6.72 and 6.85 (equiv s, external methyls), and 13.83 [s, ($\nu_1 - \nu_2$) = 2 Hz, internal methyls].

Anal. Calcd for $C_{28}H_{26}O$: C, 86.74; H, 8.23. Found: C, 86.75; H, 8.23.

When the product was treated in refluxing chloroform with manganese dioxide, a near quantitative recovery of 2-formylhexamethyldihydropyrene resulted.

Heptamethyldihydropyrene (26, R = CH_3).—Into a 300-ml three-necked flask was decanted 50 ml of a hydride solution described in the reduction of 11 to 2. To this was added dropwise over 0.5 hr a deep red solution of 400 mg of 2-formyl-hexamethyldihydropyrene in 20 ml of tetrahydrofuran and 50 ml of ether. A dark green solution immediately resulted. This slurry was heated at reflux temperature for 1 hr and, after cooling, the excess reductant was destroyed by addition of 30 ml of ethyl acetate, followed by 30 ml of water. The organic layer yielded 387 mg (99%) of a dark green solid. Recrystallization from methylene chloride–heptane gave the analytical sample: mp 213–214°; ir spectra (Nujol) showed the absence of carbonyl or hydroxy bands; nmr τ 1.40 (s, 4 H), 2.27 (s, 1 H), 6.86 (s, 1-, 3-, 6-, and 8-methyls), 7.08 (s, 2-methyl), 13.95 and 13.98 (s, internal methyls).

Anal. Calcd for $C_{28}H_{26}$: C, 91.33; H, 8.67. Found: C, 91.32; H, 8.65.

2-Hexamethyldihydropyrene Aldoxime (27).—To a slurry of 514 mg of the 2-formyl derivative **24** in 50 ml of ethanol were added 5 ml of an aqueous hydroxylamine hydrochloride solution which had been neutralized to pH 7 with sodium carbonate. This was warmed on a steam bath for 15 min, after which time thin layer chromatography showed complete conversion of starting material. Careful addition of water to the dark solution while hot resulted in a crystallization of the oxime on cooling, wt 508 mg (94%), mp 205–207°. Recrystallization from ethanol yielded olive-brown platelets: mp 210–211°; $\lambda_{max}^{CH_2Cl_2}$ 245 mμ (ϵ 12,200), 363 (106,300), 396 (32,300), 486 (8000), 610 (200), and 666 (350); ir $\nu_{max}^{CH_2Cl_2}$ 3600 cm^{-1} (s), 3300 (m), 1625 (w), and 1450 (s); nmr (DMSO-d_6) τ −1.42 (s, C=NOH), 0.96 (s, -CH=N-), 1.36 [AB quartet (J = 8 Hz), 4 H], 2.16 (s, 1 H), 6.90 (two equiv s, external methyls), and 13.94 (s, internal methyls).

Anal. Calcd for $C_{28}H_{26}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.14; H, 7.49; N, 4.09.

2-Cyanohexamethyldihydropyrene (28).—Acetic anhydride (20 ml) and 244 mg of **27** were mixed and heated at reflux temperature for 15 min. After cooling, the dark solution was poured into water. When all solvent had reacted, the mixture was extracted with a mixture of methylene chloride and ether. The residue from the organic extract was twice recovered from toluene to remove traces of acetic acid, and was chromatographed on silica gel with methylene chloride–heptane (50:50). A dark bronze band was eluted to give 99 mg (43%) of **28**, mp 218–219°. Recrystallization from methanol produced fine, olive-brown needles: mp 215–216°; $\lambda_{max}^{CH_2Cl_2}$ 365 mμ (ϵ 91,000), 402 (39,800), 505 (9700), 611 (800), and 678 (1800); ir $\nu_{max}^{CHCl_3}$ 2210 cm^{-1} (vs) and 1445 cm^{-1} (s); nmr τ 1.33 [AB quartet, (J = 8 Hz), 4 H], 2.08 (s, 1 H), 6.60 and 6.84 (equiv s, external methyls), and 13.87 (s, internal methyls).

Anal. Calcd for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47. Found: C, 87.93; H, 7.39; N, 4.51.

Registry No.—**2**, 20349-16-0; **7**, 4028-66-4; **8**, 16927-60-9; **9**, 20518-37-0; **10**, 21654-31-9; **11**, 21654-32-0; **13**, 35051-08-2; **14** (X = Ac), 32347-25-4; **14** (X = NO_2), 32347-21-0; **14** (X = CHO), 32347-27-6; **15** (X = NO_2), 33872-82-1; **15** (X = CHO), 32347-29-8; **17**, 32347-24-3; **19**, 35051-15-1; **20**, 35051-16-2; **23**, 35051-17-3; **25**, 35051-18-4; **26**, 32500-00-8; **27**, 32347-26-5; **28**, 32347-28-7.

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The Retentive Nucleophilic Displacements of α-Substituted Alkylferrocenes[1]

GEORGE W. GOKEL,[2a] DIETER MARQUARDING,[2b] AND IVAR K. UGI*[2c]

Department of Chemistry, University of Southern California, Los Angeles, California 90007

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Ferrocenylethane derivatives with suitable leaving groups [chloro, acetate (**9**), trimethylammonium (**2**)] in the α position generally undergo nucleophilic substitutions with complete retention of configuration and are useful for the preparation of a variety of chiral ferrocene derivatives. Stereochemical and kinetic evidence indicates an SN1 mechanism *via* a configurationally stable α-ferrocenylethyl carbonium ion intermediate. Departure of the leaving group and entry of the substituting nucleophile involve analogous conformations of the α-ferrocenylalkyl system. Winstein–Grunwald *m*Y analysis of ammonium compound **2** indicates only a very slight solvent effect for solvolysis in this stable carbonium ion system.

Chiral ferrocene derivatives[3] with the general formula **5** and analogous compounds may serve as asymmetrically inducing amine components[4] in stereoselective peptide synthesis by four-component condensations,[5] *i.e.*, **3** → **4**, because primary amines related to **3** are not only effective steric templates without excessive steric bulk, but their condensation products (**4**) may also be readily cleaved, **4** → **5** + **6**, under mild conditions.[5] The use of **3** as an asymmetrically inducing amine component in four-component condensations offers further advantages. Model reactions[5-7] indicate that the cleavage products can be used to resynthesize the amines. Both antipodes of optically active **1** are easy to obtain and can be effectively converted into compounds of type **1** with a sub-

(1) Stereoselective Syntheses. VIII.

