The Chemistry of Metallocenes. I. Carbonium Ion Stabilization by the Ferrocenyl Group[1,2]

T. G. Traylor and J. C. Ware

Contribution from the Department of Chemistry, Revelle College, University of California at San Diego, La Jolla, California. Received July 8, 1966

Abstract: The rapid solvolyses of α-ferrocenylcarbinyl derivatives, $FerCR_2X$, have been accurately correlated with carbonyl stretching frequencies of $FerCOCH_3$, $ArCOCH_3$, $FerArCOCH_3$, and with σ^+ values. These correlations are interpreted as evidence that the main contribution of the iron atom to the $FerC^+R_2$ stability is hyperconjugation ($\sigma-\pi$ conjugation). The σ^+ values for the ferrocenyl (Fer) group have been determined: $\sigma^+_{\alpha\text{-Fer}} = -1.35$, $\sigma^+_{p\text{-Fer}} = -0.71$, and $\sigma^+_{m\text{-Fer}} = 0$. Reactivities of metallocenes are discussed in terms of breaking and making the metal–carbon bond in a step analogous to S_E2 reactions. The presence of filled d orbitals in the metal is suggested to influence reactivities by their influence on cyclopentadienide–metal bonding rather than by direct interaction with electrophilic reagents. The terminology applied to the effects of β substituents on solvolysis reactions and mechanisms of such effects is reviewed.

The α-ferrocenylcarbonium ions I generated by solvolyses[3,4] or protonation of vinylferrocenes[5]
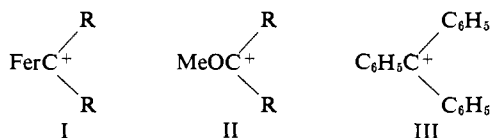
have about the same stability as α-methoxymethyl II[2] or triphenylmethyl III[3] cations and react with high stereospecificity with nucleophiles.[3b,4a]
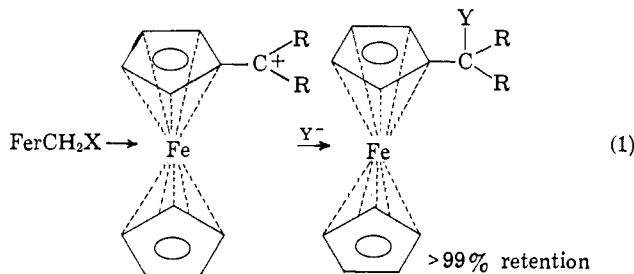
A molecular orbital description of I incorporating both direct backside participation of iron orbitals and delocalization into the ring has been formulated by Hill and Richards[3b] to explain the observed reactivity and stereospecificity of reaction 1.

A comparison of this reaction with reactions of other β-metalloalkyl derivatives[6] and a consideration of the ease of oxidation of ferrocene[7a] suggest that iron

hyperconjugation ($\sigma-\pi$ conjugation) might be exceptionally facile.

This phenomenon may also explain the observed rate acceleration and stereochemistry but can be differentiated from neighboring nucleophilic participation in several ways. In this paper we describe and document methods for differentiating these two effects and then use these methods to indicate the nature of the stabilization provided by the ferrocenyl group.

Results

We have employed four experimental methods to test whether a substituent accelerates S_N1 reactions by neighboring nucleophilic attack or by σ delocalization (including hyperconjugative or $\sigma-\pi$ delocalization). Two of these tests are well documented in the published literature and will be discussed below. We offer the following evidence for the other two.

Internal Nucleophilic Attack at the *para* Position in Benzyl Chlorides. It seems reasonable that a group which accelerates S_N1 solvolysis by neighboring nucleophilic attack
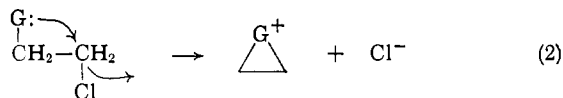
will not show this accelerating effect in the *para* position of a benzyl derivative because the aromaticity would then be lost.
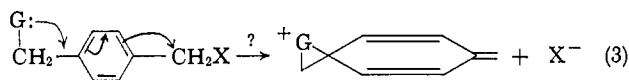
In order to determine whether such *para*-nucleophilic attack occurs to a significant extent we have studied the effect of one of the best neighboring groups (EtS–) on benzyl chloride solvolysis as shown below.

(1) Supported by Air Force Office of Scientific Research Grant AF-AFOSR-514-64.
(2) Partially reported in a previous communication: *Tetrahedron Letters*, 1295 (1965).
(3) (a) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, 81, 3484 (1959); (b) E. A. Hill and J. H. Richards, *ibid.*, 83, 3840 (1961); (c) *ibid.*, 85, 4216 (1963); (d) E. A. Hill, *J. Org. Chem.*, 28, 3586 (1963); (e) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1695 (1966).
(4) D. S. Trifan and R. Bacskai: (a) *Tetrahedron Letters*, No. 13, 1 (1960); (b) *J. Am. Chem. Soc.*, 82, 5010 (1960).
(5) G. R. Buell, W. E. McEwen and, J. Kleinberg, *Tetrahedron Letters*, No. 5, 16 (1959).
(6) (a) G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960; (b) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957; (c) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.
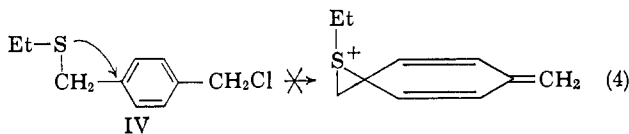(7) (a) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, John Wiley and Sons, Inc., New York, N. Y., 1965, p 63; (b) M. Rosenblum, J. O. Santer, and W. Glenn Howells, *J. Am. Chem. Soc.*, 85, 1450 (1963); (c) M. Rosenblum, *ibid.*, 81, 4530 (1959).

Table I. Carbonyl Stretching Frequency of $RCOCH_3$ in Dilute Carbon Tetrachloride Solution

	ν, cm^{-1}		
R	Present work	Jones, et al.[a]	Fuson, et al.[b]
3-Indolyl	1662.8		
2-Thienyl	1672.2		
p-$H_2NC_6H_4$	1676.2	1677	1677
Fer	1676.4		
9-Phenanthryl	1681.3		
1-Naphthyl	1681.6		
3,4-$CH_2O_2C_6H_4$	1681.9		
p-$CH_3OC_6H_4$	1682.9		1684
p-$FerC_6H_4$	1684.3		
p-$CH_3COHNC_6H_4$	1684.4[c]		1686
p-$CH_3C_6H_4$	1687.5	1687	
2-Furyl	1687.5		
m-$H_2NC_6H_4$	1688.3	1689	
p-$C_6H_5C_6H_4$	1688.5		
m-$CH_3OC_6H_4$	1689.3		
m-$CH_3C_6H_4$	1689.7		
m-$FerC_6H_4$	1690.0		
o-$FerC_6H_4$	1690.2		
p-$CH_3CO_2C_6H_4$	1690.8		
C_6H_5	1691.0	1691	1692
p-FC_6H_4		1692	
p-ClC_6H_4	1692.2	1692	1692
p-BrC_6H_4	1692.8	1693	1693
m-ClC_6H_4	1695.6	1696	
p-$O_2NC_6H_4$	1700.2	1700	1703
m-$O_2NC_6H_4$	1700.7	1701	1701
9-Anthryl	1700.8		
CH_3	1717.7		
CH_3O	1751.0		

[a] Reference 12. [b] Reference 13. [c] Limited solubility required use of expanded per cent transmission scale; position of maximum absorption is recorded.

p-Ethylthiomethylbenzyl chloride (IV) was synthesized by the reaction of the sodium salt of ethanethiol with a fourfold excess of p-xylylene dichloride. The rates of solvolysis of benzyl chloride and the substituted chloride IV in 50% aqueous dioxane were determined conductometrically. The rate constants at 80.0° were 5.90 × 10^{-5} sec^{-1} for benzyl chloride and 8.70 × 10^{-6} sec^{-1} for IV. This indicates no appreciable acceleration in benzyl chloride solvolysis by nucleophilic participation in the *para* position.[8]

Carbonyl Stretching Frequencies. The rates of solvolyses of alkyl tosylates $R_2CHOTos$ have been quantitatively correlated with carbonyl stretching frequencies in $R_2C=O$.[9] Similarly the solvolyses of aralkyl chlorides[10] $ArCHClCH_3$ may be correlated with $ArCOCH_3$ stretching frequencies[11-13] because both correlate with σ^+. It has been shown that, although neighboring groups may accelerate S_N1 solvolysis, such groups do not make a corresponding change in carbonyl stretching frequencies of the ketones.[9] In order to have a consistent set of carbonyl stretching frequen-

cies of acetophenones with which to compare the ferrocenyl derivatives we have remeasured a large number of such frequencies. The data, along with those for the ferrocenyl-substituted ketones, are shown in Table I. A plot of $\nu_{C=O}$ vs. known σ^+ values appears in Figure 1 where previously unknown σ^+ values are assigned from the measured $\nu_{C=O}$. The carbonyl stretching frequencies reported here are in good agreement with those of Jones, Forbes, and Mueller.[12] The correlation for *para* derivatives is excellent, while that for *meta* derivatives is less satisfactory. It may be that the latter should be correlated by a line of greater slope. The σ^+ values can be calculated from the equation

$$\sigma^+ = 0.0877(\nu_{C=O} - 1691.1) \qquad (5)$$

Because these frequencies can now be measured to an accuracy of ±0.5 cm^{-1}, the maximum error in σ^+ will be ±0.044. This equation should make possible the determination of σ^+_α for a variety of other aromatic systems (σ^+_α is defined as the σ^+ constant for the group at the position of reaction. Thus $\sigma^+_{\alpha\text{-Ph}} \equiv 0 \equiv \sigma^+_{p\text{-H}}$. Therefore σ^+_α includes Brown's σ^+ constants[14] and is equivalent to the σ_r and "σ" constants referred to by Streitwieser.[15]

The correlation of solvolysis rates (see below) with corresponding ketone carbonyl frequencies for α-phenethyl chlorides is shown in Figure 2. The equation of the line may be written $\log k = 0.64(\nu_{C=O} - 1691)$, as contrasted with $\log k = 0.132(\nu_{C=O} - 1720)$ found by Foote[9a] for aliphatic systems. Obviously a single line will not correlate both aralkyl and alkyl derivatives. In addition the correlation of $\nu_{C=O}$ for $RCOCH_3$ with σ^+_p of the very electronegative R groups F, Cl, Br, NH_2, CH_3O, C_6H_5O (attached directly to the carbonyl) is very poor and has a slope which reflects a very strong inductive effect on $\nu_{C=O}$. Therefore, we have omitted such groups[16,17] (as well as R = alkyl) from our plots of $\nu_{C=O}$ vs. σ^+. Each of these correlations appears to be limited to a narrow range of inductive effects. The inclusion of ferrocenyl with the aromatic series in our treatment seems justified, since it is aromatic and has an inductive effect[7a] within the range covered by the α substituents treated in Figures 1 and 2.

Syntheses. The phenylferrocenes employed in this study were synthesized by treating acetylbenzenediazonium salts with ferrocene,[7b] reducing the ketones, and treating the resulting alcohols with concentrated hydrochloric acid or dry hydrogen chloride. The analyses and nmr spectra of the intermediate products and the final chlorides are definitive for structure

(8) We also showed that p-hydroxymethylbenzyl chloride reacts with ethoxide ion at the same rate as does benzyl chloride, but this finding is not conclusive to the point due to the ease of S_N2 displacement on benzyl chloride.

