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SYNTHESIS OF [2]PARACYCLO[2]PARACYCLO[2](1,1')FERROCENOPHANE DERIVATIVES

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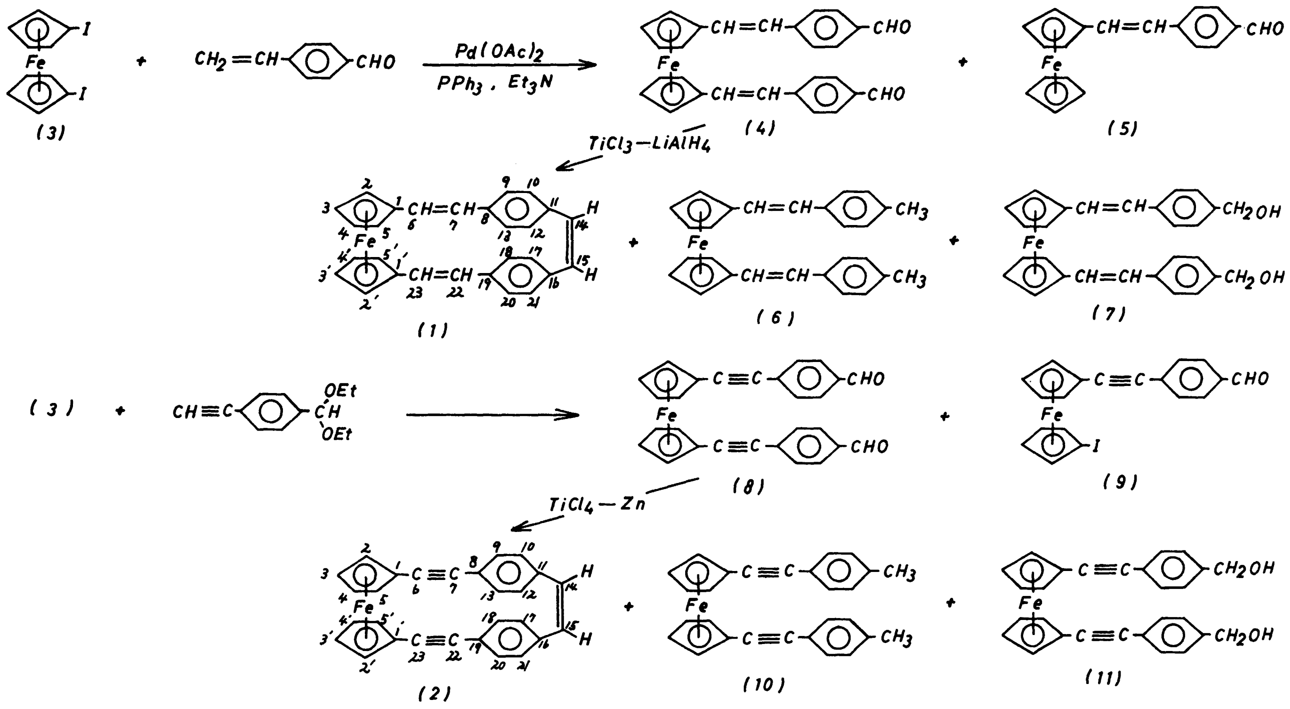
[2]Paracyclo[2]paracyclo[2](1,1')ferrocenophane derivatives having olefinic or acetylenic bonds and aromatic rings were synthesized by intramolecularly titanium-induced reductive coupling of carbonyl compounds. The transannular π-electronic interactions between two olefinic or acetylenic bonds and two benzene rings were examined on the basis of electronic spectra.

A large number of layered compounds has been synthesized and the physical and chemical properties have been studied.$^{1)}$ For example, [2.2]paracyclophane is a most typical layered compound. However, there are only a few investigation of ferrocenophane having a transannular π-electron interaction. As example of this type of ferrocenophane, the synthesis of [2.2]ferrocenophane-1,13-diyne$^{2)}$ and [2.2]ferrocenophane-1,13-diene$^{3)}$ has recently been reported. In view of the increasing interest in phane compounds, we wish to report the synthesis of [2]paracyclo[2]paracyclo[2](1,1')ferrocenophane-6,14,22-triene (1)$^{4)}$ and [2]paracyclo[2]paracyclo[2](1,1')ferrocenophane-14-en-6,22-diyne (2)$^{4)}$, both having a transannular π-electron interaction.

