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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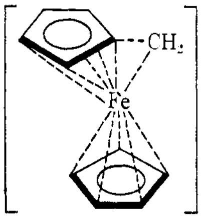
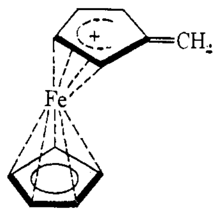
Abstract: The participation of the ferrocenyl group during solvolysis of β-ferrocenylalkyl tosylates has been demonstrated by (a) the entropy of activation, (b) the difference in solvolysis rate in acetic acid and 80% aqueous acetone, (c) the effect of methyl substitution on the α-carbon, (d) the kinetic 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 S_E2 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.



I



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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(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),

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

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

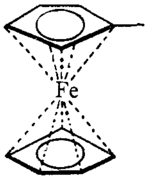
(11) J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Letters*, 1299 (1966).

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

Table I. Acetolysis Data

Compound[a]	T, ° C	$k \times 10^5$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
$FerCH_2CH_2OTs$	75.0	89.9[b]		
	59.9	17.2 ± 1.2		
	49.9	5.3 ± 0.2	22.4 ± 1.0	−8.9 ± 2.9
	39.9	1.8 ± 0.1		
	30.0	0.52[b]		
	25.0	0.27[b]		
dl-$FerCH_2CH(OTs)CH_3$	59.9	28.1 ± 1.5		
	49.9	9.4 ± 0.6	23.1 ± 0.1	−5.58 ± 0.3
	39.9	2.9 ± 0.1		
	30.0	0.852[b]		
	25.0	0.431[b]		

[a] Fer =



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

been due to electron transfer from an iron atom to a carbonium ion intermediate.[13,14]

Acetolysis rates were measured by potentiometric titration of aliquots of the degassed solvolysis mixture with sodium acetate in acetic acid, end points being determined from plots of potential against volume of base added. In many of the kinetic determinations, the infinity titer was less than expected, though the amount of toluenesulfonic acid was never less than 5–7% of the amount anticipated, a discrepancy which is smaller than the standard deviation often observed in other solvolytic systems.[15] Good first-order kinetics were obtained when the experimental infinity titer was used. Rate constants were obtained from least-squares treatment of the data and the results are shown in Table I. Other solvolyses were conducted in 80% acetone–water solutions[5] in which oxidation of the ferrocene derivatives occurs much less readily than in acetic acid. These results are shown in Table II.

Table II. Solvolysis Data in 80% Acetone–Water

Compound	Temp, °C	$k \times 10^5$, sec^{-1}
$FerCH_2CH_2OTs$	30.0	1.10 ± 0.01
$FerCH_2CD_2OTs$	30.0	0.86 ± 0.01
dl-β-$FerCH_2CH(OTs)CH_3$	30.0	1.53 ± 0.02

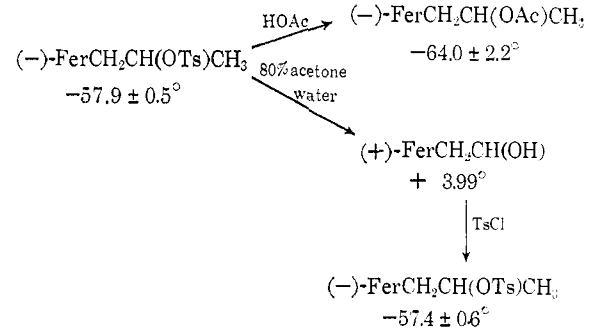
For each of the three substances discussed in this paper (2-ferrocenylethyl tosylate, 1-ferrocenyl-2-propyl tosylate, and 1,1-dideuterio-2-ferrocenylethyl tosylate), the sole products from solvolysis in either acetic acid or acetone–water are the acetates or alcohols with *unrearranged* skeletons. Nor is there any migration of deuterium; the product from 1,1-dideuterio-2-ferrocenylethyl tolsylate is exclusively 1,1-dideuterio-2-ferrocenylethanol. In fact equilibration of 1,1-dideuterio-2-ferrocenylethanol in 80% acetone–20% deuterium oxide with benzenesulfonic acid for approximately eight solvolytic half-lives gave product which showed no scrambling of deuterium by nmr (less than 5% of product with hydrogen at C-1 would have been detected).

