The authors are grateful to Prof. Emeritus M. Ishidate of the Tokyo University and to Dr. T. Ukai, President of this college, for their kind encouragement during the course of this work. The authors are also indebted to Miss Y. Saito for the elementary analyses.

Summary

Formation of N-arylmethylene-1-acylamino-1-arylmethylamine resulted in some cases when aromatic aldehyde-ammonia mixture or hydrobenzamide was allowed to react with amide. In the light of this fact the mechanism comprehensive for all the reactions which lead to the formation of N-arylmethylene-1-acylamino-1-arylmetylamine was proposed.

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157. Koji Yamakawa, Hisao Ochi, and Kiichi Arakawa : Organometallic Compounds. I. Some Transformation Reactions of 1,1'-Diacetylferrocene.

(*Tokyo Research Institute, Yawata Iron & Steel Co., Ltd.*[*1])

Since the discovery of ferrocene[1~3] in 1951 it has been found by numerous chemical confirmations that the compound undergoes facile aromatic substitution reactions.[4]

Some transformation reactions of 1,1'-diacetylferrocene has been investigated as described below.

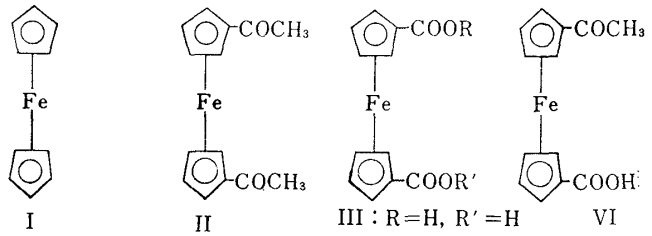
Ferrocene (I) used in these reactions was prepared by the diethylamine method described by Wilkinson,[5] though a more convenient sodium alkoxide method was reported recently by Eisenthal *et al.*[6]

1,1'-Diacetylferrocene[7~9] is one of the important disubstituted ferrocene intermediates which was first synthesized by Woodward and his co-workers,[7] employing with aluminum chloride as catalyst in the Friedel-Crafts reaction. By the modified procedure of Woodward, oxidation of 1,1'-diacetylferrocene (II) with sodium hypochlorite gave yellow sodium salt of 1,1'-ferrocenedicarboxylic acid (III) in a good yield, which was hydrolyzed to the dicarboxylic acid III.

*1 1618 Ida, Kawasaki, Kanagawa-Ken (山川浩司, 越智久雄, 荒川基一).

1) T.J. Kealy, P.L. Pauson : Nature, **168**, 1039 (1951).
2) S.A. Miller, J.A. Tebboth, J.F. Tremaine : J. Chem. Soc., **1952**, 632.
3) In this and subsequent papers from this laboratory, the generic name "ferrocene" will be used instead of the more formal dicyclopentadienyliron (II) [cf. R.B. Woodward, M. Rosenblum, M.C, Whiting : J. Am. Chem. Soc., **74**, 3458 (1952)].
4) For a reviews of the aromatic reactions of ferrocene, see *a*) P.L. Pauson : Quart. Revs., **9**, 409 (1955); *b*) A.N. Nesmeyanov, E.G. Perealova : Uspekhi Khim., **27**, 3 (1955); *c*) M.D. Rausch, M. Vogel, H. Rosenberg : J. Chem. Educ., **34**, 268 (1957); *d*) S. Yamada, M. Kumada, S. Hagiwara, H. Yamazaki : Kagaku, **14**, 358 (1959); *e*) K. Arakawa, K. Yamakawa : Kagaku no Ryoiki, **14**, 632 (1960); *f*) K. Plesske : Angew. Chem., **74**, 301, 347 (1962).
5) G. Wilkinson : Organic Syntheses, **36**, 34 (1956).
6) W.F. Little, R.C. Koestler, R. Eisenthal : J. Org. Chem., **25**, 1435 (1960).
7) R.B. Woodward, M. Rosenblum, M.C. Whiting : J. Am. Chem. Soc., **74**, 3458 (1952).
8) R. Riemschneider, D. Helm : Chem. Ber., **89**, 155 (1956).
9) G.D. Broadhead, J.M. Osgerby, P.L. Pauson : J. Chem. Soc., **1958**, 650.

