

William C. Werkheiser and Mr. John Kraus of Roswell Park Memorial Institute, Buffalo, N. Y., for their assistance in the computer analysis of the data. The

helpful criticisms of Dr. Leo R. Fedor of the State University of New York at Buffalo in the preparation of this manuscript are gratefully acknowledged.

Solvolysis of Heteroannularly Substituted Methylferrocenylcarbinyl Acetates

David W. Hall,^{1a} E. Alexander Hill,^{1b} and John H. Richards

Contribution No. 3630 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

Received January 25, 1968

Abstract: The nature of the transmission of substituent effects from one cyclopentadienyl ring of ferrocene to a reaction center on the other ring was investigated by means of solvolysis studies on heteroannularly substituted methylferrocenylcarbinyl acetates. The evidence indicates that inductive or field effects predominate, and that resonance interactions play at most a minor role. A linear relationship exists between substituent effects in the solvolysis reaction and the reversible quarter-wave potentials of the appropriately substituted ferrocenes.

Solvolyses of metallocenylcarbinyl acetates have demonstrated that an α -metallocenyl substituent imparts remarkable stability to a carbonium ion center.² The stereochemistry of these solvolyses shows that departure of the leaving acetate ion is strongly favored in the direction away from the central metal atom.³ These and other results^{1a} have been cited as evidence for the occurrence of some electron release from the central metal atom to the positive carbon, though this interpretation has recently been the subject of controversy in the literature.⁴ In this paper we report a study of the effects of several simple substituents in the heteroannular position of the ferrocenylmethylcarbinyl acetate skeleton upon the solvolysis rate and show that inductive and field effects predominate in the transmission of these effects.

Experimental Section

Substituted Acetylferrocenes. The preparation and properties of 1'-bromo-, 1'-chloro-, and 1'-cyanoacetylferrocenes have previously been reported.⁵

1'-Carbomethoxyacetylferrocene. Nesmeyanov and Reutov reported the acetylation of carbomethoxyferrocene⁶ in 58% yield.⁷ An attempt to follow their procedure led to a 30% yield of the desired product, along with recovery of 62% of the starting material. Since the conditions specified appeared to be rather mild, the reaction was repeated under more vigorous conditions.

(1) (a) Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1963. (b) Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1961.

(2) (a) J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, **81**, 3484 (1959); (b) E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961).

(3) (a) E. A. Hill and J. H. Richards, *ibid.*, **83**, 4216 (1961); (b) D. S. Trifan and R. Backsai, *Tetrahedron Lett.*, No. 13, 1 (1960).

(4) (a) J. C. Ware and T. G. Traylor, *ibid.*, 1295 (1965); (b) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *ibid.*, 1695 (1966); (c) T. T. Tidwell and T. G. Traylor, *J. Amer. Chem. Soc.*, **88**, 3442 (1966); (d) T. G. Traylor and J. C. Ware, *ibid.*, **89**, 2304 (1967); (e) J. J. Dannenberg and J. H. Richards, *Tetrahedron Lett.*, 4747 (1965).

(5) D. W. Hall and J. H. Richards, *J. Org. Chem.*, **28**, 1549 (1963).

(6) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Amer. Chem. Soc.*, **76**, 4025 (1954).

(7) A. N. Nesmeyanov and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **115**, 518 (1957); *Chem. Abstr.*, **52**, 5393 (1958).

Acetyl chloride (3.67 g, 47 mmol) was added to a stirred suspension of powdered aluminum chloride (11.5 g, 86 mmol) in methylene chloride (70 ml) under nitrogen. Over a period of 10 min, carbomethoxyferrocene (8.0 g, 32.8 mmol) in methylene chloride (80 ml) was added. The solution warmed slightly. The reaction was stirred at room temperature for 3.25 hr and poured over ice. Sufficient acid was added to allow separation of the layers, and the product was extracted into methylene chloride. The combined organic phase was washed three times with sodium bicarbonate solution and once with water. After drying over magnesium sulfate, the solvent was removed to yield a dark red solid, mp 99–100.5°. One recrystallization from heptane produced 8.59 g of dark red crystals (91.5%), mp 101–101.7° (lit.^{7,8} mp 92.5–94.5°, 102–103°).

