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SYNTHESIS OF [3.3](1,1') AND [5.5](1,1')FERROCENOPHANE DERIVATIVES

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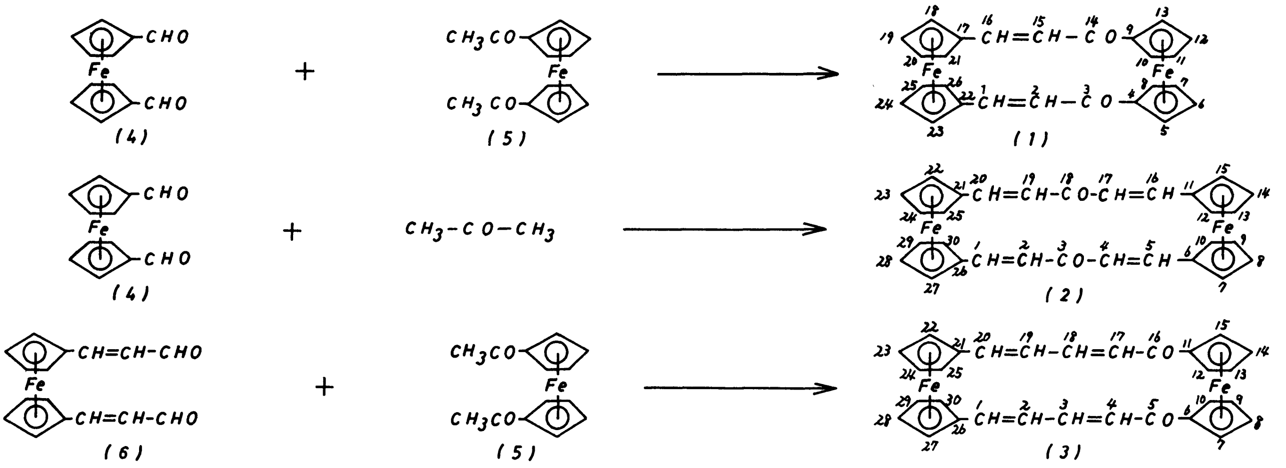
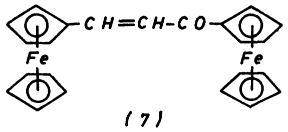
[3.3](1,1') and [5.5](1,1')Ferrocenophane derivatives with one or two olefinic linkages and one carbonyl group between ferrocene systems were synthesized by intermolecularly base-catalyzed condensation. The transannular π-electronic interaction between the olefinic groups were examined on the basis of electronic spectra.

Recently, cyclophane compounds in which two or more aromatic rings are mutually stratified have been investigated from a viewpoint of transannular π-electronic interaction.[1)] In marked contrast to the active interest shown in cyclophane compounds, the [m.n]ferrocenophane system has received little attention.[2)] We have reported on the synthesis of [2.2]ferrocenophane, in which the olefinic group are held rigidly over one another,[3)] and a strong transannular interaction in the compound led us to scrutinize the interaction in [3.3] and [5.5]ferrocenophane derivatives with one or two olefinic linkages and one carbonyl group between the two ferrocene systems.

[3.3](1,1')Ferrocenophane-1,15-diene-3,14-dione (1),[4)] [5.5](1,1')ferrocenophane-1,4,16,19-tetraene-3,18-dione (2),[4)] and [5.5](1,1')ferrocenophane-1,3,17,19-tetraene-5,16-dione (3)[4)] were synthesized by an intermolecularly base-catalyzed condensation method. In the presence of potassium hydroxide (4.4 g) in ethanol (50 ml), treatment of ferrocene-1,1'-dicarbaldehyde (4) (2.41 g, 10 mmol) with 1,1'-diacetylferrocene (5) (2.69 g, 10 mmol) in ethanol at 60°C gave 1 which was purified by recrystallisation from $CHCl_3$-hexane (35% yield, deep red crystals, mp$>$300 °C). In the same manner, an intermolecularly base-catalyzed condensation of 4 (10 mmol) with acetone (5 mmol) led to the formation of 2 (32% yield, deep red crystals, mp$>$360 °C) and the reaction of 5 (10 mmol) with 1,1'-bis(2-formylvinyl)ferrocene (6) (10 mmol) also gave 3 (30% yield, deep red crystals, mp 215°C (dec)).