The solvolysis of optically active 1-ferrocenyl-2-propyl tosylate proceeds with essentially 100% retention of configuration. 1-Ferrocenyl-2-propanol was converted to the half-phthalate ester which was resolved with strychnine. Repeated recrystallizations from acetone gave salt with $\alpha^{26}D$ −29.2 ± 1.4° which was assumed to be optically pure. Most further work was done with salt of $\alpha^{27}D$ −26.3 which is therefore 90% optically pure. Table III gives the rotations of 1-ferrocenyl-2-propanol and various derivatives each with the same absolute configuration (90% optical purity). Chart I shows the stereochemical results of solvolysis in acetic acid and 80% acetone–water. Appropriate control experiments were carried out to ensure that no significant

Table III. Rotations of 1-Ferrocenyl-2-propanol and Derivatives

	$\alpha^{27}D$
(−)-$FerCH_2CH(O_2CC_6H_4CO_2{}^{2-})$-$CH_3$·strychnine-$H^+$	−26.3 ± 0.2
(+)-$FerCH_2CH(OH)CH_3$	3.99 ± 0.07
(−)-$FerCH_2CH(OTs)CH_3$	−57.9 ± 0.5
(−)-$FerCH_2CH(OAc)CH_3$	−67.1 ± 2.2

Chart I



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(13) M. F. Hawthorne, *J. Org. Chem.*, 21, 363 (1956).

(14) H. Berger, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 2274 (1961).

(15) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," 1st ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

loss or gain of optical activity resulted from the esterification or purification procedures.

Discussion

The entropy of activation has been suggested as one test for the existence of participation by neighboring groups. For example, Winstein and Heck[16] have concluded, on the basis of rate comparisons for the solvolysis of a number of primary tosylates in ethanol, acetic acid and formic acid, that anchimerically unassisted solvolyses tend to have $\Delta S^{\ddagger}$ of about -18 ± 2 eu, while assisted solvolyses have $\Delta S^{\ddagger}$ of about -7 ± 2 eu. Thus, for 2-phenylethyl tosylate the $\Delta S^{\ddagger}$ values are, in ethanol, -20.2 eu; in acetic acid, -17.3 eu; and in formic acid, -9.5 eu. This indicates the predominance of neighboring group participation in formic acid, a conclusion which was later substantiated by experiments using ^{14}C-labeled substrates.[17] The more reactive 2,2-dimethyl-2-phenylethyl tosylate showed $\Delta S^{\ddagger} = -7 \pm 2$ eu in three solvents (ethanol, $\Delta S^{\ddagger} = 7.5$ eu, acetic acid, $\Delta S^{\ddagger} = -5.5$ eu, and formic acid, $\Delta S^{\ddagger} = -6.3$ eu).[15]

In their study, Trifan and Backsai found that in 80% acetone–water 2-ferrocenylethyl tosylate solvolyzes faster by a factor of 537 than does 2-phenylethyl tosylate but that only a factor of about 3 of this difference is reflected in the $\Delta H^{\ddagger}$ term. The remaining factor of 179 then should be accounted for by a difference in $\Delta S^{\ddagger}$ which suggests that $\Delta S^{\ddagger}$ for the solvolysis of 2-ferrocenylethyl tosylate is more positive than $\Delta S^{\ddagger}$ for the solvolysis of 2-phenylethyl tosylate by about 10 eu. As the solvolysis of 2-phenylethyl tosylate in 80% acetone–water is unlikely to be anchimerically assisted, the $\Delta S^{\ddagger}$ should be near -18 eu which would place $\Delta S^{\ddagger}$ for the solvolysis of 2-ferrocenylethyl tosylate in 80% acetone–water near -8 eu. In acetic acid, $\Delta S^{\ddagger}$ is experimentally found to be -8.9 ± 2.9 eu. Thus, both in acetic acid and 80% acetone–water the magnitude of $\Delta S^{\ddagger}$ is that thought to be symptomatic of anchimeric assistance by a neighboring group.

The effect of the two solvent systems, 80% acetone–water and glacial acetic acid, gives further information about the nature of the solvolysis process and leads to the conclusion that the solvolyses of β-ferrocenylalkyl tosylates are very nearly "limiting." The rate of solvolysis as a function of solvent can be summarized[18] in terms of the ionizing power and nucleophilicity of the solvent. When the transition state leading to the formation of the carbonium ion does not involve interaction between a solvent molecule and the electron-deficient carbon of the transition state, the solvolysis is defined as a "limiting" or SN1 process.[19] In such a limiting solvolysis, the rate depends on the ionizing power and not on the nucleophilicity of the solvent. Thus, one of the most often used criteria for a limiting solvolysis is the relative constancy of the solvolysis rate in solvents of comparable ionizing power but of different nucleophilicity. On the other hand, reactions which proceed by attack of solvent at carbon and nearly synchronous displacement of a leaving group (SN2 reactions) occur faster in more nucleophilic solvents.

Table IV. Effect of Solvent on Solvolysis Rate

Compound	Rate in 80% acetone relative to acetic acid[a]
CH$_3$CH$_2$OTs	164/1[a]
(CH$_3$)$_3$CBr	9.1/1[b]
FerCH$_2$CH$_2$OTs	2.1/1[c]
FerCH$_2$CH(OTs)CH$_3$	1.8/1[c]

[a] Based on rate constants calculated from the Winstein–Grunwald equation (see ref 15, p 73). [b] Data obtained from E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948). [c] This work.

