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Synthesis and some properties of diferrocenyl thioketones and dynamic behavior of some [1.1]ferrocenophane derivatives

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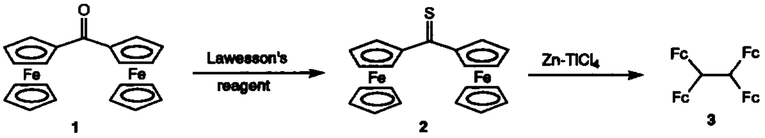
Abstract

Diferrocenyl ketone was thionated with a Lawesson's reagent to give the corresponding thioketone, which was reacted with $TiCl_4$-Zn to produce a desulfurative coupling compound. The similar reaction of [1.1]ferrocenophane-1,12-dione gave mono- and di-thiocarbonyl derivatives. [1.1]Ferrocenophane-1-one was also thionated efficiently. The dynamic behavior of some [1.1]ferrocenophane derviatives was discussed.

Introduction

Although it is well-known that the thiocarbonyl group has versatile properties [1,2], only a few ferrocene derivatives have been reported [3–6]. We here report the thiocarbonylation of diferrocenyl ketone and [1.1]ferrocenophane-1,12-dione and some properties of their thioketone products, and also the dynamic behavior of the [1.1]ferrocenophane thiones and referred [1.1]ferrocenophane-1-one derivatives.

Diferrocenyl ketone (**1**) was thionated with a Lawesson's reagent under conventional conditions to give diferrocenyl thioketone (**2**) as violet crystals in 71% yield. Because of the large deshielding effect of a thiocarbonyl group compared with a



Scheme 1.

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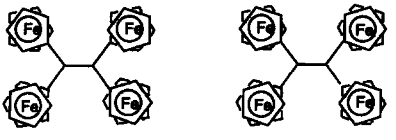


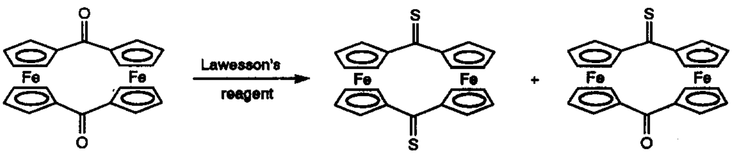
A B

Scheme 2.

carbonyl group, the α-protons of the substituted cyclopentadienyl (Cp) ring of the ferrocene nucleus appeared at the lower field (δ 5.21) in the ^{1}H NMR spectrum. Although **1** affords no coupling product in the reaction with a low valent titanium reagent (Zn-$TiCl_4$) [7], **2** reacted with Zn-$TiCl_4$ in tetrahydrofuran (THF) and the coupling product (**3**) was obtained in a low yield. Product **3** showed the molecular ion ($M^+ + 1$) at m/z 767 in the FAB mass spectrum. The ^{1}H NMR spectrum of **3** measured at room temperature showed a singlet due to the methine proton at δ 4.52, two singlets due to the protons of the unsubstituted Cp ring at δ 3.82 and 4.44, and the two sets due to the proton signals of the substituted Cp ring, in which one set resonated in a rather narrow region (δ 4.20, 4.24, 4.40, and 4.44) and the other set appeared in a rather wide region (3.25, 3.60, 3.97, and 4.27). The assignment of the signals was made by 2D COSY measurement. The NMR spectral data and the steric consideration suggest that **3** probably has a symmetrical structure **A** or **B** in which *geminal* ferrocenyl groups are *trans* to each other as shown in Scheme 2. No coupling compound was obtained by treatment of **2** with cyclopentadienyliron dicarbonyl dimer or cobalt tetracarbonyl in refluxing toluene, although the phenyl analogue was reported to give tetraphenylethylene under similar conditions [8].

[1.1]Ferrocenophane-1,12-dione (**4**) was reacted with 1.5 equivalents of Lawesson's reagent to give the dithio derivative (**5**) in 90% yield. Using a half equivalent of the Lawesson's reagent the monothio derivative (**6**) together with **5** were produced in 46 and 13% yields, respectively.