(9) (a) C. S. Foote, J. Am. Chem. Soc., 86, 1853 (1964); (b) P. R. Schleyer, ibid., 86, 1856 (1964).

(10) C. Mechelynck-David and P. J. C. Fierens, Tetrahedron, 6, 232 (1959).

(11) C. N. R. Rao and G. B. Silverman, Current Sci. (India), 26, 375 (1957).

(12) R. N. Jones, W. F. Forbes, and W. A. Mueller, Can. J. Chem., 35, 504 (1957).

(13) N. Fuson, M-L. Josien, and E. M. Shelton, J. Am. Chem. Soc., 76, 2526 (1954).

(14) H. C. Brown in "Steric Effects in Conjugated Systems," C. W. Gray, Ed., Academic Press Inc., New York, N. Y., 1958, p 109.

(15) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962: (a) p 35; (b) p 103; (c) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 326.

(16) A referee has suggested that the omission of the MeO group from Figure 1 invalidates the treatment for the ferrocenyl group. The omission of alkyl and electronegative substituents from Figure 3 or the omission of aromatic or electronegative groups in the treatment of Foote[9a] do not, in our opinion, invalidate the correlations (see ref 17).

(17) Although inductive effects appear to dominate in the carbonyl stretching frequencies of $RCOCH_3$ for MeO, Cl, etc., inductive destabilization of carbonium ions by MeO is seen to be negligibly small by the following comparison. Whereas we would calculate from eq 14 (using r 2) that $\sigma^+_{p\text{-anisyl}}$, $\sigma^+_{p\text{-MeO}}$, and $\sigma^+_{\alpha\text{-MeO}}$ should be in the ratio -0.35, -0.70, and -1.4, the observed values are -0.35, -0.78, and -1.4, in good agreement: T. Inukai, Bull. Chem. Soc. Japan, 35, 400 (1962).
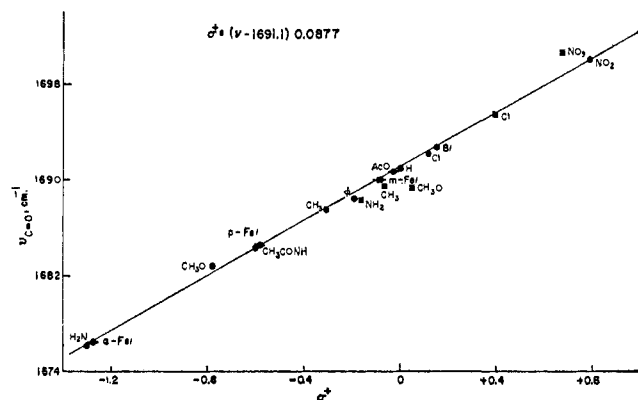
Figure 1. Plot of carbonyl stretching frequencies of substituted acetophenones against σ^+: ■, *meta* derivatives; ●, *para* derivatives; ─●─, ─■─, σ^+ values assigned by this plot.

Figure 2. Plot of carbonyl stretching frequencies of acetophenones and ferrocenyl methyl ketone against log k for chloride (RCH-ClCH₃) solvolysis.

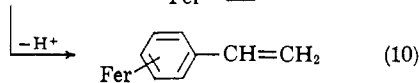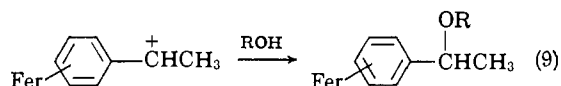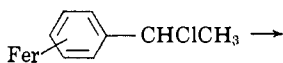proof. Other chlorides were synthesized by standard methods and similarly identified.
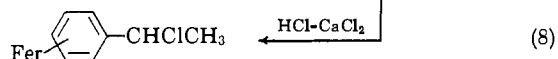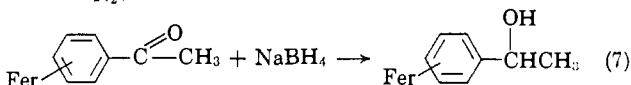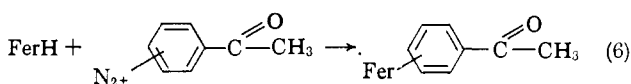
Solvolysis Products. The products of solvolyses of various α-phenethyl chlorides in ethanol–water or acetone–water are known to consist of the ether or alcohol and traces of the corresponding styrenes.[10] We have, therefore, determined only the products of the ferrocenylphenethyl chlorides under our solvolysis conditions. The products, shown in Table II, are con-

Table II. Products of Solvolysis of RC₆H₄CHClCH₃ in 95% Aqueous Ethyl Alcohol

R	Temp, °C	R'OEt[b]	R'OH[b]	R-Styrene	Other
o-Fer	40	92	3	3	...
m-Fer	70	68	3	6	...
p-Fer	0	69	4	2	Hydrocarbon,[a] ketone, etc.

[a] A small amount of unidentified high molecular weight ferrocene was obtained from the *para* derivative only. R' = RC₆H₄CHCH₃.

sistent with the SN1 mechanism previously proposed and documented for α-phenethyl chloride solvolysis.[10,18]

Figure 3. Plot of log k vs. σ^+ values for solvolyses of substituted α-phenethyl chlorides in 95% aqueous ethanol at 25°.

Kinetics. Solvolysis rates were determined by conductivity, by titration of aliquots for acid, or by pH-Stat titration. When two methods were used the agreement was good. Although limited solubilities of the ferrocenes required that we use less aqueous solvents than those reported for α-phenethyl chloride solvolyses, our data agreed with literature values after correction for solvent polarity by the method of Grunwald and Winstein.[18a] The kinetic data for solvolyses are listed together with activation parameters in Table III.

A plot of log k_{25} vs. σ^+ shown in Figure 3 yields a slope $\rho = -6.1$ and indicates that $\sigma^+_{p\text{-Fer}} = -0.7$, $\sigma^+_{m\text{-Fer}} = +0.1$, and $\sigma^+_{\alpha\text{-Fer}} = -1.4$ (off the plot).

Dimerization of the 1-(p-Ferrocenylphenyl)ethyl Carbonium Ion. p-Ferrocenyl-α-phenethyl chloride was treated with concentrated sulfuric acid in chloroform, and the resulting ferricinium products were extracted into water and reduced. A 17% yield of product whose properties agreed with the structure V was obtained. We interpret this reaction as shown below by analogy to the α-ferrocenyl carbonium ion behavior.[19,20]

(18) (a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1597 (1957); (c) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).
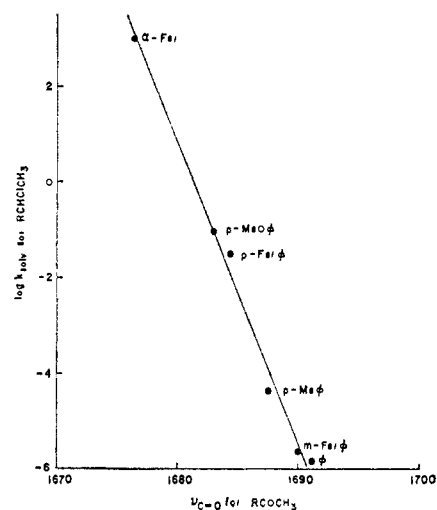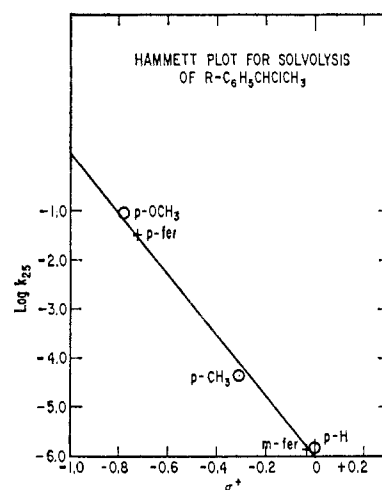
(19) K. L. Rinehart, C. J. Michejda, and P. A. Kittle, *Angew. Chem.*, **72**, 38 (1960).

(20) M. Cais and E. Eisenstadt, *J. Org. Chem.*, **30**, 1148 (1965).

Table III. Solvolyses of $RCHClCH_3$ in 95% Aqueous Ethyl Alcohol

| R	Temp, °C	$10^4 k$, sec⁻¹	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	k_{25}, sec⁻¹	$\log k_{25}$	$k_R/k_{Ph_{25}}$
⌬— [a]	60.0 / 70.0 / 78.0	0.526 / 1.16 / 2.37	19.1	−21.2	1.54×10^{-6}	−5.811	(1)
Fer—⌬— [a,t]	40.0 / 50.0 / 60.0	6.20 / 17.2 / 40.0	18.7	−13.6	1.33×10^{-4}	−3.876	86
Fer—⌬— [a]	55.0 / 60.0 / 70.0 / 80.0	0.575 / 0.918 / 2.80 / 7.32	23.3	−7.1	1.38×10^{-6}	−5.859	0.90
Fer—⌬— [a]	−9.04 / −0.02 / 10.0	5.37 / 16.6 / 59.3	18.3	−4.0	3.16×10^{-2}	−1.500	20,000
CH_3—⌬—	35.0 / 45.0 / 55.0 / 65.0	1.30 / 3.66[c] / 8.64(8.81)[d] / 23.5	19.1	−14.4	4.40×10^{-5}	−4.357	29
CH_3O—⌬—	−19.61 / −9.90 / −0.02 / +0.10	5.34 / 17.5 / 61.8 / (63.2)	16.8	−7.0	8.97×10^{-2}	−1.047	58,000
Fer—[e,f]	−66.2	5.4 ± 5				2.8[g]	4×10^8
CH_3O—[e]	−69.6	4.1 ± 4					4×10^8

[a] Containing 0.5% diethyl ether. [b] Fer = ferrocenyl. [c] Rate, 3.64×10^{-5} sec⁻¹ when the solvent contained 0.5% diethyl ether. [d] Values in parentheses were obtained titrimetrically. [e] Solvent 60:40 ether–ethanol. [f] Reference 4c. [g] Calculated using m Y relationship of ref 18 assuming $m = 1$ and Y for 60% ether–ethanol = −4.3 estimated from data of P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

(11)

VI VII VIII
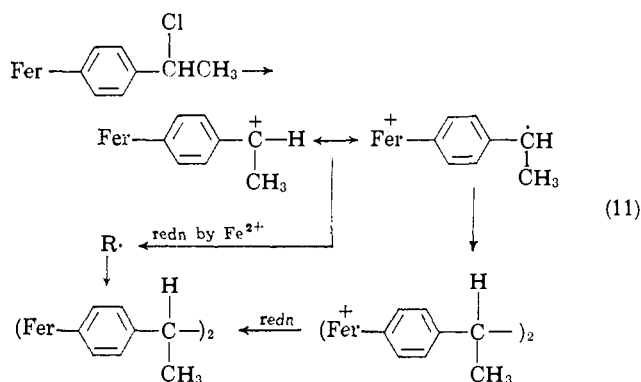
Discussion

Effects of β Substituents on Solvolysis Reactions.

Before discussing in detail the effects of β-metal substitution on solvolysis reactions, we wish to reconsider the various phenomena attributed to the effects of β substituents upon the stabilities of developing carbonium ions.

