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SYNTHESIS OF FERROCENE PARACYCLOPHANES

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Summary

Paracyclophanes containing one or two ferrocene units can be efficiently synthesized directly from 1,1′-di(hydroxymethyl)ferrocene and aromatic dithiols. In the reaction with di(4,4′-dimercaptomethylphenyl)methane the mononuclear paracyclophane was formed, while with the dithiophenols di(4,4′-dimercaptophenyl)methane and di(4,4′-dimercaptophenyl)ether, cyclophanes bearing two ferrocene units were obtained. For comparison three open-chain analogues were also prepared.

Introduction

Examples of cyclophanes incorporating the ferrocene nucleus have been described recently [1—6]. We now report an efficient synthesis of ferrocene paracyclophanes, which makes this type of compound readily accessible. Previously, the reactions of ferrocene diols with alkane dithiols were shown to provide a valuable cyclization method leading to various macrocyclic polythia- and polyoxathia-ethers bearing one or two ferrocene units [7—9]. As an extension of our work in this field we have investigated the reactions of 1,1′-di(hydroxymethyl)ferrocene with aromatic dithiols and dithiophenols.

Results and discussion

The initial aim of the work was the synthesis of organometallic paracyclophanes containing the ferrocene unit and resembling earlier synthesized and investigated [1.*n*]paracyclophanes [10,11]. It was found that only the structure of the product I was as expected, the other two syntheses yielding exclusively the cyclophanes II and III, incorporating two ferrocene units, which were formed in fairly high yields (48 and 62%, respectively).

Examination of Dreiding models suggests that the formation of mononuclear

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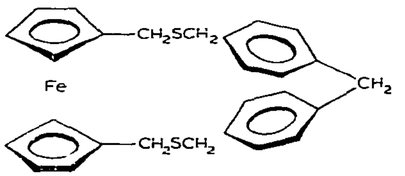
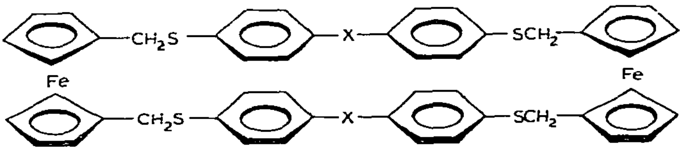
[1.*n*] type products is improbable in the cases mentioned above because of their potentially highly strained structures. The structure of I seems to be very strained, and some striking changes are observed in its ^{1}H NMR spectrum in comparison with that of the open-chain analog IV. Thus, the signal from the methylene protons in the benzhydryl position, which is a broad singlet for the open-chain model IV, is shifted upfield in I by as much as 0.9 ppm, and becomes very sharp. Although similar changes were observed earlier [11], such a large effect is so far inexplicable. On the other hand, the aromatic protons give well defined quartets for both I and IV, with almost unchanged chemical shifts.

The mass spectrum of I shows the molecular ion *m/e* 470 of low intensity and the most abundant ion peak at 244. The species *m/e* 244 may be the bridged 2-thia[3](1,1′)ferrocenophane ion. Such a course for the mass spectral fragmentation was observed earlier in the case of dithia[*n*](1,1′)ferrocenophanes [8]. Both of the binuclear products II and III give NMR spectra almost identical with those of their open-chain counterparts. The mass spectra of II and III do not exhibit molecular ions, and are not very informative, although numerous fragment ions of low mass are observed. The IR spectra of all the paracyclophanes obtained differ only slightly from those of open-chain analogs, although the bands in the spectra of the cyclic compounds are usually broader than those for the acyclic products. Unfortunately, the very poor solubility in most organic solvents used for UV spectroscopy meant that the ultraviolet absorption spectra in the region which is usually used to study π-electronic interactions in cyclophanes could not be obtained.

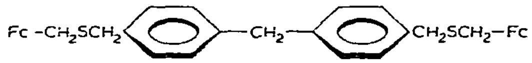
Acyclic model compounds were prepared in almost quantitative yields by reactions of ferrocenylmethanol with appropriate aromatic dithiols in methylene chloride, in the presence of a catalytic amount of trifluoroacetic acid.