In the presence of palladium(II) acetate, triphenylphosphine, and triethylamine, a palladium-catalysed substitution$^{5)}$ of 1,1'-diiodoferrocene (3) with p-formylstyrene afforded 1,1'-bis(p-formylstyryl)ferrocene (4), reddish needles, mp 218°C (dec) (55% yield) and p-formylstyrylferrocene (5), reddish needles, mp 145-147°C, (35% yield).

The reductive coupling of 4 with the low valent titanium compound ($TiCl_3$-$LiAlH_4$)$^{6)}$ led to the formation of 1,1'-bis(p-methylstyryl)ferrocene (6), reddish needles, mp 142-144°C (1.4% yield), phane compound 1, reddish needles, mp 230°C (dec) (2.2% yield), and 1,1'-bis(p-hydroxymethylstyryl)ferrocene (7), reddish yellow needles, mp 152-154°C (3.2% yield).



On the other hand, in the presence of $(Ph_3P)_2PdCl_2$, CuI, and diethylamine, a palladium-catalysed substitution[7)] of 3 with p-ethynylbenzaldehyde diethyl acetal led to the formation of 1,1'-bis(p-formylphenylethynyl)ferrocene (8), reddish needles, mp 210°C (dec) (27% yield) and 1-p-formylphenylethynyl-1'-iodoferrocene (9), reddish needeles, mp 139-141°C (45% yield) were obtained. Moreover, the intramolecularly titanium-induced reductive coupling of dialdehyde 8 with $TiCl_4$-Zn[8)] proceeded to the formation of phane compound 2, reddish needles, mp 260°C (dec) (15% yield), 1-p-formylphenylethynyl-1'-p-hydroxymethylphenylethynylferrocene (10), reddish needles, mp 190°C (dec) (6% yield), and 1,1'-bis(p-hydroxymethylphenylethynyl)ferrocene (11), reddish yellow needles, mp 195°C (dec). In the reductive coupling reaction of dialdehyde 8 with $TiCl_3$-$LiAlH_4$, the yield of the phane compound 2 was only 1.5%.

The structures of the phane compounds 1 and 2 and the other compounds were determined on the basis of IR, NMR, and MS spectra (see Table 1). In the MS spectrum of 1, the most intense peak is that due to the parent ion of m/e 414. The IR spectrum is revealed the presence of trans and cis olefinic bonds, 1,1'-disubstituted ferrocene ring, and p-disubstituted benzene rings. The NMR spectrum of 1 is also agreed with the proposed structure. In comparisson with the NMR spectrum in the reference compound, p-methylstyrylferrocene (12), the protons of aromatic and olefinic groups in phane compound 1 are shifted to upfield by about 0.6 ppm, because of a diamagnetic shielding effect due to an overlapping of two benzene rings and two olefinic groups. Furthermore,

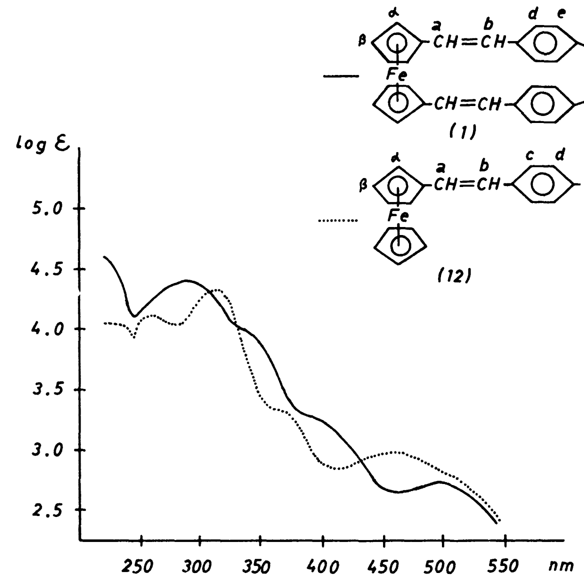


Fig. 1. Electronic spectra of 1 and 12 in dioxane.