(2) (a) National Aeronautics and Space Administration predoctoral fellow, 1969–1971. (b) Postdoctoral associate, University of Southern California, 1969–1970; Wissenschlaftliches Hauptlaboratorium, Farbenfabriken Bayer A.G., 509, Leverkusen, Germany. (c) Address correspondence to this author: Organisch-Chemisches Laboratorium, Technische Universität, 8 München 2, Arcisstrasse 21, West Germany.

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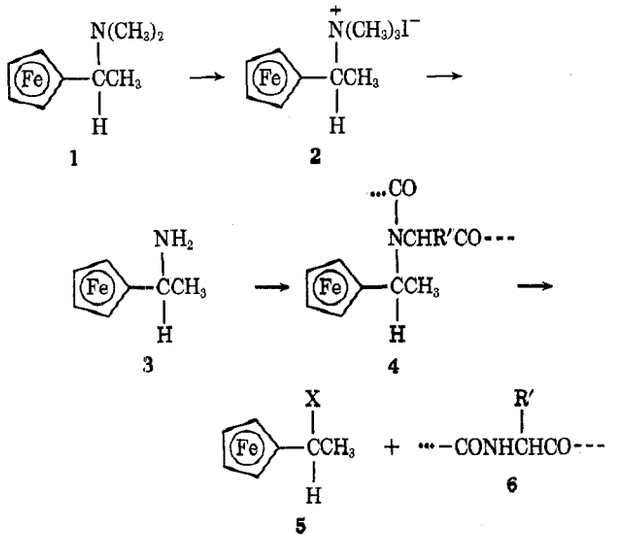
stituent in the 2 position,[8,9] and, since the ammonium group of 2 and its analogs can be replaced by a primary amino group, **3** and derivatives can be obtained conveniently and in good overall yield from readily accessible precursors (Scheme I).

SCHEME I

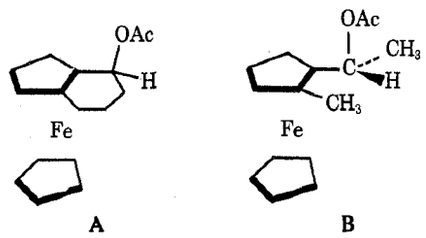


Reactions **2** → **3**, **4** → **5** + **6**, and **5** → **3** involve nucleophilic substitutions at a tetracoordinate (sp^3) center of chirality carrying a ferrocenyl ligand. Knowledge of the mechanism and stereochemical course of the latter reactions would allow full use of the potentially favorable properties of **3** and its 2-organyl derivatives.

Nucleophilic substitutions at a center of chirality with a tetrahedral skeleton proceed either with retention or with inversion of the configuration of the central chiroid. If the substitution product is homochiral[10] to its precursor, the substitution is called retentive; the substitution is considered to occur with inversion if the product is heterochiral to the initial chiral species. The product of nucleophilic substitution is called homochiral to its starting material if it is configurationally similar to the latter and not to its antipode. In this context, the entering and leaving groups are considered to be sequentially equivalent.

Retentive substitution is observed if either an SNi reaction[11] takes place or if a limiting SN1 process[12] takes place in such a manner that departure of the leaving group to give a carbonium ion and addition of the substituting nucleophile occur from the same side of the intermediate sp^2 tricoordinate skeleton of the carbonium ion.

Recent investigations of the solvolytic behavior of the α-ferrocenylalkyl systems have demonstrated the pronounced stabilization of ferrocenylalkyl cations.[13-21] This has been explained by assuming metal participation[13,15-18] or iron hyperconjugation.[16,19,20] Both interpretations imply retentive nucleophilic substitution of the SN1 type for the α-ferrocenylalkyl compounds, and there is some previous evidence[21] for the retentive nature of the above reactions. The elegant work of Richards and Hill[13] and Trifan and Bacskai[14] on cyclic and 2-substituted ferrocenyl acetates foreshadows the present results. A subtle though very important difference should be noted. The previously examined cases (see **A** and **B** below) involved systems with a ring or neighboring substituent.



To our knowledge, prior to our preliminary reports[6,7] of this phenomenon, in this context, retentive nucleophilic substitution at an acyclic chiral center without adjacent substituents had not been demonstrated. A confirmatory report has recently appeared.[22]

We have observed complete retention of the configuration of the chiral center during most of the nucleophilic substitution reactions presented in Scheme II. This is further evidence for the remarkable influence of an α-ferrocenyl group upon the stereochemistry of nucleophilic substitution.

There is a remarkable variety in the stereospecific interconversions of the α-ferrocenylethyl carbonium ions. The cycle **1** → **2** → **10** → **3** → **1** which involves transformations A, B, C, and D contains only one reaction at carbon (reaction C). Since the optical rotations of **1** were the same before and after the cycle, reaction C must occur with retention of configuration.[6] This transformation cycle defines the stereochemistry of compounds **2**, **3**, and **10** relative to **1**. The absolute configuration of **1** has been established by X-ray methods[9] and the absolute configuration of **3** has been determined independently by chemical methods.[23]