Esterification of the diacid (III) with methanol saturated with dry hydrochloric acid in ice bath gave monomethyl ester (IV), m.p. 147~148°.[10] The structure of IV was determined by elementary analysis and from the properties of this product. The reaction mixture was heated for two hours to form the dimethyl ester (V).

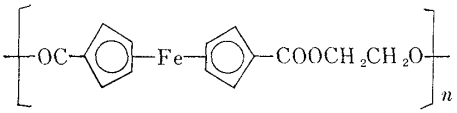


I II III : R=H, R'=H VI

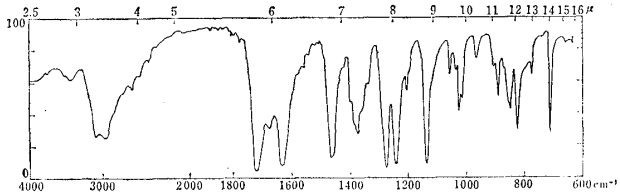
IV : R=H, R'=CH_3

V : R=CH_3, R'=CH_3

Recently, Knobloch and Rauscher,[11] and Okawara *et al.*[12] reported the condensation polymer of ferrocenes. Knobloch claimed that the polyester polymer of ferrocene was obtained from 1,1'-dimethylferrocene-carboxylate and ethylene glycol. However, the above polyester polymer has a low molecular weight and was soluble in organic solvents. Polycondensation reaction of ferrocene-1,1'-dimethyldicarboxylate (V) with ethylene glycol gave an orange brown powder of polyester polymer of ferrocene, which was insoluble in acetic acid, inconsistent with that obtained by Knobloch *et al.*[11]



Weinmayr[13] reported that oxidation of acetylferrocene with iodine in pyridine solution gave ferrocenecarboxylic acid. Therefore, 1,1'-diacetylferrocene (II) was treated with iodine in pyridine solution under the same condition. The reaction proceeded in a very smooth way and deep red crystals of m.p. 155~156° were obtained in a good yield. The pKa value 6.30 of this product agreed with that of a monoacid, considering the pKa values of ferrocenecarboxylic acid (6.78) and benzoic acid (6.32).[14] Its infrared spectrum showed strong bands at 1725 cm^{-1} (carboxylic acid) and 1637 cm^{-1} (acetylcarbonyl) in the carbonyl region. From its physical constants and elementary analysis, this compound was found to be 1-acetyl-1'-ferrocenecarboxylic acid (VI).[10,15]



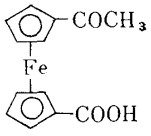


Fig. 1. Infrared Spectrum of 1-Acetyl-1'-ferrocenecarboxylic Acid (VI) (KBr Pellet)

10) A. N. Nesmeyanov, O. A. Reutov : Doklady Akad. Nauk SSSR, **115**, 518 (1958).
11) F. W. Knobloch, W. H. Rauscher : J. Polymer Sci. **54**, 651 (1961).
12) M. Okawara, Y. Takemoto, H. Kitaoka, E. Haruki, E. Imoto : Kogyo Kagaku Zasshi, **65**, 685 (1962).
13) V. Weinmayr : J. Am. Chem. Soc., **77**, 3009 (1955).
14) R. A. Benkeser, D. Goggin, G. Schroll : J. Am. Chem. Soc., **76**, 4025 (1954).
15) W. F. Little, R. Eisenthal : *Ibid.*, **82**, 1577 (1960).

