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STUDIES ON FERROCENE DERIVATIVES. XV. HYDROLYSIS OF DIESTERS CONTAINING A FERROCENE NUCLEUS

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STUDIES ON FERROCENE DERIVATIVES. XV. HYDROLYSIS OF DIESTERS CONTAINING A FERROCENE NUCLEUS*

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ABSTRACT

The hydrolysis of 1,1'-*bis*[ω -(methoxycarbonyl)alkanoyl]ferrocenes was carried out. In the compounds which have the same 1and 1'-substituents, the values of k_1 and k_2 were different. This may be caused by the electrostatic interaction between the two carbonyl groups.

INTRODUCTION

As part of the broad program investigating ferrocene derivatives, the present authors have investigated the rotation of the cyclopentadienyl (Cp) rings. The two Cp rings of an unsubstituted ferrocene freely rotate around the Cp–Fe–Cp bond axis in solution.^[2] When a substituent is introduced

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^{*}The previous part of this series can be found in Ref. [1].

on a Cp ring, it is interesting to speculate as to what happens to the rotation movement. Investigations of the ring rotation have been done by measuring the dipole moment. For example, in 1,1'-diacetyl- or dibenzoylferrocene, the free rotation of the Cp rings was reported.^[3] However, for the 1,1'-dihaloferrocenes, the rotation is restricted; the conformation in which two halogen atoms are adjacent to each other becomes unstable.^[4] Very few papers have been published on the influence of the ring rotation on the reaction of a substituent on the ferrocenyl group. In this work, the hydrolysis of 1,1'-*bis*[ω -(methoxycarbonyl)alkanoyl]ferrocenes (Fig. 1) was carried out. The results were discussed based on the specific structure of the ferrocene molecule on compared with an aliphatic dicarboxylic ester. Electrostatic interaction between the two carbonyl groups on the two Cp rings is proposed.

RESULTS AND DISCUSSION

Hydrolysis

The rate constants for the hydrolysis of the ferrocene derivatives and dimethyl sebacate are shown in Table I.

$$\begin{aligned} & \operatorname{Fc-[CO-(CH_2)_m-COOCH_3][CO-(CH_2)_n-COOCH_3]} \\ & \xrightarrow{k_1} \operatorname{Fc-[CO-(CH_2)_m-COOH][CO-(CH_2)_n-COOCH_3]} \\ & \xrightarrow{k_2} \operatorname{Fc-[CO-(CH_2)_m-COOH][CO-(CH_2)_n-COOH]} \end{aligned} \tag{Eq.1}$$



Figure 1. Compounds (1)-(4) and dimethyl sebacate.

	Table I. Rate Constants o	f Hydrolysis of Diesters	Containing a Ferroce	ne Nucleus	
Entries	Compounds	Conditions	$k_{1} \ (\times 10^{5} \text{sec}^{-1})$	$k_2 \; (\times 10^5 \text{sec}^{-1})$	$k_1/k_2 \\$
1	1,1'-bis[3-(Methoxycarbony])- pronanovllferrocene (1)	acid/MeOH	9.0 ± 0.4	9.0 ± 0.4	1.0
5	1,1'- <i>bis</i> [3-(Methoxycarbonyl)- nropanovllferrocene (1)	alkaline/MeOH	11.0 ± 0.5	3.9 ± 0.2	2.8
3	1,1'-bis[3-(Methoxycarbonyl)- propanovllferrocene (1)	alkaline/C ₆ H ₆	7.5 ± 0.3	7.5 ± 0.7	1.0
4	1,1'-bis[5-(Methoxycarbonyl)-	alkaline/MeOH	9.2 ± 0.3	4.8 ± 0.3	1.9
5	1,1'-bis[9-(Methoxycarbonyl)- nonanov]lferrocene (3)	alkaline/MeOH	5.1 ± 0.3	2.8 ± 0.3	1.8
9	1,1'-bis[9-(Methoxycarbonyl)- nonanovllferrocene (3)	alkaline/C ₆ H ₆	2.0 ± 0.1	2.0 ± 0.2	1.0
٢	1-[9-(Methoxycarbony])nona- noy]]-1'-[3-(methoxycarbo- nv])nronanov]]ferrocene (4)	alkaline/MeOH	5.6 ± 0.3	4.5 ± 0.3	1.2
8	Dimethyl Sebacate	alkaline/MeOH	2.1 ± 0.1	2.1 ± 0.1	1.0

