Metallocenyl Carbonium Ions. Stereochemistry of Participation by Ferrocene in the Solvolysis of 2-Ferrocenylalkyl Tosylates[1]

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Abstract: Studies of the acetolysis of *exo* and *endo* isomers of α-tosyloxymethyl-1,2-tetramethyleneferrocene have elucidated the stereochemical aspects of participation in β-ferrocenyl carbonium ions and have shown that, at least in these cases, participation of the electrons between the two cyclopentadienyl rings (interannular electrons) is much more effective than participation of extraannular electrons. Solvolyses of other β-ferrocenylethyl tosylates have been studied and these results are discussed.

A previous paper[3] on this subject has shown that the ferrocene nucleus effectively participates in stabilization of carbonium ions formed during solvolysis of 2-ferrocenylalkyl tosylates as evidenced by (a) the entropy of activation of these reactions, (b) the effect of solvent on the rate, (c) the effect of methyl substituents at C-1, (d) the kinetic isotope effect, and (e) the complete retention of configuration at C-1. A subsequent paper[4] discussed the stereospecific syntheses of ferrocene derivatives with leaving groups β to the metallocene. The rates of solvolysis of the related tosylates and the structures of the products of these two substances have been determined as have the rate and structures of the products of solvolysis of 2-ferrocenyl-2-propyl tosylate. The bearing these results have on the nature and stereochemical aspects of participation by ferrocene at β-carbonium ion centers forms the basis of this paper.

Results

Table I collects representative data for the solvolysis rates for *exo*- (I) and *endo*-α-tosyloxymethyl-1,2-tetramethyleneferrocene (II) and for 2-ferrocenyl-1-propyl tosylate in glacial acetic acid. Table II collects pertinent data on relative rates.

Table I. Acetolysis Data

	Temp, °C	$k \times 10^5$ sec^{-1}	ΔH, kcal/mole	$\Delta S^{\ddagger}$, eu
exo-1-Tosyloxymethyl-	100.00	39.1 ± 0.5		
1,2-tetramethylene-	89.75	13.5 ± 0.4	27.4	+1.37
ferrocene	25.00	0.0100[a]		
endo-1-Tosyloxymethyl-1,2-tetramethyleneferrocene	25.07	27.8 ± 4.5		
2-Ferrocenyl-1-propyl tosylate	25.00	1.6 ± 0.2[a]		

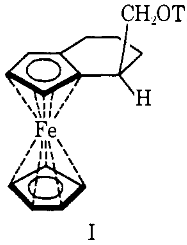
[a] Rate constant extrapolated from data at other temperatures.

The sole product of the acetolysis of the *endo* isomer II is the acetate with unrearranged carbon skeleton IV. On the other hand, acetolysis of the *exo* isomer I leads to a single acetate which does not have the carbon skeleton of I and for which structure V is proposed. This acetate is not hydrolyzed after standing for 8 days in an aqueous acetone solution of potassium carbonate at room temperature which eliminates the possibility that the acetoxy function is located on the α-carbon as such an ester (whether *endo* or *exo*) would have been extensively hydrolyzed under these conditions.[5] High intensity mass spectral peaks at m/e 311 ± 2 and 252 (corresponding to loss of acetic acid from the parent compound) and the elemental analyses show that the substance is isomeric with the acetate of unrearranged skeleton. Figure 1 shows the nmr spectrum of the acetate. These data are all consistent with the structure β-acetoxy-1,2-pentamethyleneferrocene (V) obtained by rearrangement of the substrate I.