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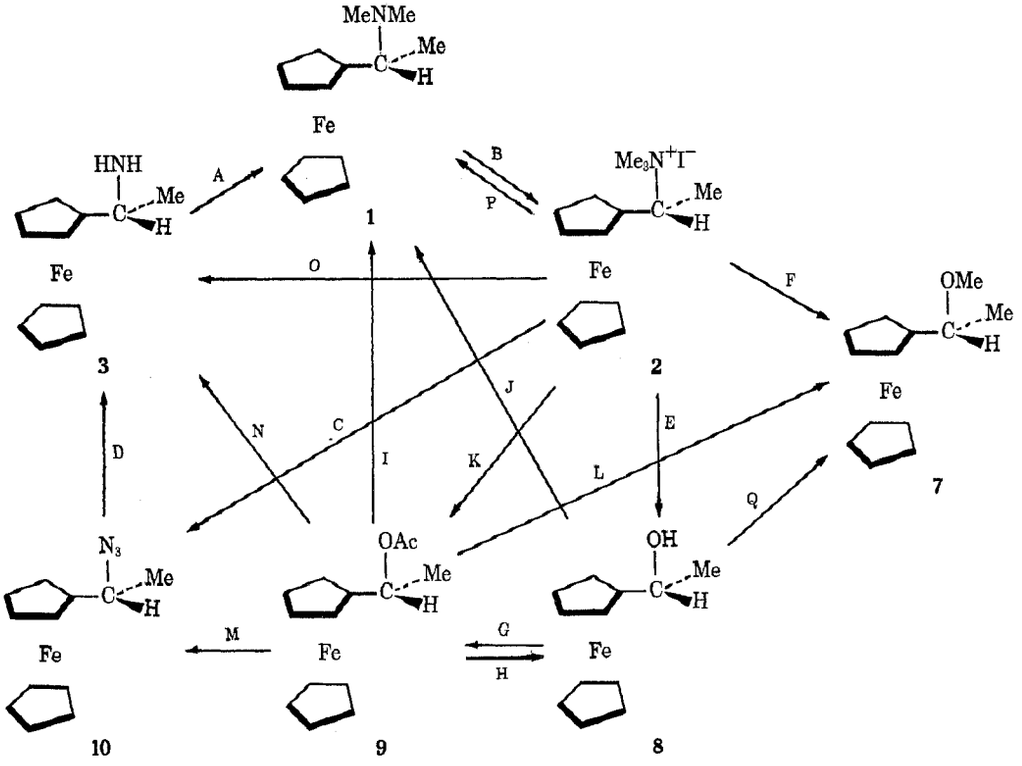
SCHEME II

STEREOSPECIFIC INTERCONVERSIONS IN THE α-FERROCENYLALKYL SYSTEM[a]



[a] A, See ref 6; B, CH_3I in acetone; C, NaN_3 in aqueous THF; D, $NaH_2Al(OCH_2CH_2OCH_3)_2$ in ether (see Experimental Section) or ref 6; E, 1:1 water–THF; F, 1:1 MeOH–MeCN; G, Ac_2O in C_5H_5N; H, aqueous THF, acetone, ethanol, etc.; I, $HNMe_2$ in aqueous MeOH; J, $COCl_2$ then $HNMe_2$; $AlCl_3$ then $HNMe_2$;[22] K, NaOAc in anhydrous DMF (partial racemization, see text); L, NaOMe in MeOH; M, NaN_3 in aqueous THF; N, aqueous NH_3 in MeOH; O, aqueous NH_3 in MeCN; P, $HNMe_2$ in MeCN; Q, *n*-BuLi then Me_2SO_4.

The degree of retention of the reactions was determined by a comparison of optical rotations before and after the cycle (Table I). Within the error of our method,

TABLE I

OPTICAL ROTATIONS FOR α-FERROCENYLETHANE DERIVATIVES[a,b]

Compd	Rotation, deg	Solvent used
1	+14.2	Ethanol
2	+43.0	2-Methoxyethanol
2	+32.5	Acetonitrile
3	−21.0	Ethanol
7	+27.5	Ethanol
8	−30.5	Benzene
9	−28.5	Ethanol
10	−69.8	Benzene

[a] Recorded at the 589-nm (D) line of Na at 25.0°. [b] For the *R* configuration.

each reaction (except K) was found to proceed with essentially complete retention (see Experimental Section for exact data). Kinetic evidence is presented below which indicates that reaction C is first order. These observations imply a configurationally stable carbonium ion intermediate. Other reactions which clearly take place at carbon and therefore involve the α-ferrocenylethyl cation are E, F, I, J, K, L, M, N, O, and P. It is less obvious that H is a retentive SNI reaction, which also involves the carbonium ion rather than a normal type of hydrolysis. That this is so was demonstrated by Richards and Hill a decade ago.[13] Dixneuf[22] has recently confirmed the stereochemistry assigned in our preliminary report[7] for **8** and the retention of reaction J, albeit by an entirely different method.

Reaction G in this cycle is normal acylation with acetic anhydride in pyridine solution. 1-Ferrocenylethanol has also been converted into 1-ferrocenylethyl acetate by refluxing the alcohol in benzene solution with an excess of glacial acetic acid and concomitant removal of water.[7,24] This reaction probably involves protonation of the alcohol and elimination of water, followed by ion-pair collapse to give the ester. A carbonium ion mechanism is believed to occur rather than a normal esterification mechanism[25] because of the stability of the carbonium ion.[21] The early work of Richards and Hill[13] indicated that the ethanolyses of α-ferrocenylcarbinyl acetates afford the ethyl ethers, and Hammond and Rudesill[26] observed that esterification of benzoic acid with triphenylcarbinol (a precursor to a stable carbonium ion) involves the trityl cation. Stephens and coworkers[27] have shown that hydroxymethyl ferrocene will esterify on heating in an acetic acid solution (greater than 60 mol of acetic acid per mole of alcohol). It is their belief that the α-ferrocenylmethyl carbonium is involved here also. In later work by this same group, hydroxymethylferrocene was converted directly into a sulfide by the action of a thiol under acetic acid catalysis. Without acetic acid to

(24) G. W. Gokel and I. K. Ugi, *J. Chem. Educ.*, **49**, 294 (1972).
(25) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).
(26) G. S. Hammond and J. T. Rudesill, *J. Amer. Chem. Soc.*, **72**, 2769 (1950).
(27) C. S. Combs, C. I. Ashmore, A. F. Bridges, C. R. Swanson, and W. D. Stephens, *J. Org. Chem.*, **33**, 4301 (1968).

protonate the alcohol and provide a good leaving group, water-insoluble mercaptans failed to react.[28]

$$FcCH_2OH \xrightarrow[1:1\ n\text{-BuSH–}H_2O]{HOAc} FcCH_2Sn\text{-Bu}$$

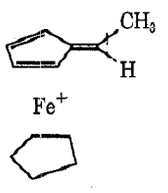
The collapse of the ion pair appears to be slow since treatment of the optically active alcohol (**8**) under these conditions results in racemic acetate.