The acetyl-carboxylic acid (VI) of ferrocene was not oxidized at low temperature, but oxidation with iodine-pyridine at 100° and treatment with diazomethane gave a diester of the dicarboxylic acid, which was prepared by Nesmeyanov, *et al.*[10]

Synthesis of divinylferrocene (VII) from diacetylferrocene was attempted by a method similar to that for monovinylferrocene.[16] 1,1′-Diacetylferrocene (II) was reduced with lithium aluminum hydride in absolute ether or tetrahydrofuran to 1,1′-bis(1-hydroxyethyl)ferrocene[17] (VIII). Dehydration of 1-hydroxyethylferrocene with alumina at 200° gave monovinylferrocene.[16] Treatment of 1,1′-bis(1-hydroxyethyl)ferrocene (VIII) through an alumina chromatographic column at room temperature gave yellow plates, m.p. 98~101°, but the product was unfortunately not divinylferrocene.

The authors[18] already suggested the predicted structure of a cyclic ether IX, which was determined by elementary analysis and from its infrared spectrum showing a strong band at 1068 cm^{-1}, attributable to a benzyl-type ether group.[19] After completion of our experiments, several workers[20~22] had observed that 1,1′-bis(1-hydroxyethyl)ferrocene (VIII) was easily converted to a cyclic ether IX and gave the same structure as ours.

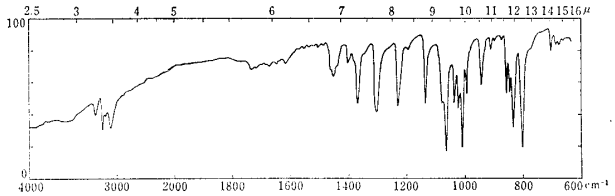


Fig. 2. Infrared Spectrum of 1,1′-(1,1′-Epoxydiethyl)-ferrocene (XI) (KBr Pellet)

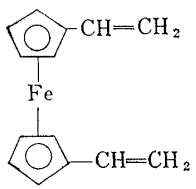
It is known that interesting heteroannular reactions, acyloin condensation[23] and dehydro-ring closure,[24] can be brought about between two cyclopentadienyl rings of ferrocene. The free rotation of ferrocene ring is completly restricted due to these cyclizations.

The cyclic ether (IX) consisted of a six-membered quasi-tetrahydropyran ring in which the central iron atom is linked to each carbon atom which formed 1-hydroxyethyl group before cyclization. Thus, the cyclic ether (IX) might have a stable quasi-eclipsed conformation. Therefore, the cyclic dimethylether IX might have *cis* and *trans* stereoisomers (*e.g.* X and XI) with reference to the two methyl groups.

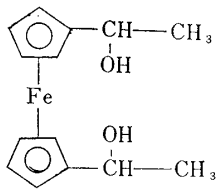
The acetyl group in 1,1′-diacetylferrocene (II), which was used as the starting material, is considered to have a steric hindrance due to the Van der Waals radii and electronic carbonyl-carbonyl repulsion between acetyl groups in the ferrocene ring. It is plausible that its more favored conformation is a *trans* form for methyl groups in 1,1′-diacetylferrocene (II). The diacetylferrocene was reduced with lithium aluminum hydride predominantly to a diol VIII. Only one of the stereoisomers was obtained.

16) F.S. Arimoto, A.C. Haven : J. Am. Chem. Soc., **77**, 6295 (1955).
17) P.J. Graham, R.V. Lidsay, G.W. Parshall, M.L. Peterson, G.W. Shitman : *Ibid.*, **79**, 3416 (1957).
18) See reference 4e p. 637.
19) L.J. Bellamy : "The Infra-red Spectra of Complex Molecules" 2nd ed. p. 114 (1958), Mathuen Co., Ltd. London.
20) T.A. Mashburn, C.R. Hauser : J. Org. Chem., **26**, 1671 (1961).
21) E.C. Winslow, E.W. Brewster : *Ibid.*, **26**, 2982 (1961).
22) K. Schögl, Mohr : Monatsh., **92**, 219 (1961).
23) K. Schögl, H. Seiler : *Ibid.*, **91**, 79 (1960).
24) K.L. Reinhart, *et al.* : J. Am. Chem. Soc., **79**, 2748, 3290 (1957); K. Schögl, H. Seiler : Tetrahedron Letters, No. 7, 4 (1960).