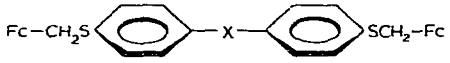
I



$X = CH_2$, II
O, III



IV



$X = CH_2$, V
O, VI

Experimental

^{1}H NMR spectra were recorded on JEOL-C-60H and Tesla BS 492C-80 spectrometers in deuteriochloroform with tetramethylsilane as internal standard. IR spectra were recorded on a Pye Unicam SP-200 spectrophotometer. Mass spectra at 70 eV were recorded on a LKB 2091 instrument with direct inlet system. Molecular weights were determined with a Hewlett Packard 302B vapour pressure osmometer or by the isothermal distillation method with a MICROMOL OX-103 apparatus (Labor MIM, Budapest). Melting points were determined on a Böetius apparatus and are uncorrected. Reagent grade solvents were used without further purification. Reactions were usually carried out under nitrogen, although neglect of this precaution did not significantly influence the yields. Open-chain compounds were prepared by to published methods [12].

General procedure

The ferrocene paracyclophane were prepared by simultaneous dropwise addition of solutions of 1,1'-di(hydroxymethyl)ferrocene in 50 ml of methylene chloride and the dithiol in 50 ml of methylene chloride/benzene (1/1) to 350 ml of vigorously stirred refluxing methylene chloride containing 5 drops of trifluoroacetic acid. The mixture was stirred at 40°C for 15 h, then cooled and washed with 5% NaOH and water, then dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was chromatographed or recrystallized. Specific details are given for each compound.

The mononuclear paracyclophane I

1,1'-Di(hydroxymethyl)ferrocene (0.98 g, 4 mmol) and 1.04 g (4 mmol) of di(4,4'-dimercaptomethylphenyl)methane were used. After the reaction the mixture was worked-up, the solution was concentrated under reduced pressure to 25 ml, and 25 ml of benzene were added. The solution was set aside overnight, and the yellow precipitate was filtered and washed several times with small portions of diethyl ether. The chromatographically pure, yellow microcrystalline product I (0.60 g, 32%) had: m.p. 147—149°C, (Found: C, 68.58; H, 5.89. $C_{27}H_{26}FeS_2$ (470.47) calcd.: C, 68.93; H, 5.57%.) Molecular weight (by osmometry) 498. NMR (ppm, in $CDCl_3$): 3.02 (s, 2 H, benzhydryl methylene); 3.38 (brs, 4 H, $FcCH_2$): 3.62 (brs, 4 H, benzyl methylene) 4.07 (m, 8 H, Fc); 7.26 (m, 8 H, phenyl). MS (*m/e*, %int.): 470 (M^+, 7), 244(100), 181(68), 180(31), 179(24), 167(22), 166(79), 165(34), 121(20), 95(22), 91(26), 85(37), 83(33), 81(26), 78(66), 71(53), 69(41), 57(72), 56(31). IR (KBr, cm^{-1}): $\nu(CH_2)$ 2920s, 2850m; $\omega(CH_2S)$ 1265s; $\delta(CH)$ 1105s(br), 1030s(br); $\gamma(CH)$ 820s(br).

The binuclear paracyclophane II

1,1'-Di(hydroxymethyl)ferrocene (0.34 g, 1.4 mmol) and 0.31 g (1.4 mmol) of di(4,4'-dimercaptophenyl)methane were used. After work-up the solution was evaporated to dryness and the crude product was chromatographed on silica gel with benzene as eluent. The first fraction yielded 0.30 g (48%) of the product II as yellow crystals of m.p. 68—70°C. Elemental analysis: Found: C, 67.77; H, 5.28. $C_{50}H_{44}Fe_2S_4$ (884.83) calcd.: C, 67.87; H, 5.01%. Molecular weight (by isothermal distillation) 812. NMR (ppm, $CDCl_3$): 3.80 (two overlapping singlets, 12 H, CH_2); 4.02 (m, 16 H, Fc); 7.08 (q, 16 H, phenyl). MS (*m/e*): 97(21), 95(22), 83(23), 81(24), 71(34), 69(47), 67(21), 57(68), 56(20), 55(71), 43(100). IR (KBr, cm^{-1}): $\nu(CH_2)$ 2920s(br), 2850m; $\omega(CH_2S)$ 1260m; ν(PhS, skeleton) 1090m; $\delta(CH)$ 1040m, 1015m; $\delta(CH)$ 805s.