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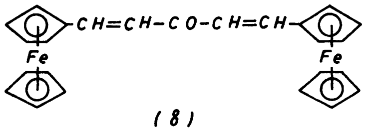

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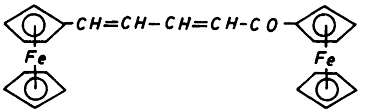

(9)

The configuration of ethylenic bonds in 1 was confirmed to be trans, because the IR spectrum in 1 exhibits a band of about 965 cm^{-1} which is characteristic of trans ethylenic linkage and the characteristic C-H out-of plane deformation modes of -CH=CH-CO- (cis) at near 820 cm^{-1} are absent. Moreover, in the NMR spectrum of 1, the coupling constant of olefinic protons is also revealed the presence of trans olefinic bonds. The NMR signals of the olefinic protons in 1 are shifted to up-field compared with those of the reference compound, 1,3-diferrocenyl-1-propen-3-one (7),$^{5)}$ because the olefinic protons in 1 are situated just above the other olefinic group. The mass spectrum of 1 at 70 eV, the most intense peak is that due to the parent ion of m/e 476; the remaining two prominent peaks at m/e 56 and 238, corresponding to Fe$^+$ and the doubly charged ion. As shown in the Figure 1, the absorption bands of 1 somewhat shifted to longer wave length and exhibit general broadening of all the absorption bands, compared to those of the reference compound 7. It is probably due to some transannular π-electronic interaction between olefinic chromopheres.

On the other hand, the IR and NMR spectra of 2 and 3 were also revealed the presence of trans olefinic linkages. The protons of the olefinic bonds in 2 and in 3 are somewhat shifted to up-field, compared with those of the reference compounds, 1,5-diferrocenylpenta-1,4-diene-3-one (8)$^{5)}$ and 1,5-diferrocenylpenta-1,3-diene-5-one (9), respectively. These up-field shifts should be attributed to the transannular shielding effect due to a magnetic anisotropy caused by the other olefinic bond. The electronic spectra of 2, 3, 8, and 9 are shown in figures 2 and 3. The spectrum of 2 shows a general broadening, an increasing of intensity, and a small blue shift of the

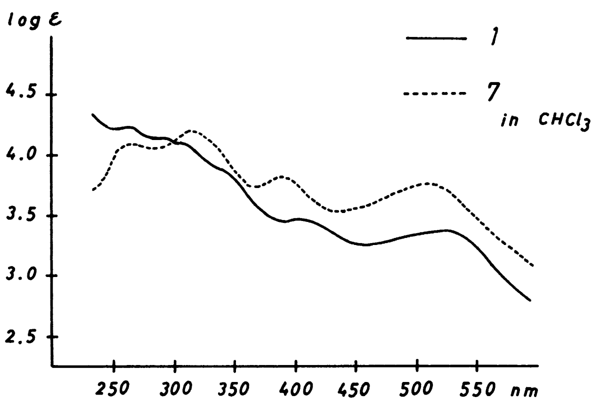

Fig. 1. Electronic spectra of 1 and 7.

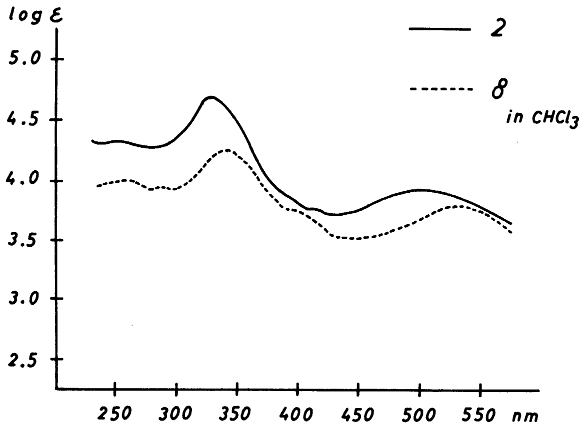

Fig. 2. Electronic spectra of 2 and 8.

the bands, compared with that of 8. In comparison with the spectrum of 9 as reference, the spectrum of 3 shows a broadening of the absorption bands and the longest wave length bands appears at longer wave length by 24 nm than that of 9. These phenomena may be due to transannular π-electronic interaction between chromopheres in 2 and in 3.