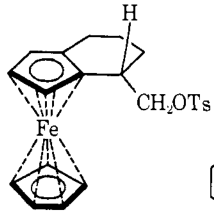
Table II. Relative Rates at 25°

Compound		
1-Tosyloxymethyltetralin (III)	1[a]	
exo-α-Tosyloxymethyl-1,2-tetramethyleneferrocene (I)	1.6[a]	1[a]
endo-α-Tosyloxymethyl-1,2-tetramethyleneferrocene (II)	4480	2780
2-Ferrocenylethyl tosylate	44	27
2-Ferrocenyl-1-propyl tosylate	256	160
1-Ferrocenyl-2-propyl tosylate	69	43

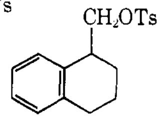
[a] Based on extrapolated rate constants.



I



II



III

Rearrangement of the carbon skeleton was also observed in the acetolysis of 2-ferrocenyl-1-propyl tosylate (VI) which gave an almost equimolar mixture of 2-ferrocenyl-1-propyl acetate (VII) and 1-ferrocenyl-2-propyl acetate (VII). The relative amount of the two isomers was determined by the relative intensity in the nmr of the methyl hydrogens of the acetoxy groups for the two isomers which had each been synthesized independently.

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(1) Supported by Grant NSF GP-24996 from the National Science Foundation.

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(3) M. J. Nugent, R. E. Carter, and J. H. Richards, *J. Am. Chem. Soc.*, **91**, 6145 (1969).

(4) M. J. Nugent and J. H. Richards, *ibid.*, **91**, 6138 (1969).

(5) E. A. Hill and J. H. Richards, *ibid.*, **83**, 4216 (1961).

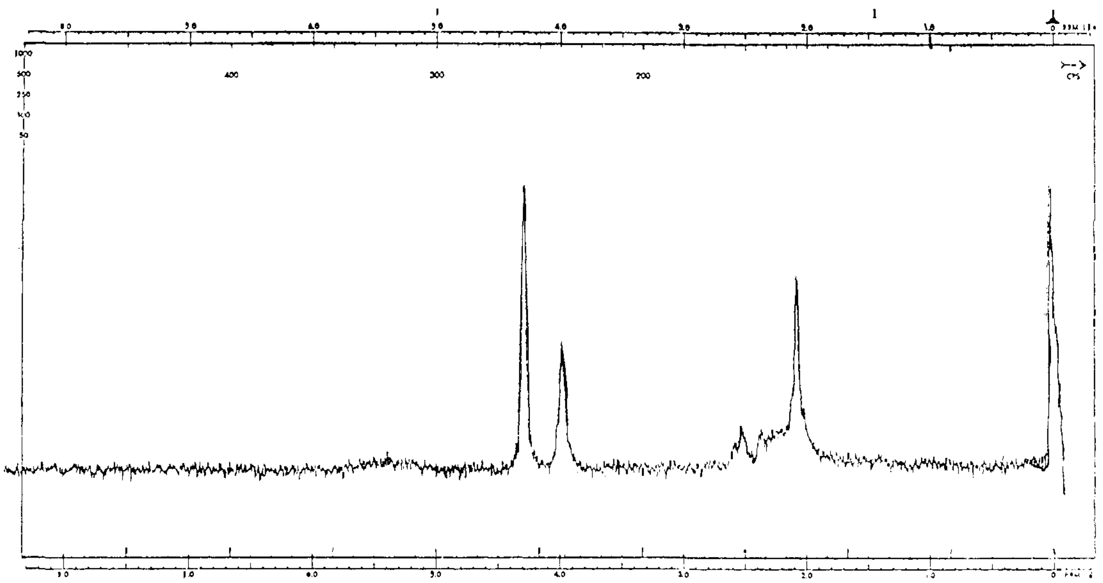
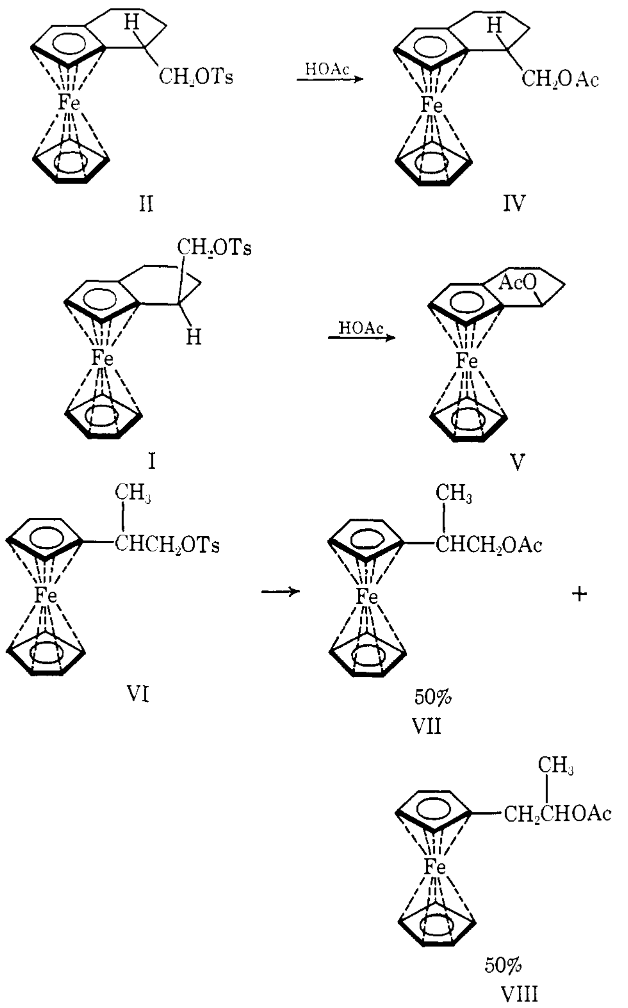