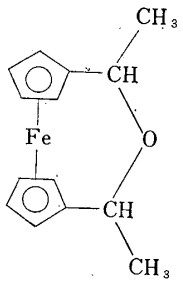
Hill and Richards[25] considered that 1-hydroxyethylferrocene is predominantly in the form of ψ-endo-configuration (XII) from its infrared spectrum.[26] Assuming that diacetylferrocene (II) would be attacked by the hydride ion from outside the two cyclopentadienyl rings for the central iron atom, this reduction might be controlled exclusively by the steric factor. Infrared spectrum in carbon disulfide solution of the diol (VIII) showed a broad band at 3310 cm^{-1}. Thus, each of the hydroxyl groups has a stable endo configuration, because the hydroxyl groups is bonded directly to the central iron atom by hydrogen bonding.



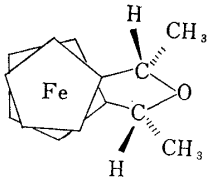
VII



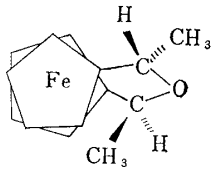
VIII



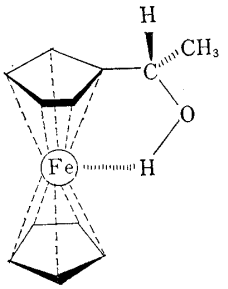
IX



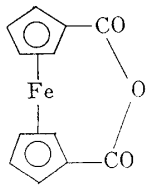
X



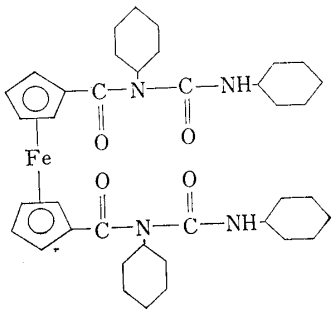
XI



XII



XIII



XIV

25) E. A. Hill, J. H. Richards : J. Am. Chem. Soc., 83, 4216 (1961).
26) D. S. Trifan, R. Bacskai : *Ibid.*, 82, 5010 (1960).

Dehydration of the diol (Ⅷ) with alumina or *p*-toluenesulfonyl chloride in benzene solution gave a cyclic ether (Ⅸ.) Consequently, it is concluded that there is a *trans*-methyl groups (Ⅺ) in the cyclic dimethyl ether (Ⅸ).

Richards and Curphey[27] previously reported that 1,2-ferrocenedicarboxylic acid was converted to the anhydride by treatmeant with N,N′-dicyclohexylcarbodiimide in anhydrous acetone solution. Assuming that 1,1′-ferrocenedicarboxylic acid (Ⅲ) might be possibly a heteroannular anhydride (Ⅻ), the dicarboxylic acid (Ⅲ) was attempted by treatment with N,N′-dicyclohexylcarbodiimide in anhydrous acetone or dioxane solution. But the product obtained as orange yellow crystals, m.p. 203～205°, was not the anhydride, since its infrared spectrum did not show the anhydride band in 1800 cm^{-1} region.[19] The compound was found to contain nitrogen by elementary analysis and from its infrared spectrum. This was proved to be an addition compound N,N′-dicyclohexyl-N,N′-bis (cyclohexylcarbamoyl)-1,1′-ferrocenedicarboxamide (XIV). The structure of this addition compound (XIV) was supported by a report on a similary addition reaction of ferrocenecarboxylic acid and N,N′-dicyclohexylcarbodiimide.[28]

Recently, Nesmeyanov and Reutov[29] synthesized 1,1′-ferrocenedicarboxylic anhydride (Ⅻ) from 1,1′-ferrocenoyl chloride with water and pyridine.

