

Fig. 1.—Quantitative relationship between experimental log k -values and log k -values calculated from eq. 9 for the saponification of 35 *m*- and *p*-substituted alkyl benzoates.

independent variables gives

$$\log k = 0.171 + 2.26\sigma + 1.51\sigma^* + 0.669E_s^c + 0.008\sigma \cdot E_s^c \quad (8)$$

(0.001) (0.001) (0.001) (0.500)

with $R = 0.996$ and $s = 0.108$. From eq. 8, it is evident that the other interaction factor, $\sigma \cdot E_s^c$, makes no contribution either.

Finally, for the combined data of Tables I, II and III, multiple regression analysis gives

$$\log k = 0.174 + 2.22\sigma + 1.53\sigma^* + 0.668E_s^c \quad (9)$$

(0.001) (0.001) (0.001)

with $R = 0.996$ and $s = 0.108$. Equation 9 is almost identical to equations 5 and 6 but is slightly more reliable since it is based on more data. The excellent quantitative relationship given by eq. 9 is shown in Fig. 1.

Experimental

Materials.—The esters were purchased from commercial sources or were prepared by well-known methods. Liquid esters were purified as described previously⁸ while solid esters were purified by recrystallization and dried *in vacuo*. The following three prepared esters were not found in the literature.

3-Pentyl benzoate was prepared by adding benzoyl chloride to a mixture of anhydrous 3-pentanol and pyridine,¹² b.p. 196° at 2.5–3 mm., n_D^{25} 1.4909. *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.97; H, 8.39; sapon. equiv., 192.26. Found: C, 74.68¹³; H, 8.42¹³; sapon. equiv., 192.33.

sec-Butyl *m*-toluate was prepared as above, b.p. 99–102° at 2.5–3 mm., n_D^{20} 1.4965. *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.97; H, 8.39; sapon. equiv., 192.26. Found: C, 74.46¹³; H, 8.44¹³; sapon. equiv., 191.19.

Isoamyl *p*-chlorobenzoate was prepared by H_2SO_4 -catalyzed direct esterification; b.p. 122–124° at 3 mm., n_D^{25} 1.5056. *Anal.* Calcd. for $C_{12}H_{15}ClO_2$: C, 63.58; H, 6.67; Cl, 15.64; sapon. equiv., 226.70. Found: C, 63.61¹⁴; H, 6.74¹⁴; Cl, 15.63¹⁴; sapon. equiv., 227.04.

Dioxane was purified as described previously.⁸ Due to limited solubility of some of the esters in lower concentrations of dioxane, it was necessary to use 60 volume % aqueous dioxane (60 volumes of dioxane diluted with deionized water to 100 volumes) in determination of the saponification rate constants.

Determination of Saponification Rate Constants at 35.00 ± 0.01°.—The method used was described previously.⁸ However, for the three fastest reactions, it was necessary to pour the ester and sodium hydroxide solutions quickly into a large test-tube and then immediately immerse a dipping conductivity cell into the reaction mixture in order to follow the reaction.

Duplicate rate constant determinations were made on 27 of the esters and three to five determinations on the other eight esters. The precision of the determinations was comparable to that reported previously.⁸

Acknowledgments.—This study was supported in part by a research grant from the Robert A. Welch Foundation. The statistical calculations were performed by the Data Processing Center, Texas Engineering Experiment Station, College Station, Texas, on IBM-650 and 704 computers.

(12) J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.*, **54**, 2088 (1932).

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Carbonium Ion Stabilization by Metallocene Nuclei. III. Evidence for Metal Participation¹

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The solvolytic behavior of diastereomeric ferrocenylcarbonyl acetates has been examined and is interpreted as indicating a direct bonding of the metal atom to the cationic carbon of the α -metallocenylcarbonium ions.

Introduction

In the first paper of this series² the unusual reactivity of carbonyl acetates with adjacent metallocenyl substituents was discussed. It had been proposed earlier³ that direct interaction be-

tween electrons of the metal component of the metallocene group and the carbonium ion center was an important factor in stabilizing certain α -metallocenyl carbonium ions. The purpose of this paper is to present additional stereochemical and solvolytic data to support this proposal.

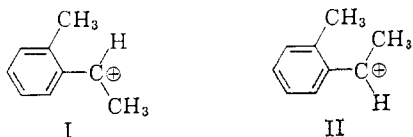
When substituents are located in *ortho* positions of a benzene derivative, steric effects between the

(1) Supported in part by a grant from the National Science Foundation and the Paint Research Institute.

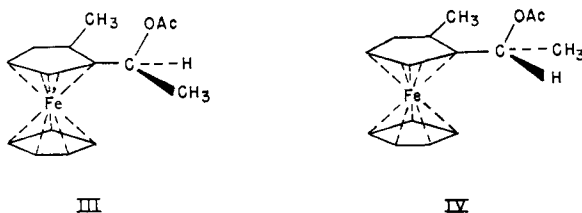
(2) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961).