Figure 1. Nmr spectrum of a carbon tetrachloride solution of the acetolysis product of α-*exo*-tosyloxymethyl-1,2-tetramethyleneferrocene with TMS internal standard.

The product distribution was shown to be the result of kinetic control because the ratio of primary to secondary acetate is unchanged after 22 hr in acetic and it is known that the secondary acetate does *not* rearrange to the primary acetate at all under these conditions.[3]

Scheme I



These results on the nature of skeletal rearrangements during solvolysis are summarized in Scheme I.

Discussion

The rate comparisons collected in Table II provide striking evidence that the sterochemical relationship between the incipient carbonium ion center and the ferrocene nucleus exerts a profound effect on the degree of interaction. Stabilization of the metallocene is much more effective when the carbonium ion can interact with electrons between the two cyclopentadienyl rings of ferrocene (the interannular electrons) relative to situations where interaction only with the extraannular π electrons is possible. Thus the *endo* isomer (II) solvolyses faster by a factor of 2780 than the *exo* isomer (I). Certainly some of the rate enhancement of the *endo* isomer II is caused not by participation of the interannular electrons, but is due to steric congestion of the ground state occasioned by interaction of the *endo*-tosyloxymethyl substituent with the hydrogen atoms and the other electrons of the ferrocene. As a result, the ground-state energies of the *exo* (I) and *endo* (II) isomers need not be the same and the rate difference of 2780 may, in part, reflect a higher ground-state energy of the *endo* isomer.

However, the production of only unrearranged acetate upon solvolysis of the *endo* isomer indicates that steric hindrance to conversion of the carbonium ion to a tetrahedral carbon by acquisition of a nucleophile from the interannular region is by no means overwhelming. Thus, on the assumption that the free energy profile for acquisition of acetate resembles that for loss of tosylate, we conclude that steric congestion in the ground state of the *endo* tosylate is not the dominant factor in the rate difference between the *endo* and *exo* isomer.