Table IV shows the rates in 80% acetone–water relative to acetic acid for some selected tosylates. While the ionizing powers of 80% acetone and acetic acid are not identical, the increase in rate due to increasing ionizing power of aqueous solvent is small as shown by the solvolysis data in Table IV for *t*-butyl bromide, the solvolysis of which is thought to be limiting and therefore independent of the nucleophilicity difference between acetone–water and acetic acid. On the other hand, the effect of the increased nucleophilicity of 80% acetone–water[20] on the rate of an SN2 reaction is more pronounced. For example, ethyl tosylate, which solvolyzes by an SN2 mechanism, reacts in aqueous acetone more rapidly by a factor of 164 than in acetic acid.[21] Thus, the observation that for 2-ferrocenyl alkyl tosylates, that there is only a small rate difference between 80% acetone–water and acetic acid, suggests strongly that these solvolyses are nearly limiting. Moreover, because primary and secondary tosylates do not generally form stable carbonium ions,[21] the stability of these primary and secondary ferrocenyl carbonium ions requires some internal source of electron supply to account for the limiting nature of these solvolyses.

The amount of rate enhancement caused by substitution of methyl for hydrogen at the carbinyl carbon can also give information about the nature of the charge distribution in the transition state. The greater is the degree of positive charge localized on the carbinyl carbon, the greater is the rate enhancement brought about by substitution of methyl for hydrogen. The theory and diagnostic application of this effect have been considered in detail for various systems.[22–25] The maximum rate enhancement attributable to substitution of methyl for hydrogen expected for a limiting solvolysis is probably that observed[21] in the ratio of the rate of formolysis of *t*-butyl bromide to the rate of formolysis of isopropyl bromide which is 10^6. Table V collects some representative data for this and other such α-methyl effects. Other systems which are thought to solvolyze by nearly limiting mechanisms give α-methyl effects of approximately 10^4, while primary systems which solvolyze by an SN2 process, give much lower values.

Low α-methyl effects are not only indicative of SN2 processes but are also observed in cases where there is participation because the positive charge of the transition state is delocalized away from the carbinyl carbon by participation. For example, α-methyl effects in Table V in those cases where the positive character of

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[16] S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 480 (1956).

[17] E. S. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

[18] S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

[19] See ref 15, p 9.

[20] H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **85**, 2181 (1963).

[21] See ref 15, p 73.

[22] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreider, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

[23] S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

[24] S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

[25] H. C. Brown and M. H. Rei, *ibid.*, **86**, 5008 (1964).

Table V. Rate Factors Due to α-Methyl Substitution

Compound pair	Solvent	Temp, °C	Ratio of solvolysis rates	Ref
CH_3CH_2OTs-CH_3OTs	EtOH	75	0.43	23
	HOAc	75	0.87	23
	HCOOH	75	1.8	23
$(CH_3)_2CHOTs$-CH_3CH_2OTs	EtOH	70	3.3	*a*
	HCOOH	75	200	23
$(CH_3)_2CHCH(OTs)CH_3$-$(CH_3)_2CHCH_2OTs$	HCOOH	75	2,240	23
	HCOOH	25	5,200	23
$(CH_3)_3CCH(OTs)CH_3$-$(CH_3)_3CCH_2OTs$	HCOOH	25	12,500	23
$(C_6H_5)CH_2CH(OTs)CH_3$-$(C_6H_5)CH_2CH_2OTs$	EtOH	30	1.6	*b*, *c*
	HOAc	50	37	*d*
	HOAc	30	31	*b*
	HCOOH	30	65	*b*
(p-$CH_3OC_6H_4$)$CH_2CH(OTs)CH_3$-(p-$CH_3OC_6H_4$)CH_2CH_2OTs	HCOOH	30	57	*c*, *d*
	HOAc	50	28	*e*
	EtOH	50	~10	*e*
$FerCH(OAc)CH_3$-$FerCH_2OAc$	80% acetone-water	30	10.5	4
$FerCH_2CH(OTs)CH_3$-$FerCH_2CH_2OTs$	80% acetone-water	30	1.4	*f*

[a] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). [b] Rates at 30° extrapolated from data at other temperatures in footnotes *c* and *d*. [c] S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Am. Chem. Soc.*, **74**, 1140 (1952). [d] S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953). [e] The rate for the primary compound was extrapolated from data in footnote *d*. [f] This work.