The terms "hyperconjugation,"[21] "elimination,"[22] "fragmentation,"[23] and "σ–π conjugation,"[24] have been applied to processes in which a carbonium ion is stabilized by π conjugation with an orbital previously bonding to another atom[25] (see VI). The names "neighboring group participation,"[26b] "anchimeric assistance,"[26]

or "synartetic acceleration"[27] are used to designate stabilization of a carbonium ion by direct bonding to a neighboring atom as in VII or VIII. In most calculations of anchimeric assistance (or bridged ion stabilities)[26c,28] some π bonding of the type VI is included, and the structure generally written is VIII. There is thus some ambiguity in these terms and we believe that this ambiguity has contributed to the controversy concerning the nature and extent of occurrence of such processes.[29]

In this discussion we will consider one extreme, VI, in which the groups G can form stable cations (G = R_2NCH_2-, C_7H_7, Li, MgX, etc.), and another extreme, VII, in which the G is a poor cation but a rather good nucleophile (G = RS, R_2N, O^-, C_2H_5, etc.). We will call VI σ–π conjugation (as a general term for hyperconjugation) and VII internal nucleophilic displacement. (The latter term has been considered synonymous with neighboring group participation.[12b]) The term "anchimeric assistance" might be applied to both extremes and to all intermediate cases (VIII). Neighbor-
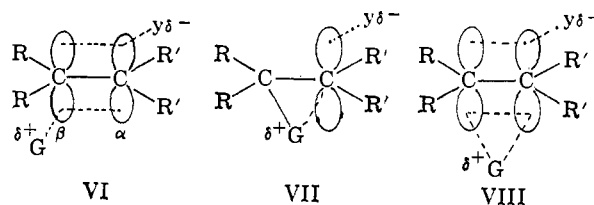
(21) M. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962; numerous references are given there.

(22) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, 1, 225 (1962).

(23) C. A. Grob, "Theoretical Organic Chemistry," The Kekule Symposium, Butterworth and Co., Ltd., London, 1959, p 114.

(24) (a) A. N. Nesmeyanov, K. A. Perchskaya, A. N. Akramovich, and L. M. Minakova, *Dokl. Akad. Nauk SSSR*, 121, 660 (1958); (b) A. N. Nesmeyanov and I. I. Kritskaya, *ibid.*, 121, 447 (1958).

(25) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 208.

(26) (a) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, 61, 1576 (1939); (b) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, 75, 147 (1953).

(27) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, 168, 65 (1951).

(28) Reference 15, p 380.

(29) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

ing aliphatic carbon is considered to use a bonding orbital to form VIII.

The $\sigma-\pi$ conjugation by the $G-C_\beta$ bond is seen by C_α as a simple π-resonance effect (see ref 15c), and will be expected to correlate quantitatively with other π-delocalization effects. In contrast, in the extreme VII, the α-carbon sees the participation of G as an SN2 process, and this process should not correlate with π delocalization. Furthermore, internal nucleophilic substitution will be expected to compete with rather than accelerate external nucleophilic attack.

Based on these considerations we have used four experimental methods which might differentiate between cases where the driving force is almost exclusively VI and those where it is VII: (1) substitution of resonance-stabilizing groups such as MeO–, HO–, ArO–, for R' in VI–VIII; such substitution has been shown essentially to destroy[30a] neighboring group participation[29] but should only reduce somewhat any resonance stabilization afforded by $R_2C(G)$ (this follows from the fact that SN1 reactions are accelerated much more by resonance stabilization than are SN2 reactions and the consideration that neighboring groups perform an internal SN2 reaction); (2) insertion of an aromatic group between the α and β carbons; whereas conjugation effects are transmitted through a p-phenylene group, neighboring nucleophilic participation is apparently not so transmitted (eq 4); (3) correlation of solvolysis rates with carbonyl stretching frequencies; this effective correlation for aryl substituents (Figure 1) fails when neighboring group participation is involved in the solvolysis;[9a,b] (4) substitution of very good π-donating substituents at the α-carbon; this accelerates both SN1 and SN2 processes, and such accelerations of SN1 reactions correlate with those of SN2 reactions[15c] whereas, by contrast, neighboring groups such as EtS, Cl, Br, and AcNH do not accelerate SN2 reactions.[15a]

Application of These Criteria to the Effect of the Ferrocenyl Group. In relating the behavior of the iron electrons in ferrocene (bonding and nonbonding) to the behavior of the electrons on the common neighboring groups EtS, R_3C, AcNH, Br, I, etc., it must be remembered that the iron electrons which are involved are probably those in the 3d orbitals whereas in most neighboring groups 2s, 2p or 3s, 3p electrons are used. This could account for some of the differences we observe.[31] However, neighboring iodine behaves like RS–[15] with respect to the criteria mentioned, and yet iodine uses much more diffuse orbitals. In the absence of evidence to the contrary we prefer to consider nucleophilic participation by d electrons to be similar to that by s and p electrons.

σ^+ **Correlations.** We propose that $\sigma-\pi$ conjugating systems will show the same kind of response to π-electron demand as do other resonance-stabilizing groups. Therefore exclusive $\sigma-\pi$ conjugation requires that any quantitative correlation which holds for conjugating aromatic groups (anisyl, thienyl, etc.) will include the ferrocenyl group. The σ^+ parameter is commonly used in such correlations, and a test of the purely resonance character of the substituent is the accuracy with which a variety of reactions correlates with the σ^+ value.

(30) (a) T. G. Traylor and C. L. Perrin, J. Am. Chem. Soc., 88, 4934 (1966); (b) T. T. Tidwell and T. G. Traylor, ibid., 88, 3442 (1966).
(31) Suggested by a referee.

We have used the carbonyl stretching frequency eq 5 to calculate $\sigma^+_{\alpha\text{-Fer}}$, $\sigma^+_{m\text{-Fer}}$, and $\sigma^+_{p\text{-Fer}}$ and compared them with those determined by other methods in Table IV.[32]

Table IV. σ^+ Values

α-Fer	σ^+ m-Fer	p-Fer	Method
−1.3	−0.09	−0.6	Carbonyl frequency vs. ArCOCH$_3$
−1.4[a]	−0	−0.7	Solvolysis of RCHClCH$_3$ vs. ArCHClCH$_3$
−1.3[b]	...	...	Basicity of RCOCH$_3$ vs. ArCOCH$_3$

[a] From Figure 1. [b] Reference 33.

Whereas neighboring nucleophilic participation in solvolysis might account for the extreme reactivity of FerCHClCH$_3$, which leads to our value for $\sigma^+_{\alpha\text{-Fer}}$ = −1.4, no such phenomenon has been observed to affect carbonyl basicities or stretching frequencies. Since these three values of $\sigma^+_{\alpha\text{-Fer}}$ are so close, it is attractive to attribute all three phenomena (including solvolysis) to $\sigma-\pi$ conjugation. This correlation is demonstrated in the plot of log k (solvolysis) vs. carbonyl stretching frequency shown in Figure 2.

Effect of Resonance-Stabilizing α Groups on α-Ferrocenyl Group Acceleration. The correlation of basicities of aromatic aldehydes with ferrocenecarboxaldehyde (eq 12) yields $\sigma^+_{\alpha\text{-Fer}}$ = 1.30.[33] In solvolysis of RCHClCH$_3$ (R = aryl, ferrocenyl), we have shown $\sigma^+_{\alpha\text{-Fer}}$ to be −1.4, in remarkably close agreement (see Table IV).

$$\overline{\text{Fe}}\text{--CHO} \quad + \text{H}^+ \quad \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \qquad (12)$$

$$\xrightarrow{k} \qquad (13)$$
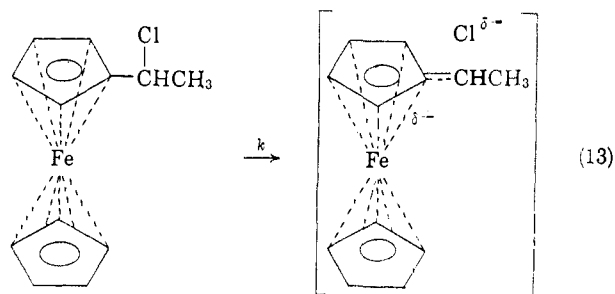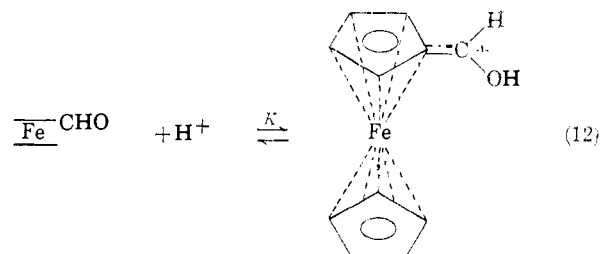
Since substitution of a methoxy group on a carbonium ion completely removes the participation by neighboring carbon,[30a] clearly, if there is participation by iron, it is not like that by neighboring carbon.

(32) A. N. Nesmeyanov, E. G. Perevalova, S. P. Gubin, K. I. Grandberg, and A. G. Kozlovsky, Tetrahedron Letters, 2381 (1966), have calculated $\sigma^+_{\alpha\text{-Fe}_i}$ = −1.09 from rates of protonolysis of R_2Hg. Because this reaction does not follow σ^+ we feel that the number is less reliable than our value of − 1.35. We find the ratio $\sigma_p^+/\sigma_\alpha^+$ to be 2.1 for either MeO or Fer, while they use the value 1.55 determined from σ_α/σ_p rather than from $\sigma_\alpha^+/\sigma_p^+$.
(33) E. M. Arnett and R. D. Bushick, J. Org. Chem., 27, 111 (1962).

Transmission of Resonance Effects through a Phenylene Group.

The basis of the $\rho\sigma^+$ treatment is the transmission of resonance effects through a phenylene group.[14] Furthermore, a phenylene transmission coefficient, τ, independent of substituent, may be defined.[34]

$$\log k/k_0 = \tau(\rho\sigma^+) \qquad (14)$$

This implies that the free-energy difference introduced in the transition state by α substitution should be proportional to that caused by *para* substitution of the same substituent if steric effects are small.

$$\Delta\Delta F^{\ddagger}_{(\alpha\text{-MeO})} = \tau\Delta\Delta F^{\ddagger}_{(p\text{-MeO})} \qquad (15)$$

If the ferrocenyl (or any other) group stabilizes only by conjugation the same relationship should hold.
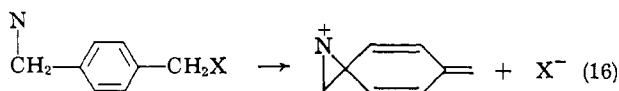
$$\Delta\Delta F^{\ddagger}_{(\alpha\text{-Fer})} = \tau\Delta\Delta F^{\ddagger}_{(p\text{-Fer})}$$

Thus

$$\log k_{\alpha\text{-Fer}}/k_{\alpha\text{-MeO}} = \tau \log k_{p\text{-Fer}}/k_{p\text{-MeO}}$$

and if $k_{\alpha\text{-Fer}} = k_{\alpha\text{-MeO}}$ then $k_{p\text{-Fer}} = k_{p\text{-MeO}}$. This is the reason we chose to compare the ferrocenyl group with the methoxyl group.[35]

On the other hand, transmission of a neighboring group effect through a phenylene group destroys the aromaticity

$$(16)$$

and, as we have shown, does not occur. If the ferrocenyl group is acting as a neighboring nucleophile, it should be without effect in the *para* position. If it is acting in both ways, then it should lose (relative to *p*-methoxyl) a fraction, $1/\tau$, of the free energy contributed by neighboring group participation when insulated by a phenyl group. Because we are discussing $\Delta\Delta F_\alpha^{\ddagger}$ values of about 18 kcal and $\tau \cong 2$, this test is a sensitive one. The relevant rate data are shown in Table V.