In contrast to paracyclophanyl systems,[6] however, the steric repulsions in the *endo* derivatives of ferrocene systems are not large enough to compensate for the greater availability of interannular electrons (as contrasted to the extraannular electrons) in the ferrocene

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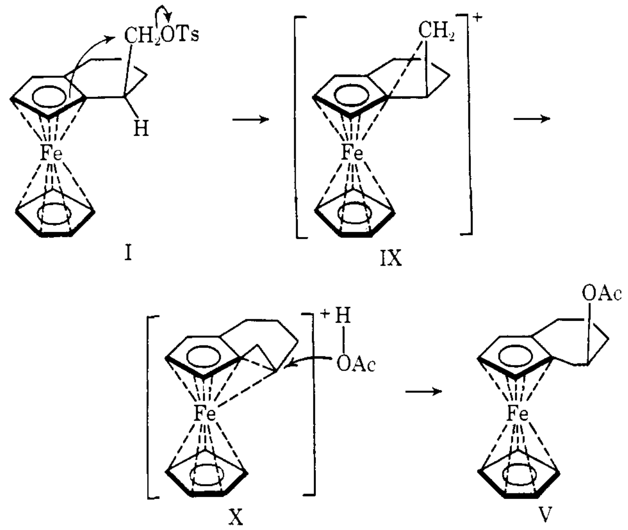
(6) D. J. Cram and L. A. Singer, *J. Am. Chem. Soc.*, 85, 1075 (1963).

Scheme II

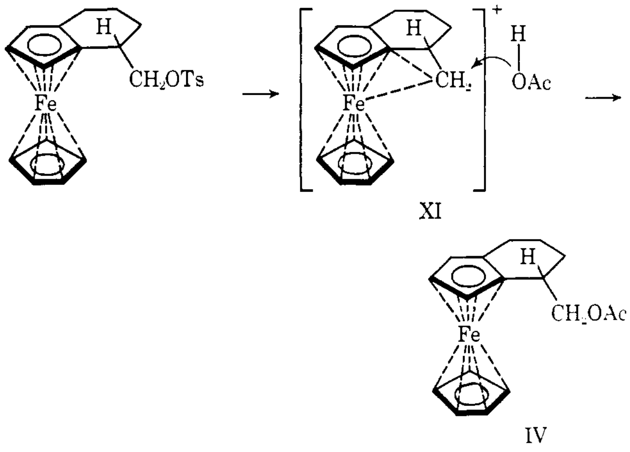


derivative and this leads to a higher rate for the *endo* than the *exo* isomer. As a result, *endo* orientation of the alkyl chain leads to the most favorable positioning of the electron-deficient carbon atom and is postulated to give, in general, the more favorable transition state for acetolysis of 2-ferrocenylalkyl tosylates, whereas *exo* orientation of the chain is postulated in the paracyclophanyl system.

Further information regarding the effectiveness of participation by the extraannular electrons relative to participation of the π electrons of a phenyl ring can be obtained from Table II. Acetolysis of 1-tosyloxymethyltetralin involves participation by the π electrons of the phenyl ring resulting in partial rearrangement to a secondary tosylate which then reacts further at a rate about 200 times faster than cyclohexylcarbinyl tosylate and which gives only rearranged product.[7] The fact that α-*exo*-tosyloxymethyl-1,2-tetramethyleneferrocene, in which overlap between the developing p orbital of the electron-deficient *exo* carbon and the interannular ferrocene orbitals is not possible, solvolyses with skeletal rearrangement (see subsequent discussion) and at nearly the same rate as its phenyl analog indicates that participation of the extraannular π electrons is about as effective as participation by the π electrons of a phenyl ring in stabilizing an incipient β-carbonium ion, a result which is similar to that encountered for α-carbonium ions.[8]

There is, however, an interesting difference between the rates observed for the phenyl derivative 1-tosyloxymethyltetralin and the *exo* isomer (I). During the acetolysis of I no induction period is observed. In contrast, an induction period is characteristic of the primary phenyl systems which rearrange to secondary sulfonates during solvolysis. Of course, no induction period will be observed if the solvolysis rate of the secondary system exceeds by approximately two or more orders of magnitude that of the unrearranged primary system. However, the absence of an induction period is completely compatible with a mechanism in which the extraannular participation IX during departure of the tosylate anion is succeeded by rearrangement to allow participation of the interannular electrons (X). This intermediate (X) is then stabilized by acquisition of a nucleophile from the *exo* direction to give the product V (see Scheme II).