Table VI[a]

Compound	Reaction	Atoms of D	k_H/k_D (obsd)	k_H/k_D[b] (cor)	Ref
1-Deuteriocyclopentyl tosylate	HOAc, 50°	1.07	1.15	1.16	*c*
1-Deuterio-1-p-tolylethyl chloride	Aqueous acetone	1.00	1.10	1.11	26
1-Deuterio-1-methylheptyl brosylate	MeOH	1.00	1.10	1.11	*d*
2-Deuterio-2-propyl brosylate	HOAc, 70°	1.01	1.12	1.14	*e*
1-Deuteriocyclohexyl tosylate	HOAc, 75.4°	1.03	1.19	1.22	*e*
1-Deuteriocyclodecyl tosylate	HOAc, 25°	1.05	1.17	1.17	*e*
1-Deuteriobenzyl tosylate	HOAc, 50°	1.00	1.12	1.13	*e*
1,1-Dideuteriobenzyl tosylate	HOAc, 50°	2.06	1.25	1.14	*e*
1,1-Dideuterio-2-phenylethyl tosylate	HCOOH, 75.3°	1.83	1.17	1.11	*f*
1,1-Dideuterio-2-p-anisylethyl tosylate	HCOOH, 50°	2.0	1.20	1.11	*g*
1,1-Dideuterio-2,2-diphenylethyl tosylate	HCOOH, 75°	2.0	1.21	1.12	*g*
1,1-Dideuterio-2-p-anisylethyl tosylate	HOAc, 75° $LiClO_4$	2.0	1.18	1.11	*d*
1,1-Dideuterio-2,2-diphenylethyl tosylate	HOAc, 75°	2.0	1.21	1.12	*g*
1,1-Dideuterio-2-ferrocenylethyl tosylate	Acetone, water 30°	2.0	1.27	1.14	

[a] Adapted and expanded from Table IV in S. Selzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961). [b] The k_H/k_D ratio is corrected to 30.0 and for only one α-deuterium. In cases where more than the theoretical number of atoms of deuterium was present, the theoretical value for m in eq i was used. [c] A. Streitwieser, Jr., R. H. Jagow, R. C. Fakey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958). [d] See ref 2 and footnote *d*, Table V. [e] K. Mislow, S. Borčič, and V. Prelog, *Helv. Chim. Acta*, **40**, 2477 (1957). [f] W. H. Saunders, S. Ašperger, and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958). [g] W. H. Saunders and R. Glaser, *ibid.*, **82**, 3586 (1960).

the transition state is delocalized by participation or conjugation range from 65 for the 2-phenylalkyl systems to 10 for ferrocenyl carbinyl derivatives. The low value for the β-ferrocenyl alkyl system thus provides evidence for the presence of anchimeric participation of the ferrocenyl substituent in the solvolysis of these β-ferrocenylalkyl tosylates.

The substitution of hydrogen by deuterium at the carbinyl carbon gives rise to a secondary deuterium isotope effect which the results in Table VI show to average about 10–15% per deuterium for limiting, carbonium ion processes. These data have been corrected for the number of deuterium atoms per molecule and for the effect of temperature by eq i which relates the isotope effect to the difference in free energy of activation between deuterated and undeuterated molecules and in which m is the number of deuterium atoms per molecule.[26]

$$(RT/m)(\ln k_H/k_D) = \Delta(\Delta F_a) \qquad \text{(i)}$$

The anticipated isotope effect can be calculated on the assumption that the change in zero point energy between hydrogen and deuterium is the dominant effect[27,28] by a modified Bigeleisen equation[29] (ii) which

$$k_H/k_D \cong \pi \exp\left[\left(1 - \frac{1}{1.35}\right)\frac{h}{kT}(\nu_H - \nu_{H_1})\right]/2 \qquad \text{(ii)}$$

includes the approximation that $\nu_0 = \nu_H/1.35$.[30]

The frequencies which have been assigned to the in-phase and out-of-phase C–H stretching vibrations of a secondary C–H bond (in $-CH_2-$) in the ground state are 2926 ± 10 and 2853 ± cm^{-1}, respectively.[31] The deformation or bending modes of these hydrogens give rise to absorption close to 1465 ± 20 cm^{-1}. In β-ferro-

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(26) R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.*, 52 (1958).

(27) See Table VI, footnote *c*.

(28) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press, New York, N. Y., 1960, p 89.

(29) J. Bigeleisen, *J. Chem. Phys.*, 17, 675 (1949).

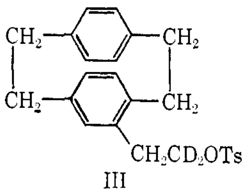
(30) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1950, p 227.

(31) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, pp 13, 34.

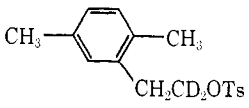
cenylethyl tosylate these three bands occur at 2920, 2856, and approximately 1465 cm^{-1}. Using an aldehydic hydrogen as the model for the solvolytic transition state, in which case values of 2985 and 3085 cm^{-1} are assigned[32,33] to the symmetrical and asymmetrical modes, respectively, one calculates an isotope effect (corrected for the presence of two α deuterium atoms) in an SN1 solvolysis at 30° $k_H/k_D = 1.46$. If, on the other hand, an olefinic C–H of a *trans*-CH=CH– is used as a model for the transition state (for example, in the solvolysis of cyclopentyl tosylate) and the frequency changes 2890–3025 cm^{-1} (C–H stretching), 1340–965 cm^{-1} (C–H out-of-plane bending), and 1340–1300 cm^{-1} (C–H in-plane binding) are considered, the calculated isotope effect becomes 1.18, in excellent agreement with the observed value. In both the aldehyde and olefin models for the transition state, the carbon has been transformed from sp^3 to sp^2; in the former case, the model has considerable positive character on the carbon in question; whereas in the olefin model this carbon is neutral. However, Streitwieser has pointed out that "the presence of net positive charge on trigonal carbon apparently does little to the vibration frequencies of attached bonds."[34]