It is possible that the racemization is due to the presence of vinylferrocene as an intermediate in this reaction. The ease of elimination of α-ferrocenylethanol to vinylferrocene[29] and the documented ease of addition of acetic acid to this molecule[15] seem to support this hypothesis.

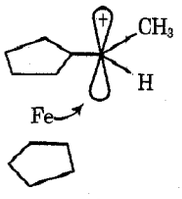
This racemization phenomenon also discounts a normal esterification mechanism because, if nucleophilic attack by the alcohol occurred at the acetic acid carbonyl, the stereochemistry of the resulting compound should be unaffected.

We have found that reaction K proceeds to give acetate (**9**) with partial racemization. The optical rotation of **9** produced from reaction G is 28.5° and, when produced by reaction K, it is 21° or only 73.5% optically pure. One possible explanation for this behavior is that, in the case of weak nucleophiles, the ion pairs collapse more slowly and partial racemization occurs in the interim.

We have interpreted the observed stereospecificity of the α-ferrocenylethyl cation in terms of a structure like **11** in our preliminary report.[6] This structure



11



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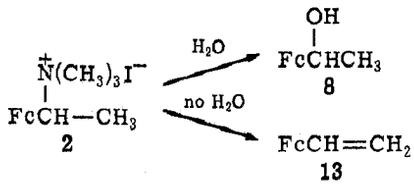
seemed best able to explain the stereochemical retention. After this work was submitted, the report of the stereospecific hydrolysis of optically active β-ferrocenylpropyl tosylate appeared.[30] Clearly, a structure like **11** cannot account for β stereospecificity, whereas some iron lone pair overlap might. On the other hand, structure **12** does not reasonably account for the ability of the dimethylferrocenyl carbinyl cation to undergo cycloaddition.[31] Although the exact nature of the carbonium ion stabilization is still not completely elucidated, recent work by several groups bears on this point.[32–34]

Our interest in this system led us to measure the kinetic dependence of some of the reactions shown in Scheme II. We have determined kinetic parameters for reactions C, E, and H in that scheme. In addition, we have determined Winstein–Grunwald "*m*" values for reactions E and H. The reaction which often competes with SN1 reactions in this system is the E1 reaction of **2** to give vinylferrocene (**13**). We have also



measured the kinetics of this reaction. Results for the reactions illustrated above are given in Table II. All

TABLE II

RATES OF DISPLACEMENT AND ELIMINATION REACTIONS OF **2**[a]

Reaction[b]	Solvent[c]	Temp, °C	k, sec^{-1} [d]
2 + H_2O ⟶ **8**	50% THF	30.0	$9.92 \pm 0.95 \times 10^{-5}$
2 + H_2O ⟶ **8**	50% THF	40.0	$3.62 \pm 0.01 \times 10^{-4}$
2 + H_2O ⟶ **8**	50% THF	50.0	$1.61 \pm 0.13 \times 10^{-3}$
2 + NaN_3 ⟶ **10**[e]	50% THF	50.0	$2.26 \pm 0.01 \times 10^{-3}$
2 + NaN_3 ⟶ **10**[f]	50% THF	50.0	$2.17 \pm 0.07 \times 10^{-3}$
2 ⟶ **13**	MeCN	40.0	$3.44 \pm 0.16 \times 10^{-4}$
2 ⟶ **13**	MeCN	45.0	$8.16 \pm 0.23 \times 10^{-4}$
2 ⟶ **13**	MeCN	50.0	$2.04 \pm 0.15 \times 10^{-3}$

[a] Determined polarimetrically at the 589-nm line of Na. [b] Concentration of **2** is *ca.* 0.05 *M* unless otherwise noted. [c] Solvent mixtures are vol./vol. [d] Average of two or more runs. [e] Concentration of **2** is 0.013 *M*; concentration of NaN_3 is 0.026 *M*. [f] Concentration of **2** is 0.013 *M*; concentration of NaN_3 is 0.048 *M*.

rates were determined by performing the reaction on the appropriate optically active substrate in a thermostated polarimeter tube, where the time dependence of the optical rotation was used as a measure of the extent of reaction.

We have confirmed that, in the concentration range examined, reaction C in Scheme II is first order. The *m* value obtained from reaction H indicates that in this case a carbonium ion mechanism is also operative. The hydrolysis of **2** follows first-order kinetics, although the possibility that it is pseudo-first order cannot be rigorously excluded. The implication that all of the substitution reactions in Scheme II are SN1 is clear, but this was not specifically confirmed for each case.

We have determined activation parameters for the hydrolysis of **2** in 50% aqueous THF and for the E1 reaction of **2** in anhydrous acetonitrile. The hydrolysis of **2** (Scheme II, reaction E) had E_a = 27.2 kcal/mol and ΔS is 5.2 eu. The elimination of **2** to vinylferrocene had E_a = 35.6 kcal/mol and ΔS = −31.6 eu. In our efforts to determine Arrhenius parameters for the latter reaction, it was found that the reactivity of the carbonium ion formed from **2** is sufficiently high toward water that any traces of water in the solvent caused formation of the alcohol, detected by a slight negative rotation at infinity. In the solvolysis of **2**, on the other hand, no vinylferrocene was detected in the product when nmr analysis was applied to crude alcohol obtained from a small-scale preparation.