This table shows first that the EtSCH$_2$– group, which is an excellent neighboring group, has little effect in the *para* position. Secondly, although the data for the α-MeO and α-Fer are rather inaccurate, it is clear that (within a factor or two)

$$\frac{k_{\alpha\text{-FerCHClCH}_3}}{k_{\alpha\text{-MeOCHClCH}_3}} = \frac{k_{p\text{-FerC}_6\text{H}_4\text{CHClCH}_3}}{k_{p\text{-MeOC}_6\text{H}_4\text{CHClCH}_3}}$$

In addition to these solvolysis data, the carbonyl stretching frequencies for α- and p-ferrocenyl ketones indicate almost identical transmission coefficients for phenylene.

$$\left(\frac{\sigma^+_{\alpha\text{-Fer}}}{\sigma^+_{p\text{-Fer}}}\right)_{CO\ stretch} = \frac{1.3}{0.6} = 2.1$$

and

$$\left(\frac{\sigma^+_{\alpha\text{-Fer}}}{\sigma^+_{p\text{-Fer}}}\right)_{solvolysis} = \frac{1.4}{0.7} = 2.0$$

Therefore, this criterion also indicates that neighboring nucleophilic participation makes a negligible contribu-

(34) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.
(35) A better choice would have been the *p*-aminophenyl group except for synthetic and analytic difficulties (see ref 16).

**Table V.** Relative Solvolysis Rates of Alkyl Chlorides at 25°

Compd	Rel rate	Compd	Rel rate
EtCl	(1)		(1)
MeOCHCl^a / CH$_3$	10^{14}	MeO—⬡—CHCl^a / CH$_3$	5×10^4
FerCHCl^b / CH$_3$	10^{14}	Fer—⬡—CHCl^a / CH$_3$	2×10^4
EtSCH$_2$CH$_2$Cl^c	10^7	EtSCH$_2$—⬡—CH$_2$Cl^{a,d}	1.6^d
$\overline{\text{O}}$CH$_2$CH$_2$Cl^c	10^{10}	Fer—⬡—CHCl^a / CH$_3$	1.0
		MeO—⬡—CHCl^e / CH$_3$	0.5

^{a} This work. ^{b} Reference 3c. ^{c} Reference 15c. ^{d} Relative to benzyl chloride. ^{e} From $\sigma^+_{m\text{-MeO}} = +0.05$, $\rho = -6.1$.
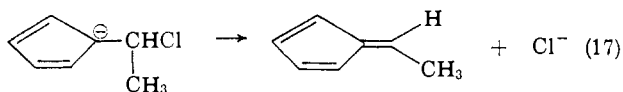
tion to the stabilization of α-ferrocenyl carbonium ions. The neighboring iron has little in common with other neighboring groups.

Correlation of SN1 with SN2 Reactions on Ferrocenylmethyl Chloride.

We have recently reported[30b] that ferrocenylmethyl chloride is about eight times more reactive than methoxymethyl chloride toward either SN1 ethanolysis or bimolecular reaction with ethoxide ion. Since ferrocenylmethyl chloride competes with methoxymethyl chloride as well in SN2 as in SN1 reactions and neighboring group participation does not accelerate SN2 reactions, we concluded that no such acceleration was indicated in the SN1 reaction of ferrocenylmethyl chloride.

Mechanism of Solvolysis.

Having presented experimental evidence against neighboring nucleophilic participation, we must account for rate acceleration, *exo:endo* rate ratios in IX, and retention of configuration in some other way.

IX
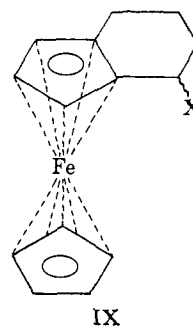
We conceive the metallocene structure to be a rather basic aromatic system, which might be expected of a somewhat complexed cyclopentadienide anion. Thus, although reaction 17 would certainly be too fast to measure reducing the negative charge by bonding to

$$\text{[cyclopentadienyl]}^{\ominus}\text{--CHCl} \atop \text{CH}_3 \quad \rightarrow \quad \text{[cyclopentadiene]}{=}\text{CH} \atop \text{CH}_3 + H \quad + \text{Cl}^- \quad (17)$$

Fe^{2+} (eq 18) would make the reaction sufficiently slow

$$(18)$$
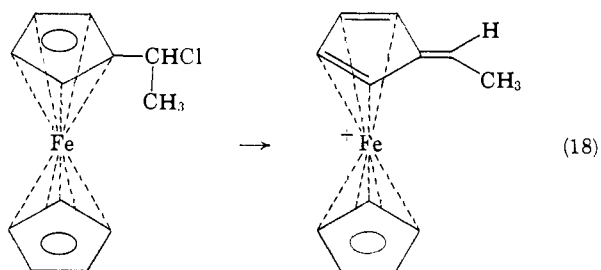
to be observable. (Cr^0 may be *donating* in $(C_6H_6)_2Cr$.) The rate acceleration (relative to phenyl) is therefore easily explained.

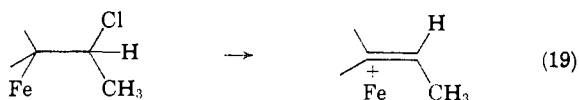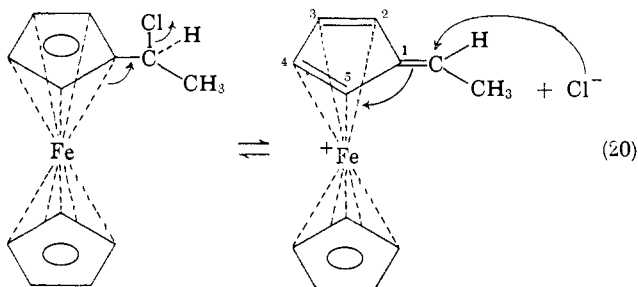The only thing which would differentiate this system (reaction 19) from other aromatic systems is the Fe–C bonding, which we conceive to be greatly weakened in the transition state by σ–π conjugation.[36a,b] This will

$$(19)$$

determine the stereochemistry because such conjugation is much more facile when the two groups are in a *trans* configuration.[37]

$$(20)$$

By microscopic reversibility, the lowest energy reaction path for the reverse process takes the same *trans* geometry and gives retention of configuration.[38a] Therefore this process (which might be compared to an E2 elimination if the second cyclopentadienide ring is considered as the base) gives the same stereochemistry as would nucleophilic participation by unshared electrons on iron. For the same reasons, the *exo*:*endo* rate ratios in the solvolyses of IX are clearly consistent with the σ–π conjugation mechanism.

Either neighboring nucleophilic attack as we describe it or "direct back-side participation of iron elec-

(36) (a) Rosenblum has formulated this stabilization similarly: ref 7a, p 133; (b) the weakening of the iron carbon bonds on formation of an α-ferrocenylcarbonium ion has been suggested and documented by Nesmeyanov, *et al.* For example, the diphenylferrocenyl carbonium ions readily dissociate to 6,6-diphenylfulvenes; (c) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Dokl. Akad. Nauk SSSR*, 154, 1393 (1964); (d) A. V. Nesmeyanov, V. A. Sazonova, V. N. Drozd, N. A. Rodionova, and G. I. Zudkova, *Izv. Akad. Nauk SSSR*, 2061 (1965).

(37) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, 82, 2655 (1960).

(38) (a) In the process shown in eq 20 all the upper Fe–C bonds are conceived to be weakened in going to the ion but the Fe–C₁ bond should probably weaken much more than the others. We have called this process "elimination" or "σ–π conjugation." The latter term is probably preferable since the iron atom is not removed from the molecule. (b) We do not mean to imply that the carbonium ion has no positive character at the α-carbon. Rather the resonance hybrid XV $\longleftrightarrow$ XVI looks more like XVI than like XV (see nmr section for structures).

trons"[3b] as formulated by Hill and Richards suggests that the Fe–C_α distance decreases during ionization to the cation I whereas the σ–π conjugation mechanism predicts no appreciable decrease.[3b] A comparison of the crystal structure of the cation salt with that of the alcohol should be very informative.

Comparison of Ferrocene Reactions with Those of Alkylmetal Compounds. Cyclopentadienylmetal compounds other than those of transition metals react rapidly with electrophiles and show other chemical behavior typical of alkylmetal compounds.[39a,b]

$$(21)$$

Ferrocene and other metallocenes are much less reactive toward electrophiles than are other cyclopentadienylmetal compounds.[6,40-42] They are also much more stable toward homolysis than are alkyl transition metal compounds. On the other hand, rates of substitution on the ring in ferrocene are much faster than those on benzene. Typical reactions which are much faster on ferrocene than on benzene are depicted in eq 1, 22, and 23.

$$(22)$$

$$(23)$$
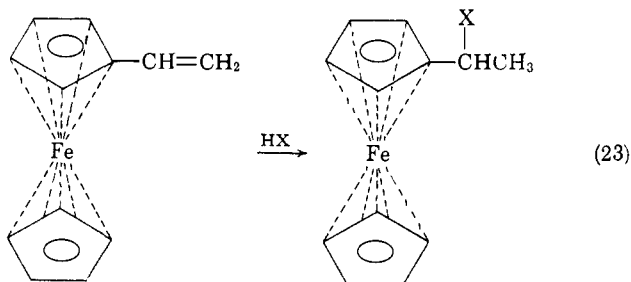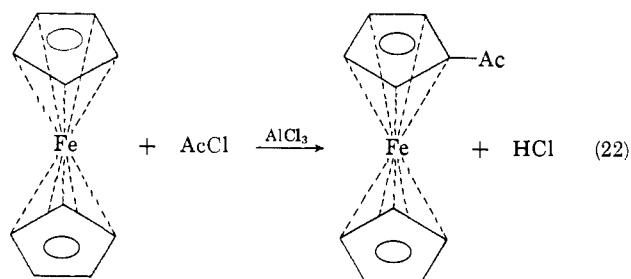
A popular mechanism which has been considered general for these processes is[6,39c,d]

$$(24)$$
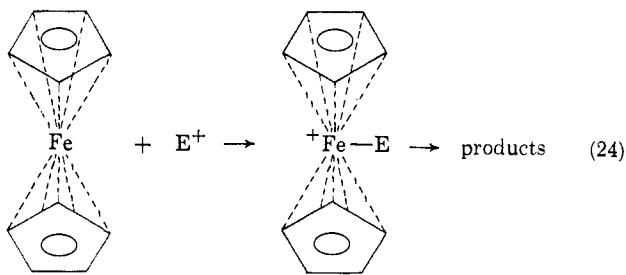
(39) (a) P. L. Pauson, *Quart. Rev.* (London), 9, 391 (1955); W. F. Little, "Survey of Progress in Chemistry," Vol. 1, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1963: (b) p 188; (c) p 153; (d) however, see M. Rosenblum and F. W. Abbate, *J. Am. Chem. Soc.*, 88, 4178 (1966), where additional results suggest that attack on iron is not a necessary part of the mechanism of electrophilic substitution on ferrocenes.

(40) T. J. Kealy and P. L. Pauson, *Nature*, 168, 1039 (1951).

(41) S. A. Miller, J. A. Tebboth, and J. F. Treamine, *J. Chem. Soc.*, 632 (1952).