(3) J. H. Richards and E. A. Hill, *ibid.*, **81**, 3484 (1959).

two *ortho* groups may be anticipated. Thus in the solvolysis of 2-substituted phenylethyl derivatives, two carbonium intermediates are possible (I and II). Steric interaction is minimized in I and solvolysis will be expected to proceed mainly through a carbonium with this structure. Since, however,



the carbonium ion has a plane of symmetry, optically isomeric derivatives differing only in configuration about the carbonyl carbon will show identical behavior on solvolysis. In a metallocenyl derivative there is an additional element of asymmetry due to the metal atom and second ring, such that homoannular ring-substituted derivatives with asymmetric carbonyl carbons will exist in two diastereomeric forms (*e.g.*, III and IV). It would be anticipated that isomeric species of this type would be separable and that the two isomers



would behave differently on solvolysis. The synthesis and solvolytic behavior of such isomeric pairs is the subject of this paper.⁴

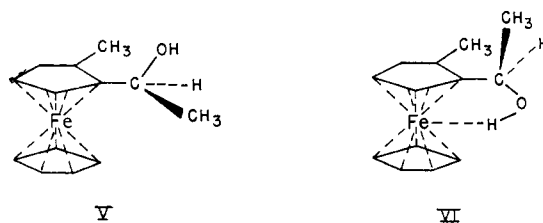
Results

Reduction of the appropriate ketones by lithium aluminum hydride led to mixtures of two isomeric carbinols that could be separated by chromatography on alumina. Thus reduction of 2-methylacetoferrocene, 2,1'-dimethylacetoferrocene and 2-,1,1'-trimethyleneacetoferrocene yielded pairs of isomeric carbinols, one of which was significantly more readily eluted from alumina than its companion. The hydroxyl stretching frequencies, summarized in Table I, are the basis for assigning to one of the isomers a ψ -*endo* configuration (*cf.* V, VI),⁵ and to the other a ψ -*exo* configuration. It is believed that the interaction between the methyl group on the carbonyl carbon and the substituent on the α -position of the ring will be sufficient to make that rotational conformation which possesses this interaction unfavorable relative to alternative

(4) In the case of 3-alkylferrocenylcarbinyl derivatives, however, the ring substituent is sufficiently removed that the chemical and solvolytic properties of the two isomers would be indistinguishable. This is the observed behavior of such 3-alkylferrocenylcarbinyl derivatives. They will be discussed in a subsequent paper which will deal with the general question of substituent effects uncomplicated by stereochemical factors.

(5) In these systems the term *exo* will signify that the group so designated is *trans* to the metal component of the metallocene. An *endo* substituent is *cis* to the metal atom. The term ψ -*exo* is used where there is free rotation about the bond between the metallocene and the carbon carrying the substituent; but where for steric, or other reasons, one rotational conformation is preferred and where this preferred conformation has the substituent in an *exo* orientation to the metal. ψ -*Endo* has an analogous meaning.

conformations in which this steric interaction is minimized. This accounts for the ψ -*exo* and ψ -*endo* isomers assuming preferential conformations



such as are shown in V and VI; these conformations explain, in turn, the observed properties of these isomers. Thus, the ψ -*endo* isomer in each case has a stronger hydroxyl stretching absorption in the infrared in the region of 3580 cm^{-1} . This absorption has been assigned^{2,6} to a hydroxyl group, the hydrogen of which is intramolecularly hydrogen bonded to the iron atom. The ψ -*exo* isomer in each case has the stronger hydroxyl band in the vicinity of 3605 cm^{-1} .

TABLE I
PROPERTIES OF ISOMERS

| Compound | Infrared in CS_2 , cm^{-1} | Order of elution from alumina | Ratio of <i>endo/exo</i> or ψ - <i>endo/</i> ψ - <i>exo</i> |
|---|--|-------------------------------|---|
| Methyl(2-methylferrocenyl)-carbinol | | | |
| ψ - <i>endo</i> isomer | 3580 (strong) | 1 | |
| | 3595 (slight sh.) | | 49:51 |
| ψ - <i>exo</i> isomer | 3604 (strong) | 2 | |
| | 3580 (weak) | | |
| Methyl-2-(1,1'-dimethylferrocenyl)-carbinol | | | |
| ψ - <i>endo</i> isomer | 3605 (shoulder) | 1 | |
| | 3578 (strong) | | 43:57 |
| ψ - <i>exo</i> isomer | 3604 (strong) | 2 | |
| | 3581 (weak) | | |
| Methyl-2-(1,1'-trimethyleneferrofenyl)-carbinol | | | |
| ψ - <i>endo</i> isomer | 3609 (shoulder) | 1 | |
| | 3575 (strong) | | 80:20 |
| ψ - <i>exo</i> isomer | 3602 | 2 | |
| α -Hydroxy-1,2-tetramethyleneferrocene | | | |
| <i>endo</i> isomer | 3561 | 1 | |
| <i>exo</i> isomer | 3610 | | 90.5:9.5 |