Compound **5** showed the molecular ion (M^+) at m/z 456 in the mass spectrum and the proton signals of the Cp rings appeared as multiplets at δ 4.02, 4.14, 4.22, and 4.79 in the ^{1}H NMR spectrum. No change in the NMR spectral pattern was observed in the temperature range from -40 to $+60$°C, indicating that **5** has a rigid structure, in contrast to fluxional **4** [9*]. This may be probably because of the large size of the sulfur atom and the length of the C=S bond compared with that of



4 5 6

Scheme 3.

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* Reference number with asterisk indicates a note in the list of references.

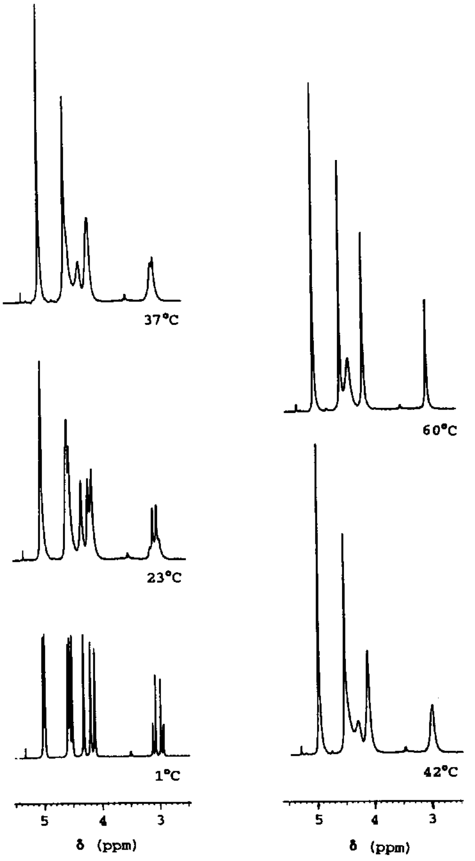


Fig. 1. Variable temperature 400 MHz NMR spectra of [1.1]ferrocenophane-1-one (7) in $CDCl_3$.

the C=O bond. Compound **6** showed the molecular ion (M^+) at m/z 440 in the mass spectrum. In the IR spectrum the carbonyl stretching appeared at 1604 cm^{-1}, but the absorption due to the thiocarbonyl group was not assigned. The ^1H NMR spectrum of **6** was broadened at room temperature and became more complex upon cooling but underwent no further significant changes below −5°C, indicating the presence of a similar dynamic process as observed in [1.1]ferrocenophane [10] and [1.1]ferrocenophane-1-one derivatives (see below). Treatment of **5** with tri-n-butylphosphine for 10 h at 150°C gave only the recovered starting material. When **5** was treated with Zn-$TiCl_4$, no coupling product was observed, and instead [1.1]ferrocenophane (4%), [1.1]ferrocenophane-1-one (**7**) (21%), and [1.1]ferrocenophane-1-one-12-thione (**6**) (trace) were obtained.

On the other hand, **4** was reacted with Zn-$TiCl_4$ in THF by action of an ultra sound to give [1.1]ferrocenophane-1-one (**7**) in 55% yield, which was previously prepared from MnO_2 oxidation of [1.1]ferrocenophane [11]. The ^1H NMR spectrum of **7** was also broadened at room temperature and became more complex upon cooling but showed no further change below 1°C (Fig. 1).

The eight signals for the ferrocenyl ring protons of **7** are observed at δ 5.33, 5.02, 4.98, 4.60, 4.57, 4.51, 4.32, 4.20, and 4.12 and the methylene protons

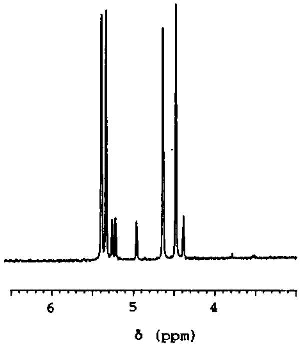
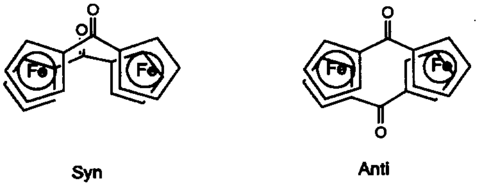
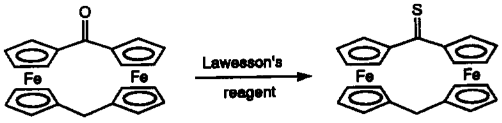