In the solvolysis of the *endo* isomer, participation of the interannular electrons leads directly to an intermediate XI (similar to X) which acquires a nucleophile to yield unrearranged product IV.



These results do not show whether the interannular electron participation involves the nonbonding electrons of the iron or is due to interaction of the d-π electrons involved in iron–carbon bonding. The former would be analogous to the interaction postulated to occur in protonated metallocenes,[9] while the latter would be closer to the suggestions of Rosenblum[10] and Traylor and Ware.[11]

The solvolysis of 2-ferrocenyl-1-propyl tosylate provides an interesting and somewhat perplexing example because in this case of an open chain derivative the incipient cation can adopt either an *exo* or *endo* orientation relative to the ferrocene ring system, and both structural rearrangement and retention are observed in about equal amounts.

The primary tosylate may, by internal return, rearrange to the secondary 1-ferrocenylpropyl tosylate from which rearranged acetate is produced. However, the secondary tosylate solvolyses more slowly by a factor of about 4; so if this rearrangement did occur by internal return, one should observe a decrease in the rate of solvolysis of 2-ferrocenyl-1-propyl tosylate with time. In fact, the rate is linear to at least 85% completion. Thus the structural rearrangement observed occurs during or after departure of the tosylate anion.

We have conceived of no simple rationalization for this observation. One possibility is that, in this open chain derivative, participation by both *intra*- and *extra*-annular electrons compete more effectively than in the case of the cyclic derivatives. The fraction of solvolysis that occurs with initial participation of the extraannular electrons could lead to rearrangement, while that fraction of solvolysis that proceeds with participation of the interannular electrons would give product with an unrearranged skeleton (Scheme III).

Alternately, a single initial intermediate involving participation only of the interannular electrons could be

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(7) R. Huisgen, G. Seidl, and I. Wimmer, *Tetrahedron*, **20**, 623 (1964).

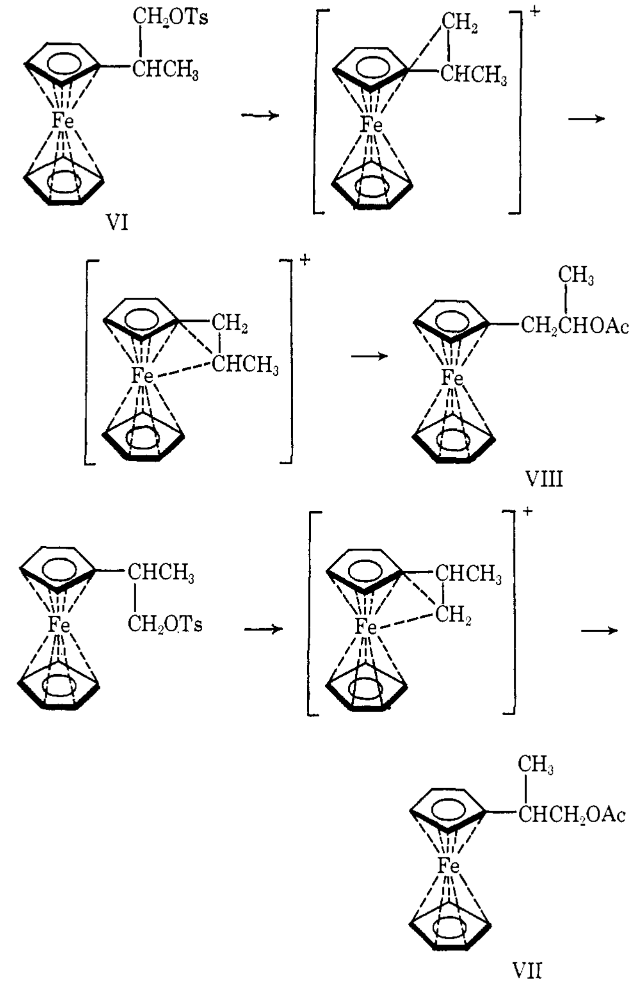
(8) D. S. Trifan and R. Backsai, *Tetrahedron Letters*, No. **13**, 1 (1960).