Reduction of α -keto-1,2-tetramethyleneferrocene produced a mixture of carbinols. The isomer that passed through an alumina column more rapidly showed hydroxyl absorption in the infrared at 3561 cm^{-1} . The presence of such absorption and the ease of elution of this carbinol from alumina permit the assignment to it of an *endo* configuration VII. A second isomeric carbinol was subsequently eluted from the alumina column. It showed hydroxyl absorption at 3610 cm^{-1} and is accordingly assigned the *exo* configuration VIII. The n.m.r. spectra, which will be discussed in detail in a separate paper, are also in accord with these assignments. The two isomers were isolated in an

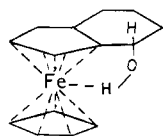
(6) D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **82**, 5010 (1960).

TABLE II
 SOLVOLYTIC RATE DATA

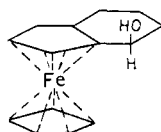
| Compound | $k_{30}^{\circ} \times 10^5$ | Rel. k_{30}° | ΔH^{\ddagger} kcal/mole | ΔS^{\ddagger} e. u. | Ratio of rate of <i>exo/endo</i> isomer |
|--|------------------------------|-----------------------|---------------------------------|-----------------------------|---|
| Methylferrocenylcarbinyl acetate | 17.02 | 1.000 | 19.0 \pm 0.6 | -13.2 | |
| Methyl-(2-methylferrocenyl)-carbinyl acetate | | | | | |
| <i>ψ-exo</i> isomer | 72.8 | 4.28 | 19.4 \pm 0.3 | - 8.9 | 12.7 |
| <i>ψ-endo</i> isomer | 5.73 | 0.337 | 19.2 \pm 0.5 | -14.9 | |
| Methyl-2-(1,1'-dimethylferrocenyl)-carbinyl acetate | | | | | |
| <i>ψ-exo</i> isomer | 128.8 ^a | 7.55 | 18.5 \pm 0.6 | -10.8 | 11.9 |
| <i>ψ-endo</i> isomer | 10.85 | 0.636 | 18.5 \pm 0.4 | -15.7 | |
| Methyl-2-(1,1'-trimethyleneferrocenyl)-carbinyl acetate | | | | | |
| <i>ψ-exo</i> isomer | 46.7 | 2.74 | 18.2 \pm 0.4 | -13.8 | 157 |
| <i>ψ-endo</i> isomer | 0.297 | 0.0174 | 22.2 \pm 0.8 | -10.6 | |
| α -Acetoxy-1,2-tetramethyleneferrocenylcarbinyl acetate | | | | | |
| <i>exo</i> isomer | 72.1 | 4.24 | 18.5 \pm 0.4 | -12.0 | 2570 |
| <i>endo</i> isomer | 0.028 ^a | 0.00165 | 23.5 \pm 1.3 | -11.0 | |

^a Extrapolated from data at other temperatures.

endo/exo ratio of 90.5/9.5.⁷ The predominance of the *endo* isomer, formed by preferential hydride attack from the upper side of the ring, is a further argument in favor of the assigned structures.^{9,10}



VII



VIII

The acetates were prepared from the carbinols by acetylation with acetic anhydride in pyridine; as this reaction does not disturb the alkyl-oxygen bond, the configurations about the carbinyl carbon have not been altered. The equilibrium between the *endo*- and *exo*- α -acetoxy-1,2-tetramethyleneferrocenes was determined in acetic acid solution at 50° and, as would be expected, demonstrated that the *exo* isomer is much the more stable. Also, a limited attempt to equilibrate the *ψ -exo*- and *ψ -endo*-methyl-(2-methylferrocenyl)-carbinyl acetates showed that the *ψ -exo* isomer is the more stable.

Solvolyses of the substances referred to above were carried out in 80% aqueous acetone solution¹ and were cleanly first order. The rate data are summarized in Table II.

(7) Trifan and Backsai⁸ have independently investigated the solvolysis of *exo*- and *endo*- α -acetoxy-1,2-tetramethyleneferrocene. In their reduction of α -keto-1,2-tetramethyleneferrocene they reported the isolation of the isomeric carbinols in a ratio of *endo/exo* of 89/11.

(8) D. S. Trifan and R. Backsai, *Tetrahedron Letters*, No. 13, 1 (1960).

(9) Because of the hydrogen bond interaction, the *endo*-carbinol may well be the more stable, a point presently under investigation.

(10) An interesting reduction of the cobalticinium ion by sodium borohydride has recently been reported by Wilkinson.¹¹ In this case, the reducing hydride apparently occupies an *endo* configuration in the product π -C₅H₅(C₅H₅)Co. Such a stereochemical result is probably due to an interaction of the attacking anion with the positive metal atom of the metallocene, a situation which is analogous to the postulated interaction between neutral metallocenes of the group VIII metals and electrophiles. Its bearing on the stereochemistry expected from hydride reduction of α -keto metallocenes is, therefore, relatively remote, as these latter reductions are probably controlled almost exclusively by steric factors.