It has been recognized for some time,[35] if not specifically stated, that the Winstein–Grunwald *m***Y** cor-

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TABLE III

SOLVENT DEPENDENCE OF THE HYDROLYSES OF 2 AND 5[a]

Expt no.	Solvolysis of compd no.	Solvent[b]	Y[c]	Substrate concn M[d]	K, sec^{-1}[e]
1	2	90% acetone	−1.856	0.050	$2.56 \pm 0.16 \times 10^{-3}$
2	2	80% acetone	−0.673	0.052	$2.02 \pm 0.03 \times 10^{-3}$
3	2	70% acetone	0.130	0.051	$2.16 \pm 0.19 \times 10^{-3}$
4	2	60% acetone	0.796	0.026	$2.28 \pm 0.22 \times 10^{-3}$
5	2	90% ethanol	−0.747	0.064	$5.77 \pm 0.23 \times 10^{-3}$
6	2	80% ethanol	0.000	0.054	$4.90 \pm 0.27 \times 10^{-3}$
7	2	70% ethanol	0.595	0.036	$3.88 \pm 0.21 \times 10^{-3}$
8	2	60% ethanol	1.124	0.038	$3.45 \pm 0.20 \times 10^{-3}$
9	9	90% acetone	−1.856	0.056	$1.58 \pm 0.17 \times 10^{-4}$
10	9	80% acetone	−0.673	0.054	$1.65 \pm 0.02 \times 10^{-3}$
11	9	75% acetone	−0.250[f]	0.054	$3.28 \pm 0.03 \times 10^{-3}$
12	9	70% acetone	0.130	0.053	$6.17 \pm 0.29 \times 10^{-3}$

[a] Determined polarimetrically at the Na 589-nm line (expt 1–8) or at the Hg 546-nm line (expt 9–12). [b] Solvent mixtures are vol./vol. [c] Y values from A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956). [d] Average of several runs. [e] At 50.0 ± 0.1°, average of at least two runs. [f] Determined graphically from data taken from footnote *c*.

relation[36] is not generally applicable to charged substrates like sulfonium salts and therefore presumably also to ammonium salts. The extensive investigations of Hyne and coworkers in this field[37-41] have established clearly an increase in rate of solvolysis of sulfonium salts with decrease in solvent dielectric constant. This corresponds to a negative m value in the Winstein–Grunwald treatment. That this should be so is not surprising and indeed was predicted by Hughes and Ingold many years ago.[42]

We have now observed this phenomenon in α-ferrocenylethyl ammonium compounds. The data are summarized in Table III, and show that solvolyses of **2** and **9** give remarkably different m values. The m value for **2** in aqueous acetone at 50° (expt no. 1–4) is −0.008, and in aqueous ethanol at 50° (expt no. 5–8) it is −0.131. The m value determined for **9** in aqueous acetone (expt no. 9–12) is 0.807, the value anticipated for an SN1 reaction with charge separation and in excellent agreement with the titrimetrically determined value of 0.8 determined by Hill and Richards.[13]

The retentive nucleophilic substitutions of the α-ferrocenyl cation in combination with the facile synthesis and resolution of **1**[7,24,43] and the stereorelating syntheses demonstrated for the ferrocene series[8] give a general entry into a great variety of ferrocenes which may be both central and planar chiroids. The recent X-ray configuration determination[9] of a 1,2-disubstituted derivative of optically active **1** solidifies the stereochemical assignments presented herein and may serve as a foundation for other configuration determinations.

Experimental Section

General.—Optical rotations were determined at the 589-nm (D) line of Na in a 10-cm microcell, thermostated at 25° unless otherwise indicated, using a Perkin-Elmer 141 digital polarimeter. Solvents were AR grade. Melting points were determined using a Thomas–Hoover capillary melting apparatus, and are uncorrected. Infrared spectra were recorded on a P.E. 457, and nmr spectra were recorded on either a Varian A-60 or Varian T-60, using TMS as internal standard.

Kinetic Procedure.—All kinetic runs were done using a Perkin-Elmer 141 digital polarimeter. The cell used is a jacketed 1-dl microcell heated by a Bronwill Scientific circulating thermostat calibrated and maintained at each temperature to t ± 0.1°. All runs utilized the 589-nm (D) line of sodium except the solvolyses of **9** (expt. no. 9–12), which utilized the 546-nm line of Hg. In each case, the substrate was weighed in an erlenmeyer flask; then the appropriate solvent (preheated to the required temperature) was pipetted into the flask containing substrate; the timer was started simultaneously. The flask was stoppered and swirled vigorously for 25 sec; then the solution was transferred to the preheated cell; and the readout was switched on. The first reading was generally taken at 100-sec elapsed time; this allowed about 50 sec for instrumental equilibration. Solvent mixtures were prepared by mixing the specified volume of each at 25°. Water was aspirated and then distilled. Acetone and ethanol (AR grade) were redistilled. Acetonitrile (MCB–AR) was refluxed over excess P_2O_5 and then distilled through a 50-cm vacuum jacketed column packed with Raschig rings. The dry acetonitrile was stored under dry N_2 in a serum bottle and transferred by syringe.

The data utilized were taken for a minimum of three half-lives and the infinity point was experimentally determined. The best fit of the data was obtained by least-squares analysis carried out on an IBM 360 computer.

All compounds are known; physical and spectral properties agree with literature values.

***N,N*-Dimethyl-1-ferrocenylethylamine (1).**—Preparation was as described in ref 43. For resolution data see ref 24.

(*R*)-(+)-*N,N,N*-Trimethyl-1-ferrocenylethylammonium Iodide (2) (Scheme II, Reaction B). (*R*)-(+)-**1** [26 g, 0.1 mol; $[\alpha]^{25}D$ 14.2 (*c* 2.0, ethanol)] is dissolved in 50 ml of dry acetone and cooled to 0°. Iodomethane (64 g, 0.45 mol, 28 ml) is added in a thin stream with stirring. The flask is stoppered and stirred at 0° for 30 min. The solution is diluted with 200 ml of ether; the product separates as an oil which solidifies quickly to a yellow solid and is isolated by filtration: yield 39 g (97%); mp 132–133° (dec); $[\alpha]^{25}D$ +43° (*c* 0.6, 2-methoxyethanol; rotation diminishes on standing in solution); $[\alpha]^{25}D$ +32.5° (*c* 1.4, acetonitrile).

