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THE PREPARATION OF FERROCENETHIOCARBOXYLIC ACID DERIVATIVES AND THEIR SPECTRAL PROPERTIES

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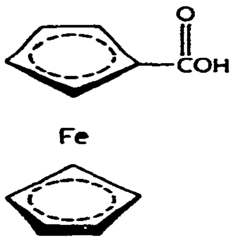
Summary

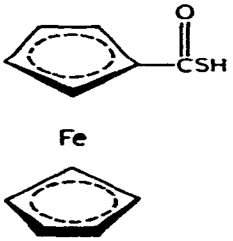
Ferrocenethiocarboxylic acid (FcCOSH) has been synthesized by the reaction of ferrocenecarboxylic acid chloride with sodium hydrogen sulfide. Treatment of this thioic acid and its ammonium salts with electrophiles gave derivatives such as phenylcarbamoyl ferrocenethiocarboxylate, methyl ferrocenethiocarboxy late, bis(ferrocenecarbonyl) disulfide and bis(ferrocenecarbonyl) sulfide in good yields.

Introduction

Although ferrocenecarboxylic acid (I) [1] and ferrocenedithiocarboxylic acid (III) [2] and their derivatives have been reported, the corresponding ferrocenethiocarboxylic acid (II) has not been described. The present paper describes the preparation of ferrocenethiocarboxylic acid (II) and various derivatives and reports pertinent spectral data.



(I)



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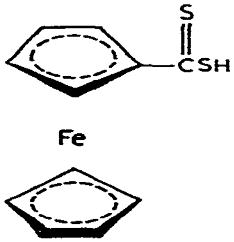

(III)

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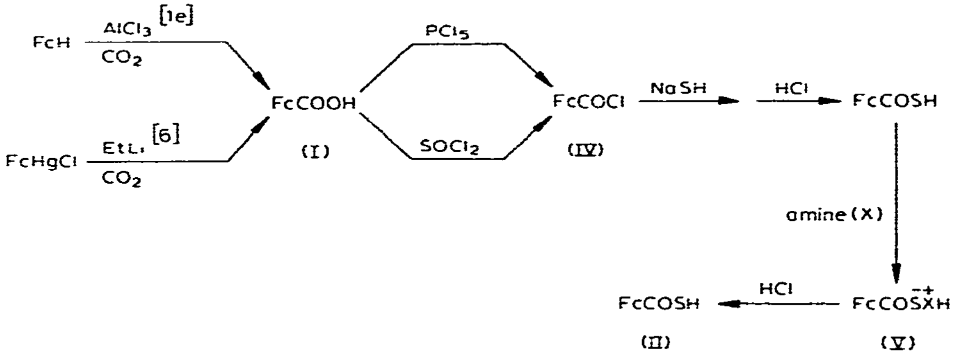
Results and discussion

Preparations

Ferrocenethiocarboxylic acid (II) and its ammonium salt (V) were prepared by the reaction sequence shown in Scheme 1.

SCHEME 1



Ferrocenecarboxylic acid chloride [3] (IV) was obtained as red-brown crystals by reaction of I and thionyl chloride in petroleum ether at reflux for 1.5 h. This material was used in the following reaction without further purification. Treatment of crude IV with an excess of ethanolic sodium hydrogen sulfide gave ferrocenethiocarboxylic acid (II) as dark purple crystals.