Fig. 2. ^{1}H NMR spectrum of [1.1]ferrocenophane-1,12-dione (**4**) at −41°C (400 MHz, $CDCl_3$).

resonated as an AB pattern at δ 3.09 and 2.94 at around 0°C. The activation energy ($\Delta G^\ddagger$) of the dynamic process for the conformational change in **7** was calculated from the coalescence temperature ($T_c = 315$ K) of the methylene protons to be 64.5 kJ/mol. It was reported [9] that **4** was also fluxional. In the ^{1}H VT–NMR spectrum of **4** in $CDCl_3$ the nearly averaged spectrum was observed at 60°C and the static spectrum corresponding to the one fixed conformer at −41°C. The activation energy ($\Delta G^\ddagger$) of the dynamic process for the conformational change of **4**, calculated from the coalescence temperature ($T_c = 303$ K) of the β ring proton signals in **4**, was 58.7 kJ/mol, whose value is somewhat smaller than that ($\Delta G^\ddagger = 64.5$ kJ/mol) of **7**. This may be explained by the different direction of bulkiness of the methylene group compared with the carbonyl group, since their bulk based on the van der Waals radii are nearly similar. The C–O bond of the carbonyl group is expanded in the same plane as the Cp ring of ferrocene, while the C–H bond of the methylene group is expanded in the plane perpendicular to the Cp ring of ferrocene. Curiously, one more set of the signals (δ 4.37, 4.94, 5.20, and 5.24) for the ferrocenyl ring protons appeared at the low-temperature spectrum of **4** (Fig. 2). These signals are coalesced with those of the main set for the ferrocenyl ring protons at about 10°C, and finally only the two signals (δ 4.50 and 5.27) are observed in the nearly averaged spectrum at 60°C. These signals seem therefore to be due to the existence of the *anti*-conformer in addition to the *syn*-conformer. The conversion between the conformers may be possible because of the differently expanded direction of bulkiness for a carbonyl group compared with that of a methylene group (see above), although the *anti*-conformer of [1.1]ferrocenophane is fixed and not exchangeable with the *syn*-conformer [10].



Scheme 4.



7 8

Scheme 5.

Ketone **7** was refluxed with a Lawesson's reagent in toluene to give the thiocarbonyl derivative (**8**) in 94% yield. Compound **8** gave the nearly sharp ^1H NMR spectrum even at room temperature, in which two sets of the proton signals of the Cp rings were observed. The fixed structure of **8** at low temperature seems to take a *syn* conformation similar to other [1.1]ferrocenophanes [10]. It is interesting to note that the thiocarbonyl compound **8** takes a fixed structure, while the carbonyl-thiocarbonyl compound **6** is fluxional at room temperature. The easier mobility of **6** compared with **8** is consistent with the fact described above that **4** is more fluxional than **7**.

Experimental

Melting points were measured with a differential scanning calorimeter (Seiko DSC-20). Electronic spectra were recorded on a Shimadzu UV2100 spectrophotometer. The IR spectra were taken with a Hitachi 270–50 IR spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-400 Spectrometer.

Materials. Diferrocenyl ketone [12] and [1.1]ferrocenophane-1,12-dione [11] were prepared according to the literature. The Lawesson's reagent was commercially obtained (Aldrich).

Diferrocenylthioketone (2). A solution of diferrocenyl ketone (150 mg, 0.38 mmol) and Lawesson's reagent (120 mg, 0.20 mmol) in benzene (30 ml) was refluxed for 3 h under nitrogen. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel by elution of dichloromethane to give the title compound as violet crystals which were recrystallized from hexane (112 mg, 71%). M.p. 135°C (dec.). Found: C, 60.95; H, 4.49%. $C_{21}H_{18}SFe_2$ calcd.: C, 60.91; H, 4.38%. ^1H NMR ($CDCl_3$): δ 4.19 (5H), 4.68 (2H), 5.21 (2H).