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Acid or Alkaline Catalyzed Hydrolysis of 1,1'-*bis*[3-(Methoxycarbonyl)-propanoyl]ferrocene (1) in Methanol

No difference was recognized in the rate constants of the first and second step hydrolysis under acidic conditions (Table I, entry 1). Namely, the two methoxycarbonyl groups could be independently hydrolyzed under acidic conditions. In contrast, under alkaline conditions, the rate constant of the first step, k_1 , was greater than that of the second step, k_2 ; the first step reaction proceeded faster than the second step (Table I, entry 2).

To confirm whether or not this result is applicable to a compound not containing a ferrocene nucleus, the following experiments were performed. Considering that one ferrocenyl group corresponds to three methylene groups in length, an aliphatic dicarboxylic acid having a length equal to compound (1) is sebacic acid. The hydrolysis of dimethyl sebacate was then carried out under alkaline conditions.

Alkaline Catalyzed Hydrolysis of Dimethyl Sebacate

The rate constants, k_1 and k_2 , were approximately equal for the alkaline catalyzed hydrolysis of dimethyl sebacate that contains no ferrocene nucleus (Table I, entry 8). In general, the difference between the rate constants, k_1 and k_2 , of an aliphatic diester becomes smaller with increasing number of methylene groups between both ester groups.^[5] The hydrolysis by sodium hydroxide converts one ester group to COO⁻. The COO⁻ group electrostatically interacts with another ester group, so that the hydrolysis of this group is inhibited. However, for the higher members of diesters that have a longer methylene chain, for example, dimethyl sebacate, such an interaction is not possible. Thus, the two ester groups would be independently hydrolyzed, so that k_1 and k_2 were approximately equal.

Alkaline Catalyzed Hydrolysis of 1,1'-*bis*[5-(Methoxycarbonyl)pentanoyl]-(2) and 1,1'-*bis*[9-(Methoxycarbonyl)nonanoyl]ferrocene (3) in Methanol

The hydrolysis of compounds (2) and (3), which have longer methylene chains (n = 4 and 8), was carried out under alkaline conditions. A difference between k_1 and k_2 was recognized in compounds (2) and (3) as well as in compound (1) (Table I, entries 4 and 5). This was not noted for aliphatic dimethyl sebacate which has a shorter molecular length. The differences that lead to different rate constants may be caused by the structure of the diesters containing the ferrocene nucleus.

To ascertain whether or not a difference between the rate constants is found for unsymmetrically substituted ferrocenes, the hydrolysis was carried out with a ferrocene derivative which has different 1 and 1' substitutents.

Alkaline Catalyzed Hydrolysis of 1-[9-(Methoxycarbonyl)nonanoyl]-1'-[3-(methoxycarbonyl)propanoyl]ferrocene (4) in Methanol

The k_1 and k_2 values were approximately equal for the hydrolysis of compound (4) (Table I, entry 7). Thus, the hydrolysis of the two ester groups proceeded independently.

Interaction Between the 1- and 1'-Substituents of the 1,1'-bis[ω-(Methoxycarbonyl)alkanoyl]ferrocenes Comparison of Acid and Alkaline Catalyzed Hydrolysis

In general, under alkaline conditions, a methoxycarbonyl group is hydrolyzed to a carboxylate ion.^[5] In 1,1'-*bis*[ω -(methoxycarbonyl)alkanoyl]-ferrocenes, the formed carboxylate ion possibly can interact electrostatically with the remaining methoxycarbonyl group which has not been yet hydrolyzed (Fig. 2).