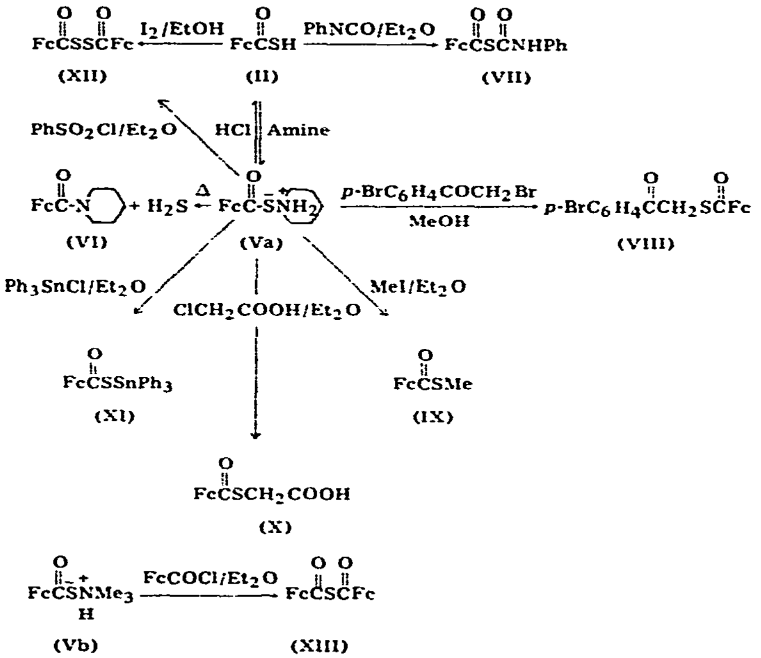
The reaction of II with amines such as piperidine and trimethylamine gave the corresponding piperidinium and trimethylammonium ferrocenethiocarboxylate (Va and Vb) in high yield. The ammonium salts V obtained were fairly stable crystalline solids and did not change on exposure to the atmosphere during more than 2 weeks. However, when salt Va was heated to above its melting point, it decomposed to *N*-pentamethylene ferrocenylcarbamide (VI) in 70% yield with the evolution of hydrogen sulfide. Moreover, these salts V reacted readily with a variety of electrophilic reagents to give the corresponding esters in good yields. Treatment of Va with alkyl halides having an electron-withdrawing group in the α-position, such as *p*-bromophenacyl bromide, methyl iodide and monochloroacetic acid, gave *p*-bromophenacyl ferrocenethiocarboxylate (VIII), methyl ferrocenethiocarboxylate [4] (IX) and α-thioferrocenyl acetic acid (X) in yields of 85, 43, and 54%, respectively. Va afforded the corresponding triphenyltin ester (XI) in 77% yield on treatment with triphenyltin chloride in dry ether. Bis(ferrocenecarbonyl) disulfide (XII) was obtained in 86% yield on treatment of Va with a catalytic amount of benzenesulfonyl chloride, or on treatment of Va with iodine. Vb was converted to bis(ferrocenecarbonyl) sulfide (XIII) in 93% yield on reaction with ferrocenecarboxylic acid chloride (VI) in dry ether. Moreover, thioic acid II reacted readily with phenyl isocyanate to give phenylcarbamoyl ferrocenethiocarboxylate (VII) in 60% yield.

These conversions are summarized in Scheme 2 and Table 1.

Spectral data

IR spectra. The infrared spectra of ferrocenethiocarboxylic acid (II) and its

SCHEME 2



esters (VIII—XIII) have two characteristic bands near 1650 (ν(C=O)) and 700 cm^{-1} (ν(C—S)). Generally, carbonyl stretching absorption bands for the RCO$_2^-$ group are observed around 1500 cm^{-1}, while ν(C=O) for their esters are seen at 1650—1750 cm^{-1}. Similar shifts toward low wave numbers would be expected for amine salts V. The amine salts V obtained in this study showed a strong absorption band near 1500 cm^{-1}, considered to be ν(C=O) of thiocarboxylate group (RCOS$^-$). The IR spectrum of phenacylcarbamoyl ferrocenethiocarboxylate (VII) did not show its N—H stretch in the expected range (3100—3400 cm^{-1}). Instead, we observed a new band near 2900 cm^{-1}, attributable to ν(N—H). Furthermore, a shift of the carbonyl stretching frequency of VII (ca. 45 cm^{-1}) to lower wave number, compared with that of corresponding thiocarboxylic acid (II), was observed. Such an unusually large shift in ν(N—H) and ν(C=O) suggests a structure containing an intramolecular hydrogen bond between oxygen and hydrogen (Fig. 1). The NMR spectrum of VII (NH, δ 11.5 ppm) further supported this suggestion.

