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Synthesis and characterization of 1,1′-bis[1-(carboxymethyl)thioalkyl]ferrocenes and 1,1′-bis[1-(carboxymethyl)thio-1-phenylmethyl] ferrocene

D. Scutaru, I. Mazilu, Lucia Tătaru, Tatiana Lixandru and Cr. Simionescu

Department of Organic Chemistry, Polytechnic Institute of Iassy, Str. 23 August, Nr. 11,
6600 Iassy (Romania)

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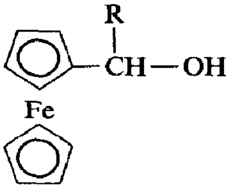
Abstract

The reactions of the 1,1′-bis(1-hydroxyalkyl)ferrocenes and 1,1′-bis(1-hydroxy-1-phenylmethyl)ferrocene with thioglycolic acid give the 1,1′-bis[1-(carboxymethyl)thioalkyl]ferrocenes and 1,1′-di[1-(carboxymethyl)thio-1-phenylmethyl]ferrocene which have been characterized by IR and ^{1}H NMR spectroscopy.

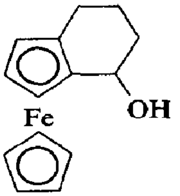
Introduction

The reaction of ferrocenylmethanol with thioglycolic acid, first investigated by Combs et al. [1], under rather vigorous conditions gives *S*-(ferrocenylmethyl)thioglycolic acid.

Ratajczak et al. [2,3] have made some *S*-modified derivatives of the thioglycolic acid, by its reaction with alcohols of type I[R = H, CH_3, C_2H_5, $CH(CH_3)_2$, C_6H_5], II or III in methylene chloride or acetone (solvent), in the presence of trifluoroacetic acid (TFA) for 12 h.



I



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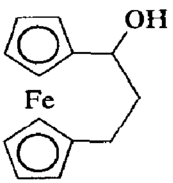
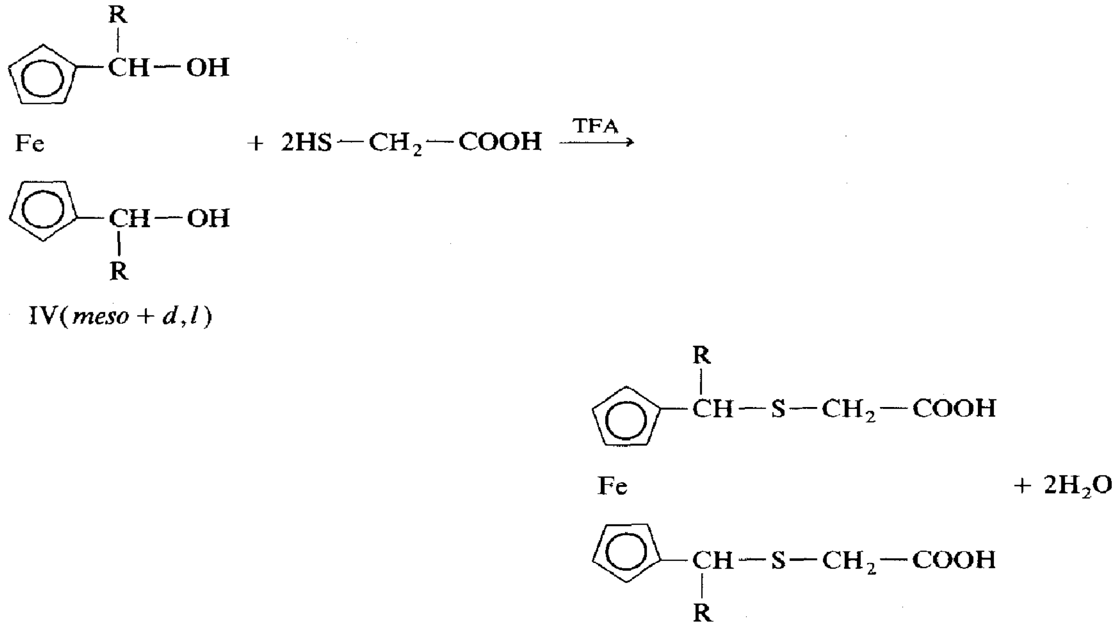


III

Results and discussion

The method proposed by Ratajczak was extended by us to the synthesis of a number of type V acids, starting from dihydroxylated derivatives of the type IV, according to the reaction:



IV(*meso* + *d*,*l*)

V(*meso* + *d*,*l*)

Attempts to separate the type V stereoisomers, by qualitative or preparative TLC were unsuccessful.