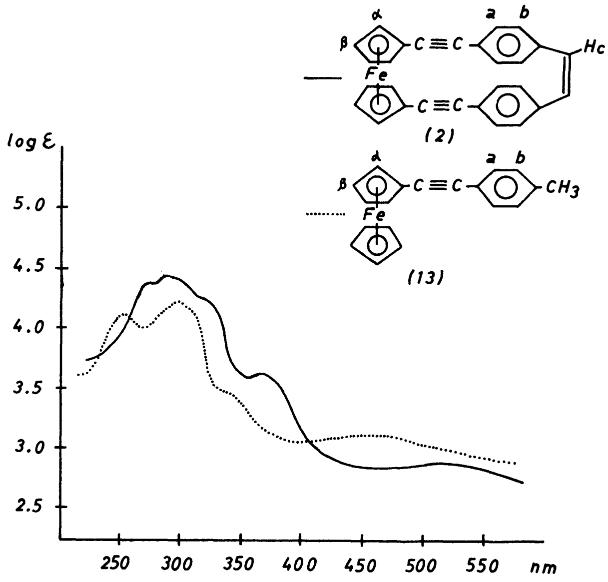


Fig. 2. Electronic spectra of 2 and 13 in dioxane.

as seen in the Figure 1, the absorption bands of 1 somewhat shifted to longer wavelength and show an increase of intensity of the bands compared with the spectrum of the reference compound 12. It is probably due to some transannular π-electron interaction between two benzene rings and olefinic bonds, respectively.

On the other hand, the IR, NMR, and MS spectra of phane compound 2 were completely consistent with the proposed structure. The IR spectrum is revealed the presence of triple bonds, p-disubstituted benzene rings, and 1,1'-disubstituted ferrocene ring. In comparison with the NMR spectrum of the reference compound, p-tolylethynylferrocene (13), the protons of the benzene rings in 2 are shifted to up-field by about 0.6 ppm. This phenomenone may be caused by the diamagnetic shielding effect between two benzene rings. Moreover, in the electronic spectra of 2 and the reference compound 13 (see Fig. 2), the absorption bands of 2 are shifted to longerwavelength, compared with that of 13, and exhibit strong bathochromic and hyperchromic effects due to a transannular π-electron interaction between the two benzene rings and two triple bonds.

Table 1. The IR, NMR, and MS spectral data of 1, 2, 12, and 13.$^{a)}$

1 IR: 3100, 1400, 805 (ferrocene ring), 1630, 950 (trans -CH=CH-), 730 (cis -CH=CH-), 1600, 1580, 820 cm^{-1} (p-disub. benzene ring). NMR: δ 4.24 (m, 4H, H), 4.42 (m, 4H, H), 5.98 (d, 2H, H_b, J=16 Hz), 6.29 (d, 2H, H_a, J=16 Hz), 6.49 (d, 4H, H_e, J=8 Hz), 6.71 (d, 4H, H_d, J=8 Hz), and 7.17 ppm (s, 2H, H_c). MS: m/e

414 (M^+).

2 IR: 3100, 1400, 810 (ferrocene ring), 2200 (-C≡C-), 1640, 730 (cis -CH=CH-), 1600, 1580, and 820 cm^{-1} (p-disub. benzene ring). NMR: δ 4.24 (m, 4H, H_β), 4.47 (m, 4H, H_α), 6.47 (d, 4H, H_b, J=8 Hz), 6.82 (d, 4H, H_a, J=8 Hz), and 7.18 ppm (s, 2H, H_c). MS: m/e 410 (M^+).

12 Mp 130-131°C, reddish crystals. IR: 3080, 1410, 1100, 995, 810 (ferrocene ring), 1625 and 960 cm^{-1} (trans -CH=CH-). NMR: δ 2.29 (s, 3H, $-CH_3$), 4.13 (s, 5H, Cy ring protons), 4.27 (m, 2H, H_β), 4.47 (m, 2H, H_α), 6.60 (d, 1H, H_b, J=16 Hz), 6.83 (d, 1H, H_a, J=16 Hz), 7.12 (d, 2H, H_d, J=8 Hz), and 7.31 ppm (d, 1H, H_c, J=8 Hz). MS: m/e 302 (M^+). This compound was synthesized by the palladium-catalysed substitution[5)] of iodoferrocene with p-vinyltoluene.

13 Mp 109-110°C, reddish crystals. IR: 3100, 1410, 1100, 1000, 810 (ferrocene ring), and 2200 cm^{-1} (-C≡C-). NMR: δ 2.29 (s, 3H, $-CH_3$), 4.21 (m, 7H, Cy ring protons + H_β), 4.48 (m, 2H, H_α), 7.10 (d, 2H, H_b, J=8 Hz), and 7.38 ppm (d, 2H, H_a, J=8 Hz). MS: m/e 300 (M^+). This compound was synthesized by the palladium-catalysed substitution[7)] of iodoferrocene with p-ethynyltoluene.

a) All compounds gave correct elemental analysis. Furthermore, the IR and NMR spectra and the elemental analysis of the compounds 4, 5, 6, 7, 8, 9, 10, and 11 were all consistent with the proposed structures.

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