UV and visible spectra. The absorption maxima (λ_{max}) and their molecular coefficients are listed in Table 1. Ferrocenethiocarboxylic acid derivatives have three characteristic maxima at 270—285 nm (ϵ 6000—15000), 330—350 (ϵ 700—2200), and 455—475 (ϵ 400—1400), respectively. It may be considered that the former two bands are due to the $\pi \to \pi^*$ transition and the third to the $n \to \pi^*$ transition of the carbonyl group. We have reported that the molecular extinction coefficients for the $n \to \pi^*$ transition of the thiocarbonyl group in the visible spectra of ferrocenedithiocarboxylic acid derivatives were 10—15 times

TABLE 1

YIELDS AND SOME PHYSICAL PROPERTIES OF FERROCENETHIOCARBOXYLIC ACID DERIVATIVES

No	Compound	Yield (%)	M.p. (°C)	Color [b]	Analysis (Found (calcd.)) (%)			
					C	H	S	N
II	FcCOSH	60 [a]	46—47	DP	53.56 (53.70)	4.04 (4.07)	13.09 (13.01)	
Va	$FcCOS^{-}cyclo\text{-}C_5\overset{+}{N}H_{12}$	62 [a]	120—121	OY	57.76 (58.04)	6.44 (6.35)	9.58 (9.67)	4.40 (4.23)
Vb	$FcCOS^{-}\ {}^{+}NHMe_3$	48 [a]	81—83	OY	55.01 (55.12)	6.30 (6.23)	10.29 (10.50)	4.65 (4.59)
VII	FcCOSCONHPh	66	82—83	RP	59.36 (59.21)	4.14 (4.11)	8.72 (8.77)	3.89 (3.84)
VIII	$p\text{-}BrC_6H_4COCH_2SCOFc$	85	128—130	OY	51.32 (51.50)	3.42 (3.39)	7.30 (7.23)	
IX [4]	FcCOSMe	54	42—43	OY	55.38 (55.43)	4.59 (4.62)	12.34 (12.32)	
X	$FcCOSCH_2CO_2H$	60	93—95	OY	51.18 (51.35)	4.00 (3.95)	10.45 (10.53)	
XI	$FcCOSSnPh_3$	84	135—136	RY	58.39 (58.55)	4.05 (4.04)	5.33 (5.38)	
XII	$(FcCOS)_2$	86	145—150 (dec.)	RY	53.99 (53.92)	3.70 (3.68)	13.10 (13.07)	
XIII	$(FcCO)_2S$	93	149—150	RY	57.85 (57.69)	3.97 (3.93)	7.04 (6.99)	
I	$FcCO_2H$							
III	$FcCS_2H$							
	PhCOSH							

[a] Isolated yield (based on the ferrocenecarboxylic acid (I) used). [b] DP: Dark Purple, OY: Orange Yellow, RP: Reddish Purple, RY: Reddish Yellow. [c] Solvent ethanol. [d] Shoulder. [e] Refs. 1a, 5. [f] Ref. 2.

greater than expected either for an aromatic dithioic acid or for ferrocenecarboxylic acid (I). In ferrocenethiocarboxylic acid derivatives, however, the enhanced extinction coefficients for the $n{\rightarrow}\pi^*$ transition of the carbonyl group were not observed. This result might indicate that the through-space interaction between the iron and carbonyl oxygen atom, or a conjugative effect of the

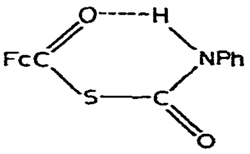


Fig. 1.

phenyltin chloride [7] were prepared according to literature procedures. The other reagents used were commercial materials. All solvents were carefully dried and distilled before use. New compounds were identified by their elemental analyses and spectral data (Table 1).