Experimental*2

Ferrocene (I)——a) According to the modification of the procedure described by Wilkinson,[5] the procedure for isolation of ferrocene from the reaction products was improved. The crude ferrocene was subjected to steam distillation and recrystallization from EtOH gave orange prisms, m.p. 171～172°. IR ν_{max}^{KBr} cm^{-1} : 3075, 1408, 1101, 992, 810 (CH); UV λ_{max}^{EtOH} mμ (ε) : 323 (57), 439 (102).

b) According to the procedure described by Eisenthal, *et al.*[6] freshly distilled cyclopentadiene*3 and EtONa in abs. EtOH were added to activated $FeCl_2$. Ferrocene (I) m.p. 170～173°(reported[5] m.p. 173～174°), was obtained in 80% yield.

1,1′-Diacetylferrocene (II)——According to the procedure reported by Reimschneider and Helm,[8] freshly distilled 64.5 cc. of AcCl and 70.0 g. of ferrocene in dry CS_2 (450 cc.) were slowly added with vigorous stirring to 150 g. of anhyd. $AlCl_3$ suspended in 600 cc. of dry CS_2. The reaction mixture was refluxed with stirring for 4 hr. and allowed to stand over night. Then the mixture was poured into ice water to precipitate 92 g. of red crystals of 1,1′-diacetylferrocene, m.p. 102～124°.

Recrystallization from benzene-hexane gave 75 g. (73.5%) red needles, m.p. 122～124°(reported[7,8] m.p. 130～131°). IR ν_{max}^{KBr} cm^{-1} : 1660, 1115 ($COCH_3$), UV λ_{max}^{EtOH} mμ (ε) : 263 (12,000), 461 (530).

1,1′-Ferrocenedicarboxylic Acid (III)——a) With NaOCl : Cl_2 gas was passed through a solution of NaOH in distilled H_2O in ice bath. After absorption 19 g. of Cl_2 gas, 80 cc. of MeOH was added. To this solution 160 cc. of MeOH solution of 7.0 g. of diacetylferrocene was added with stirring at 5° during 30 min. and the temperature was raised to 50° over a period of 35 min. Cooling and filtration of the reaction mixture gave yellow crystals of the Na salt of the diacid (Ⅲ). The Na salt was dissolved in 80 cc. of H_2O and acidification with 10% HCl gave orange red crystals, m.p. 210° (subl.) (kofl.), in a quantitative yield (7.95 g.). Recrystallization from AcOEt gave orange red prisms, m.p. 240°(decomp.), yield, 6.2 g. (87.5%). pKa 6.80 (25°, 50% MeOH). IR ν_{max}^{KBr} cm^{-1} : 1690, 1403 (COOH). UV λ_{max}^{EtOH} mμ (ε) : 255 (9,900), 445 (300). *Anal.* Calcd. for $C_{12}H_{10}O_4Fe$: C, 52.57; H, 3.65; O, 23.32. Found : C, 52.72; H, 3.74; O, 23.46.

b) With NaOI : To 2.7 g. of diacetylferrocene (Ⅱ) in 60 cc. of MeOH solution I_2 16 g. in 16 cc. of MeOH and NaOH-MeOH solution (NaOH 10.0 g., H_2O 15 cc. and MeOH 20 cc.) were added with stirring at 50° during 1 hr. The reaction mixture was allowed to stand overnight and concentrated to half its volume in a reduced pressure. To this solution 100 cc. of H_2O was added and extracted with Et_2O.

*2 All melting points are uncorrected. Infrared spectra were measured with a Nippon Bunko Model IR-S and Hitachi Model EPI-2 double-beam spectrophotometers. Ultraviolet spectra were measured with a Beckman Model DB double beam spectrophotometer.

*3 The authors thank the Yawata Chemical Industry Co., Ltd., for supplying 98% dicyclopentadiene.

