CH_3CN (or CD_3CN) at 100 MHz relative to internal TMS

c: in CH_3CN relative to CS_2

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* To whom all correspondences should be addressed.

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