Preparation of ferrocenecarboxylic acid chloride (IV)

To a suspension of ferrocenecarboxylic acid (I) (460 mg, 2.0 mmol) in petroleum ether (b.p. 40—45°C) (20 ml) was added dropwise an excess of thionyl chloride (2.0 g, 16 mmol) at room temperature. The resulting mixture was stirred for 2 h at 50°C. The solvents were evaporated at reduced pressure, and the residue was extracted several times with petroleum ether. Evaporation of the petroleum ether extracts was followed by washing of the residual solid with a small portion of petroleum ether to give ferrocenecarboxylic acid chloride (IV) (320 mg, 64%, m.p. 48.0—49.0°C). IV was obtained as red crystals; IR (KBr): 1750 and 1725 cm^{-1} (ν(C=O)). It was used for the following reactions directly, without any further purification.

Preparation of piperidinium ferrocenethiocarboxylate (Va)

Two molar equivalents of freshly prepared sodium hydrogen sulfide in dry ethanol (30 ml) was added gradually to a solution of IV prepared from I (460 mg, 2.0 mmol) in petroleum ether (20 ml) under cooling with ice water. The resulting solution was stirred for 1 h. The reaction mixture was concentrated to about 1 ml and poured into 50 ml of 10% HCl at 5°C. This mixture was extracted with 50 ml of ether. The ether layer was separated and extracted with 50 ml of 10% KOH solution. The resulting dark red aqueous layer was acidified with 50 ml of 10% HCl and then extracted with 50 ml of ether at 5°C. The ether extracts were washed with water, dried over anhydrous magnesium sulfate and treated with 1.8 mmol of piperidine at 5°C. Filtration of the resulting residue and recrystallization from n-hexane/CH_2Cl_2 gave orange needle crystals of piperidinium ferrocenethiocarboxylate (Va) (410 mg, 62%).

Preparation of ferrocenethiocarboxylic acid (II)

Concentrated HCl (20 ml) was added to a suspension of salt Va (330 mg, 1.0 mmol) in ether (100 ml) and the mixture was shaken vigorously. The ether layer was separated, washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo gave dark purple crystals of pure ferrocenethiocarboxylic acid (II) (230 mg, 94%).

Thermolysis of piperidinium ferrocenethiocarboxylate (Va)

The piperidinium salt Va (330 mg, 1.0 mmol) was heated in a nitrogen-filled sealed tube without solvent at 130°C for 18 h. After cooling, the tube was opened. The presence of hydrogen sulfide was confirmed by the colorization of lead acetate paper. The decomposition products were Soxhlet-extracted with ether. Concentration of the extracts and filtration of the resulting precipitate gave 210 mg (70%, m.p. 129—130°C) of *N*-pentamethylene ferrocenylcarbamide as dark brown crystals, identified by means of its IR spectrum as well as by elemental analysis. Found: C, 64.77; H, 6.38, N, 4.56. $C_{16}H_{19}NOFe$ calcd.: C, 64.69; H, 6.40; N, 4.72%. IR (KBr) ν(C=O) 1615 cm^{-1}.

IR (KBr) (cm^{-1})			UV(CH$_2$Cl$_2$) λ max (nm)(ε max)		
ν(N—H) or ν(S—H)	ν(C=O)	ν(C—S)			
2475(SH)	1642	700	271(6500) [269(6300)	337(1700) 298(3600)^{d}	457(530) 464(680)]^{c}
3000—2250(NH)	1484	722	271(6100)	328(860)	456(390)
3450(NH)	1512	730	278(10900)	—	456(410)
	1598, 1700	694	283(10200)	353(730)	476(640)
	1642, 1688	700	280(13700)	—	457(560)
	1655	702	285(6000)	331(700)	455(360)
	1655, 1728	710	278(7600)	343(1950)	461(750)
	1608	698	279(8200)	341(890)	463(660)
	1678	700	282(15400)	343(2250)	462(1400)
	1658, 1688	698	280(11500)	355(710)	471(1200)
			261(4100)^{d} [	311(1000) 342(361)	448(220) 445(223)]^{c,e}
			265(6500) [264(5400)	319(9200) 319(7400)	556(2500) 554(1530)]^{c,f}
			248(9800) [243(7600)	— 290(5700)	— 419(55)]^{c}

ferrocenyl moiety through the bond to the carbonyl group, is of little importance in ferrocenethiocarboxylic acid and its derivatives.

