CHEMISTRY LETTERS, pp. 1039-1042, 1980.

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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 intra-molecularly reductive coupling of 1,1'-bis(m-formylphenyl)ferrocene with TiCl_A -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-3,18diene.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⁾ (<u>1</u>) 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 LiAlH₄ 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 CHCl₃ 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 TiCl₄ (9.49 g, 50 mmol) in dry THF (180 ml), the mixture was refluxed



for 1.5 h under a nitrogen atmosphere. To the metal complex solution thus obtained was added dropwise a solution of $\underline{4}$ (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 CHCl₃. The extract was washed with water, and dried over MgSO₄. The phane compound <u>1</u> (reddish needles, mp 193-195°C, 16.6% yield), 1,1'-di-m-tolylferrocene (<u>5</u>) (orange yellow needles, mp 115-117°C, 2.5% yield), and <u>3</u> (yellowish needles, mp 125-127°C, 45.2% yield) were obtained after separation by silica gel column chromatography.

The structures of the phane compound <u>1</u> 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 <u>1</u> was confirmed to be cis, because the IR spectrum of <u>1</u> 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 <u>1</u>, it is noteworthy that the vinyl protons (H_e) of <u>1</u>, 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 <u>1</u> are shifted to higher field than the corresponding protons of the reference compounds, <u>5</u> and m-tolylferrocene⁹) (<u>6</u>), whereas the H_{b-d} signals of <u>1</u> 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 nonplanar 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 <u>1</u>. Furthermore, an ex-



amination with Dreiding model suggests that anti form $(\underline{7})$ is difficult to form due to its highly strained structure.

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 <u>5</u> and <u>6</u> as a reference. These are probably due to some transannular π -electronic interactions between the two benzene rings in <u>1</u>.

Table 1. The IR, NMR, and mass spectra data of the compounds.^{a)} Compound

- <u>1</u> IR: 3100, 805 (1,1'-disubstituted Fc ring), 860, 800 (m-disubstituted benzene ring), 1625, 720 and 680 cm⁻¹ (cis -CH=CH-). NMR: **6** 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⁺).
- <u>2</u> IR: 3100, 805 (1,1'-disubstituted Fc ring), 1720 (-COOMe), 860 and 800 cm⁻¹ (m-disubstituted benzene ring). NMR: **6** 3.91 (s, 6H, -CH₃), 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⁺).
- <u>3</u> IR: 3250, 1020 (-OH), 3100, 805 (1,1'-disubstituted Fc ring), 860 and 800 cm⁻¹ (m-disubstituted benzene ring). NMR: 5 2.10 (br. s, 2H, -OH), 4.28 (m, 4H, Fc ring protons), 4.47 (m, 4H, Fc ring protons), 4.54 (s, 4H, -CH₂-),

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

- <u>4</u> IR: 3100, 805 (1,1'-disubstituted Fc ring), 2820, 1690 (-CHO), 860 and 800 cm⁻¹ (m-disubstituted benzene ring). NMR: **5** 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: § 2.26 (s, 6H, -CH₃), 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⁺).
- <u>6</u> NMR: **8** 2.31 (s, 3H, -CH₃), 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 CDCl₃ at 90 MHz with TMS as standard.

References

- 1) S. Misumi and T. Otsubo, Acc. Chem. Res., <u>11</u>, 251 (1978).
- 2) M. Rosenblum, N. M. Brawn, D. Clappenelli, and J. Tancrede, J. Organomet. Chem., 24, 469 (1970).
- 3) A. Kasahara and T. Izumi, Chem. Lett., 1978, 21.
- 4) A. Kasahara, T. Izumi, and I. Shimizu, Chem. Lett., 1979, 1119.
- 5) A. Kasahara, T. Izumi, and I. Shimizu, Chem. Lett., 1979, 1317.
- 6) The nomenclature and numbering system of the phane compound <u>1</u>, as illustrated in the scheme, is modification of that proposed by F. Vogtle and P. Neumann (Tetrahedron, <u>26</u>, 5847 (1970)).
- 7) T. Mukaiyama, T. Sato, and J. Hanna, Chem. Lett., <u>1973</u>, 1041.
- 8) V. Boekelheide and R. A. Hollins, J. Am. Chem. Soc., <u>92</u>, 3512 (1970).
- 9) W. L. Baun, Anal. Chem., <u>31</u>, 1308 (1959).

(Received May 22, 1980)

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