(11) M. L. H. Green, L. Pratt and J. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

From either the *exo*- or *endo*- α -acetoxy-1,2-tetramethyleneferrocene the product consisted solely (at least 99%) of the *exo*-alcohol. In the other six cases, the sole alcohol product recovered was of the same configuration as the starting acetate. The only other products observed were small amounts of ethers formed during the isolation procedure. Thus, in all cases, there is a complete stereospecificity in the solvolysis reaction.

Discussion

The solvolysis of the two isomers of α -1,2-tetramethyleneferrocene will be considered first. The rate constant observed for the faster *exo* isomer is very close to that for methyl-(3-methylferrocenyl)-carbinyl acetate^{4,12} and to that for the faster of the 2-methyl isomers. The rate increase over that of a derivative unsubstituted in the ring is thus of the magnitude expected for acceleration by electron release from an alkyl group. The *endo* isomer, however, is slower than its diastereomer by a factor of 2570. Essentially all of this rate decrease arises from the increased enthalpy of activation. It is, therefore, enormously more favorable for the acetate group to leave from that side of the carbinyl carbon which is *trans* to the metal. This fact is evidence that the metal electrons participate in the cationic center which develops as the acetate ion leaves. From the enthalpies of activation one might estimate that this participation is roughly equal to the difference in activation energies, or 4.5 kcal., a conclusion independently reached by Trifan and Backsai.⁸ As the *exo* isomer is the more stable, the observed rate difference is *not* due to the instability of the ground state of the *exo* relative to the *endo* isomer.

While metal participation may be the dominant consideration in interpretation of the rate factor of 2570, other effects may also be significant. Thus departure of the acetate group from the *endo* isomer may be sterically hindered by the opposite ring. Moreover, it is conceivable that the leaving acetate group with its developing negative charge may experience repulsion by the filled orbitals of the iron atom.

(12) E. A. Hill and J. H. Richards, unpublished results.

It has been reported⁸ that α -tetralyl acetate solvolyzes more slowly than the *endo* isomer by a factor of 600, which is entirely due to a less favorable entropy of activation. It was therefore concluded that no residual driving force is still present in the *endo* isomer relative to its phenyl analog. If repulsion to the departing acetate group and other effects mentioned above contribute appreciably to the high enthalpy of activation for *endo*- α -acetoxy-1,2-tetramethyleneferrocene, then the results for α -tetralyl acetate are readily rationalized. α -Tetralyl acetate is a secondary arylmethyl acetate; solvolysis of such compounds may well involve a carbon-solvent interaction with significant covalent character in the transition state, *i.e.*, need not be completely limiting.¹³ Thus, nucleophilic solvent participation may make an important contribution, with an attendant decrease in entropy of activation.¹⁴ Stabilization of the positive charge by delocalization of the ring π -electrons in *endo*- α -acetoxy-1,2-tetramethyleneferrocene may still be slightly more effective than in a benzene analog.² However, the steric hindrance to departure of the acetate group may overpower this slightly greater resonance stabilization and so increase the enthalpy of solvolysis of the *endo* isomer.

The isolation of only *exo*-alcohol from either *endo*- or *exo*- α -acetoxy-1,2-tetramethyleneferrocene is further strong evidence for backside metal participation which permits solvent collapse only from the *exo* side. It has been suggested⁸ that the *endo/exo* isomer ratio of 9:1 observed in the reduction of the ketone would be a reasonable estimate of *endo* to *exo* solvent collapse in the absence of iron participation. This probably is not a valid argument as reduction of ketones with lithium aluminum hydride is known¹⁵ to show "product development control," in which case the more stable isomer is produced.

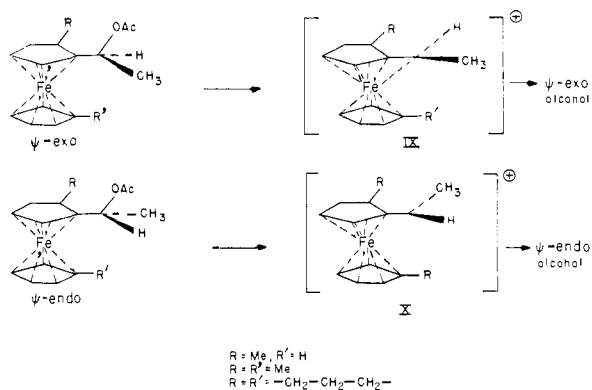
In the solvolysis of the *endo* isomer, the acetate group must first leave before the iron electrons can effectively participate. Though the experimental results do not demand a common intermediate in the solvolysis of the *exo* and *endo* isomers, it is attractive to consider that after departure of the acetate ion from the *endo* isomer the same intermediate, stabilized by iron participation, intercedes eventually in both cases.