The binuclear paracyclophane III

1,1′-Di(hydroxymethyl)ferrocene (0.49 g, 2 mmol) and 0.46 g (2 mmol) of di(4,4′-dimercaptophenyl)ether were used. Yellow crystals (0.55 g, 62%) of III were obtained by the procedure described for II. M.p. 181—183°C, elemental analysis: Found: C, 64.62; H, 4.56. $C_{48}H_{40}Fe_2O_2S_4$ (888.78) calcd.: C, 64.87; H, 4.54%. Molecular weight (by isothermal distillation) 821. NMR (ppm, $CDCl_3$): 3.82 and 3.91 (two singlets, 8 H, CH_2); 4.07 (m, 16 H, Fc); 7.07 (q, 16 H, phenyl). MS (*m/e*): 446(17), 234(93), 213(100), 135(27), 125(33), 110(20), 109(29), 97(29), 69(37), 65(48), 45(28). IR (cm^{-1}, KBr). $\nu(CH_2)$ 2930s, 2845s; $\omega(CH_2S)$ 1265s; $\nu(C—O)$ 1240m(br), $\nu(PhS)$ 1100s(br); $\delta(CH)$ 1030s(br); $\gamma(CH)$ 825s(br).

The open chain compounds IV—VI, which are brown, viscous oils, were obtained in yields of >95%, and had properties as follows: IV, Found: C, 67.50; H, 5.61. $C_{37}H_{36}Fe_2S_2$ (656.51) calcd.: C, 67.69; H, 5.53%. NMR (ppm, $CDCl_3$): 3.40 (s, 4 H, $FcCH_2$); 3.61 (brs, 4 H, benzyl protons); 3.92 (brs, 2 H, benzhydryl methylene); 4.07 (br, 18 H, Fc); 7.15 (m, 8 H, phenyl). MS (*m/e*): 656(7), 458(37), 426(33), 232(26), 231(38), 227(25), 200(36), 199(100), 195(31), 165(20), 121(49), 56(20). IR (cm^{-1}, KBr): $\nu(CH_2)$ 2940s, 2880m, $\omega(CH_2S)$ 1240m; $\delta(CH)$ 1100s, 1040m, 1020s, 1000m; $\gamma(CH)$ 820s. V, Found: C, 66.58; H, 5.28. $C_{35}H_{32}Fe_2S_2$ (628.45) calcd.: C, 66.89; H, 5.13%. NMR (ppm, $CDCl_3$): 3.80 (two overlapping singlets, 6 H, CH_2); 4.02 (m, 18 H, Fc); 7.08 (q, 8 H, phenyl). MS (*m/e*): 628 (M^+, 4), 430(20), 232(20), 200(18), 199(100), 121(24), 43(34). IR (cm^{-1}, KBr): $\nu(CH_2)$ 2940s, 2880m; $\omega(CH_2S)$ 1235, $\delta(CH)$ 1100s, 1030s, 1010s, 995s; $\gamma(CH)$ 800s. VI, Found: C, 64.72; H, 4.50. $C_{34}H_{30}Fe_2OS_2$ (630.42) calcd.: C, 64.78; H, 4.80%. NMR (ppm, $CDCl_3$): 3.81 (s, 4 H, CH_2); 4.03 and 4.08 (two singlets, 18 H, Fc); 7.05 (q, 8 H, phenyl). MS (*m/e*): 630 (M^+, 3), 474(16), 460(17), 430(20), 354(15), 234(20), 200(22), 199(100), 121(24), 56(22), 43(28). IR (cm^{-1}, KBr): $\nu(CH_2)$ 2920m; $\omega(CH_2S)$ + $\nu(C—O)$ 1260s(br); $\delta(CH)$ 1110s, 1045m, 1030m, 1010m; $\gamma(CH)$ 835 s(br).

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