27) J. H. Richards, T. J. Curphey : Chem. & Ind. (London), **1956**, 1456.
28) H. H. Lau, H. Hart : J. Org. Chem., **24**, 280 (1959); E. M. Acton, R. M. Silverstein : *Ibid.*, **24**, 1487 (1959).
29) N. A. Nesmeyanov, O. A. Reutov : Doklady Akad. Nauk SSSR, **120**, 1267 (1958).

The extract was washed with 10% $Na_2S_2O_3$ and was reextracted with 10% NaOH. Removal of Et_2O left a dark orange red solid which was identified with the starting material (II) by IR spectrum.

The above alkaline solution was acidified with HCl, extracted with Et_2O, and the extract was dried. Evaporation of Et_2O gave orange red crystals (1.58 g.). Recrystallization from AcOEt gave 1.55 g. (56.5%) of orange red prisms, m.p. 240° (decomp.). It was identified by IR spectrum with the dicarboxylic acid (III) obtained by the above method a).

Esterification of the Diacid (III)——a) A solution of 0.3 g. of the above diacid (III) in 100 cc. of abs. MeOH was saturated with dry HCl with cooling (−8 to −3°) and poured into ice water. The separated orange yellow crystalline solid (0.05 g.), m.p. 240°, was identified with the starting diacid (III) by IR spectrum. The filtrate was extracted with $CHCl_3$. The extract was dried, and evaporated in a reduced pressure. There was obtained 0.2 g. (63.5%) of the monomethyl ester (IV) (m.p. 142~145°) of III, soluble in 5% $NaHCO_3$. Recrystallization from benzene-benzin (1:1) afforded 0.1 g. (31.7%) of yellow needled, m.p. 147~148°. *Anal.* Calcd. for $C_{12}H_{12}O_4Fe$: C, 54.45; H, 4.16. Found : C, 54.63; N, 4.46.

b) A solution of 5.0 g. of the diacid (III) in 950 cc. of abs. MeOH, saturated with dry HCl by the above procedure a), was refluxed for 2 hr. and concentrated under reduced pressure at 40°. The residue was poured into ice water and 4.88 g. of the dimethyl ester (V) separated as a yellow crystalline solid, m.p. 102~108°. Recrystallization from petr. benzin afforded 4.5 g. (82%) of yellow orange needles, m.p. 112~115°. IR : ν_{max}^{KBr} 1704 cm^{-1}(COOMe). UV λ_{max}^{EtOH} mμ (ε) : 277 (10,000), 446 (340). *Anal.* Calcd. for $C_{14}H_{14}O_4Fe$: C, 55.66; H, 4.67. Found : C, 55.98; H, 4.95.

Polycondensation of Dimethyl Ester (V) and Ethylene Glycol[30]——In a polymer tube bearing a side arm 0.3 g. of the dimethyl ester (V), 0.3 g. of freshly distilled ethylene glycol, 0.002 g. of $(AcO)_2Ca \cdot H_2O$, and 0.0005 g. of Sb_2O_3 were placed. The tube was partially immersed in an ethylene glycol bath to allow the mixture to melt at 110° and a capillary tube was inserted to the bottom of the tube. A stream of N_2 was passed through the melt and the reaction mixture changed its color to brown black. After heating at 175~178° for 3 hr., the polymer tube was transferred to a diethyl terephthalate bath whose temperature was raised to 283° over a period of 30 min. The mixture was heated for further 2.5 hr. at 283° at 30 to 8 mm. Hg pressure. When cooled, the products was washed with excess Et_2O in a soxhlet apparatus and 0.2 g. of dark brown powder, m.p. ca. 200° (a part sublimed), was obtained. This compound was insoluble in benzene, Et_2O, CCl_4, CS_2, MeOH, EtOH, AcOEt, and dimethylformamide, and slightly soluble in AcOH and $CHCl_3$. IR ν_{max}^{Nujol} cm^{-1} : 1720 (s), 1705 (s), 1260 (s), 1130 (m, broad), 1075 (m, broad).