(42) R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, 74, 3458 (1952).

where E^+ can be the external electrophiles Ac^+, H^+, $HgOAc^+$, RN_2^+, or the internal electrophiles C^+R_2, CH_2OH.[43] We offer an alternative view which proposes that an individual cyclopentadienylmetal bond in a metallocene retains some of the characteristics which are generally associated with carbon–metal bonds.[6] Thus with regard to a single Fe–C bond we might consider ferrocene to be a more covalent counterpart of cyclopentadienyllithium. According to this interpretation the cyclopentadienide moiety has higher electron density on the metal side than on the opposite side of the ring (X),[36a] just as ethyllithium has greater electron density on the lithium side of the carbon than on the opposite side (XI).
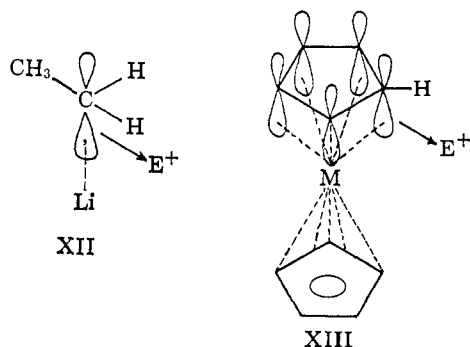

X

XI
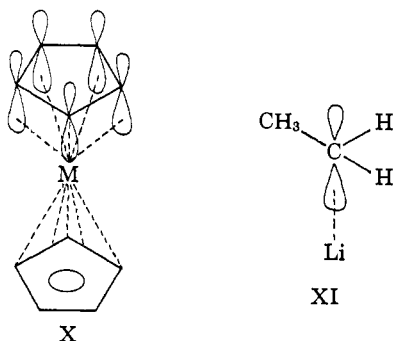
Let us consider reactions 1, 22, and 23 with reference to structures X and XI and the known stereochemical behavior of organometallic compounds.[44] Electrophilic attack on XI is facile and occurs with retention of configuration[6,44a,b] by attack on the electron-rich side as shown in XII. Similarly (under conditions which

XII

XIII

inhibit S_E1 reactions), attack should occur preferentially on the metal side of the cyclopentadienide moiety XIII whether the compound is the σ-bonded lithium derivative, X, or the covalent sandwich, ferrocene.


$$+ \quad M^+ \quad (25)$$
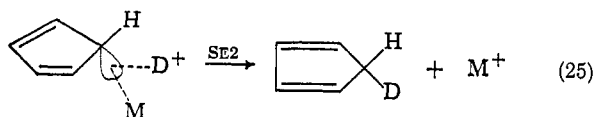
Likewise the addition of HX to vinylferrocene, as in reactions of other allylmetal compounds,[45] should be facile.

(43) See ref 7a for a review of these studies.

(44) (a) R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950); (b) S. Winstein, T. G. Traylor, and C. S. Garner, *ibid.*, **77**, 3741 (1955). See also ref 6c, p 116, for a review.

(45) (a) H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, **2**, 119 (1964); (b) P. D. Sleezer, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **85**, 1890 (1963); (c) B. M. Mikhailov and A. Ya. Bezmenov, *Izv. Akad. Nauk SSSR*, 904 (1965)

$$(26)$$

$$(27)$$

$$(28)$$
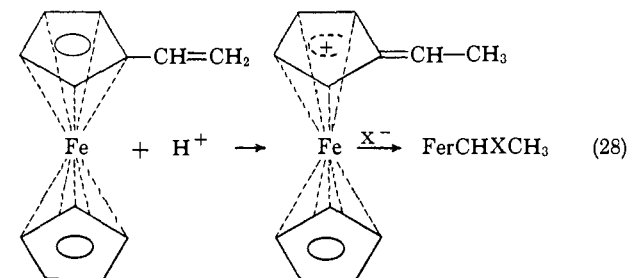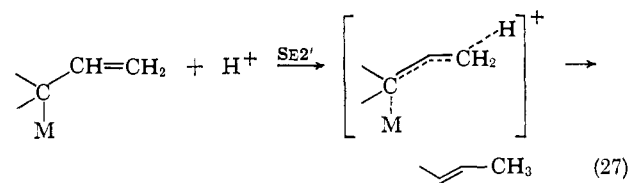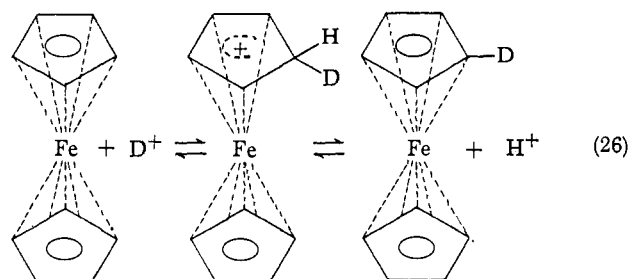
The well-known elimination of organometallic compounds,[6] *e.g.*

$$(29)$$
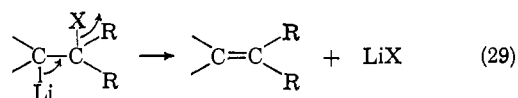
might also be expected to occur rather readily with metallocene compounds as discussed above and shown in eq 20.

Participation in β-Ferrocenylethyl Tosylate Solvolysis. The formation of cyclopropanes from γ-metalloalkyl halides is well known.[46]

$$BrCH_2CH_2CH_2Br + Mg \longrightarrow [BrCH_2CH_2CH_2MgBr] \longrightarrow$$
$$cyclopropane + MgBr \quad (30)$$

$$R_2\overset{OH}{\overset{|}{B}}CH_2CH_2CH_2Cl \longrightarrow cyclopropane + R_2BOH + Cl^- \quad (31)$$
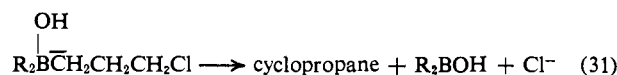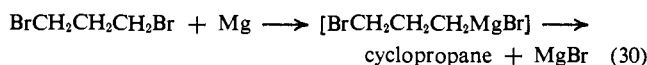
If we write these reactions with the usual retention of configuration observed for carbon–metal bond cleav-

age,[44] it becomes clear that cyclopentadienyl compounds of this type should show the same stereochemical preference whether they are σ bonded or sandwich compounds (eq 32 and 33).
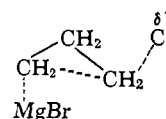
The intermediate formed from solvolysis of β-ferrocenylethyl tosylate is pictured as a structure like the phenonium ion, but it is formed by a simple S_E2 attack on the cyclopentadienyl carbon. The rapid rate of solvolysis of this tosylate (500 times that of phenethyl tosylate) observed by Trifan and Bacskai[4a] is entirely

(46) (a) L. H. Sommer, R. E. van Strien, and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 3056 (1949); (b) M. F. Hawthorne, *ibid.*, **82**, 1886 (1960); (c) P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).

$$(32)$$

$$\xrightarrow{\text{SE2 by } CH_2^+} \qquad \xrightarrow{\text{SE2 by } M}$$

$$(33)$$
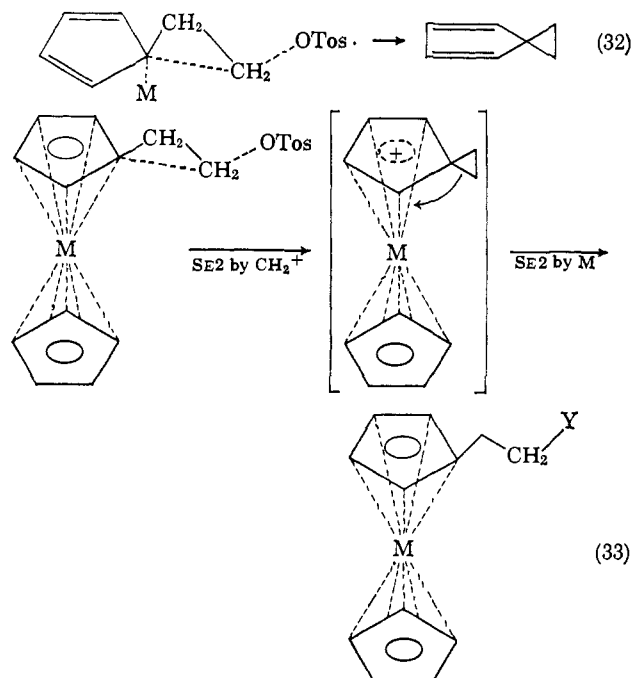
consistent with the mechanisms we propose. Indeed, we would suggest that this reaction would be much more facile if iron were replaced by, e.g., magnesium, which has no d electrons because C–Mg is more ionic than C–Fe.

In all these proposed reaction mechanisms, the difference between "ionic" or σ-bonded RM compounds and covalent sandwich compounds is considered to be that in the latter the metal is retained by bonding to the remaining diene group whereas in the σ-bonded compounds the metal does not bind with dienes and is lost.[38]

Nmr Spectra of Metallocenylmethyl Cations. The chemical shifts of ring (H_2, H_3) and α hydrogens (H_1) in XIV[47] and XV[3e] have been interpreted by Fitzpatrick,

XIV   XV
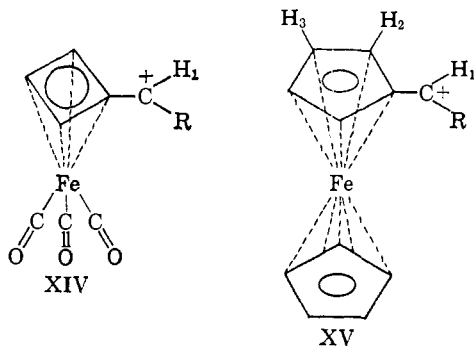
Watts, and Pettit[47] in terms of structures such as XVI and by Cais, et al.,[3e] in terms of structure XVII. While

XVI   XVII

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

Table VI. Nmr Spectra of Cations and Olefins

R	$\Delta \nu^{b,d}$	$\delta_{H_1}{}^{a,b}$	$\delta_{H_1}{}^{a,c}$	$\delta_{H_1}{}^{a,b}$
H	118	5.75	5.3	
CH_3	94	7.03	5.70	
Isopropyl	93	6.98	...	
Cyclohexyl	...	...	5.64	
t-Butyl	90	7.07	5.65	
C_6H_5	66	7.92	6.16	9.80
p-MeC$_6$H$_4$	71	7.94	6.21	
p-MeOC$_6$H$_4$	79	7.96	6.26	9.06

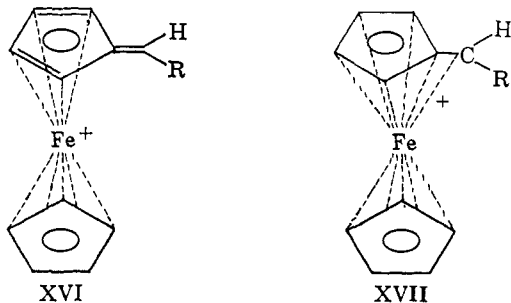^{a} Chemical shift in parts per million from TMS. ^{b} Reference 3e. ^{c} Reference 48a. The data were given in cps downfield from water. We have used $\delta_{H_2O} = 5.00$ to compute the chemical shifts in ppm. ^{d} $\Delta \nu = (\delta_{H_3} - \delta_{H_2})60$.

we agree that the data of Cais, et al.,[3e] may be explained by structure XVII, they do not appear to exclude XVI. In Table VI are listed the data for the α protons in ions XV, and in similarly substituted olefins and carbonium ions.