(*R*)-(−)-1-Ferrocenylethylazide (10) (Scheme II, Reaction C).—The solution of (*R*)-(+)-**2** [4.0 g, 0.01 mol; $[\alpha]^{25}D$ +32.5° (*c* 1.4, MeCN)] and NaN_3 (3.9 g, 0.06 mol) in 50% THF is refluxed for 2 hr, diluted with 100 ml of ether, and the phases are separated. The organic phase is washed with three 100-ml portions of water and dried over $MgSO_4$, and the solvent is removed *in vacuo:* yield 2.12 g (82%) of a red-brown oil; bp 80° (0.02 Torr); $[\alpha]^{25}D$ −69.8° (*c* 1.1, benzene). *Caution: This compound is known to explode on distillation.*

(*R*)-(−)-1-Ferrocenylethylamine (3) (Scheme II, Reaction D).—For reduction of **10** with $K_2[Sn(OH)_4]$, see ref 6.

(*R*)-(−)-**10** [2.6 g, 0.01 mol; $[\alpha]^{25}D$ −69.8° (*c* 1.1, benzene)] is dissolved in 50 ml of ether and sodium bis(methoxyethoxy)alu-

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minum hydride (SDMEA)[44] (2.8 ml, 0.02 mol) in 10 ml of ether is added dropwise. The solution is refluxed for 1 hr and then poured into water. The layers are separated, the ether layer is dried (K_2CO_3), and the solvent is removed *in vacuo* [yield, 2.0 g (87%) of an amber oil]. This material is dissolved in ether, gaseous HCl is added, and the yellow HCl salt is collected by filtration. The salt is washed quickly with ether, added to 20% NaOH, and extracted with CH_2Cl_2. The solvent is removed *in vacuo*, leaving material with $[\alpha]^{25}D$ −21.0° (*c* 2, ethanol). If the amine is allowed to stand open to the air even for a brief time, the oil converts to a yellow solid, presumably the hydroxylamine.[45] The rotation of this solid is *ca.* 30–35° in EtOH, depending on purity.

(*R*)-(−)-1-Ferrocenylethanol (8) (Scheme II, Reaction E).—A solution of (*R*)-(+)-**2** [10 g, 0.025 mol; $[\alpha]^{25}D$ +32.5° (*c* 1.4, MeCN)] in 200 ml of 50% THF is refluxed for 2 hr. Water (200 ml) is added and the phases are separated. The aqueous layer is extracted with ether; the organic material is combined, washed with water and brine, and dried ($MgSO_4$). Evaporation of the solvent gives an orange solid, 5.3 g (77%), which is recrystallized from *n*-heptane (10 ml/g of solute). The bright yellow product has mp 72–73°; $[\alpha]^{25}D$ −30.5° (*c* 1.1, benzene).

(*R*)-(+)-1-Ferrocenyl-1-methoxyethane (7) (Scheme II, Reaction F).—A solution of (*R*)-(+)-**2** [2.0 g, 0.05 mol; $[\alpha]^{25}D$ +32.4 (*c* 1.0, MeCN)] in 50 ml of 1:1 methanol–acetonitrile is stirred at ambient temperature for 20 hr. The solution is diluted with 100 ml of ether and 100 ml of water and the phases are separated. The organic phase is washed with brine and dried ($MgSO_4$), and the solvent is removed *in vacuo* [yield is 1.0 g (83%), of a dark brown oil which partially solidifies on standing, $[\alpha]^{25}D$ 27.5° (*c* 2, EtOH)].

(*R*)-(−)-1-Ferrocenylethyl Acetate (9) (Scheme II, Reaction G).—A solution of (*R*)-(−)-**8** [1.15 g, 0.005 mol; $[\alpha]^{25}D$ −30.5° (*c* 1.1, benzene)] is dissolved in 5 ml of pyridine; Ac_2O (2 ml) is added; and the flask is stoppered and allowed to stand at ambient temperature overnight. The solution is then reduced *in vacuo* to minimum volume and the residue is dissolved in ether. The resulting solution is washed with ice water (3 × 100 ml) and brine (1 × 100 ml) and dried over 3A molecular sieves. Evaporation of the solvent gives 1.18 g (87%) of a yellow solid which is recrystallized from Skelly A (30 ml) at −60°: mp 70–71°; $[\alpha]^{25}D$ −27.8° (*c* 1.15, EtOH). Sublimation of the recrystallized acetate (45°, 0.4 Torr) raises the rotation, $[\alpha]^{25}D$ −28.5 (*c* 1.4, EtOH). The same experiment performed on (*S*)-(+)-**8** gave (*S*)-(+)-**9** with $[\alpha]^{25}D$ +28.7° (*c* 1.5, EtOH). (Rotation diminishes on standing in solution.)

(*S*)-(+)-1-Ferrocenylethanol (8) (Scheme II, Reaction H).—A solution of (*S*)-(+)-**9** [0.5 g, 0.00218 mol; $[\alpha]^{25}D$ +28.7 (*c* 1.5, EtOH)] in 25 ml of 50% acetone is allowed to stand for 20 hr at ambient temperature. The solution is diluted with water (25 ml), extracted with ether (3 × 25 ml), and dried over K_2CO_3, and the solvent is removed *in vacuo* [yield 0.39 g (78%)]. Recrystallization from *n*-heptane (4 ml) affords (*S*)-(+)-**8** as a yellow powder: $[\alpha]^{25}D$ +30.1° (*c* 1.2, benzene).

(*R*)-(+)-*N*,*N*-Dimethyl-1-ferrocenylethylamine (1) (Scheme II, Reaction I).—A solution of (*R*)-(−)-**9** [1.0 g, 3.68 mmol; $[\alpha]^{25}D$ −29.4° (*c* 1.3, ethanol), optical purity 96.5%], 25% aqueous dimethylamine (3.5 ml, 20 mmol), and methanol (20 ml) is allowed to stand for 2 days. Ice (50 g) is added and the product is extracted with ether (50 ml), then extracted into 8.5% H_3PO_4, washed with ether (50 ml), neutralized with 20% NaOH, and returned to ether. Evaporation of the solvent yields 943 mg (94%) of (*R*)-(+)-**1**: $[\alpha]^{25}D$ 13.6° (*c* 1.2, EtOH) (optical purity 96%).