These results hold further implications for the solvolysis of other metallocenylcarbinyl acetates. First, since the backside of the forming carbonium ion is bonding to iron, these solvolyses should be quite limiting¹³ in nature. Second, these results predict that solvolyses of other α -metallocenylcarbinyl acetates should proceed with retention of configuration, particularly when the carbinyl carbon is structurally free to rotate.

This latter anticipation is amply demonstrated by the complete stereochemical specificity observed in the solvolysis of ψ -*exo* and ψ -*endo*-methyl-(2-methylferrocenyl)-carbinyl acetate and

related compounds. Between ψ -*exo*- and ψ -*endo*-methyl-(2-methylferrocenyl)-carbinyl acetate and between ψ -*exo*- and ψ -*endo*-methyl-2-(1,1'-dimethylferrocenyl)-carbinyl acetate the ratio of rates of the ψ -*exo* to the ψ -*endo* isomer is observed to be 12.7 and 11.9, respectively. The equilibration experiments cited earlier, which demonstrate that the ψ -*exo* isomer is the more stable, indicate that the rate difference is caused by steric hindrance in achieving the planar carbonium IX that would result from the ψ -*endo* isomer. That this must be the ion formed is a direct manifestation of the overwhelming requirement for the acetate group to leave *trans* to the iron atom. This hindrance between adjacent positions of the ring of metallocenes is less pronounced than that between adjacent positions of a benzene derivative,¹⁶ but is still clearly seen in the observed rate differences. In the case of the ψ -*exo* isomer, which will solvolyze *via* the ion IX,² there is no appreciable hindrance; the rate observed is almost exactly that expected for an alkyl-substituted ferrocenylcarbinyl acetate. On the other hand, carbonium ion X derived from the ψ -*endo*-acetate has the methyl group on the carbinyl carbon and the R group on the α -position of the ferrocene ring forced together, an interaction which destabilizes this carbonium ion relative to IX and accounts for the decreased rates of solvolysis of the ψ -*endo* isomers.

The fact that rotation about the ring-carbinyl bond is prevented in the transition state does not of itself require metal participation, for it has been shown¹⁷ that such rotation does not occur



in the allylic butenyl cation under solvolytic conditions. However, the absolute stereospecificity of product production and rate differences between the ψ -*exo* and ψ -*endo* isomers, when taken together, are further evidence for metal participation.

The case of ψ -*exo*- and ψ -*endo*-methyl-2-(1,1'-trimethyleneferrocenyl)-carbinyl acetates shows similar stereospecific solvolyses, with the ratio of solvolysis rates of the ψ -*exo* to the ψ -*endo* isomer being 157. Both isomers are slower than would be anticipated for a heteroannular dialkylferrocenylcarbinyl acetate, which fact can be attributed to a tilting of the two cyclopentadienyl rings relative to one another. This aspect of these and re-

(13) S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(14) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956); R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957).

(15) W. G. Dauben, G. J. Fonken and D. S. Noyce, *ibid.*, **78**, 2579 (1956).

(16) K. L. Rinehart, Jr., K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

(17) W. G. Young, S. H. Sharman and S. Winstein, *ibid.*, **82**, 1376 (1960).

lated compounds will be discussed in a subsequent paper. The central point for present purposes is that this additional pair of isomeric substances shows solvolytic behavior that is most readily interpreted as arising from direct participation of iron electrons at the backside of the developing α -metallocenylcarbonium ion.

Experimental¹⁸

Methylacetoferrocenes.—Methylferrocene (13.0 g., 65 mmoles) and acetic anhydride (6.62 g., 64.8 mmoles) were dissolved in methylene chloride (150 ml.) in a 200-ml. flask equipped with a stirrer and a gas bubbling tube. The reaction mixture was cooled to 0° and saturated with boron trifluoride. Stirring was continued for 1.25 hr. at 0°; the mixture was then allowed to warm to room temperature over a period of 2.75 hr. The reaction mixture was poured into an excess of aqueous sodium acetate, sufficient ascorbic acid was added to reduce the ferricinium ion, and the aqueous phase was extracted several times with methylene chloride. The organic layer was washed twice with saturated aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of the solvent yielded a red-brown oil, which was dissolved in benzene-hexane and chromatographed on 1220 g. of acid-washed alumina (52 × 5.5 cm. column). A yellow band containing the starting material (0.80 g., 6.1%, m.p. 36–37.5°) was eluted in fraction 1 with about 1.1 l. of benzene-hexane. Development and elution of the monoacetylated products were carried out with benzene-ether mixtures. A faster-moving band of light orange partially separated from the major orange band, but no visible resolution of the larger band appeared to occur. The product was collected in 25 fractions.

