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Preliminary communication

Synthesis and absolute configuration of optically pure tricarbonyl(2,4-cycloheptadienonium)iron tetrafluoroborate

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Abstract

Optically pure tricarbonyl(2,4-cycloheptadienonium)iron tetrafluoroborate was prepared. Its absolute configuration was determined by way of its being related to tricarbonyl(2,4-cycloheptadienone)iron.

Tricarbonyl(tropone)iron (**1**) is a useful complex as a starting material for organic syntheses of compounds containing seven-membered ring system [1], especially for the syntheses of natural products [2]. Therefore, it is very significant to obtain optically active **1** on a preparative scale. We have already reported optical resolution of **1** by HPLC using CHIRAL PAK OT(+) [3]. The drawback of this method is that optical resolution is limited to a small scale. Moreover, the high cost of optical resolution columns precludes their use on a large scale. It was known that **1** and tricarbonyl(2,4-cycloheptadienonium)iron tetrafluoroborate (**4**) are readily converted into each other. Here we report a new procedure to obtain optically pure cations (+)-**4** and (−)-**4** starting from *l*-mentyloxy derivatives **2** and **3** on a preparative scale, and the determination of the configuration of optically active **4** and **1** by their being related to optically active tricarbonyl(2,4-cycloheptadienone)iron (**6**).

Racemic tricarbonyl(2,4-cycloheptadienonium)iron ion (**4**) [4,5] was obtained from tricarbonyl(tropone)iron (**1**) by treatment with concentrated H_2SO_4, the excess of which was neutralized with solid Na_2CO_3 in methylene chloride containing a large excess of *l*-menthol, to give a 1/1 diastereoisomeric mixture of ether com-

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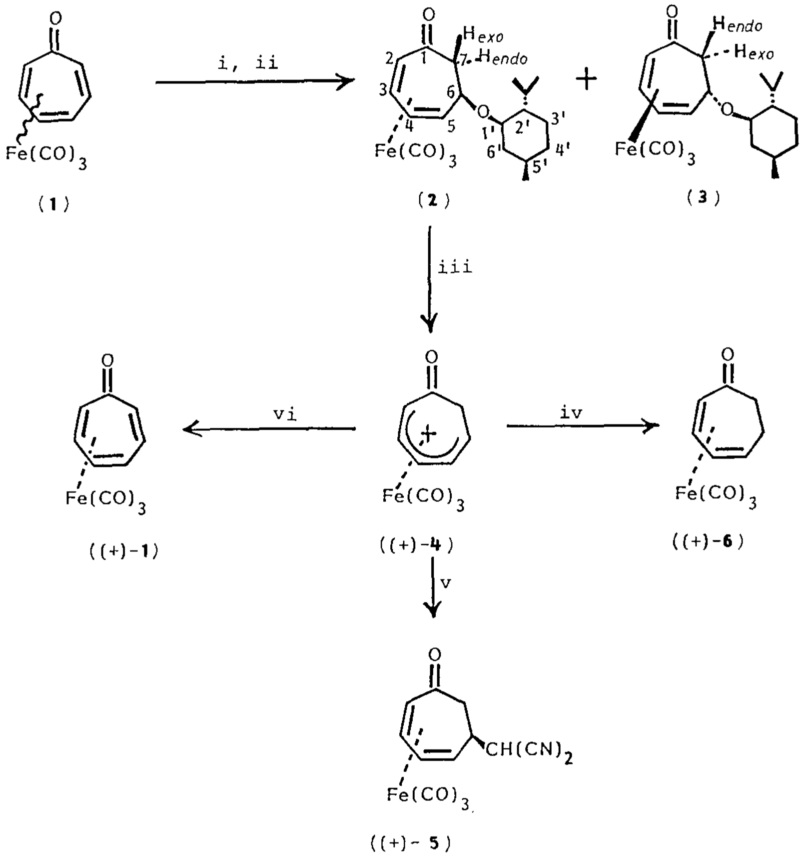

Scheme 1. Reagents: i, conc. H_2SO_4; ii, Na_2CO_3/*l*-menthol; iii, 42% HBF_4/Ac_2O; iv, Et_3SiH/ CF_3COOH; v, $LiCH(CN)_2$; vi, Et_3N.

plexes **2** (m.p. 144.5–145.5°C(dec.)) and **3** (m.p. 137–138°C(dec.)) * in 73% yield, which were easily separated by column chromatography on silica gel or by medium pressure liquid chromatography. The complex **4** has been known to be attacked by nucleophiles such as methanol on the face opposite to iron [4,5]. By analogy to the ^1H NMR of the methyl ether complex [6], the structures of **2** and **3** were assigned accordingly. These complexes gave almost the same CD spectra except for the sign of the Cotton effect as shown in Fig. 1, although their correlations were diastereoisomeric. This suggests that the absolute configuration of the metal-ligand π bonding moiety is a dominant factor in these CD spectra.