Table VI shows a striking similarity between the α-substituent effects on the chemical shifts of H_1 in ferrocenylmethyl cations and those in olefins.[48a,c] It is especially striking that anisyl substitution (R = anisyl) has no greater effect than phenyl substitution (R = phenyl) in olefins and in the cations XV. This differs from the effects of anisyl vs. phenyl substitution in other carbonium ions.[29]

Similarly, the changes in $\Delta \nu$ shown in Table VI and attributed by Cais, et al., to changes in extent of iron participation are also explicable by formulation XV. Such $\Delta \nu$ values have been observed for metal π complexes of butadiene and cyclopentadiene.[48d-f] Furthermore, the $\Delta \nu$'s within the aryl series are inconsistent with the notion of decreased iron participation with increased electron supply from R.
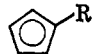
Therefore, we believe that either the proposal of Pettit, et al., or that of Cais, et al., is consistent with the nmr data now vailable. Neither the chemical shifts of the α protons nor those of the ring protons differentiate between these proposals.

Conclusion

The results of this study appear to be inconsistent with a mechanism of solvolysis of FerCR$_2$X involving the same kind of neighboring group participation usually displayed by carbon or by RS groups. While we cannot exclude some novel involvement of filled d orbitals which might be consistent with our findings, we consider a mechanism of σ-π conjugation simpler and preferable at this time.

(48) (a) W. Brügel, T. Ankel, and F. Krückeburg, *Z. Elektrochem.,* **64**, 1121 (1960); (b) G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.,* **83**, 2045 (1961); (c) C. Pascual, J. Keier, and W. Simon, *Helv. Chem. Acta,* **49**, 164 (1966); (d) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.,* 3759 (1959); (e) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.,* **1**, 12 (1964); (f) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *ibid.,* **3**, 96 (1965).

Table VII. Nmr Absorptions in Units of τ

Isomer	CH$_3$	⬠	⬠-R	Ar	—CH	OH
			FerC$_6$H$_4$COCH$_3$			
o	7.92	5.92	5.62 (quartet)	2.9–2.1 (complex)		
m	7.39	5.98	5.50 (sextet)	2.9–1.9 (complex)		
p	7.43	5.98	5.45 (sextet)	2.30 (quartet)		
			FerC$_6$H$_4$CH(OH)CH$_3$			
o	8.58 (doublet)	5.92	5.8–5.5^a	2.9–2.1 (complex)	a	8.36 (complex)
m	8.49 (doublet)	5.98	5.53 (sextet)	2.9–2.5 (complex)	5.17 (triplet)	8.07 (broad)
p	8.50 (doublet)	5.98	5.54 (sextet)	2.8–2.5 (complex)	5.14^b	8.14 (broad)

^{a} Unresolved from CH. ^{b} Not fully resolved.

This interpretation is similar to that proposed earlier by Hill and Richards[3b] (delocalization into the ring) with respect to the major stabilization of α-ferrocenylcarbonium ions (i.e., about 80% of the stabilization energy). Our interpretations differ mainly with respect to the stereospecific solvolyses, the exo:endo rate ratios in IX, and the position of the iron atom in the carbonium ion. Thus we suggest that there is no detectable bonding between iron and C_α in the carbonium ion whereas Richards, et al., and Trifan, et al., postulate that such bonding is sufficient to govern stereochemistry and exo:endo rate ratios.[48g]

Experimental Section[49]

The procedures followed for all preparations of substituted acetophenones and α-phenethyl alcohols are the same as those used for p-ferrocenyl derivatives.

p-Ferrocenylacetophenone. p-Aminoacetophenone (11.0 g, 0.0814 mole) was dissolved in 100 ml of 25% fluoroboric acid and cooled to 0° in an ice-salt bath. An ice-cold solution of 6.3 g of sodium nitrite in water was added dropwise, keeping the temperature below 5°, until a positive test was obtained with starch–iodide paper. The white precipitate was collected on a suction filter and washed with small amounts of water, ethanol, and ether. It was suspended in 50 ml of cold acetic acid–water (1:1) and added dropwise to a cooled, stirred suspension of 15 g (0.805 mole) of ferrocene in 600 ml of acetic acid. After addition was complete, the solution was stirred overnight at room temperature. Then 2 l. of water was added, and the mixture was filtered. The solid was washed with water and sodium carbonate solution, dissolved in benzene, and dried. It yielded 10.4 g of a brick red solid on evaporation. The solid was chromatographed on neutral activity II alumina using petroleum ether–benzene mixtures. First, 5.9 g of ferrocene (acetophenone odor) was eluted with petroleum ether (bp 30–60°). Then 5.4 g of p-ferrocenylacetophenone was eluted with 1:1 petroleum ether–benzene, mp 173–174°, after recrystallization from cyclohexane (lit.[7b] mp 176–178°). No attempt was made to isolate other products in any of the arylation reactions. Anal. Calcd for C$_{18}$H$_{16}$FeO: C, 71.07; H, 5.30. Found: C, 71.07; H, 5.21.

The aqueous layer was reduced with stannous chloride to yield 2.53 g of a brown solid. This was chromatographed in a similar manner and yielded 2.35 g of ferrocene. There were several other bands on the column but only a trace of the desired ketone. Yield of p-ferrocenylacetophenone based on unrecovered ferrocene was 49%.

m-Ferrocenylacetophenone. m-Aminoacetophenone (11.0 g, 0.0815 mole) was diazotized and the salt added to 30 g (0.161 mole) of ferrocene in 1 l. of acetic acid. The ether-soluble portion of the

product on chromatography yielded 13.8 g of ferrocene. The desired ketone (6.0 g, 31% yield) was eluted next with 1:1 benzene-petroleum ether. It formed orange-brown prisms, mp 73.5–74°, after two recrystallizations from ethanol. Anal. Calcd for C$_{18}$H$_{16}$FeO: C, 71.07; H, 5.30. Found: C, 71.39; H, 5.27.

From the blue aqueous layer there was isolated 5.4 g of a brown solid, much of it evidently ferric oxide, which on chromatography afforded 3.4 g of ferrocene and 0.4 g of m-ferrocenylacetophenone.

o-Ferrocenylacetophenone. o-Aminoacetophenone (5.0 g, 0.037 mole) was diazotized and added to 10.0 g (0.0538 mole) of ferrocene in 300 ml of acetic acid. Following work-up as usual, the ether-soluble product was chromatographed. Ferrocene (3.6 g) was eluted first, followed by the ketone (2.9 g, 35% yield), which was eluted with 1:1 benzene–petroleum ether. It was recrystallized from ethanol to form brown-red prisms, mp 87–87.5°. Anal. Calcd for C$_{18}$H$_{16}$FeO: C, 71.07; H, 5.30. Found: C, 70.83; H, 5.23.

Ferrocene (1.4 g, mp 171–173°) precipitated from the aqueous layer on reduction with stannous chloride. The infrared spectrum showed no detectable impurities.

α-(p-Ferrocenylphenyl)ethyl Alcohol. A solution of 3.0 g (0.0097 mole) of p-ferrocenylacetophenone in 50 ml of isopropyl alcohol was refluxed for 4 hr with 6 g of sodium borohydride. Excess sodium borohydride was then destroyed with acetone, and a few drops of water were added. The solvent was removed by evaporation and the residual yellow solid recrystallized from cyclohexane, mp 113–114°, yield 96%. Anal. Calcd for C$_{18}$H$_{18}$FeO: C, 70.61; H, 5.92. Found: C, 70.30; H, 5.96.

α-(m-Ferrocenylphenyl)ethyl Alcohol. The carbinol, prepared in 85% yield, was recrystallized from ether-petroleum ether, mp 86.5–87°. Anal. Calcd for C$_{18}$H$_{18}$FeO: C, 70.61; H, 5.92. Found: C, 70.62; H, 6.05.

α-(o-Ferrocenylphenyl)ethyl Alcohol. The carbinol was obtained as yellow needles, mp 113.5–114.5°, following recrystallization from cyclohexane; yield of purified material 80%. Anal. Calcd for C$_{18}$H$_{18}$FeO: C, 70.61; H, 5.92. Found: C, 70.41; H, 5.95.

α-(p-Tolyl)ethyl Alcohol. The crude reduction product was distilled at reduced pressure. The alcohol [bp 113° (13 mm)] was obtained in 80% yield; n^{22}D 1.5205 (lit.[10] n^{20}D 1.5232).

α-(p-Anisyl)ethyl Alcohol. The yield of purified alcohol [bp 128° (15 mm), lit.[50] bp 109–110° (2.5 mm)] was 71%; n^{22}D 1.5335 (see Table VII for nmr readings).

α-(p-Ferrocenylphenyl)ethyl Chloride. Procedure A.[10] A solution of 0.2 g of α-(p-ferrocenylphenyl)ethyl alcohol in 50 ml of ether was cooled to 0°. Several pieces of calcium chloride were added. The solution was purged with nitrogen, and then hydrogen chloride was passed into it for 1 hr.

Procedure B.[51] To the cooled ethereal solution of the carbinol was added 10 ml of concentrated hydrochloric acid. The mixture was shaken and kept at 0° for 1 hr. About 50 ml of petroleum ether was added, and the layers were separated.

The ethereal solution was dried with calcium chloride for 1 hr and filtered and the solvent removed at reduced pressure. Two portions of dry petroleum ether were added and evaporated. The residual

(48g) Note Added in Proof. After this paper was submitted M. Cais [Organometal. Rev., 1, 435 (1966)] criticized our initial[2] proposal of σ–π conjugation. The suggestions of Cais should be compared with results presented here.

(49) Melting points are uncorrected. Analyses were performed by Dr. Franz Pascher, Bonn, Germany.

(50) R. Fuchs and C. A. Vander Werf, J. Am. Chem. Soc., 76, 1631 (1954).

(51) Procedure of J. F. Norris, M. Watt, and R. Thomas, ibid., 38, 1071 (1916).

yellow solid, mp 83–84°, was highly reactive and was used without further purification. Analysis indicated that it contained 8% of starting material. *Anal.* Calcd for $C_{18}H_{17}ClFe$: C, 66.59; H, 5.28; Cl, 10.92. Found: C, 67.23; H, 5.78; Cl, 10.03.

α-(*m*-Ferrocenylphenyl)ethyl Chloride. Procedure B was used and the crude product, mp 86.5–88.5°, was chromatographed on activity II basic alumina, using petroleum ether. It was eluted rapidly, mp 90–90.5°, after recrystallization from petroleum ether. *Anal.* Calcd for $C_{18}H_{17}FeCl$: C, 66.59; H, 5.28; Cl, 10.92. Found: C, 66.04; H, 5.29; Cl, 10.94.

α-(*p*-Methylphenyl)ethyl Chloride.[52] α-(*p*-Methylphenyl)ethyl alcohol (2 ml) was dissolved in dry benzene and cooled in an ice bath. Then 0.9 ml of phosphorus trichloride was added cautiously. A second phase appeared within 1 min. The mixture was kept at 0° for 1.5 hr. Then solid lithium carbonate was added and the solvent almost entirely removed at reduced pressure. The residual mass was suspended in petroleum ether and chromatographed on activity II basic alumina. The chloride was eluted before the carbinol. Portions of eluate were evaporated, and the infrared spectra of the chloride thus obtained were checked for absence of hydroxyl. The rest of the chloride-containing eluate was stored as the petroleum ether solution in the freezer in order to discourage polymerization; $n^{22}D$ 1.5242 (lit.[10] $n^{20}D$ 1.5232).