The alkaline catalyzed hydrolysis is initiated by the attack of a hydroxide ion to a carbonyl carbon. The attack would be inhibited by the interaction shown in Fig. 2. In the second step of the hydrolysis of the ferrocenes containing two ester groups, the attack of the hydroxide ion on another carbonyl carbon is sterically protected, so that the rate constant is lower than that of the first step. In contrast, under acidic conditions, the carboxyl group exists as the free acid form. Such an interaction found under alkaline conditions is impossible, so that both rate constants, the first- and the second steps, are approximately equal.



Figure 2. The interaction between methoxycarbonyl group and carboxylate ion.

To confirm the above discussion, the following experiment was done. In the presence of a crown ether, an alkaline hydrolysis was carried out in benzene solution. No differences were found between k_1 and k_2 for both compounds (1) and (3) (Table I, entries 3 and 6). Under these conditions, the hydroxide ion is not solvated, that is to say, it exists as a naked anion. The naked ion is sterically small,^[6] so that no steric hindrance to the attack of a carbonyl carbon appears, even under alkaline conditions, which results in the interaction shown in Fig. 2. As a result, no difference between the k_1 and k_2 rate constants would be recognized.

Chain-Length Effect

In compounds (1), (2) and (3), in which the 1- and 1'-substituents are the same, the values of k_1 and k_2 are different. This would be caused by the electrostatic interaction between the two carbonyl groups because these groups are adjacent to each other. In contrast, in compound (4) having different substituents, the two ester groups are sterically separated, so that no interaction occurs. Thus, each substituent will be independently hydrolyzed.

The values of k_1/k_2 for compounds (1), (2) and (3) were obtained. For compound (1), which has a shorter methylene chain (n = 2), this value was 2.8. For the higher members (n = 4 and 8), compounds (2) and (3), the values were 1.8–1.9. For the conformations in which the 1- and 1'-substituents are adjacent (Figs. 3a and 3a'), the two carbonyl groups are able to approach more easily than for the lower member compound (1). As a result, the interaction mentioned above easily occurs. Thus, compound (1) forces a stronger interaction between the two carbonyl groups.



Figure 3. The five antiprismatic conformers of 1,1'-disubstituted ferrocene.

On the other hand, in dimethyl sebacate, which is considered to have the same molecular length, no difference between k_1 and k_2 was found. Therefore, the interaction found in the ferrocene derivatives is not present in the aliphatic diester, which has no ferrocene nucleus but only a methylene chain.

Conclusion

In 1,1'-bis $[\omega$ -(methoxycarbonyl)alkanoyl]ferrocenes (1)–(3), the values of k_1 and k_2 were different. This would be caused by the electrostatic interaction between the two carbonyl groups. The result means that the two Cp rings of these ferrocenes are restricted to rotate around the Cp–Fe–Cp bond axis. Thus, the electrostatic interaction between the two carbonyl groups would suppress the rotation movement.

EXPERIMENTAL

Synthesis

The $[\omega$ -(methoxycarbonyl)alkanoyl]ferrocenes [compounds (1)–(4)] were prepared by known method.^[7,8] The compounds were identified by ¹H NMR, IR, and mass spectra. ¹H NMR was measured at room temperature using a JEOL A-400 spectrometer. IR spectra were recorded on a Shimadzu FTIR 8400 spectrometer. Mass spectra were obtained by a Shimadzu LCMS-QP8000 mass spectrometer. The ionization mode was that of the Atmospheric Pressure Chemical Ionization (APCI) method. The negative ion mode was used for the half esters and dicarboxylic acid and the positive mode for diesters. The data are shown in Tables II and III.

Hydrolysis

Acid Catalyzed Hydrolysis in Methanol

In a screw-capped test tube, 1.5 mL methanol, 1.5 mL H₂O and 10.5 mL of 0.12 N HCl were added. The tube was kept at 40 °C. A quantity of 0.12 mmol of a ferrocene derivative was dissolved in 10 mL methanol, and the solution was added to the test tube. When the materials were added, the rate measurement was initiated. Sampling of the reaction mixture was carried out at regular intervals. The amounts of the substrate and products were determined by HPLC.