The magnitude of the isotope effect for the solvolysis of 1,1-dideuterio-2-ferrocenylethyl tosylate in 80% acetone–water is clearly very similar to that for other systems where ionization proceeds with little, if any, participation of solvent, and quite unlike that found for SN2 processes (for example, the reaction of isopropyl bromide with sodium ethoxide has $k_H/k_D = 1.00$).[35] The observed isotope effect is also compatible with the presence of some neighboring group participation as evidenced by comparison with situations in which such participation is known to exist from independent experiments and in which an α-deuterium isotope effect of similar magnitude is observed, for example, in the acetolysis and formolysis of 1,1-dideuterio-2-anisylethyl tosylate which gives k_H/k_D of 1.11 per deuterium at 30°.[36]

The stereochemistry of participation in the solvolysis of 2-ferrocenylethyl tosylate must be such that in the intermediate carbonium ion the two methylene groups of the aliphatic chain do not become equivalent. For the alcohol obtained after solvolysis of 1,1-dideuterioferrocenylethyl tosylate in 80% acetone–water, or after equilibration of 1,1-dideuterio-2-ferrocenylethanol in 80% acetone-d_6–20% deuterium oxide with benzenesulfonic acid for eight solvolytic[37] half-lives, shows no scrambling of deuterium between the α and β positions which is detectable by nmr analysis of the product alcohol (sensitive to 5%). Thus, the two methylene groups do not become equivalent. Cram and Singer[39] have observed an exactly analogous result in the case of the acetolysis or formolysis of 4-(2-tosyloxyethyl-2,2-dideuterio)[2.2]paracyclophane (III) even under conditions when the carbonium ion was repeatedly formed. On the other hand the deuterium of 1,1-dideuterio-2-(2,5 dimethylphenyl)ethyl tosylate (IV) was scrambled in the acetolysis (46% C_β-*d*) and solvolysis in 80% acetone–water (26% C_β-*d*) products. Moreover, the entropy of activation of the paracyclophenyl derivatives indicate significant aryl participation (acetolysis of III, $\Delta S^{\ddagger} = -11.7$ eu, solvolysis of IV in 80% acetone–water, $\Delta S^{\ddagger} = -15.0$ eu).



III



IV

The absence of deuterium scrambling and of any bridged products such as 1,1′-dimethyleneferrocene makes unlikely a type of participation in which the carbonium ion interacts with the heteroannular cyclopentadienyl ring. Cram and Singer[39] have argued on similar grounds against analagous participation in the paracyclophenyl derivatives.

The final evidence for participation of the ferrocenyl group in solvolysis of 2-ferrocenylalkyl tosylates is the complete retention of configuration in the acetolysis and solvolysis in 80% acetone–water of (−)-1-ferrocenyl-2-propyl tosylate. The products are, moreover, obtained with no detectable rearrangement of the carbon skeleton, (−)-1-ferrocenyl-2-propyl acetate or (+)-1-ferrocenyl-2-propanol (which has the same stereochemistry as the (−) esters) being formed exclusively.

The effectiveness of 2-ferrocenyl participation exceeds that of 2-aryl participation by a significant amount as shown in Table VII which collects appropriate relative rate data.

Table VII. Relative Acetolysis Rates of B-Phenyl and B-Ferrocenylalkyl Systems

	Relative rate
Primary systems at 75°	
$C_6H_5CH_2CH_2OTs$	1
p-$CH_3OC_6H_4CH_2CH_2OTs$	23.9
p-Cyclophenylethyl tosylate	3.09
$FerCH_2CH_2OTs$	3120[a]
Secondary systems at 50°	
$C_6H_5CH_2CH(OTs)CH_3$	1
p-$CH_3OC_6H_4CH_2CH(OTs)CH_3$	20.5
$FerCH_2CH(OTs)CH_3$	161

[a] Extrapolated from data at other temperatures.

The ferrocenyl group has thus been shown to assist by anchimeric participation the acetolysis and solvolysis of 2-ferrocenylalkyl tosylates as evidenced by (a) the solvent effect on the reaction, (b) the effect of α-methyl substitution, (c) the α-deuterium secondary isotope effect, and (d) the complete retention of stereochemistry in the acetolysis and solvolysis of 1-ferrocenyl-2-propyl tosylate. The effectiveness of this participation exceeds that of phenyl, anisyl, or [2,2]paracyclophanyl in analogous 2-aryl systems by about an order of magnitude, and, as in the paracyclophanyl case, the two methylene

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(32) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), A175, 208 (1940); N. Sheppard and D. M. Simpson, *Quart. Rev.* (London), 6 (1952).