Carbinols. The 1'-bromo-, 1'-chloro-, 1'-carbomethoxy-, and 1'-cyanoacetylferrocenes were reduced to the corresponding carbinols with sodium borohydride in methanol.

The general procedure consisted in adding sodium borohydride powder over a period of 2–5 min to a methanolic solution of the ketone stirred with a magnetic stirrer. A gentle stream of nitrogen was directed onto the surface of the solution during the reaction. The reductions were generally complete in about 0.5 hr. The solutions changed from the red-orange color of the ketones to the straw-yellow color of the alcohols. After approximately 1 hr, excess sodium borohydride was decomposed with acetone. The reaction mixture was poured into approximately 200 ml of water and ammonium chloride was added until the solution tested weakly basic. The alcohol was extracted with dichloromethane. Ether formation may occur if the solution of the alcohol is dried over anhydrous magnesium sulfate or chromatographed on acid-washed alumina. For this reason, the dichloromethane solutions were worked up by adding them to an equivalent volume of benzene in a solvent stripping apparatus, and then distilling solvent under reduced pressure. The last traces of solvent were removed either at room temperature or else on a warm water bath maintained at a temperature no greater than 50°. The crude alcohol was used directly to prepare the acetate or else it was further purified by chromatography on neutral or basic alumina that had been deactivated by the addition of water (roughly 5% by weight). The crude alcohol was used directly to prepare the acetate only when its infrared spectrum indicated that none of the starting ketone remained unreduced. Liquid methylferrocenylcarbinols in general give poor elemental analyses whereas the liquid acetates give satisfactory analyses. For this reason all the carbinols were not themselves analyzed, but rather only the corresponding acetates were analyzed.

Acetates. The carbinols were converted into the corresponding acetates with acetic anhydride in pyridine according to the pro-

(8) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953.

cedure of Arimoto and Haven.⁹ About 1 g of the alcohol was mixed with pyridine (5 ml) and acetic anhydride (2 ml) and allowed to stand overnight at room temperature under a nitrogen atmosphere. Pyridine and acetic anhydride were distilled at a pressure of 0.5 mm and temperatures up to 50°. The crude acetate was dissolved in a small amount of dichloromethane and transferred to a molecular distillation apparatus. The bulk of the dichloromethane was removed by evaporation with a stream of nitrogen. The last traces of solvent were removed by placing a stopper in place of the cold finger of the still, and then maintaining a pressure of 0.5–1.0 mm for about 0.5 hr.

The molecular still used in the present study for the purification of all acetates except methyl(1'-acetylferrocenyl)carbinyl acetate had a heating chamber 25 mm in diameter with a path length between base and the cold finger of 20 mm. The chamber was fitted with a removable oil bath heating assembly. Since the heating chamber was in contact with a glass sleeve rather than the oil bath itself, the temperature of the material in the heating chamber was probably somewhat less than the temperature of the oil bath. For this reason the temperatures reported below for the distillation of the acetates should be regarded as maximum temperatures to be employed if a conventional molecular still were to be used to purify these acetates.

The purified acetates were transferred either to tared vials and stoppered under a nitrogen atmosphere or else to tared ampoules and sealed under a nitrogen atmosphere. When the acetate was stored in a tared vial, it was used within 1 day after it was collected from the distillation.

Methyl(1'-bromoferrocenyl)carbinol was prepared by reducing 1'-acetyl bromoferrocene (1.37 g, 4.5 mmol). The infrared spectrum of the crude alcohol displayed no bands in the carbonyl region.