Oxydation of II with Iodine and Pyridine——To a solution of 10.0 g. of diacetylferrocene (II) in 25 cc. of pyridine, 11.0 g. of I_2 was added with stirring at room temperature, and after 3 hr., additional 10 cc. of pyridine was added to prevent solidification and stirred for 8 hr. The reaction mixture was allowed to stand overnight, extracted with 10% KOH, and acidified with 10% HCl to precipitate 11.1 g. of light brown solid.

The solid was dissolved in AcOEt and filtered. The filtrate was extracted with 10% NaOH and acidified with 10% HCl to 3.3 g. (33%) of scarlet prisms, m.p. 155~156°, of 1-acetyl-1'-ferrocenecarboxylic acid. IR ν_{max}^{KBr} cm^{-1} : 1725 (COOH), 1637 ($COCH_3$). UV λ_{max}^{EtOH} mμ (ε) : 227 (14,200), 455 (420). *Anal.* Calcd. for $C_{13}H_{12}O_3Fe$: C, 57.38; H, 4.45. Found : C, 56.91; H, 4.49.

A solution of 2.5 g. of the monoacetylmonocarboxylic acid (VI) in 160 cc. of abs. MeOH was saturated with dry HCl in an ice bath and allowed to stand over night in a refrigerator. This was evaporated to half its original volume under reduced pressure at 40°. The residue was poured into ice water, extracted with Et_2O, and the extract was washed with 5% $NaHCO_3$ and H_2O. The Et_2O was evaporated to leave 2.3 g. (85.2%) of the methyl ester, m.p. 76~84°, of the (V). Recrystallization from Et_2O afforded orange red prisms, m.p. 91~94°. UV λ_{max}^{EtOH} mμ (ε) : 277 (14,000), 455 (430). *Anal.* Calcd. for $C_{14}H_{14}O_3Fe$: C, 58.77; H, 4.93; O, 16.78. Found : C, 58.49; H, 5.19; O, 17.35.

Further oxidation of the above acetyl-carboxylic acid (VI) under the same condition for 24 hr. and treatment with the above procedure afforded 2.0 g. of a crude solid. The solid which was immediately dissolved in 80 cc. of abs. MeOH was esterified and afforded orange red prisms, m.p. and mixed m.p. 80~86° with the authentic methyl ester of V.

1,1'-Bis(1-hydroxyethyl)ferrocene (VIII)——This was prepared by the modified procedure of that described by Graham, *et al.*[19] To a suspension of 1.0 g. of $LiAlH_4$ in 50 cc. of abs. tetrahydrofuran 2.5 g. of diacetylferrocene (II) was added with stirring at room temperature. The mixture was refluxed for 2 hr. on a steam bath. When cooled, AcOEt was added to destroy the excess reagent. A mixture of 0.6 cc. of H_2O, 4 cc. of EtOH, and 8 cc. of Et_2O was then cautiously added to the above mixture and resulting yellow suspension was filtered, washed well with Et_2O, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a crystalline solid, m.p. 64~67°, which was taken up in hot hexane. Cooling of the hexane solution in a refrigerator gave 2.85 g. (74%) of the glycol (VIII) as yellow

30) cf. W. R. Sorenson, T. W. Cambell : "Preparative Methods of Polymer Chemistry" p. 113 (1961) Interscience Publishers, Inc., Now York.

needles, m.p. 69～71°. (reported[19] m.p. 69～71°). IR $\nu_{max}^{CS_2}$ cm^{-1}: 3310, 1365, 1097 (OH); ν_{max}^{KBr} cm^{-1}: 3300, 1365, 1098 (OH). UV λ_{max}^{EtOH} mμ (ε): 322 (150), 429.5 (150).