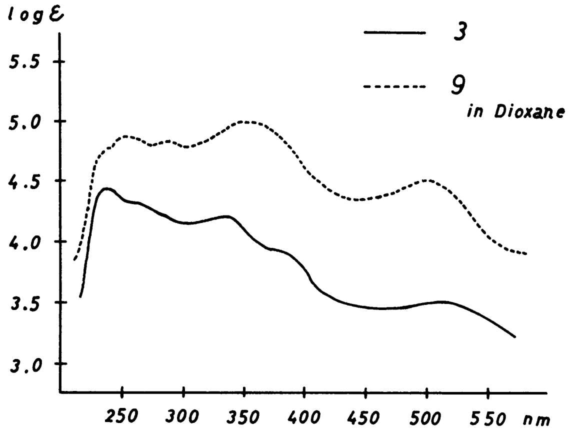

Fig. 3 Electronic spectra of 3 and 9.

Table 1. The IR, NMR, and MS spectral data of the compounds.[a)]

Compound

1 IR: 1645 (C=O), 1590, 965 (trans -CH=CH-), 3100, 805 cm^{-1} (1,1'-disubstituted Fc ring). NMR: δ 4.83 (m, 8H, Fc ring protons), 4.56 (br-s, 8H, Fc ring protons), 6.37 (d, 2H, J=16 Hz, Fc-C=CH-CO-), and 7.55 ppm (d, 2H, J=16 Hz, Fc-CH=C-CO-). MS: m/e 476 (M^+), 238 (m/2e), and 56 (Fe^+).

2 IR: 1610 (C=O), 1590, 965 (trans -CH=CH-), 3100, 805 cm^{-1} (1,1'-disubstituted Fc ring). NMR: δ 4.45 (m, 8H, Fc ring protons), 4.55 (m, 8H, Fc ring protons), 6.24 (d, 4H, J=16 Hz, Fc-C=CH-CO-), and 7.46 ppm (d, 4H, J=16 Hz, Fc-CH=C-CO-). MS: m/e 528 (M^+), 264 (m/2e), and 56 (Fe^+).

3 IR: 1665 (C=O), 1580, 960 (trans -CH=CH-), 3100, 1400, and 805 cm^{-1} (1,1'-disubstituted Fc ring). NMR: δ 4.36 (m, 8H, Fc ring protons), 4.55 (m, 4H, Fc

ring protons), 4.84 (m, 4H, Fc ring protons), 6.01-6.61 (m, 6H, Fc-C=CH-CH=CH-CO-), and 7.15 ppm (d-d, 2H, Fc-CH=C-). MS: m/e 528 (M^+), 264 (m/2e), and 56 (Fe^+).

7[5] NMR: δ 4.21 (s, 10H, Fc ring protons), 4.51 (m, 2H, Fc ring protons), 4.62 (m, 4H, Fc ring protons), 4.92 (m, 2H, Fc ring protons), 6.82 (d, 1H, J=15 Hz, Fc-C=CH-CO-), and 7.82 ppm (d, 1H, J=15 Hz, Fc-CH=C-CO-).

8[5] NMR: δ 4.20 (s, 10H, Fc ring protons), 4.48 (m, 4H, Fc ring protons), 4.58 (m, 4H, Fc ring protons), 6.63 (d, 2H, J=16 Hz, Fc-C=CH-CO-), and 7.66 ppm (d, 2H, J=16 Hz, Fc-CH=C-CO-).

9 Mp 172-173°C (dec), reddish crystals. IR: 1640 (C=O), 1600, 1575, 960 (trans -CH=CH-), 3100, 1400, 1100, 995, and 805 cm^{-1} (monosubstituted Fc ring). NMR: δ 4.13 (s, 5H, Fc ring protons), 4.19 (s, 5H, Fc ring protons), 4.36 (m, 2H, Fc ring protons), 4.46 (m, 2H, Fc ring protons), 4.51 (m, 2H, Fc ring protons), 4.82 (m, 2H, Fc ring protons), 6.39-6.78 (m, 3H, Fc-C=CH-CH=CH-CO-) and 7.45 (d-d, 1H, Fc-CH=C-). MS: m/e 450 (M^+). This compound was synthesized by the base-catalyzed condensation of acetylferrocene with 3-ferrocenyl-2-propenal.

a) All compounds gave correct elemental analyses. All IR spectra were measured on KBr disks and NMR spectra were observed in $CDCl_3$ at 90 MHz or 100 MHz with TMS as standard.

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