Experimental

All melting points were obtained on a hot-stage type Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were recorded on the Hitachi R-24 (60 MHz) and R-22 (90 MHz) with tetramethylsilane as internal standard. IR spectra were measured on a JASCO grating infrared spectrophotometer IR-G. UV and visible spectra were obtained using a Hitachi 124 spectrophotometer. Microanalyses were carried out by the Elemental Analyses Center of Kyoto University.

Materials

Monochloromercuriferrocene [6], ferrocenecarboxylic acid [1e,6] and tri-

Reaction of ferrocenethiocarboxylic acid (II) with phenyl isocyanate

Phenyl isocyanate (120 mg, 1.0 mmol) was added dropwise to a solution of ferrocenethiocarboxylic acid (245 mg, 1.0 mmol) in dry ether (40 ml) and stirred for 2 h at room temperature. After removal of the solvent, filtration of the resulting crystalline precipitate and washing with small portions of ether gave 240 mg (60%) of phenylcarbamoyl ferrocenethiocarboxylate (VII).

Reaction of piperidinium salt Va with p-bromophenacyl bromide

Equimolar quantities of the piperidinium ferrocenethiocarboxylate (Va) (330 mg, 1.0 mmol) and *p*-bromophenacyl bromide (285 mg, 1.0 mmol) in methanol (20 ml) were stirred for 24 h at room temperature. Filtration of the precipitate which formed was followed by washing with water and methanol to give 380 mg (85%) of *p*-bromophenacyl ferrocenethiocarboxylate (VIII).

Reaction of piperidinium ferrocenethiocarboxylate (Va) with methyl iodide

A slight excess of methyl iodide was added to a solution of the salt Va (330 mg, 1.0 mmol) in dry ether (30 ml) and the mixture was stirred for 2 h at room temperature. After removal of the precipitate by filtration, evaporation of the filtrate and recrystallization of the resulting residue from n-hexane gave pure methyl ferrocenethiocarboxylate (IX) (140 mg, 54%).

Reaction of piperidinium ferrocenethiocarboxylate (Va) with monochloroacetic acid

A mixture of the piperidinium salt (Va) (330 mg, 1.0 mmol) and monochloroacetic acid (115 mg, 1.2 mmol) in dry ether (20 ml) was stirred for 2 h at room temperature. After filtering the insoluble solids, evaporation of the filtrate and recrystallization of the residue from ether/petroleum ether gave orange-yellow crystals of α-thioferrocenyl acetic acid (X) (180 mg, 60%).

Reaction of piperidinium ferrocenethiocarboxylate (Va) with triphenyltin chloride

Equimolar amounts of the salt Va (330 mg, 1.0 mmol) and triphenyltin chloride (380 mg, 1.0 mmol) in ether (20 ml) were stirred at room temperature for 3 h. Filtration of the precipitate, evaporation of the solvent and recrystallization of the resulting residue from ether/petroleum ether gave triphenyltin ferrocenethiocarboxylate (XI) (485 mg, 84%).

Reaction of piperidinium ferrocenethiocarboxylate (Va) with benzenesulfonyl chloride

To a suspension of the piperidinium salt Va (330 mg, 1.0 mmol) in ethanol (10 ml) was added four drops of benzenesulfonyl chloride, and the resulting solution was stirred for 1 h at room temperature under argon. The insoluble crystals were filtered and washed with water and ethanol to give 285 mg (86%) of pure bis(ferrocenecarbonyl) disulfide (XII). The melting point and IR spectrum agreed with those of an authentic sample prepared by treatment of the piperidinium salt Va with iodine [8].

Reaction of trimethylammonium ferrocenethiocarboxylate (Vb) with ferrocenecarboxylic acid chloride (IV)

The mixture of the salt Vb (305 mg, 1.0 mmol) and ferrocenecarboxylic acid chloride (IV) (250 mg, 1.0 mmol) in dry ether (10 ml) was stirred at room temperature for 1 h. Filtration of the precipitate and subsequent washing with water and ethanol, gave 440 mg (93%) of bis(ferrocenecarbonyl) sulfide (XIII).

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