(9) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5249 (1960).

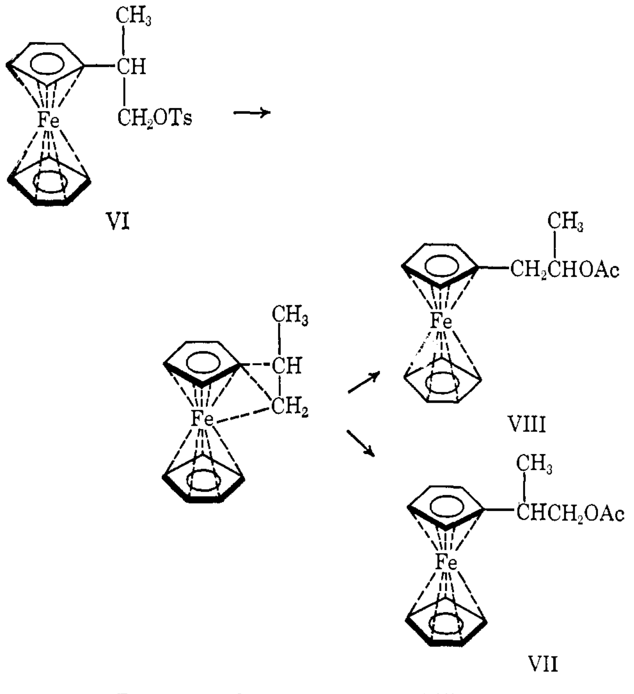
(10) M. Rosenblum, "Chemistry of the Iron Group Metallocenes; Ferrocene, Ruthenocene, Osmocene," Interscience Publishers, New York, N. Y., 1965, p 133.

(11) T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967).

Scheme III

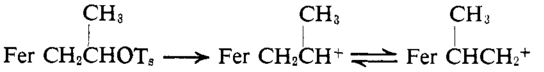


Scheme IV



formed. Because of the greater stability of secondary relative to primary carbonium ions, there may be sufficient charge at the secondary center in this intermediate to give rise to rearranged product. One must then account for formation of rearranged product in this case when none was observed in the analogous cyclic derivative, α-tosyloxymethyl-1,2-tetramethyleneferrocene. One possibility is that there is a greater barrier to formation of rearranged acetate imposed in the latter case by steric constraints imposed on the cyclic molecule (II) which are absent in the open chain derivative. This possibility is outlined in Scheme IV.

There is also the possibility that complete retention of optical activity in the solvolysis of 1-ferrocenyl-2-propyl tosylate[3] is due to a rapid equilibration as has been suggested by Brown.[12] If this explanation is indeed valid in the present situation one can put a lower limit on the rate of equilibration in either direction, a rate which must be faster than the rate of rotation about the carbon–carbon single bond between the α-carbon and the ring carbon of the ferrocene. Otherwise some rearranged acetate would be observed during the solvolysis of 1-ferrocenyl-2-propyl tosylate and none is, in fact, detected.[3]



$$\text{Fer } CH_2\overset{CH_3}{\overset{|}{C}}HOTs \longrightarrow \text{Fer } CH_2\overset{CH_3}{\overset{|}{C}}H^+ \rightleftharpoons \text{Fer } \overset{CH_3}{\overset{|}{C}}HCH_2^+$$

Experimental Section

The kinetic procedure is that described previously.