(*S*)-(−)-*N*,*N*-Dimethyl-1-ferrocenylethylamine (1) (Scheme II, Reaction J).—Phosgene (3.0 g, 0.03 mol) is dissolved in 50 ml of dry ether in a 250-ml three-necked flask equipped with overhead stirrer, nitrogen inlet, and dropping funnel. The phosgene solution is cooled in a Dry Ice–ethanol bath to −20°. The solution of (*S*)-(+)-**8** [4.6 g, 0.02 mol; $[\alpha]^{25}D$ +27.6° (*c* 1.6, benzene) (optical purity 91%)] in 50 ml of ether is added dropwise with stirring. Stirring is continued at −20° for 15 min, and then at ambient temperature for 15 min. The solution is then transferred to a dropping funnel and added in a thin stream to a stirred solution of anhydrous $HNMe_2$ (4.5 g, 0.1 mol) in 100 ml of *i*-PrOH at −20°. When the solution reaches ambient temperature, it is filtered to remove $HNMe_2 \cdot HCl$ and evaporated. The residue is dissolved in 100 ml of ether, extracted into 8.5% H_3PO_4 (3 × 75 ml), washed with ether (100 ml), made basic with solid Na_2CO_3, and returned to ether. The solution is dried (K_2CO_3) and evaporated to yield, after distillation [bp 110° (0.5 Torr), 3.0 g (58%)], a brown oil: $[\alpha]^{25}D$ −12.9° (*c* 1.3, EtOH) (optical purity 91.5%)].

(*R*)-(−)-1-Ferrocenylethyl Acetate (9) (Scheme II, Reaction K).—A solution of (*R*)-(+)-**2** [2.0 g, 0.005 mol; $[\alpha]^{25}D$ +32.4° (*c* 1.4, MeCN)] and anhydrous NaOAc (2.05 g, 0.025 mol) in 50 ml of anhydrous DMF is allowed to stand for 24 hr at ambient temperature, and then diluted with ether (100 ml) and water (100 ml). The ether solution is washed repeatedly with water to remove DMF, dried over $MgSO_4$, and the solvent is removed *in vacuo* to leave a yellow-orange oil (solidifies on standing). The crude material is sublimed (50°, 0.5 Torr) to give 100 mg (7.4%) of pure **9**: $[\alpha]^{25}D$ −21.0° (*c* 0.6, EtOH) (optical purity 73.5%).

(*S*)-(−)-1-Ferrocenyl-1-methoxyethane (7) (Scheme II, Reaction L).—A solution of (*S*)-(+)-**9** [0.50 g, 0.0025 mol; $[\alpha]^{25}D$ +28.7° (*c* 1.5, EtOH)] in 25 ml of dry MeOH is allowed to stand for 24 hr at ambient temperature. Evaporation of the solvent *in vacuo* leaves **7** as a light brown oil: yield 390 mg (63%); $[\alpha]^{25}D$ −27.0° (*c* 1.9, EtOH).

(*R*)-(−)-1-Ferrocenylethyl Azide (10) (Scheme II, Reaction M).—A solution of (*R*)-(−)-**9** [3.0 g, 0.011 mol; $[\alpha]^{25}D$ −20.1° (*c* 1.4, EtOH) (optical purity 70.5%)] and sodium azide (4.0 g, 0.061 mol) in 300 ml of 25% MeOH is stirred overnight at ambient temperature. Most of the MeOH is removed *in vacuo*, saturated salt solution (75 ml) is added, and the product is extracted with three 50-ml portions of CH_2Cl_2. The combined extracts are dried over $MgSO_4$ and the solvent is removed *in vacuo* to give 2.0 g (70%) of a brown oil: ir 2100 cm^{-1}; $[\alpha]^{25}D$ −47.5° (*c* 2.5, benzene) (optical purity 68%). *Caution*: product is explosive.

(*R*)-(−)-1-Ferrocenylethylamine (3) (Scheme II, Reaction N).—A solution of (*R*)-(−)-**9** [3.0 g, 0.011 mol; $[\alpha]^{25}D$ −20.1° (*c* 1.4, EtOH) (optical purity 70.5%)] in 10 ml of concentrated aqueous NH_3 solution and 150 ml of MeOH is stirred for 10 hr at ambient temperature. The MeOH is then removed *in vacuo* and the residue is treated with 8.5% H_3PO_4 and ether. The acid solution is washed with ether and made basic with 20% NaOH, and the product is extracted with CH_2Cl_2. The solution is dried (K_2CO_3) and the solvent is removed *in vacuo*. The residue (1 g, 40%) has $[\alpha]^{25}D$ −14.5° (*c* 1.3, EtOH) (optical purity 69%). {Vacuum sublimation [40° (1 Torr)] affords a yellow solid, probably the hydroxylamine.[45]}

(*R*)-(−)-1-Ferrocenylethylamine (3) (Scheme II, Reaction O).—A solution of (*R*)-(+)-**2** [4.0 g, 0.01 mol; $[\alpha]^{25}D$ +32.4° (*c* 1.0, MeCN)] in 25 ml of concentrated aqueous NH_3 solution and 25 ml of acetonitrile is stirred for 20 hr at ambient temperature. Work-up is the same as for reaction N above. Yield was 1.58 g (69%) of a red-brown oil: $[\alpha]^{25}D$ −20.7 (*c* 1.2, EtOH)

(*R*)-(+)-*N*,*N*-Dimethyl-1-ferrocenylethylamine (1) (Scheme II, Reaction P).—A solution of (*R*)-(+)-**2** [4.0 g, 0.01 mol; $[\alpha]^{25}D$ +32.4° (*c* 2, MeCN)] in 100 ml of MeCN saturated with anhydrous $HNMe_2$ is allowed to react overnight at ambient temperature. The mixture is diluted with water (150 ml) and extracted with ether. The ether solution is extracted with 8.5% H_3PO_4, washed with ether, and made basic with solid Na_2CO_3, and the amine is returned to ether. The ether solution is dried (K_2CO_3) and the solvent is removed *in vacuo* to give (*R*)-(+)-**1**: yield 1.8 g (70%); $[\alpha]^{25}D$ +13.9° (*c* 1.1, ethanol).