α-(*p*-Methoxyphenyl)ethyl Chloride. Procedure B was used. The infrared spectrum of the product, $n^{22}D$ 1.5370, showed no hydroxyl absorption. When a weighed portion of the chloride was added to water it liberated 99.6% of the theoretical amount of hydrochloric acid, as determined by titration with sodium hydroxide. The nuclear magnetic resonance spectrum, taken in carbon tetrachloride solution, had a three-proton doublet centered at τ 8.26 (side-chain methyl), a three-proton sharp peak at 6.32 (methoxy), a one-proton quartet centered at 5.01 (tertiary hydrogen), and a four-proton quartet centered at 2.99 (aromatic hydrogen).

p-Ferrocenylstyrene. A petroleum ether solution of α-(*p*-ferrocenylphenyl)ethyl chloride was passed over a column of basic activity II alumina. Immediately a green-brown band appeared on the column. Rapid elution yielded an orange-yellow solid, mp 128–128.5°, after recrystallization from petroleum ether, in about 50% yield. (Other products were not examined.) The presence of peaks at 1623, 991, and 910 cm⁻¹ in the infrared spectrum of the material (carbon tetrachloride solution) was indicative of a styrene derivative. *Anal.* Calcd for $C_{18}H_{16}Fe$: C, 75.02; H, 5.39. Found: C, 75.19; H, 5.33.

α-Chloroethyl methyl ether was prepared by the method of Henze and Murchison.[53]

Products of Solvolysis of α-Ferrocenylphenylethyl Chlorides.
A. α-(*o*-Ferrocenylphenyl)ethyl Chloride. A solution of 0.0105 g (3.23 × 10⁻⁴ mole) of α-(*o*-ferrocenylphenyl)ethyl chloride in 95% ethyl alcohol was purged with nitrogen for 15 min. After the solution had been immersed in a 40° bath for 3.5 hr, the solvent was removed with a rotary evaporator. The residue was chromatographed on basic activity II alumina. Petroleum ether first eluted 0.003 g of a material (3%) whose infrared spectrum was characteristic of a styrene. This was followed by 0.099 g of a yellow solid, mp 71–72°, after recrystallization from ether–petroleum ether. It showed strong absorption in the infrared at 1090 cm⁻¹, and analysis confirmed its identity as ethyl α-(*o*-ferrocenylphenyl)ethyl ether (92% yield). *Anal.* Calcd for $C_{20}H_{22}FeO$: C, 71.87; H, 6.64. Found: C, 71.96; H, 6.80. Increasing proportions of benzene then eluted 0.003 g (3%) of a yellow solid, shown by its infrared spectrum to be α-(*o*-ferrocenylphenyl)ethyl alcohol.

B. α-(*m*-Ferrocenylphenyl)ethyl Chloride. A solution of 0.100 g (3.08 × 10⁻⁴ mole) of α-(*m*-ferrocenylphenyl)ethyl chloride in 95% ethyl alcohol was purged with nitrogen and then held at 70° for 7 hr. The solvent was removed with a rotary evaporator and the residue, a dark orange oil, chromatographed on neutral activity II alumina. About 0.009 g of the residue, dark brown in color, was insoluble. Petroleum ether first eluted 0.005 g of a yellow solid (6%) judged to be a styrene from its infrared spectrum. The styrene was followed by 0.070 g (68%) of an orange-yellow solid, mp 59.5–60.5° after two recrystallizations from petroleum ether. On the basis of infrared spectrum and elementary analysis it was identified as ethyl α-(*m*-ferrocenylphenyl)ethyl ether. *Anal.* Calcd for $C_{20}H_{22}FeO$: C, 71.87; H, 6.64. Found: C, 72.03; H, 6.75.

Benzene–ether solutions eluted about 0.003 g (3%) of α-(*m*-ferrocenylphenyl)ethyl alcohol, which was incompletely separated from a carbonyl-containing material (*ca.* 0.003 g), judging from infrared spectra. Some remaining darkly colored bands were very reluctantly eluted with ethanol and acetic acid and could not be characterized further.

C. α-(*p*-Ferrocenylphenyl)ethyl Chloride. A solution of 0.416 g of α-(*p*-ferrocenylphenyl)ethyl chloride (1.18 × 10⁻³ mole, allowing for 8% carbinol contamination) was dissolved in 100 ml of 95% ethyl alcohol that had been cooled to 0° and purged with nitrogen. After 3 hr at 0°, the solvent was removed by rotary evaporator. The dark orange oil was dissolved in petroleum ether and chromatographed on basic activity II alumina. Petroleum ether rapidly eluted 0.006 g (2%) of a yellow solid, shown by comparison of infrared spectra to be *p*-ferrocenylstyrene. The styrene was followed by 0.273 g (69%) of an orange oil which crystallized after vacuum drying, mp 47.5–48.5° after recrystallization from ethyl alcohol. On the basis of infrared and nmr spectra and elementary analysis it was identified as ethyl α-(*p*-ferrocenylphenyl)-ethyl ether. *Anal.* Calcd for $C_{20}H_{22}FeO$: C, 71.87; H, 6.64. Found: C, 72.00; H, 6.61.

The nmr spectrum in deuteriochloroform had a triplet centered at τ 8.85 and a quartet centered at 6.69 (ethoxy), a doublet centered at 8.63 (methyl β to aromatic ring), a singlet at 6.03 (unsubstituted ferrocene ring), a sextet centered at 4.65 (substituted ferrocene ring), and a quartet centered at 2.76 (aromatic ring). The tertiary hydrogen was not resolved from the sextet at 5.65.

The ether was followed by 0.029 g (8% by weight) of a yellow solid which was eluted very slowly by petroleum ether and had mp 190–210°. It was poorly soluble in ordinary solvents, and a portion which was recrystallized from cyclohexane melted from 195 to 210°. Nearly the same melting range (195–205°) was shown by a portion which was recrystallized from ethanol. The infrared spectrum showed no bands that could not arise from a ferrocene nucleus with a hydrocarbon side chain. Lack of material and insolubility prevented obtaining a good nmr spectrum, the only clear peak being that at *ca.* τ 6, characteristic of unsubstituted ferrocene rings. *Anal.* (relative to those for 2,3-di-*p*-ferrocenylphenyl-butane): Calcd for $C_{36}H_{34}Fe_2$: C, 74.76; H, 5.93; mol wt, 576. Found: C, 75.62; H, 8.02; mol wt, 611 (melting point depression).

Small percentages of benzene in the eluate brought off 0.017 g of an orange-red oil, the infrared spectrum of which had a carbonyl peak at *ca.* 1690 cm⁻¹. Its infrared spectrum consisted of the peaks characteristic of *p*-ferrocenylacetophenone, but there were others as well, in particular, one at 1090 cm⁻¹ (strong), possibly an ether. Attempts to rechromatograph this fraction were unsuccessful because decomposition occurred after prolonged contact with the adsorbent.

Benzene–petroleum ether (1:3) eluted 0.049 g (4.5% allowing for that initially present) of α-(*p*-ferrocenylphenyl)ethyl alcohol, characterized by melting point and infrared spectrum. The small amount of material remaining on the column, eluted with mixtures ranging to 100% ether, could not be identified. The infrared spectra were complex, and prominent in all was a strong peak at *ca.* 1680 cm⁻¹. The "9–10 bands" characteristic of unsubstituted ferrocene rings were also evident.

Kinetic Measurements. The solvents were made up by volume at room temperature, using redistilled water, USP absolute alcohol, ethanol which had been refluxed and distilled over calcium hydride (for ethanol–ether mixtures), and sodium-dried reagent ethyl ether. These were saturated with nitrogen both before and after dilution. Temperature control in the range −20 to +80° was ±0.02° or less; the very low temperatures are estimated to be accurate within ±0.3°. Thermometers in the normal range were calibrated against an NBS thermometer, and the low temperatures were measured with a vapor pressure thermometer.

The reactions were run in conductance cells unless titration procedures were to be used. Generally, the thermally equilibrated solvent was added to the substrate in the cell. The ferrocene derivatives had to be dissolved in a small amount of ether in order to effect immediate solution. It was necessary to use quite dilute solutions (*ca.* 0.001 *M*) in order to avoid a falloff in rate which became pronounced after one half-life.[54] Insolubility of the fer-

(52) K. Schlögel, *Monatsh.*, **88**, 601 (1957).
(53) H. R. Henze and J. T. Murchison, *J. Am. Chem. Soc.*, **53**, 4077 (1931).

(54) It is unlikely that this rate change is due to internal return. We tested for ether cleavage by allowing α-(*p*-tolyl) ethyl ethyl ether and 0.004 *M* HCl to stand in the solvolysis solvent for several half-lives of solvolysis and found no change in conductance. We conclude that the rate decrease results from readdition to the product styrene.

rocene derivatives also necessitated dilute solutions. Infinity readings were taken after at least ten half-lives. Under optimum conditions, good first-order rate plots for up to three half-lives were obtained. Conductance was shown to be proportional to hydrochloric acid concentration under the conditions employed.

Three or more runs were made at each temperature, and a typical rate measurement follows in Table VIII.

Table VIII. Run 118, Solvolysis of α-(m-Ferrocenylphenyl)ethyl Chloride, 0.00161 M, at 55.00°

Time, sec	10^6L, ohm^{-1}	Time, sec	10^6L, ohm^{-1}	Time, sec	10^6L, ohm^{-1}
293	2.1	4066	31.3	9,560	52.8
386	2.7	4692	35.7	10,074	55.0
501	3.7	5838	38.8	10,797	58.8
593	4.7	6459	41.0	15,550	70.2
890	7.2	6786	41.8	16,483	76.0
1530	12.7	7200	43.0	17,247	78.3
1909	15.7	7622	44.7	17,641	79.6
2471	20.0	8464	47.3	17,988	80.4
3275	26.2	8770	49.1	79,200	121.5
3798	28.8	9303	51.3	165,600	123.6

$$k_1 = 5.68 \times 10^{-5} \text{ sec}^{-1}$$

The solvolysis rate of α-(p-methylphenyl)ethyl chloride at 55° was also determined by titration of liberated hydrochloric acid with sodium hydroxide. It was necessary to add an excess of 2,6-lutidine to the reaction mixture, which was more than ten times as concentrated as the conductance solutions, in order to avoid a severe drop in first-order reaction rate with time.

The solvolyses of α-(p-methoxyphenyl)ethyl chloride at 0° and of α-chloroethyl methyl ether at −70° were followed by an *in situ* titration procedure. Sodium ethoxide in the ether–ethanol kinetics solvent[55] was dropped in as needed in order to keep the reaction mixture at the green end point of brom thymol blue. The titrant, contained in a bulb, was forced out by mercury from a 5-mm buret. Addition rate was controlled manually, using the valve from a Radiometer titrator TTT1. The height of the mercury in the buret was sensed by a transducer, and this mercury pressure was recorded as a function of time. Thus, a continuous record of volume of sodium ethoxide added (and of hydrochloric acid formed) could be obtained. Good linear first-order plots were obtained from these measurements, and rates compared well with those determined conductometrically.

Activation parameters were calculated by the method of least squares, and these values were used to calculate rates at 25°.

Measurement of Carbonyl Frequencies. The ketone carbonyl frequencies were measured as 0.002–0.004 M solutions in carbon tetrachloride, using the double beam mode of a Cary-White Model 90 infrared spectrophotometer. The slit width was 1.4 cm^{-1} and cell thickness 1 mm. The instrument was calibrated against water vapor peaks in the 1700-cm^{-1} region. The mid point of the peak at half its maximum intensity was taken as the absorption maximum. The uncertainty in the absolute values is estimated to be about 0.5 cm^{-1}. Uncertainties in relative values are smaller.