The solid fractions and their neighboring semi-solid fractions were worked up by a number of crystallizations to yield pure products. There was thus obtained 2-methylacetoferrocene (1.59 g.), m.p. 62.2–63.2°.

Anal. Calcd. for $C_{13}H_{14}OFe$: C, 64.55; H, 5.83; Fe, 23.04. Found: C, 64.66; H, 5.72; Fe, 23.34.

The second isomer eluted from the column is 1-methylacetoferrocene (2.07 g.), m.p. 42.7–43.2°. Found: C, 64.70; H, 5.84; Fe, 23.20.

The third isomer eluted from the column is 3-methylacetoferrocene (1.09 g.), m.p. 57.5–61.5°. Found: C, 64.61; H, 5.92; Fe, 23.22.

These structures were assigned on the basis of appropriate spectral comparisons.^{16,19,20}

α -Keto-1,1'-trimethyleneferrocene.—Trifluoroacetic anhydride (73 g., 350 mmoles) was added to 250 ml. of carbon tetrachloride (previously bubbled out with nitrogen for about 10 min.) in a 500-ml. round-bottomed flask wrapped in foil. β -Ferrocenylpropionic acid (7.38 g., 28.6 mmoles) was introduced under a stream of nitrogen, and the reaction mixture was allowed to stand at room temperature (30–35°) with occasional swirling for 4 hr. The contents of the flask were poured into a suspension of 70 g. (0.83 mole) of sodium bicarbonate in 150 ml. of water, and the aqueous layer was extracted with portions of methylene chloride until the extracts were nearly colorless. After the organic phase had been washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate, the solvent was evaporated to yield a dirty red-orange solid. This was chromatographed on 400 g. of alumina with ether-benzene mixtures (1 to 5% ether). After sufficient separation had occurred, the column was extruded. The product band was separated and extracted with acetone, and the solvent was removed at reduced pressure to yield a solid, m.p. 143–144°. Crystallization from heptane produced 4.72 g. of orange rods, m.p. 144.5–145.5° (lit.²¹ m.p. 144–144.5°).

Acidification of the aqueous phase with concentrated hydrochloric acid precipitated 1.10 g. (15%) of starting material, m.p. 117–118.5°. The yield of bridged ketone

was 69%, or 81% on the basis of unrecovered starting material.

1,1'-Trimethyleneferrocene.— α -Keto-1,1'-trimethyleneferrocene (5.23 g., 21.9 mmoles) was hydrogenated over a platinum oxide catalyst at 2–2.5 atm. in 150 ml. of glacial acetic acid. A total of 1.13 g. of catalyst in two portions was required to bring about consumption of the theoretical quantity of hydrogen in a period of 22.5 hr. The catalyst was removed by filtration and some of the solvent distilled until a yellow solid had begun to precipitate. The mixture was added to an excess of sodium bicarbonate solution, and the product was extracted with petroleum ether. This extract was dried and chromatographed on 215 g. of neutral alumina. Elution of the major, yellow product band with benzene-hexane (20–80) and removal of the solvent yielded 4.45 g. (90.5%) of yellow plates, m.p. 106–107°. Successive recrystallizations from hexane and methanol raised the melting point to 106.7–107.2° (lit. m.p. 106–107°,²² 105–106°²³).

2,1'-Trimethylenecetoferrocenes.—Acetylation of 1,1-trimethyleneferrocene (5.65 g., 25 mmoles) by the usual procedure with acetic anhydride-boron trifluoride²⁴ was followed by chromatography of the resulting product mixture on neutral alumina. By repeated recrystallizations and rechromatography of mother liquors there were obtained in 65% over-all yield (based on unrecovered starting material) two isomeric products. The first to be eluted from the column is 2,1'-trimethylenecetoferrocene, m.p. 77.5–78.5°.

Anal. Calcd. for $C_{15}H_{16}OFe$: C, 67.19; H, 6.02; Fe, 20.83. Found: C, 67.48; H, 6.27.

The second isomer eluted from the column is 2,1'-trimethylenecetoferrocene, m.p. 100–101°. Found: C, 67.09; H, 6.08; Fe, 20.65.

α -Keto-1,2-tetramethyleneferrocene.—Cyclization of γ -ferrocenylbutyric acid (1.01 g., 3.7 mmoles) with trifluoroacetic anhydride by the same procedure used in the preparation of α -keto-1,1'-trimethyleneferrocene, except that the reaction time was reduced to 2.25 hr., produced α -keto-1,2-tetramethyleneferrocene (0.64 g., 68%) as a red solid that upon recrystallization from hexane has m.p. 85–85.5° (lit.²¹ 85.4–85.7°).