Table II. Analytical and F	hysical Data of Su	ıbstitut	ed Ferrocer	les	
Compounds	Empirical Formulas	MM	Yield (%)	APCI-MS	Melting Points (°C)
1,1'-bis[3-(Methoxycarbonyl)propanoyl]ferrocene (1) 1-(3-Carboxypropanoyl)-1'-[3-(methoxycarbonyl)-	$C_{20}H_{22}FeO_6$ $C_{19}H_{20}FeO_6$	414 400	27 3.5	415 (M+1) 399 (M-1)	$162.0{-}163.5$
propanoyl]terrocene 1,1'-bis(3-Carboxypropanoyl)ferrocene	$\mathrm{C_{18}H_{18}FeO_6}$	386	36	385 (M-1)	179.3-181.0
1,1'-bis[5-(Methoxycarbonyl)pentanoyl]ferrocene (2)	$C_{24}H_{30}FeO_6$	400	19	471 (M+1)	113.9–114.5
1,1'-bis(5-Carboxypentanoyl)ferrocene	$C_{22}H_{26}FeO_6$	386	23	441 (M-1)	Ι
1,1'-bis[9-(Methoxycarbonyl)nonanoyl]ferrocene (3)	$\mathrm{C_{32}H_{46}FeO_6}$	582	20	583 (M+1)	80.5-82.2
1,1'-bis(9-Carboxynonanoyl)ferrocene	$\mathrm{C}_{30}\mathrm{H}_{42}\mathrm{FeO}_{6}$	554	29	553 (M-1)	1138.8-115.0
1-[9-(Methoxycarbonyl)nonanoyl]-1'-	$C_{26}H_{34}FeO_6$	498	19	499 (M+1)	Ι
[3-(methoxycarbonyl)propanoyl]ferrocene (4)					
1-(3-Carboxypropanoyl)-1'-[9-(methoxycarbonyl)-	$C_{25}H_{32}FeO_6$	484	1.2	483 (M-1)	Ι
nonanoyl]ferrocene					
1-(9-Carboxynonanoyl)-1-(3-carboxypropanoyl)-	$C_{24}H_{30}FeO_6$	470	20	469 (M-1)	72.3–74.1
ferrocene					

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Table III. ¹ H NMR ³	ind IR Data of Substituted Ferrocenes	
Compounds	Chemical Shifts (ppm)	$v(C=O)^d$ (cm ⁻¹)
1,1'- bis [3-(Methoxycarbonyl)propanoyl]ferrocene (1) ^a	4.89 (t, J = 7.9 Hz, 4 H), 4.59 (t, J = 7.9 Hz, 4 H), 3.78 (s, 6 H), 3.03 (t, J = 6.2 Hz, 4 H), 2.71 (t, J = 6.2 Hz, 4 H)	1736
1-(3-Carboxypropanoyl)-1'-[3-(Methoxycarbonyl)- propanoyl]ferrocene ^b	4.95 (t, J = 7.9 Hz, 4 H), 4.68 (t, J = 7.9 Hz, 4 H), 3.67 (s, 3 H), 3.31 (t, J = 6.2 Hz, 4 H), 2.65 (t, J = 6.2 Hz, 4 H)	1736, 1673
1,1'- <i>bis</i> (3-Carboxypropanoyl)ferrocene ^c	4.89 (t, J = 7.9 Hz, 4 H), 4.64 (t, J = 7.9 Hz, 4 H), 3.37 (t, J = 6.2 Hz, 4 H), 3.06 (t, J = 6.2 Hz, 4 H)	1673
1,1'-bis[5-(Methoxycarbonyl)pentanoyl]ferrocene (2) ^a	4.80 (t, J = 7.9 Hz, 4 H), 4.55 (t, J = 7.9 Hz, 4 H), 3.65 (s, 6 H), 2.39 (t, J = 6.2 Hz, 4 H), 2.35 (t, J = 6.2 Hz, 4 H), 1.70 (m, 8 H)	1730
1,1'- <i>bis</i> (5-Carboxypentanoyl)ferrocene ^b	4.80 (t, $J = 7.9$ Hz, 4 H), 4.55 (t, $J = 7.9$ Hz, 4 H), 2.35 (t, $J = 6.2$ Hz, 4 H), 2.35 (t, $J = 6.2$ Hz, 4 H), 1.70 (m, 8 H)	1667
1,1'- bis [9-(Methoxycarbonyl)nonanoyl]ferrocene (3) ^a	4.81 (t, J = 7.9 Hz, 4 H), 4.56 (t, J = 7.9 Hz, 4 H), 3.61 (s, 6 H), 2.73 (t, J = 6.2 Hz, 4 H), 2.31 (t, J = 6.2 Hz, 4 H), 1.63 (m, 8 H), 1.37 (m, 16 H)	1732
1,1'- <i>bis</i> (9-Carboxynonanoy1)ferrocene ^b	4.82 (t, $J = 7.9$ Hz, 4 H), 4.56 (t, $J = 7.9$ Hz, 4 H), 2.73 (t, $J = 6.2$ Hz, 4 H), 2.30 (t, $J = 6.2$ Hz, 4 H), 1.61 (m, 8 H), 1.37 (m, 16 H)	1678