(33) See ref 30, p 43.

(34) See Table VI, footnote *c*.

(35) V. J. Shiner, *J. Am. Chem. Soc.*, **74**, 5258 (1952).

(36) See Table VI, footnote *g*.

(37) This calculation is based on a first-order rate constant of 8.67 × 10^{-7} sec^{-1} for 1,1-dideuterio-2-ferrocenylethyl tosylate and on the approximation that the tosylate solvolyzes faster by a factor of 3.8 than the protonated alcohol.[38]

(38) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953); see also ref 15.

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

groups of the side chain do not become equivalent during the reaction. The actual structure of the intermediate involved in this participation will be considered in a subsequent paper.

Experimental Section

2-Ferrocenylethanol. This alcohol is prepared according to the procedure of Hauser and coworkers[40] from lithium aluminum hydride reduction of ferrocenylacetic acid.

The deuterated alcohol, 1,1-dideuterio-2-ferrocenylethanol, was also prepared by this method. Lithium aluminum deuteride (98.8%) was purchased from Metal Hydrides Inc., Beverly, Mass. After two crystallizations from petroleum ether (bp 60–70°), the deuterated alcohol melted at 37–38°. Nmr analysis showed that at least 98% of the α-hydrogens were substituted by deuterium.

2-Ferrocenylethyl *p*-Toluenesulfonate. The crude alcohol (46 g, 204 mmoles) was dissolved in 75 ml of pyridine which had been stored over barium oxide. An equivalent amount of the crystallized *p*-toluenesulfonyl chloride was then added and the reaction mixture was allowed to stand in the stoppered flask at 0° overnight. The contents of the flask were then poured into a mixture of ice, 75 ml of concentrated phosphoric acid, and methylene chloride. The organic layer was extracted and washed three times with water. The aqueous washings were then extracted once with methylene chloride. Combined methylene chloride extracts were dried over sodium sulfate and then added dropwise to boiling hexane. Orange crystals were obtained from the cold hexane solution in 24% yield, mp 78–79° after two crystallizations.

Anal. Calcd for $C_{19}H_{20}O_2Fe$: C, 59.38; H, 5.25; Fe, 14.53. Found: C, 59.47; H, 5.24; Fe, 14.59.

2-Ferrocenylethyl Acetate. 2-Ferrocenylethanol (250 mg, 1.09 mmole) and acetic anhydride (0.5 ml) were allowed to react in pyridine (1.3 ml) for 24 hr at room temperature. All volatile material was evaporated under vacuum leaving a dark oil which was crystallized from ethanol–water to yield 236 mg (80%) of white-yellow crystals: mp 40–42°; ir (CCl_4) at 1745 and 1250 cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_2Fe$: C, 61.79; H, 5.93; Fe, 20.52. Found: C, 61.78; H, 6.19; Fe, 20.56.

1-Ferrocenyl-2-propanone. Crude, dry ferrocenylacetic acid (133 g, 545 mmoles) was extracted from a soxhlet thimble into 650 ml of anhydrous ether. A residue of 18 g remained in the thimble. Methyllithium, 860 ml of a 2 *M* etheral solution (Lithium Corp. of America), was slowly added to the suspension of 115 g (472 mmoles) of acid in 1.5 l. of anhydrous ether at −10°. A static pressure of purified nitrogen was maintained over the reaction mixture, which was stirred at high speed. After the reaction mixture had been allowed to stand for 5 hr at −10°, it was refluxed for 5 additional hr. Stirring was then discontinued and the mixture was allowed to stand at room temperature overnight. Phosphoric acid (200 ml of a 5% aqueous solution) was then added dropwise with stirring while methane was continuously evolved. The ethereal layer was then extracted, washed once with saturated sodium bicarbonate solution, and dried over sodium sulfate. The product ketone was not isolated because of its instability as evidenced by the fact that the low-temperature evaporation of ether produced only tars.

1-Ferrocenyl-2-propanol. The ethereal solution of 1-ferrocenyl-propanone, obtained above, was added dropwise to a suspension of 18.1 g (79 mmoles) of lithium aluminum hydride. The reaction mixture was refluxed for 12 hr; after which excess hydride was decomposed by the dropwise addition of water. The ethereal layer was extracted, washed three times with water, and dried over sodium sulfate. The ether was removed at reduced pressure, and the crude alcohol was obtained as a viscous orange-brown oil in 76% yield. The alcohol was purified by chromatography on grade III, neutral alumina. It was eluted from the column with 1:1 methylene chloride–hexane: ir (CCl_4) 1020, 1140, and 3100, and 3480 cm^{-1}; nmr 4.23 (singlet), 3.07 (multiplet), 3.09 (singlet), 2.61 (doublet), and 1.23 ppm (doublet).