1,1'-Dimethylferrocene.—Aluminum chloride (8.50 g., 64 mmoles) in ether (150 ml.) was added under nitrogen over a period of 3 min. to a stirred suspension of lithium aluminum hydride (2.50 g., 66 mmoles) in ether (250 ml.) in a 1-l. flask equipped in the customary manner. After 5 min. of stirring, dicarbomethoxyferrocene²⁵ (6.38 g., 21.1 mmoles) was added. Since the diester proved insufficiently soluble in ether to add in a convenient volume, part was added as a solid. The mixture was refluxed for 40 min. in addition to the 30 min. required to add the ester. Ethyl acetate (20 ml.) and water (20 ml.) were added over a period of 30 min., the reaction mixture was filtered through Celite and the solvent was distilled to yield an orange oil. This was chromatographed on 250 g. of alumina with a 50–50 mixture of hexane and benzene. The major product band was rapidly eluted, and the solvent was removed to yield 3.13 g. (69%) of orange solid, m.p. 39–40.5° (lit.²⁶ m.p. 32.5–33°).

Dimethylacetoferrocenes.—A solution of dimethylferrocene (3.11 g., 14.6 mmoles) and acetic anhydride (1.50 g., 0.0147 mole) in methylene chloride (90 ml.) was saturated with boron trifluoride at 0°. The mixture warmed to room temperature during a 3.5-hr. period of stirring. The reaction mixture was decomposed, and a non-crystalline red-orange oil was isolated by the usual extraction procedure (see procedure for acetylation of methylferrocene).

Chromatography on acid-washed alumina produced complete separation when graded benzene-ether mixtures were used as solvents. There was obtained after recrystallization from pentane 0.77 g. (20.6%) of 2,1'-dimethylacetoferrocene, m.p. 25–26.5° (lit.¹⁶ m.p. 15–16°) and, after re-

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crystallization from hexane, 1.26 g. (33.8%) of 3,1'-dimethylacetoferrrocene, m.p. 51.7–53° (lit.¹⁶ m.p. 46°).

Isomeric Methyl-(methylferrocenyl)-carbinyl Acetates.—Reduction of 2-methylacetoferrrocene (0.61 g., 2.5 mmoles) with lithium aluminum hydride (0.20 g., 5.3 mmoles) according to the procedure reported earlier² produced a mixture of two isomeric carbinols, which was separated by chromatography on neutral Merck alumina which had been deactivated by allowing it to stand in air up to 5 hours. The first band eluted from the column afforded 0.29 g. (47%) of the ψ -endo-alcohol, m.p. 55–56°. ψ -endo-Methyl-(2-methylferrocenyl)-carbinyl acetate was prepared as previously described; it was a liquid and was purified by molecular distillation.

Anal. Calcd. for C₁₅H₁₈O₂Fe: C, 62.96; H, 6.34. Found: C, 63.19; H, 6.54.

The second band eluted from the column yielded 0.3 g. (49%) of a liquid alcohol; this was converted to ψ -exo-methyl-(2-methylferrocenyl)-carbinyl acetate, which was a solid. After recrystallization from hexane, it had m.p. 54–55.2°.

Anal. Calcd. for C₁₅H₁₈O₂Fe: C, 62.96; H, 6.34. Found: C, 63.28; H, 6.46.

Isomeric α -Acetoxy-1,2-tetramethyleneferrrocenes.—Reduction of α -keto-1,2-tetramethyleneferrrocene (0.48 g., 1.9 mmoles) with lithium aluminum hydride (0.18 g., 4.8 mmoles) produced a mixture of two isomeric carbinols, which could be separated by chromatography on neutral alumina (see above). The first band eluted from the column yielded 0.44 g. (87%) of the liquid *endo*- α -hydroxy-1,2-tetramethyleneferrrocene. The acetate was prepared by the pyridine method. After recrystallization it had m.p. 48.5–49.5° (lit.⁸ m.p. 49–50°).

The second band was eluted from the column by adding a trace of methanol to the solvent. This fraction weighed 0.046 g. (9.2%). The *exo*- α -hydroxy-1,2-tetramethyleneferrrocene crystallized as a yellow solid, m.p. 70.5–72° (lit.⁸ m.p. 71.5–72.5°). Acetylation by the pyridine method yielded α -acetoxy-1,2-tetramethyleneferrrocene, m.p. 65–66° (lit.⁸ m.p. 64–65°).

Isomeric Methyl-2-(1,1'-dimethylferrocenyl)-carbinyl Acetates.—Reduction of 2-acetyl-1,1'-dimethylferrocene (0.71 g., 2.6 mmoles) with lithium aluminum hydride (0.17 g., 4.5 mmoles) produced a mixture of two isomeric alcohols, which was separated by chromatography on neutral aluminum (see above). The first alcohol eluted from the column yielded 0.271 g. (38%) of a cloudy orange oil, ψ -endo-methyl-2-(1,1'-dimethylferrocenyl)-carbinol.

Anal. Calcd. for C₁₄H₁₈OFe: C, 65.14; H, 7.03; Fe, 21.64. Found: C, 65.24; H, 6.94; Fe, 22.06.