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III.	
Table	

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Compounds	Chemical Shifts (ppm)	$v(C=O)^d$ (cm ⁻¹)
1-[9-(Methoxycarbonyl)nonanoyl]-1'-[3-(methoxy- carbonyl)propanoyl]ferrocene (4) ^a	4.84 (t, $J = 7.9$ Hz, 2H), 4.72 (t, $J = 7.9$ Hz, 2H), 4.58 (t, $J = 7.9$ Hz, 2H), 4.55 (t, $J = 7.9$ Hz, 2H), 3.67 (s, 3H), 3.65 (s, 3H), 3.05 (t, $J = 6.2$ Hz, 2H), 2.77 (t, $J = 6.2$ Hz, 2H), 2.60 (t, $J = 6.2$ Hz, 2H), 2.39 (t, $J = 6.2$ Hz, 2H), 1.65 (m, 4H), 1.35 (m, 8H)	1736
1-(3-Carboxypropanoyl)-1'-[9-(methoxycarbonyl)- nonanoyl]ferrocene ^b	$\begin{array}{l} 4.84 \ (t, \ J=7.9 Hz, \ 2 H), \ 4.72 \ (t, \ J=7.9 Hz, \ 2 H), \\ 4.59 \ (t, \ J=7.9 Hz, \ 2 H), \ 4.55 \ (t, \ J=7.9 Hz, \ 2 H), \\ 3.68 \ (s, \ 3 H), \ 3.07 \ (t, \ J=6.2 Hz, \ 2 H), \\ 2.77 \ (t, \ J=6.2 Hz, \ 2 H), \ 2.61 \ (t, \ J=6.2 Hz, \ 2 H), \ 2.38 \ (t, \ J=6.2 Hz, \ 2 H), \ 1.35 \ (m, \ 8 H) \end{array}$	1736, 1675
1-(9-Carboxynonanoyl)-1'-(3-carboxypropanoyl)- ferrocene ^b	4.85 (t, J = 7.9 Hz, 2 H), 4.72(t, J = 7.9 Hz, 2 H), 4.59(t, J = 7.9 Hz, 2 H), 4.55(t, J = 7.9 Hz, 2 H), 3.05(t, J = 6.2 Hz, 2 H), 2.75(t, J = 6.2 Hz, 2 H), 2.62(t, J = 6.2 Hz, 2 H), 2.38(t, J = 6.2 Hz, 2 H), 1.65(m, 4 H), 1.35(m, 8 H)	1675
^a in CDCI ₃ . ^b in acetone-d ₆ . ^c in DMSO-d ₆ . ^d The signals by carbonyl of ketone were not detected.		