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* Spectral data of **2**: $[\alpha]_D^{22°C}$ +116° (*c* 0.1198, $CHCl_3$), IR (KBr): 2070, 2000, 1995, 1900, 1660, 1645 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm) 5.78 (ddd, *J* 6.3, 5.6, 1 Hz, H(3)), 5.53 (ddd, *J* 7.6, 5.6, 1 Hz, H(4)), 4.07 (ddd, *J* 10.5, 5.4, 1.6 Hz, H(6)), 2.9–3.4 (m, H(2), H(5), and H(1')), 1.93 (t, *J* 11 Hz, $H(7_{exo})$), 0.9–2.5 (m, 10H), 0.94 (d, *J* 6.5 Hz, Me), 0.86 (d, *J* 7.2, Me), 0.69 (d, *J* 6.9 Hz, Me). Spectral data of **3**: $[\alpha]_D^{22°C}$ −242° (*c* 0.1493, $CHCl_3$), IR (KBr): 2060, 2010, 2000, 1990, 1980, 1945, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 5.78 (t, *J* 5.5 Hz, H(3)), 5.51 (dd, *J* 7.7, 5.5 Hz, H(4)), 4.06 (ddd, *J* 10.8, 5.8, 1.6 Hz, H(6)), 3.1–3.4 (m, H(2), H(5), H(1')), 2.39 (ddm, *J* 11, 5.5 Hz, $H(7_{endo})$), 2.00 (t, *J* 11 Hz, $H(7_{exo})$), 0.7–2.2 (m, 9H), 0.93 (d, *J* 7 Hz, Me), 0.89 (d, *J* 5.9 Hz, Me), 0.82 (d, *J* 7 Hz, Me).

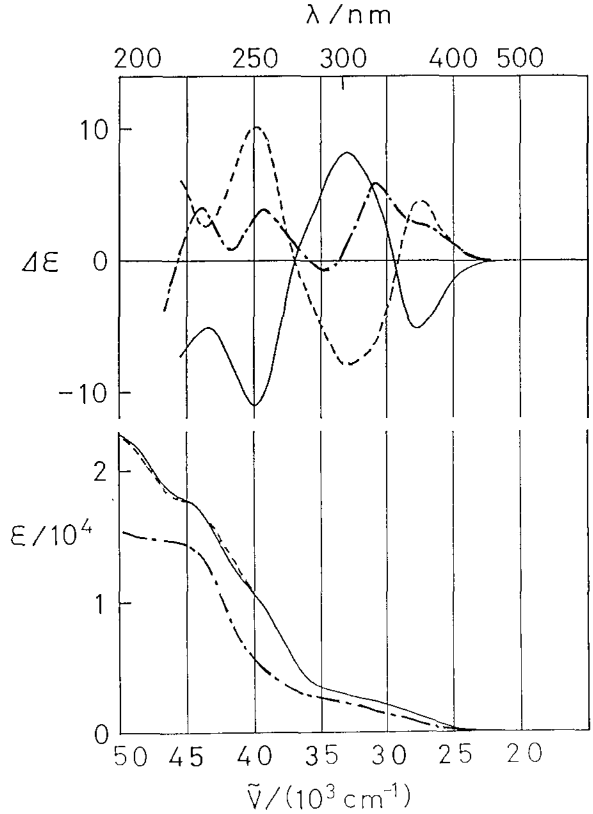

Fig. 1. Absorption (bottom) and CD (top) spectra of (+)-2 (——— in CH_3OH), (−)-3 (------ in CH_3OH) and (+)-4 (–·–·–· in CH_3CN) at room temperature.

Complex **2** was added to tetrafluoroboric acid in acetic anhydride at 0°C to afford optically pure tetrafluoroborate (+)-**4** as a white solid in quantitative yield; m.p. 145.5–146.5°C(dec) $[\alpha]_D^{20°C}$ +311° (c 0.203, CH_3CN) [6]. Similarly, complex **3** gave (−)-**4**; m.p. 146–147°C(dec.), $[\alpha]_D^{20°C}$ −311° (*c* 0.197, CH_3CN). The CD spectrum of (+)-**4** (Fig. 1) is different from those of optically active **6** and its related complexes [3,8]. Thus, optically active cations (+)-**4** and (−)-**4** can be obtained on a preparative scale.

Optical purity of (+)-**4** is 100% ee, because (+)-**4** reacted with the lithium salt of malononitrile to give an optically pure adduct (+)-**5**, whose optical purity was checked by HPLC with CHIRAL CEL OC [7].

Since the absolute configuration of (+)-**6** was found to be 2*R* configuration by X-ray crystallography [8], the absolute configuration of (+)-**4** thus was also determined to be 2*R* by its reaction with triethylsilane in CF_3COOH [5] to give optically pure (+)-**6** in 87% yield. As a result, absolute configurations of all of these complexes were established and are depicted in Scheme 1.

Treatment of (+)-**4** with triethylamine in CH_2Cl_2 gave optically active (+)-**1** in 95% yield, $[\alpha]_D^{20°C}$ +1665° (*c* 0.0209, $CHCl_3$), optical purity of 98% ee was found by HPLC with CHIRAL CEL OB. The decrease in optical purity is due to racemization during isolation.

Further work as to the scope and utility of the optically active **4** is now in process.

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