1-Ferrocenyl-2-propyl *p*-Toluenesulfonate. The procedure for the preparation of this tosylate was the same as that described above for 2-ferrocenylethyl *p*-toluenesulfonate. The yield of yellow crystalline product, mp 71–72°, was 33%.

Anal. Calcd for $C_{20}H_{22}O_3Fe$: C, 60.31; H, 5.58; O, 12.05. Found: C, 60.16; H, 6.02; O, 12.03.

1-Ferrocenyl-2-propyl Acetate. This compound was prepared in 95% yield according to the procedure described above for 2-ferrocenylethyl acetate. A red-brown oil was obtained by molecular distillation at 71° (18 μ), ir 1250 and 1745 cm^{-1}.

Anal. Calcd for $C_{15}H_{18}O_2Fe$: C, 62.96; H, 6.34. Found: C, 63.10; H, 6.43.

Resolution of 1-Ferrocenyl-2-propanol. 1-Ferrocenyl-2-propyl Acid Phthalate. 1-Ferrocenyl-2-propanol (2 g of uncrystallized oil) was dissolved in dry pyridine (3 ml). Phthalic anhydride (1.4 g, 9.5 mmoles) was added and the mixture gently warmed to assist solution. After sitting at room temperature overnight, the solution was heated on the steam bath for 0.5 hr, and then poured into a mixture of ice and excess hydrochloric acid. The phthalate ester was extracted with chloroform and the extract was washed with water and dried on a column of anhydrous sodium sulfate. After evaporation of the solvent, the residue was treated with excess sodium carbonate (10%). The yellow solid thus produced was collected and washed on the filter with ether to remove unreacted alcohol. The solid was then dissolved in ether and the ethereal solution washed with cold phosphoric acid. The ethereal solution was then washed with water and dried over anhydrous sodium sulfate containing a small amount of ascorbic acid to prevent oxidation. The oil which remained after the evaporation of the solvent was recrystallized from benzene–petroleum ether (bp 30–60°) to yield a yellow powder (2.19 g, 70%, mp 121–125°). A second recrystallization produced material of mp 125–127°.

(−)-1-Ferrocenyl-2-propyl Acid Phthalate Strychnine Salt. A chloroform solution of 4.87 g (14.6 mmoles) of strychnine was added to an acetone solution of 5.73 g (14.6 mmoles) of 1-ferrocenyl-2-propyl acid phthalate. The reaction mixture was stirred overnight. The volume was reduced, and the unreacted strychnine was removed by filtration. The filtrate was cooled, and yellow crystals of the levorotatory salt were collected. Six recrystallizations from acetone produced material which melted at 175–177°, with $\alpha^{26}\text{D}$ 29.2 ± 1.4° (*c* 9.2, methanol). Measurements of rotations could not be carried out visually because all other solutions are deeply colored. Polarimetric determinations were, therefore, made on an ETL-NPL electric polarimeter, Type 143-A. A quartz cell (0.1 dm) and a glass cell (0.4 dm) were used for each determination. The melting point and specific rotation did not change on further recrystallization.

Anal. Calcd for $C_{42}H_{42}N_2O_6Fe$: C, 69.41; H, 5.48; O, 13.21; N, 3.86; Fe, 7.67. Found: C, 69.50; H, 5.76; O, 13.28; N, 3.84; Fe, 7.62.

(+)-1-Ferrocenyl-2-propanol. An excess of aqueous ammonia was added to an ethanolic solution (1.42 g/50 ml) of (−)-1-ferrocenyl-2-propyl acid phthalate strychnine salt, $\alpha^{27}\text{D}$ 26.3° (*c* 5.1, methanol). Precipitated strychnine was filtered and concentrated hydrochloric acid was added to bring the filtrate to pH 6. The acidic solution was then extracted with ether, the organic layer dried over sodium sulfate and evaporated. The resulting brown oil was suspended in a benzene–ether solution and added to a suspension of 0.2 g (50 mmoles) of lithium aluminum hydride in ether. The reaction mixture was then refluxed for 6 hr, after which water was added to destroy the unreacted hydride and the organic layer was extracted and evaporated. Chromatography of the residue yielded 58% of dextrorotatory alcohol, which was dried at 55° (1 mm) for 1 hr. This compound had $\alpha^{26}\text{D}$ +3.99° (*c* 15.2, carbon tetrachloride).

(−)-1-Ferrocenyl-2-propyl *p*-Toluenesulfonate. This sulfonic ester was prepared according to the method described above for 2-ferrocenylethyl *p*-toluenesulfonate. The starting material, (+)-1-ferrocenyl-2-propanol, had $\alpha^{26}\text{D}$ 3.99° (*c* 3.2, carbon tetrachloride). Bright yellow crystals of tosylate were obtained in 57% yield. After two recrystallizations, the solid melted at 78–81°, and had $\alpha^{26}\text{D}$ −57.9 ± 0.5° (*c* 3, carbon tetrachloride).