2-Ferrocenyl-1-propyl *p*-Toluenesulfonate. A solution of 0.590 g (1.48 mmoles) of 2-ferrocenyl-1-propyl *p*-toluenesulfonate in purified acetic acid was degassed as described above. After the solution had been thermostated at 60° for 11 hr (ten half-lives of 2-ferrocenylethyl *p*-toluenesulfonate), it was added to 25 ml of dry pyridine and evaporated to dryness at 30° (1 mm). The residue was chromatographed on grade III neutral alumina. Only one colored band formed. This band was eluted with hexane, and no further separation was achieved by thin layer chromatography on silica gel in a 1:9 acetone–hexane solvent system. Control experiments indicated that 2-ferrocenyl-1-propyl acetate would not be separated from 1-ferrocenyl-2-propyl acetate by these methods. The infrared spectrum of this product and the nmr spectrum can be completely described as a composite of the spectra of the isomeric 1-ferrocenyl-2-propyl and 2-ferrocenyl-1-propyl acetates. There is no spectral evidence of the presence of any other acetates. This experiment was repeated with an acetic acid solution of 0.300 g (0.753 mmoles) of tosylate which was thermostated at 60° for 22 hr. Spectral analysis of this reaction mixture showed that both the primary and secondary acetates were present in nearly identical amounts. The over-all yield of acetate product was 85%.

***endo*-α-Tosyloxymehyl-1,2-tetramethyleneferrocene.** No specific acetolysis experiment was carried out in this case; instead, the products were recovered from the acetolysis mixtures, which had been used for kinetic determinations. Each titrated aliquot of the reaction mixture was poured into a solution of potassium carbonate in aqueous acetone. A period of 2 weeks elapsed between neutralization of the first aliquot and isolation of the products. The basic solution was extracted with ether until the aqueous layer was colorless. The ethereal extract was dried over sodium sulfate and evaporated to yield a brown oil, which was chromatographed on grade III, neutral alumina. The product, α-*endo*-acetoxymethyl-1,2-tetramethyleneferrocene, was eluted with hexane in 80% yield; 10% of the unrearranged alcohol was also obtained. A small amount of decomposed material remained at the top of the column. The yield of *p*-toluenesulfonic acid from this *endo*-tosylate was 96.8 ± 0.6%. This yield was also independent of the acetolysis temperature.

***exo*-α-Tosyloxymethyl-1,2-tetramethyleneferrocene.** The products of this acetolysis were isolated in the manner described above for the *endo* isomer. A period of *ca.* 8 days elapsed between the titration of the first aliquot and the isolation of the acetolysis products. Chromatography of the reaction mixture (1.79 g) on grade III, neutral alumina produced three bands. The first band, eluted with hexane, was an orange oil (30 mg), which exhibited broad infrared absorption from 1000 to 1125 cm^{-1}, and had no other ab-

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[12] H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, 87, 2137 (1965).

sorptions indicative of any functional groups. This material was not identified. The second band eluted with hexane was a solid (350 mg), which melted at 79.0–80.5° after three crystallizations from hexane. This material was shown by mass spectral analysis to have a molecular weight of 311 ± 2; this spectrum also exhibited a high intensity peak at *m/e* 252. The infrared spectrum of this product showed absorptions at 1003 and 1107 cm^{-1} indicative of a homoannularly substituted ferrocene; acetate absorptions were at 1250 and 1735 cm^{-1}. Spectral comparisons showed that this material was not α-*exo*-acetoxymethyl-1,2-tetramethyleneferrocene. The nmr spectrum is shown in Figure 1.

Anal. Calcd for $C_{17}H_{20}O_2Fe$: C, 65.40; H, 6.46; Fe, 17.89. Found: C, 65.20; H, 6.47; Fe, 17.96.

The third band (1.11 g) was eluted with 1:1 hexane–methylene chloride and was shown by mixture melting point, infrared, and nmr spectral analysis to be unreacted *exo*-tosylate starting material.

