CHEMISTRY LETTERS, pp. 1039-1042, 1980. © The Chemical Society of Japan 1980

SYNTHESIS OF [0]METACYCLO[2]METACYCLO[0](1,1')FERROCENOPHANE-7-ENE

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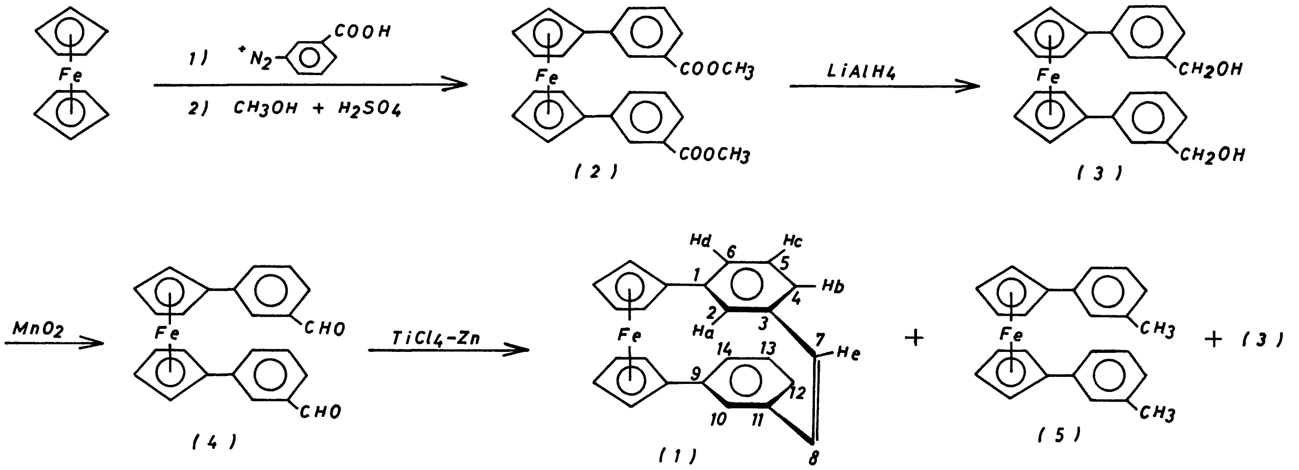
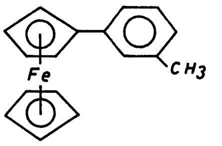
[0]Metacyclo[2]metacyclo[0](1,1')ferrocenophane-7-ene revealing transannular electronic interactions was synthesized via the intramolecularly reductive coupling of 1,1'-bis(m-formylphenyl)ferrocene with $TiCl_4$-Zn.

Transannular interactions between two benzene rings in cyclophanes attracted much attention and a large number of phane compounds in corporating various benzenoid and heteroaromatic rings have been synthesized.1) However, there are only a few investigations of ferrocenophane revealing transannular electronic interattions: [2.2]ferrocenophane-1,13-diyne,2) [2.2]ferrocenophane-1,13-diene,3) [2]paracyclo[2]paracyclo[2](1,1')ferrocenophane derivatives,4) [3.3](1,1')ferrocenophane-1,15-diene-3,14-dione,5) and [5.5](1,1')ferrocenophane-1,4,16,19-tetraene-3,18-diene.5) As a part of our studies on metallocenophane chemistry, we wish to report the synthesis of [0]metacyclo[2]metacyclo[0](1,1')ferrocenophane-7-ene6) (1) in order to examine the interaction between two benzene rings.

Gomberg's arylation of ferrocene with diazonium salts derived from m-aminobenzoic acid and the subsequent esterification of the reaction products in methanol afforded 1,1'-bis(m-methoxycarbonylphenyl)ferrocene (2), orange yellow needles, mp 113-114 °C, in 19.5% yield. Reduction of 2 with $LiAlH_4$ in ether-benzene yielded 1,1'-bis(m-hydroxymethylphenyl)ferrocene (3), yellowish needles, mp 125-127 °C, in 95% yield. Oxidation of 3 with active MnO_2 in $CHCl_3$ led to the formation of 1,1'-bis(m-formylphenyl)ferrocene (4), reddish needles, mp 133-134 °C, in 66% yield. The reductive coupling of 4 with the low valent titanium reagent was carried out according to Mukaiyama's procedure.7) After Zn dust (6.5 g, 100 mmol) was added to a solution of $TiCl_4$ (9.49 g, 50 mmol) in dry THF (180 ml), the mixture was refluxed





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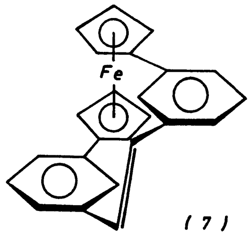

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for 1.5 h under a nitrogen atmosphere. To the metal complex solution thus obtained was added dropwise a solution of 4 (3.9 g, 10 mmol) and dry pyridine (0.75 g) in dry THF (550 ml) for 18 h under refluxing. The mixture was then refluxing for additional 10 h and quenched with 20% aqueous solution. After filtration, the filtrate was extracted with $CHCl_3$. The extract was washed with water, and dried over $MgSO_4$. The phane compound 1 (reddish needles, mp 193-195 °C, 16.6% yield), 1,1'-di-m-tolylferrocene (5) (orange yellow needles, mp 115-117 °C, 2.5% yield), and 3 (yellowish needles, mp 125-127 °C, 45.2% yield) were obtained after separation by silica gel column chromatography.