In order to show that there was no optical fractionation of (−)-1-ferrocenyl-2-propyl *p*-toluenesulfonate during its crystallization, nearly equivalent amounts of pure, racemic tosylate (mp 71–72°) and optically active ($\alpha^{26}\text{D}$ −57.9 ± 0.5°) material were mixed, and recrystallized twice from hexane. The calculated value of the specific rotation of this mixture was −29.1°; the values obtained after the first and second crystallizations were −28.6 and −29.1°, respectively.

(−)-1-Ferrocenyl-2-propyl Acetate. This ester was prepared by the same methods as were used for the racemic compound. A sample prepared from alcohol with $\alpha^{26}\text{D}$ +3.99° (*c* 15.2, carbon tetrachloride) gave acetate with $\alpha^{28}\text{D}$ −67.1 ± 2.2° (*c* 3.1, carbon tetrachloride). Appropriate control experiments showed that

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(40) D. Lednicer, J. K. Lindsay, and C. R. Hauser, *J. Org. Chem.*, **23**, 653 (1958).

no racemization occurred either during chromatography of the liquid acetate, or drying at 55° (1 mm).

Kinetic Methods. Du Pont glacial acetic acid was purified according to the procedure described by Wiberg.[41] Approximately 0.5 g of ferrocenyl alkyl tosylate was dissolved in 50.00 ml of purified acetic acid. Aliquots (5.00 ml) were then added to each of nine previously prepared constricted tubes which were fitted with a 19/38 joint. The tubes were stoppered, cooled to $-196°$, then attached to a degassing apparatus. Three freeze-thaw degassing cycles at 1 μ were carried out, after which the tubes were sealed at the constriction. The samples were then thermostated. Ampoules were withdrawn at various intervals, quenched by shaking in an ice slush, and opened. The contents were poured into a beaker containing a small amount of purified acetic acid. The ampoule was rinsed three times with acetic acid and the washings were added to the beaker. The acetic acid solution was then titrated with 0.2 *N* sodium acetate in acetic acid; the end point was determined from a potentiometric plot. Rate constants were obtained from a least-squares fit of the data to the first-order rate expression.

Solvolysis Products. Acetolysis containing about 0.5 g of ferrocenylalkyl tosylate in 10 ml of purified acetic acid were degassed according to the above procedure. After ten half-lives in a sealed ampoule at the desired temperature, the reaction mixture was added to excess dry pyridine. The solvent was then evaporated at room temperature (1 mm), and the resulting oil was chromatographed on grade III, neutral alumina. Unrearranged acetates were obtained in yields of 90%, and identified by comparison of their infrared and nmr spectra with those of authentic samples.

Acknowledgment. This work was supported by a grant from the National Science Foundation, NSF GP-5190, and a grant from the Paint Research Institute.

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New Organogold Chemistry. I.[1]

Synthesis and Fluorine-19 Nuclear Magnetic Resonance Studies of Some Fluoroorganogold Compounds

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Abstract: Four fluorophenyl(fluorophenyl isocyanide)gold(I) isomers, representatives of a new class of organogold compounds, were prepared from *m*- and *p*-fluorophenyl isocyanide. ^{19}F nmr studies show that the gold atom withdraws electron density strongly from the isocyanide ligand, but is a weak donor into the fluorobenzene ring. Infrared spectral shifts for the isocyanide absorption support this conclusion. Oxidative addition of bromine to pentafluorophenyl(triphenylphosphine)gold(I) has given compound **13**, a new type of gold(III) compound. The electronic effects of the isocyanide group are discussed relative to structure.

Although the organometallic chemistry of most transition metals has been of high interest in recent years, relatively little work has been reported on gold.[4,5] Calvin[6] has prepared a series of monomeric compounds of the type R_3PAuR' ($R = C_2H_5$ or C_6H_5, $R' = CH_3$, C_6H_5, etc.). When R is acetylacetonate, the diketone is bonded to gold through carbon.[7] The preparation, structure, and reactions of polymeric gold acetylides have been studied by two groups.[8,9] Hüttel prepared a variety of olefin–gold chloride complexes,[10–13] as well as cyclopentadienylgold,[14] and other olefin complexes were described by Chalk.[15]

Gold(III) compounds have also recently been of interest. Two tertiary phosphine complexes of trimethylgold were prepared for studies of infrared spectra, dipole moments, and thermal decomposition.[16] Some dialkylgold(III) dialkyldithiocarbamates have been synthesized starting from gold(I) dialkyldithiocarbamates or N-ethylpiperidinium tetrachloroaurate.[17] Dimethylgold(III) halides have been treated with sodium trimethylsiloxide to give the dimer $[(CH_3)_2AuOSi(CH_3)_3]_2$,[18] and with 8-hydroxyquinoline to give the monomeric, internally coordinated compound $(CH_3)_2Au(C_9H_6NO)$.[19] Several water-soluble salts, prepared from dimethylgold(III) hydroxide, have

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