1,1,2,2-Tetraferrocenylethane (3). To a solution of low valent titanium prepared from zinc powder (72 mg, 1.1 g atom) and titanium (IV) chloride (0.06 ml, 0.55 mmol) in THF (distilled from lithium aluminium hydride) at −18°C, was added diferrocenylthioketone (124 mg, 0.3 mmol) at 0°C under nitrogen. The mixture was stirred for 10 h and then hydrolyzed with 10% aqueous potassium hydroxide (20 ml). After filtration, the organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue chromatographed on silica gel. The following three products were obtained: diferrocenyl-thioketone (**2**) (39.6 mg, 33%); diferrocenylmethane (41.3 mg, 36%); 1,1,2,2-tetraferrocenylethane (**3**) (11.5 mg, 10%). Yellow crystals (m.p. 277°C). Found: C, 65.86; H, 5.00%. $C_{42}H_{38}Fe_4$ calcd.: C, 65.84; H, 5.00%. ^1H NMR ($CDCl_3$): δ 3.25 (s, 2H), 3.80 (s, 2H), 3.82 (s, 10H), 3.97 (s, 2H), 4.20 (s, 2H), 4.24 (s, 2H), 4.27 (s, 2H), 4.40 (s, 2H), 4.44 (s, 10H), and 4.52 (s, 2H).

Thionation of [1.1]ferrocenophane-1,12-dione (4). A solution of **4** (127 mg, 0.3 mmol) and the Lawesson's reagent (180 mg, 0.45 mmol) in toluene (10 ml) was refluxed for 2 h under nitrogen. After the solution had been cooled, the resulting crystals of [1.1]ferrocenophane-1,12-dithione (**5**) were filtered. Yield: 123 mg (90%). Violet crystals (m.p. 386°C). Found: C, 58.16; H, 3.52%. $C_{22}H_{16}S_2Fe_2$ calcd.: C, 57.92; H, 3.53%. ^1H NMR ($CDCl_3$): δ 4.02 (s, 2H), 4.14 (s, 2H), 4.22 (s, 2H), and 4.79 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 76.52, 75.40, 75.24, and 69.44. The reaction of **4** (0.3 mmol) and the Lawesson's reagent (0.15 mmol) gave **5** (13 mg, 13%) and [1.1]ferrocenophane-1-one-12-thione (**6**) (34 mg, 46%). Violet crystals (m.p. 287°C). Found: C, 60.03; H, 3.83%. $C_{22}H_{16}OSFe$ calcd.: C, 60.04; H, 3.66%. ^1H NMR ($CDCl_3$, -5°C): δ 4.32 (s, 2H), 4.47 (s, 2H), 4.52 (s, 2H), 4.77 (2H), 5.12 (s, 2H), 5.27 (s, 2H), 5.33 (s, 2H), and 5.39 (s, 2H).

Reduction of 4 with low valent titanium. To a solution of low valent titanium prepared from zinc powder (246 mg, 3.6 g atom) and titanium(IV) chloride (0.2 ml, 1.8 mmol) in THF (distilled from lithium aluminium hydride) at -20°C, was added **4** (257 mg, 0.6 mmol) at 0°C under nitrogen. The ultra sound irradiation was applied for 4 h followed by hydrolysis with 10% aqueous potassium hydroxide (30 ml). The mixture was filtered, and the organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation, the residue was chromatographed on silica gel to give [1.1]ferrocenophane-1-one (**7**) (135 mg, 55%), along with a trace of [1.1]ferrocenophane. ^{13}C NMR ($CDCl_3$, -20°C): δ 195.92 (CO), 87.04, 80.37, 72.49, 71.93, 71.52, 70.51, 70.10, 69.35, 68.66, 68.10, and 20.42.

[1.1]Ferrocenophane-1-thione (8). A solution of **7** (60 mg, 0.15 mmol) and Lawesson's reagent (40 mg, 0.08 mmol) in toluene (15 ml) was refluxed for 1 h under nitrogen. After evaporation, the residue was chromatographed on silica gel to give **8** (60 mg, 94%) as violet crystals (m.p. 199°C). Found: C, 61.87; H, 4.35%. $C_{22}H_{18}SFe$ calcd.: C, 62.01; H, 4.26%. ^1H NMR ($CDCl_3$): δ 2.82 (d, $J = 20.9$ Hz, 1H), 2.93 (d, $J = 20.9$ Hz, 1H), 3.99 (m, 1H), 4.14 (m, 1H), 4.25 (m, 1H), 4.45 (m, 1H), 4.75 (m, 1H), 4.81 (m, 1H), 5.26 (m, 1H), and 5.17 (m, 1H).

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