The structures of the phane compound 1 and the other compounds were determined on the basis of IR, NMR, and mass spectra and the elemental analyses (see Table 1). The configuration of ethylenic bond in 1 was confirmed to be cis, because the IR spectrum of 1 exhibits a band at about 720 cm^{-1} which is characteristic of cis ethylenic linkage and the characteristic C-H out-of deformation modes of trans -CH=CH- at near 960 cm^{-1} are absent. In the NMR spectrum of 1, it is noteworthy that the vinyl protons (H_e) of 1, which can be easily assigned by relative intensities, appear at lower field than the aromatic protons (H_{a-d}) similarly to the case of [2.2.2](1,3,5)-cyclophane-1,9,17-triene.8) The H_a protons in 1 are shifted to higher field than the corresponding protons of the reference compounds, 5 and m-tolylferrocene9) (6), whereas the H_{b-d} signals of 1 were observed at the nearly same positions as those of 5 and 6. These phenomena suggest that, by the short length of the side chain which is bridging the meta position, the planes of the two benzene rings in 1 are not parallel and the cyclopentadienyl and benzene rings have a non-planar orientation. The H_a protons consequently lie closer to opposed benzene ring than the H_{b-d} protons and the difference of the chemical shifts may be due to the difference in ring current effect of the opposed benzene ring on the four protons (H_a and H_{b-d}) of 1. Furthermore, an examination with Dreiding model suggests that anti form (7) is difficult to form due to its highly strained structure.

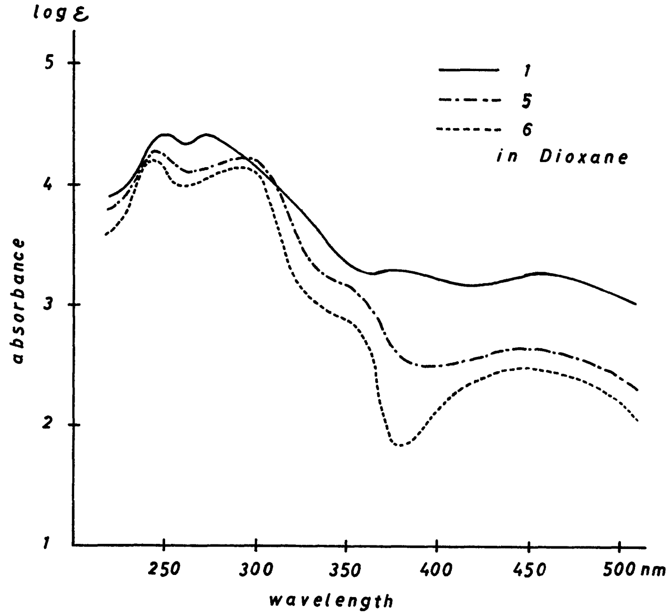

Fig. 1. UV spectra of 1, 5, and 6.

As seen in the Figure 1, in the spectrum of 1 there are somewhat bathochromic and hyperchromic shifts and unambiguous broadening of the longest wavelength band, compared with that of 5 and 6 as a reference. These are probably due to some transannular π-electronic interactions between the two benzene rings in 1.

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

Compound

1 IR: 3100, 805 (1,1'-disubstituted Fc ring), 860, 800 (m-disubstituted benzene ring), 1625, 720 and 680 cm^{-1} (cis -CH=CH-). NMR: δ 4.29 (m, 8H, Fc ring protons), 6.57 (s, 2H, H_a), 7.01-7.30 (m, 6H, H_b + H_c + H_d), and 7.53 ppm (s, 2H, H_e). MS: m/e 362 (M^+).

2 IR: 3100, 805 (1,1'-disubstituted Fc ring), 1720 (-COOMe), 860 and 800 cm^{-1} (m-disubstituted benzene ring). NMR: δ 3.91 (s, 6H, $-CH_3$), 4.26 (t, 4H, Fc ring protons), 4.55 (t, 4H, Fc ring protons), and 7.10-7.75 ppm (m, 8H, benzene ring protons). MS: m/e 454 (M^+).

3 IR: 3250, 1020 (-OH), 3100, 805 (1,1'-disubstituted Fc ring), 860 and 800 cm^{-1} (m-disubstituted benzene ring). NMR: δ 2.10 (br. s, 2H, -OH), 4.28 (m, 4H, Fc ring protons), 4.47 (m, 4H, Fc ring protons), 4.54 (s, 4H, $-CH_2-$),

and 7.11 (m, 8H, benzene ring protons). MS: m/e 398 (M^+).

4 IR: 3100, 805 (1,1'-disubstituted Fc ring), 2820, 1690 (-CHO), 860 and 800 cm^{-1} (m-disubstituted benzene ring). NMR: δ 4.31 (t, 4H, Fc ring protons), 4.57 (t, 4H, Fc ring protons), 7.28-7.53 (m, 8H, benzene ring protons), and 9.87 ppm (s, 2H, -CHO). MS: m/e 394 (M^+).

5 IR: 3100, 805 (1,1'-disubstituted Fc ring), 860 and 800 cm^{-1} (m-disubstituted benzene ring). NMR: δ 2.26 (s, 6H, $-CH_3$), 4.19 (t, 4H, Fc ring protons), 4.43 (t, 4H, Fc ring protons), and 7.09-7.28 ppm (m, 8H, benzene ring protons). MS: m/e 366 (M^+).

6 NMR: δ 2.31 (s, 3H, $-CH_3$), 4.01 (s, 5H, Fc ring protons), 4.26 (t, 2H, Fc ring protons), 4.58 (t, 2H, Fc ring protons), and 7.04-7.20 ppm (m, 4H, benzene ring protons).

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

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(Received May 22, 1980)