(*R*)-(+)-1-Ferrocenyl-1-methyldimethyl Ether (7) (Scheme II, Reaction Q).—A solution of *n*-butyllithium in hexane (15 ml, 2 *M*) is added dropwise to an ether solution of (*R*)-(−)-**8** [4.6 g, 0.02 mol; $[\alpha]^{25}D$ −18.5 (*c* 2.3, benzene) (optical purity 60.6%)] and refluxed for 1 hr. Me_2SO_4 (2.8 g, 0.022 mol) in ether (25 ml) is added dropwise at reflux and heating is continued for 2 hr. The mixture is then poured into ice water (100 ml); the organic phase is washed with water (3 × 100 ml) and brine (100 ml) and dried ($MgSO_4$). Removal of the solvent *in vacuo* gives a viscous amber oil (4.8 g). Chromatography over silica gel (5.5 × 50 cm, J. T. Baker, no. 3405, 60–200 mesh) gives the following fractions: Skelly B, 90 mg (2.1%) of vinylferrocene; 1:5 acetone–Skelly B, 1.1 g (22.5%) of (*R*)-(+)-**7** {$[\alpha]^{25}D$ +16.2° (*c* 0.9, EtOH) (optical purity 59%)}; 1:3 acetone–Skelly B, 3.3 g of a mixture of **7** and **8**.

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Reaction of (*S*)-(+)-1-Ferrocenylethanol (8) with Acetic Acid in Benzene.—A solution of glacial HOAc (6 g, 0.1 mol) and (*S*)-(+)-**8** [4.6 g, 0.02 mol, $[\alpha]^{25}D$ +29.3° (*c* 1.7, benzene)] in 130 ml of dry benzene is refluxed for 4 hr while water separates (Dean-Stark trap). The solvent is removed *in vacuo* and the crude acetate (**9**) (4.9 g, 90%) is purified by chromatography (activated alumina, 5.5 × 20 cm, MCB, 80–325 mesh, eluent-Skelly B). The resulting yellow solid is sublimed: 35° (1 Torr), $[\alpha]^{25}D$ 0 (ethanol).

Registry No.—**2**, 11136-56-4; **9**, 11136-55-3.

Nucleophilic Substitutions Initiated by Electrochemical Oxidation. I. Intramolecular Nucleophilic Substitutions

G. POPP

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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The overcrowded 8-*tert*-butyl-1-(2-pyridyl)naphthalenes **1a–c** have been anodically oxidized to give the zwitterions **2a–c** after treatment of the initial reaction mixtures with aqueous base. The initial product of the two-electron oxidation of **1a** was the isolable perchlorate **3**, which slowly eliminates the *tert*-butyl group. The overall mechanism of the formation of zwitterions **2a–c** can be viewed as an electrochemically initiated intramolecular nucleophilic substitution reaction.

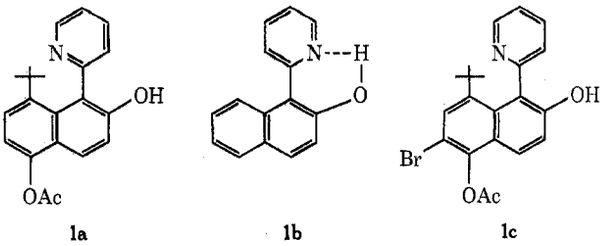
Anodic substitution reactions have been the subject of research for many years, with numerous investigations being described in the literature and summarized in review articles.[1–4] There has been much discussion of the mechanism of these reactions; recent studies have been concerned mainly with the pyridination of substituted anthracenes. Mechanisms proposed for these reactions include (a) the initial formation of a dication and subsequent attack by the nucleophile;[5–7] (b) the formation of a radical cation, attack of this species by the nucleophile, and further electron transfer (ECE mechanism);[8] and (c) disproportionation of the initial radical cation and attack of the resulting dication by the nucleophile.[9]

In all these mechanisms the proton can be considered as the leaving group. Reports of anodic substitution reactions with leaving groups other than the proton are scarce, but such reactions might prove more tractable and thereby offer useful mechanistic insight. The anodic nucleophilic displacement of bromine has been reported for 9,10-dibromoanthracene.[10] However, the authors did not elaborate on the chemical nature of the leaving group. Other communications have dealt with the replacement of a *tert*-butyl group during the course of the anodic oxidation of 2,4,5-tri-*tert*-butylphenol[11] and of 2,4,6-tri-*tert*-butylaniline[12] in acetonitrile solution.

We have investigated intramolecular nucleophilic substitution reactions of highly sterically hindered 8-*tert*-butyl-1-(2-pyridyl)naphthalenes[13] initiated *via* electrochemical oxidation. The leaving group in this case is also the *tert*-butyl group. However, when the oxidations are carried out under suitable reaction conditions, the intermediate cationic species, which still incorporate the *tert*-butyl group, can be isolated as their perchlorate salts. Decomposition of these salts yields isobutylene and zwitterions as the final products. One of these novel zwitterions was observed earlier[13] when 2-hydroxy-5-acetoxy-8-*tert*-butyl-1-(2-pyridyl)-naphthalene was treated with cupric chloride in refluxing ethanol. Although a two-electron oxidation product was obtained from this reaction, the polarographic oxidation was then described as a one-electron exchange. The suggested mechanism included the hitherto unprecedented oxidative coupling of a pyridyl radical through nitrogen rather than carbon. Our own studies on the anodic substitution of a *tert*-butyl group of 2,4,6-tri-*tert*-butylphenol by pyridine, which we shall describe in another paper, led us to the assumption that this intramolecular reaction may also proceed *via* a nucleophilic substitution. Therefore, the objective of this work was to explore the scope and mechanism of the oxidative formation of the zwitterions from their pyridyl naphthol precursors.

Results and Discussion

Cyclic Voltammetric Studies.—Upon scanning anodically from 0.0 V, compounds **1a–c**, all of which have



1a **1b** **1c**

a free hydroxyl group, show three "irreversible" responses A, B, and C, the peak potentials of which are given in Table I. Response C, which is near the solvent cutoff, is often ill-defined; therefore, no effort was made to elucidate its nature.

Compounds **1a–c** do not show a cathodic response between 0 and −2.0 V if the scan is started at 0 V.

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