The acetate was prepared from this carbinyl in the usual manner and yielded ψ -exo-methyl-2-(1,1'-dimethylferrocenyl)-carbinyl acetate. A satisfactory analysis for this particular acetate could never be obtained, though its solvolysis was linear to 100% reaction and the alcohol, recovered in good yield, gave a correct analysis.

The second alcohol eluted from the column was a cloudy oil, weighing 0.366 g. (51%), of ψ -exo-methyl-2-(1,1'-dimethylferrocenyl)-carbinol. The acetate was prepared in the usual manner in pyridine and yielded, as an oil, ψ -exo-methyl-2-(1,1'-dimethylferrocenyl)-carbinyl acetate.

Anal. Calcd. for C₁₆H₂₀O₂Fe: C, 64.02; H, 6.72; Fe, 18.61. Found: C, 63.96; H, 6.62; Fe, 18.91.

Isomeric Methyl-2-(1,1'-trimethyleneferrrocenyl)-carbinyl Acetates.—Reduction of 2,1'-trimethyleneferrrocene (1.12 g., 4.0 mmoles) with lithium aluminum hydride (0.21 g., 5.5 mmoles) yielded a mixture of isomeric alcohols,

which were separated by chromatography on neutral aluminum (see above).

The first alcohol to be eluted (0.70 g., 63%) crystallized to a yellow solid, melting point 80–81°, of ψ -endo-methyl-2-(1,1'-trimethyleneferrrocenyl)-carbinol.

Anal. Calcd. for C₁₅H₁₈OFe: C, 66.69; H, 6.71; Fe, 20.67. Found: C, 66.95; H, 6.50; Fe, 20.65.

ψ -endo-Methyl-2-(1,1'-trimethyleneferrrocenyl)-carbinyl acetate was prepared from the alcohol in the usual manner and was obtained as a solid, m.p. 60–61°.

Anal. Calcd. for C₁₇H₂₀O₂Fe: C, 65.40; H, 6.46; Fe, 17.89. Found: C, 65.14; H, 6.41; Fe, 18.31.

The second alcohol eluted from the column yielded 0.18 g. of ψ -exo-methyl-2-(1,1'-trimethyleneferrrocenyl)-carbinol, which melted at 160–161.5°.

Anal. Calcd. for C₁₅H₁₈OFe: C, 66.69; H, 6.71; Fe, 20.67. Found: C, 66.55; H, 6.55; Fe, 20.68.

The acetate was prepared in the usual manner and crystallized to a yellow-orange solid, m.p. 74.7–75.7°, of ψ -exo-methyl-2-(1,1'-trimethyleneferrrocenyl)-carbinyl acetate.

Anal. Calcd. for C₁₇H₂₀O₂Fe: C, 65.40; H, 6.46; Fe, 17.89. Found: C, 65.19; H, 6.39; Fe, 18.12.

Kinetic Procedures.—The kinetic procedures used in these experiments were identical to those reported in the earlier paper.² All solvolyses were carried out in 80% acetone-water solutions. The results are summarized in Table III.

TABLE III
RATE DATA

| Compound | T, °C. | 10 ⁴ k | |
|--|--------------|-------------------|--------------|
| Methyl-2-(1,1'-dimethylferrocenyl)-carbinyl acetate | 0.00 | 3.99 ± 0.04 | |
| | ψ -exo | 10.00 | 1.38 ± .2 |
| | ψ -endo | 0.00 | 0.335 ± .009 |
| | 10.00 | 1.07 ± .02 | |
| | 30.00 | 10.6 ± .5 | |
| Methyl-2-(2-methylferrocenyl)-carbinyl acetate | 0.00 | 1.91 ± 0.03 | |
| | 10.00 | 6.90 ± .09 | |
| | ψ -exo | 30.00 | 72.8 ± .8 |
| | ψ -endo | 10.00 | 0.50 ± .01 |
| | 30.00 | 5.7 ± .2 | |
| 40.00 | 14.4 ± .3 | | |
| 45.00 | 23.8 ± .1 | | |
| Methyl-2-(1,1'-trimethyleneferrrocenyl)-carbinyl acetate | 0.00 | 1.53 ± 0.02 | |
| | 10.00 | 5.07 ± .08 | |
| | ψ -exo | 30.00 | 46.7 ± .9 |
| | ψ -endo | 30.00 | 0.297 ± .006 |
| | 45.00 | 1.70 ± .02 | |
| 70.32 | 2.56 ± 1.5 | | |
| α -Acetoxy-1,2-tetramethyleneferrrocene | 0.00 | 2.10 ± 0.05 | |
| | 10.00 | 7.64 ± .11 | |
| | <i>exo</i> | 25.00 | 40.4 ± .3 |
| | 30.00 | 72.1 ± .5 | |
| | <i>endo</i> | 45.00 | 0.187 ± .004 |
| 63.50 | 1.57 ± .08 | | |
| 80.00 | 8.2 ± .3 | | |