1,1′-(1,1′-Epoxydiethyl)ferrocene (IX)——a) With Ac_2O: To a solution of 3.0 g. of the glycol (X) in 10 cc. of dry pyridine 4 cc. of Ac_2O was added with cooling. After standing overnight at room temperature, the reaction mixture was poured into ice water, extracted with benzene, and the solvent was evaporated from the extract under reduced pressure to leave a semi-solid. The product was dissolved in benzene-petr. ether and chromatographed on 50 g. of alumina, employing petr. ether as the eluent. Orange yellow plates, m.p. 98～102°, were obtained. IR ν_{max}^{KBr} cm^{-1}: 1138, 1068 (-CH_2-O-CH_2-). UV λ_{max}^{EtOH} mμ (ε): 319 (110), 440 (140). *Anal.* Calcd. for $C_{14}H_{16}OFe$: C, 65.52; H, 6.25. Found: C, 65.01; H, 6.26.

b) With *p*-toluenesulfonyl chloride: A solution of 0.1 g. of the glycol (X) in 50 cc. of benzene and 0.01 g. of *p*-toluenesulfonyl chloride was refluxed for 30 min. The reaction mixture was poured into ice water and washed with 5% $NaHCO_3$ and H_2O. The benzene layer was dried and evaporated in a reduced pressure to give 0.092 g. (98.5%) of a crystalline solid, m.p. 90～98°. Recrystallization from EtOH gave yellow plates, m.p. 98～101°. It showed no depression of the melting point on admixture with the cyclic ether (IX) from the above method a).

c) From diacetylferrocene (II): To a solution of 0.12 g. of $LiAlH_4$ in 30 cc. of abs. Et_2O, 1.0 g. of diacetylferrocene (II) was added with stirring at room temperature. The reaction mixture was refluxed for 3 hr. and allowed to stand overnight. Dilute HCl was added to destroy the reagent. The ethereal layer was washed with H_2O, dried over Na_2SO_4, and evaporated to give yellow platet, m.p. 90～98°. with the authentic sample of the cyclic ether (IX).

N,N′-Dicyclohexyl-N,N′-bis(cyclohexylcarbamoyl)-1,1′-ferrocenedicaboxamide (XIV)——To a solution of 0.2 g. of 1,1′-ferrocenedicarboxylic acid (III) in 60 cc. of anhyd. Me_2CO 0.25 g. of N,N′-dicyclohexylcarbodiimide was added with stirring during 8 hr. at room temperature. There was obtained 0.19 g. of orange yellow crystals, m.p. 201～205°. Recrystallization from EtOH-$CHCl_3$ afforded orange prisms, which melt in the range of 203～205.2, solidified on further heating, and kept solid form until at least 300°. This product was soluble in benzene and $CHCl_3$, slightly soluble in Me_2CO and AcOEt, and insoluble in Et_2O, petr. benzin, and 10% $NaHCO_3$. *Anal.* Calcd. for $C_{38}H_{54}O_4N_4Fe$: C, 66.46; H, 7.93; N, 8.16. Found: C, 66.64; H, 8.02; N, 8.55. IR λ_{max}^{Nujol} cm^{-1}: 3220 (NH), 1700, 1595, 1535, 720(-CONH-).

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Summary

Oxidation of 1,1′-diacetylferrocene with sodium hypochlorite and iodine-pyridine gave 1,1-ferrocenedicarboxylic acid (III) and 1-acetyl-1′-ferrocenecarboxylic acid (VI), respectively. The polyester polymer of ferrocene was obtained from dimethyl-1,1′-ferrocenecarboxylate (V) and ethylene glycol. 1,1′-Bis(1-hydroxyethyl)ferrocene (VIII) was converted to 1,1′-(1,1′-epoxydiethyl)ferrocene (IX) by chromatographic method or with *p*-toluenesulfonyl chloride. Stereochemistry of the cyclic dimethyl ether (IX) is discussed. Treatment of 1,1′-ferrocenedicarboxylic acid with N,N′-dicyclohexylcarbodiimide gave N,N′-dicyclohexyl-N.N′-bis(cyclohexylcarbamoyl)-1,1′-ferrocenedicarboxamide (XIV).

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