All of the ketones were carefully purified. The more volatile ones were purified by vpc, using a silicone column in an Aerograph Model A-700 "Autoprep" gas chromatograph. Acetophenone and its *m*- and *p*-chloro, methyl, and methoxy derivatives were purified in this way. Amino, nitro, and phenyl derivatives were recrystallized to constant melting point. *p*-Acetoxyacetophenone was prepared from *p*-hydroxyacetophenone by the pyridine method.[56a] *p*-Acetamidoacetophenone was obtained by acetylation[55b] of the corresponding amino derivative, mp 173–174°, after recrystallization from ethyl alcohol (lit.[51] mp 167°).

9-Acetylanthracene, Chemicals Procurement Laboratories material, was chromatographed on neutral activity II alumina with petroleum ether. Anthracene was eluted first, followed imme-

diately by 9-acetylanthracene, which was recrystallized from methanol to yield yellow prisms, mp 75–77° (lit.[57] mp 75–76°).

9-Acetylphenanthrene, obtained from Aldrich, was treated with Norit and recrystallized twice from methyl alcohol to yield colorless needles, mp 73–74° (lit.[58] mp 73–74°).

3-Acetylindole was treated with Norit and recrystallized from benzene. Colorless needles, mp 194.5°, were obtained (lit.[59] mp 191°).

2-Acetylfuran was treated with Norit and recrystallized from ether at 0°. It was stored in the refrigerator, since the melting point is 29°.[60]

1-Acetonaphthone, Eastman Kodak Technical, was separated with difficulty from 2-acetonaphthone by vapor phase chromatography, using a 5% Apiezon L on Chromosorb column ($^1/_8$ in. × 10 ft) at 180°. The collected material showed only a single peak when rechromatographed.

3,4-Methylenedioxyacetophenone, obtained from Aldrich, was treated with Norit and recrystallized from ether to yield colorless prisms, mp 86–87° (lit.[61] mp 88°).

2-Acetylthiophene was obtained from Matheson Coleman and Bell and its purity was checked by vapor phase chromatography on a DEGS column (0.25 in. × 10 ft) at 120°. A single peak was observed.

Preparation and Solvolysis of *p*-Hydroxymethylbenzyl Chloride. *p*-Xylylenediol (10 g, 0.0724 mole) was added to a mixture of 150 ml of carbon tetrachloride and 50 ml of 6 N HCl at 0°. The glycol dissolved, and the aqueous layer turned yellow. The mixture was stored in the freezer for 2 days and then warmed to room temperature. A carbon tetrachloride extract at that time yielded nothing, but after 1 hr much yellow oil had appeared between the two layers. The oil was removed and extracted with ether to yield white crystals, mp 55–58°, melting point unchanged after recrystallization from carbon tetrachloride. The aqueous layer had developed by then a white precipitate, which was extracted into ether; mp 53–55°.

All the crystals were combined, dissolved in chloroform, and crystallized by adding petroleum ether to the solution. In this way there was obtained 1.35 g of crystals, mp 55.5–57.5°.

A second crop, 0.49 g, was obtained in the same way, mp 56–57.5°. The second crop was sublimed at 65° (1 mm), and white crystals, mp 55–60°, were obtained. Resublimation afforded 0.224 g of material of mp 59–60°. This sample was used for analysis and kinetics. (The compound was found to be quite irritating to the skin.) *Anal.* Calcd for C_8H_9ClO: C, 61.35; H, 5.97; mol wt, 157. Found: C, 60.99; H, 5.63; mol wt, 174.

The chlorohydrin yielded 99% of the anticipated amount of hydrochloric acid when hydrolyzed by 50% aqueous acetone (0.1 M in NaOH) at 35° for 3 days.

Kinetics. The substrate (0.04–0.09 M) was dissolved in ethyl alcohol containing 0.1 M NaOEt at 55°. Aliquots were quenched with hydrochloric acid and back-titrated with sodium ethoxide. In both instances the reaction followed second-order kinetics. For *p*-xylene dichloride, k_2 was 6.20 × 10^{-4}, and for the chlorohydrin, k_2 = 6.21 × 10^{-4} l mole^{-1} sec^{-1}.

Dimerization of *p*-Ferrocenylphenethyl Carbonium Ions. A solution of 0.406 g (0.00125 mole) of α-(p-ferrocenylphenyl)ethyl chloride in 7 ml of chloroform was added to 10 ml of 1:1 sulfuric acid–chloroform at 0°.[62] After 1 hr the mixture was warmed to room temperature. It stood for 3 days, after which 35 ml of water was added. The dark green aqueous layer was separated from a pale yellow organic layer. The latter yielded only a few milligrams of yellowish oil on evaporation and was not examined further. The green solution was reduced with stannous chloride and extracted with benzene to yield 0.280 g of a yellow-brown solid.

The solid was chromatographed on neutral activity II alumina with benzene–petroleum ether mixtures. An orange solid (0.065 g), mp 220–225° and only slightly soluble, was eluted with 0.5% benzene. The infrared spectrum was consistent with that of a ferrocenyl hydrocarbon although it was very weak. A petroleum

(55) An adaptation of the apparatus used for continuous pressure recording; see T. G. Traylor and C. A. Russell, *J. Am. Chem. Soc.*, 87, 3698 (1965).

(56) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964: (a) p 247; (b) p 259.

(57) C. Merritt, Jr., and C. E. Braun, "Organic Syntheses," Coll. Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1963, p 8.

(58) H. F. Miller and G. B. Bachman, *J. Am. Chem. Soc.*, 57, 766 (1935).

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(60) H. D. Hartough and A. I. Kosak, *J. Am. Chem. Soc.*, 69, 1012 (1947).

(61) E. Mameli, *Gazz. Chim. Ital.*, 39, II, 165 (1909).

(62) Conditions used were those of A. Berger, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, 83, 2274 (1961).

ether extract of the material yielded 0.005 g, mp 188–210°. The insoluble material then melted at 225–228°. Limited solubility of the latter forced use of such a high spectral amplitude that only a qualitative nmr could be obtained (benzene). Neither chloroform, DMSO, nitromethane, nor DMF would dissolve enough of the material for a spectrum. There appeared to be the following absorptions: a doublet at τ 8.96 and 8.87; sharp peak at 6.30 (unsubstituted ferrocene ring); and two poorly resolved triplets at 6.13 and 5.73 (substituted ferrocene ring). Aromatic proton absorption could not be distinguished from that of the solvent. *Anal.* Calcd for $C_{36}H_{34}Fe_2$: C, 74.76; H, 5.93; Fe, 19.31; mol wt, 576. Found: C, 74.47; H, 5.89; Fe, 19.73; mol wt, 549. This represents a 17% yield of dimer, based upon amount of starting chloride.

Elution mixtures containing 5–10% benzene eluted 0.010 g of solid of mp 258–261°. *Anal.* Found: C, 69.58; H, 6.52; mol wt, 3092.

Increasing amounts of benzene eluted additional amounts of solids, which had very wide melting ranges and variable but limited solubility. These could not be recrystallized, and infrared spectra indicated little because of insolubility. Mulls were also unsatisfactory. It was assumed that these fractions were polymers of a polystyrene type.

Preparation and Solvolysis of *p*-Chloromethylbenzyl Ethyl Sulfide (IV). A solution of 13 ml (0.17 mole) of ethanethiol in 100 ml of absolute alcohol containing 0.40 g (0.16 g-atom) of sodium as sodium ethoxide was added to 61 g (0.34 mole) of α,α'-*p*-xylylene dichloride in 700 ml of *t*-butyl alcohol (precipitate). The mixture was maintained at 70–75° during the addition which required about 15 min. After an additional hour stirring at this temperature the mixture was cooled to 0° for a few hours to precipitate the excess dichloride and filtered and the solvent evaporated. The product was distilled through a short Vigreux column at reduced pressure. Four fractions were obtained at 0.4 mm. The first two cuts, bp 103–104.5°, solidified and were shown by their infrared spectra to contain starting dichloride. The third cut, 3 g, bp 104.5–106.4°, $n^{21.5}$D 1.5686, showed none of the dichloride absorption at 14.4 μ in the infrared. The fourth cut, bp 106.5–115°, $n^{21.5}$D 1.5691, also showed no dichloride. Thin layer chromatography of cuts 3 and 4 using silica gel and cyclohexane–benzene also demonstrated the absence of dichloride, but cut 4 contained appreciable amounts and cut 3 a small amount of a second, slower moving component, presumably the disulfide. Fraction 3, which was used in kinetic runs, gave the following. *Anal.* Calcd for $C_{10}H_{13}SCl$: C, 59.98; H, 6.54; Cl, 17.70; S, 15.90. Found: C, 60.00; H, 6.73; Cl, 15.58; S, 18.10.

Nmr. Whereas α,α'-dichloro-*p*-xylene showed singlets at τ 5.56 and 2.77, fractions 3 and 4 had the spectra shown in Table IX. Solvolyses of benzyl chloride, α,α'-dichloro-*p*-xylene, and IV in 50 vol. % aqueous dioxane, followed as described above, gave the first-order rate constants shown in Table X.

Table IX

| | Areas under nmr peaks | | | | |
	CH_3—CH_2	–S–CH_2—C_6H_4—CH_2 –Cl			
Position, τ	8.9	7.7	6.42	2.82	5.58
Areas, fraction 3	2.9	1.9	1.8	3.9	2.2
Areas, fraction 4	3.6	2.2	2.0	3.6	1.7

Table X

| | Rate constants, $k \times 10^5$, sec^{-1} | | |
	60°	80°	90°
Benzyl chloride		5.73, 6.10	
α,α'-Dichloro-*p*-xylene		5.08, 5.27	
IV	1.57, 1.45	8.53, 8.81, 8.74	21.6, 21.0

$\Delta H^{\ddagger}_{IV} = 20.4$ kcal, $\Delta S^{\ddagger} = -19$ eu

Substituent Effects in the Chronopotentiometric Oxidation of Ferrocene Derivatives. Internal Solvation of Certain Substituted Ferricenium Ions[1]

David W. Hall[2] and Charles D. Russell

Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology,[3] Pasadena, California, and the Marathon Oil Company, Denver Research Center, Littleton, Colorado. Received August 12, 1966

Abstract: Chronopotentiometric quarter-wave potentials of a number of substituted ferrocenes were measured in acetonitrile solution. These new data, together with previously published data, indicate that substituent effects in this reaction are best correlated by a blending of Hammett σ_m and σ_p constants, rather than by the Hammett σ_p constants alone as was previously suggested. The quarter-wave potentials of acetamido- and urethano-substituted ferrocenes are anomalously low compared with those of the other compounds studied. This unusual behavior is explained in terms of direct interaction of the acetamido and urethano substituents with the positive iron atom in the oxidized species.

The degree of correlation of chronopotentiometric quarter-wave potentials of substituted ferrocenes with substituent constants such as Taft's polar constants,[4] Brown's σ^+ constants,[5] and Hammett's σ_m

(1) (a) Presented in part at the 34th Annual Meeting of the Colorado–Wyoming Academy of Science, Colorado State University, Fort Collins, Colo., May 1963. The experimental portion of this paper is taken from: (b) the Ph.D. Thesis of D. W. Hall, California Institute of Technology, Pasadena, Calif., 1963; (c) the Ph.D. Thesis of C. D. Russell, California Institute of Technology, Pasadena, Calif., 1963.

(2) To whom correspondence should be addressed at the Chemistry Department, University of British Columbia, Vancouver 8, Canada.

(3) Contribution No. 3462.

(4) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(5) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).