In an effort to recover any alcohols, which are usually formed under the basic work-up conditions of the other tosylate solvolysis mixtures, the tosylate obtained from chromatography and before crystallization was treated with pyridine and acetyl chloride at room temperature for 24 hr. The acetylated reaction mixture was then rechromatographed; however, only tosylate was obtained, no traces of other acetates were evident. The purity and quality of all of these separations were checked by thin layer chromatography on silica gel in a 9:1 hexane–acetone solvent system.

Metallocenyl Carbonium Ions. Participation by Ferrocene in the Solvolysis of β-Ferrocenylalkyl Tosylates

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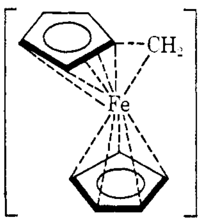
Abstract: The participation of the ferrocenyl group during solvolysis of β-ferrocenylalkyl tosylates has been demonstrated by (a) the entropy of activation, (b) the difference in solvolysis rate in acetic acid and 80% aqueous acetone, (c) the effect of methyl substitution on the α-carbon, (d) the kinetic isotope effect in the solvolysis of 1,1-dideuterio-2-ferrocenylethyl tosylate, and (e) the complete retention of configuration in the solvolysis of optically active 1-ferrocenyl-2-propyl tosylate.

The unusual stability of α-metallocenyl carbonium ions has been demonstrated.[3–6] Though the exact structure of these cations is the subject of some debate,[3–10] there is general agreement that electrons from the region between the two cyclopentadienyl rings are most effective in accounting for this stability. The open question is the degree of bonding between the iron atom of the metallocenyl residue and the α carbon, one group[3–7] feeling that there is significant bonding between these two atoms (structure I) and another group[8–10] favoring a structure such as II[11] which is similar to the breaking and reformation of the metal–carbon bond in a step analogous to an SE2 reaction.

The work reported in this and the succeeding papers is concerned with the stabilization of cationic centers that are removed from the ferrocenyl group by one carbon atom (2-ferrocenylalkyl cations). Trifan and Backsai[4] first observed that 2-ferrocenylethyl *p*-toluenesulfonate solvolyzes more rapidly by a factor of 537 than 2-phenylethyl *p*-toluenesulfonate in 80% acetone water.



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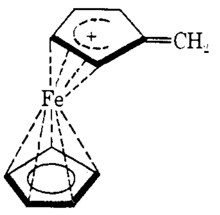

II

They suggested that this rate enhancement was due to participation by the ferrocenyl group. The point of this paper is to provide evidence that the 2-ferrocenylalkyl cation is stabilized by the neighboring ferrocenyl group and in a succeeding paper to show that electrons in the interannular region of the ferrocene are most effective in providing this stabilization. The question of whether the electrons involved in this stabilization are those which in the ground state form carbon–iron bonds or are localized on the iron atom is not resolved by this work.

Results

All acetolyses were carried out in carefully degassed ampoules. No oxidative formation of ferricinium salts[12] was observed when a degassed solution of methylferrocene in acetic acid was maintained at a typical solvolysis temperature for extended periods of time. In some of the solvolyses, however, small amounts of ferricinium ion formation were observed which might have

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(2) Academy for Chemistry, Nobel Institute, Stockholm 53, Sweden.

(3) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3483 (1959).

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

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

(6) E. A. Hill and J. H. Richards, *ibid.*, **83**, 4216 (1961).

(7) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, No. 15, 1965 (1966).

(8) J. C. Ware and T. G. Traylor, *ibid.*, 1295 (1965).

(9) T. T. Tidwell and T. G. Traylor, *J. Am. Chem. Soc.*, **88**, 3442 (1966).

(10) T. G. Traylor and J. C. Ware, *ibid.*, **89**, 2304 (1967).

(11) J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Letters*, 1299 (1966).

(12) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952).