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Alkaline Catalyzed Hydrolysis in Methanol

A quantity of 35 mL of methanol and 0.06 mmol of a ferrocene derivative were mixed in a three-necked flask and stirred at 40 °C. Five mL of 0.1 N NaOH were added to the flask. The same procedure as described above was then followed.

Alkaline Catalyzed Hydrolysis in Benzene

A quantity of 35 mL benzene, 0.24 mmol of ferrocene derivative and 2 mmol (0.53 g) 18-crown-6 were mixed in a three-necked flask and stirred at $40 \text{ }^{\circ}\text{C}$. Five mL of 0.4 N NaOH were added to the flask. The same procedure as mentioned above was followed.

Alkaline Catalyzed Hydrolysis of Dimethyl Sebacate in Methanol

A quantity of 135 mL of methanol and 5 mL of 1 N NaOH were mixed in a three-necked flask, and stirred at 40 °C. A 0.24 mmol (0.055 g) sample of dimethyl sebacate was dissolved in 5 mL of methanol, and the solution was added to the above flask. Titration with NaOH was carried out to determine the amount of methyl sebacate and sebacic acid.

Calculation of Rate Constants

The measurement of the hydrolysis rate was carried out at least two times. The values in Table I are the average of these results.

The concentration of acid or alkali was much higher than that of the esters. The rate constants were then calculated for a pseudo-first order reaction of the substrate. The first-step rate constant, k_1 , was calculated from the decrease of the amount of the 1,1'-*bis* derivative (diester). The second-step, k_2 , was determined as follows: in compounds (1) and (4) for which the half esters were synthesized, the hydrolysis of these half esters was carried out under the same conditions. The amount of the half esters was determined, and k_2 was calculated from the decrease of the amount of the half esters. In the other case, in which the corresponding half esters were not prepared, a simulation method^[9] was employed. The amount of the substrate and two products (half ester and dicarboxylic acid) were calculated from the experimental k_1 and a hypothetical k_2 , and then compared with the experimental values. The best-fitted values of k_2 were employed as calculated values.

REFERENCES

- Part XIV: Okada, Y.; Nakagawa, T.; Hayashi, T. Studies on Ferrocene Derivatives. XIV. Oxidation Reaction of (2,6-Disubstituted phenyl)ferrocenes. Inorg. Chim. Acta 2001, 312, 197–200.
- Richmond, H.H.; Freiser, H. The Electric Moments of Mono- and Diacetylferrocene. J. Am. Chem. Soc. 1955, 77, 2022–2023.
- Sorriso, S.; Lumbroso, H. Sur Les Conformations des Molecules de Diacetyl-1,1' et de Dibenzoyl-1,1'-ferrocenes. Tetrahedron 1970, 26, 2695–2701.
- Sorriso, S. Energy Barrier to Internal Rotation in Some Ferrocene Derivatives from Dielectric Measurements. J. Organomet. Chem. 1979, 179, 205–213.
- 5. Ritchie, M. Saponification of Diesters. J. Chem. Soc. 1931, 3112-3125.
- Pedersen, C.J. Cyclic Polyethers and their Complexes with Metal Salts. J. Am. Chem. Soc. 1967, 89, 2495–2496.
- Rinehard, K.L.; Curby, R.J.; Scokol, P.E. Organic Chemistry of Ferrocene. II. The Preparation of ω-Ferrocenyl Aliphatic Acids. J. Am. Chem. Soc. 1957, 79, 3420–3424.
- Dabard, R.; Patin, H. Contribution a l'Etude des Metallocenes. VII. Synthese et Etudes Physicochimiques de Diacyl-1,1'-ferrocenes et de Diacyl-2,1' et 3,1'-Alcoylferrocenes. Nouveaux Ferrocenophanes. Bull. Soc. Chim. Fr. 1973, 2158–2164.
- Noggle, J.H. Practical Curve Fitting and Data Analysis; PTR Prentice Hall, Inc.: Englewood Cliffs, New Jersey, 1993; 146–158.

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