Owing to the low stability of the synthesized acids in the reaction medium, after 12 h there were some degradation products present; to avoid their formation, the conversion of the ferrocene derivative was followed by TLC (10/2 benzene-acetone). The obtained data show that the reaction occurs rapidly, at temperatures between 20 and 30 ° C, the transformation of the diols IV is almost complete after 10–15 minutes of reaction (when $R = C_6H_5$, the disappearance of the spot corresponding to the diol is observed after one minute).

In view of the extremely short reaction time, a series of the compounds as described by Ratajczak were synthesized, starting from the derivatives I the reaction was monitored by TLC. The reaction was usually complete after 10–15 minutes, and similar structures (IR, ^{1}H NMR) and in similar yields were obtained.

Chromatography of samples taken at intervals from the reaction mixture indicated that under certain conditions, some secondary by-products had formed. IR and ^{1}H NMR spectroscopy permitted assignment of a number of vinylic structures to the secondary products; probably formed by monomolecular eliminations (except when $R = C_6H_5$) that often accompany S_N^1 reactions.

The monomolecular character of the above mentioned reactions has been established by determining the kinetic parameters [4] of the exemplary reaction of 1-ferrocenylethanol with thioglycolic acid. The marked increase in the reaction rate observed when the substituent was modified, may be attributed to the increase in the stability of the α -ferrocenylalkyl or α -ferrocenylmethylphenyl cations that act as the intermediates.

The main characteristics of the synthesized products are listed in Table 1.

Table 1

Characteristics of some *S*-modified derivatives of the thioglycolic acid

No.	R	Yield (%)	m.p. (°C)	IR cm^{-1}		^1H NMR (in $CDCl_3$, δ, ppm)	Recrystallised from:
				C=O(s)	OH(w)		
1	CH_3	90	113	1700	2580 2690	1.72 (d, 6H, $-CH_3$), 3.25 (s, 4H, $-S-CH_2-$), 4.00 (q, 2H, CH), 4.22 (s, 8H, 1,1'-$C_{10}H_8Fe$)	toluene-n-hexane
2	CH_2CH_3	89	oil	1715	2585 2690	1.14 (t, 6H, $-CH_3$), 2.04 (m, 4H, $-CH_2-$), 3.16 (s, 4H, $-S-CH_2-$), 3.70 (t, 2H, CH), 4.12 (s, 8H, 1,1'-$C_{10}H_8Fe$)	–
3	$CH_2CH_2CH_3$	87	106–109	1710	2570 2685	1.08 (d, 6H, $-CH_3$), 1.76 (m, 8H, $-CH_2CH_2-$), 3.16 (s, 4H, $-S-CH_2-$), 3.74 (t, 2H, CH), 4.12 (s, 8H, 1,1'-$C_{10}H_8Fe$)	toluene
4	$CH(CH_3)_2$	80	97–100	1713	2565 2685	0.94 (d, 12H, $-CH_3$), 2.24 (m, 2H, $-CH$), 3.32 (s, 4H, $-S-CH_2-$), 3.86 (d, 2H, $-CH-S-$), 4.12 (s, 8H, 1,1'-$C_{10}H_8Fe$)	benzene-n-hexane
5	C_6H_5	75	oil	1705	2570 2680	3.05 (s, 4H, $-S-CH_2-$), 4.25 (s, 8H, 1,1'-$C_{10}H_8Fe$), 5.10 (s, 2H, $-CH$), 7.40 (m, 10H, $-C_6H_5$)	–

Experimental

Instrumentation

The ^1H NMR spectra were recorded on a JEOL 60 MHz instrument, in $CDCl_3$ solutions with TMS as internal standard. The IR measurements were performed by use of a Carl Zeiss UR 20 type spectrometer on solutions of the compounds in CCl_4. The melting points were determined with a Bõetius equipment and are uncorrected. The degree of purity of the obtained products was estimated by TLC, on Silicagel FG-254 supplied by Merck. The plates were activated at 110 °C for 1 h before use.

Starting materials

The diols IV were synthesized by reduction of the corresponding 1,1'-diacylferrocenes with $NaBH_4/CH_3OH$, and purified by chromatography on an Al_2O_3 column.

General procedures

To a solution of diol IV (30 mmol) in anhydrous CH_2Cl_2 (100 ml), was added thioglycolic acid (90 mmol (8.29 g)) and of TFA (0.05 ml). The mixture was stirred for 15 min at room temperature and the disappearance of the diol from the system was followed by TLC (10/2 benzene-acetone). The mixture was washed with water (3 × 25 ml) and extracted with saturated Na_2CO_3 solution. The aqueous phase was acidified with 10% HCl (*p*H ca. 4.5–5.0), extracted with CH_2Cl_2 (3 × 25 ml), dried over anhydrous $MgSO_4$, and then evaporated in vacuo. The oils that result slowly crystallise in the freezer. Purification was by recrystallisation (Table I).

References

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4 Unpublished results from this laboratory.