Methyl(1'-bromoferrocenyl)carbinyl acetate was prepared from the crude alcohol as described above and then distilled at 80° at approximately 5- μ pressure. The product was a red oil (1.2 g, 75% yield based on 1'-acetyl bromoferrocene used in the reduction reaction), n_D^{25} 1.5959. The nuclear magnetic resonance spectrum was compatible with the assigned structure. The infrared spectrum (liquid smear) displayed a carbonyl absorption centered at 1736 cm^{-1} . Although the analysis listed below is not entirely satisfactory, the material was apparently quite pure since the experimental infinity titers for two out of three solvolysis runs done at 45° were within 1% of the theoretical values. The experimental infinity titer for the third run was within 2% of the theoretical value.

Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{BrO}_2\text{Fe}$: C, 47.90; H, 4.31; Br, 22.77. Found (Elek): C, 48.44; H, 4.37; Br, 23.10.

Methyl(1'-carbomethoxyferrocenyl)carbinol. Reduction of 1'-carbomethoxyacetylferrocene (1.15 g, 4.0 mmol) with sodium borohydride (1.0 g) in methanol (75 ml) followed by chromatography on alumina and recrystallization from hexane gave 0.65 g (56% yield) of methyl(1'-carbomethoxyferrocenyl)carbinol melting at 57.5–58.5°. A second fraction collected (0.20 g, 17% yield) had a melting point of 56.5–58.2°. The infrared spectrum (CCl_4) displayed a doublet carbonyl absorption at 1724 and 1705 cm^{-1} , suggesting that the hydroxyl group is hydrogen bonding to the carbonyl oxygen of the ester group. The 1705- cm^{-1} band disappeared when the hydroxyl group was methylated or acetylated. This compound also displayed bands at 3605, 3552, and 3508 cm^{-1} in the O–H stretching region.

Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Fe}$: C, 58.45; H, 5.60; Fe, 19.37. Found (Spang): C, 58.37; H, 5.64; Fe, 19.59.

Methyl(1'-carbomethoxyferrocenyl)carbinyl acetate was prepared by the usual procedure from the carbinol. Distillation gave an oil, n_D^{25} 1.5721. The infrared spectrum exhibited a carbonyl absorption at 1720 cm^{-1} with a shoulder at 1725 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_4\text{Fe}$: C, 58.20; H, 5.49. Found (Elek): C, 58.13; H, 5.64.

Methyl(1'-chloroferrocenyl)carbinyl acetate was prepared by reducing 1'-chloroacetylferrocene (0.55 g, 2.1 mmol) and esterifying the crude alcohol in the usual manner. The acetate was purified by distillation over a 4-hr period at 60–80° and 5–10 μ .

The product was a red-orange oil (0.5 g, 86% yield based on the amount of 1'-acetylchloroferrocene used in the reduction reaction), n_D^{25} 1.5806. The infrared spectrum was determined from a liquid smear and from a carbon tetrachloride solution; the carbonyl absorption occurred at 1735–1740 cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{ClO}_2\text{Fe}$: C, 54.85; H, 4.93; Cl, 11.57. Found (Spang): C, 54.79; H, 5.06; Cl, 11.45.

Methyl(1'-cyanoferrocenyl)carbinol was prepared from 1'-acetylcyanoferrocene in the usual way. The alcohol was isolated in nearly a quantitative yield after chromatography on alumina. The infrared spectrum of this crude material showed no band in the carbonyl region.

Methyl(1'-cyanoferrocenyl)carbinyl acetate was prepared in the usual manner and distilled during an 8-hr period at 110° and 5–10 μ . The product was a red oil, n_D^{25} 1.5849. The infrared spectrum (carbon tetrachloride) displayed a carbonyl absorption at 1740 cm^{-1} and a nitrile absorption at 2235 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{Fe}$: C, 60.63; H, 5.09; N, 4.71. Found (Elek): C, 60.87; H, 5.26; N, 4.53.

Methyl(1'-acetylferrocenyl)carbinol was prepared by partially reducing crude 1,1'-diacetylferrocene¹⁰ (6.0 g, 22 mmol) with sodium borohydride (1.0 g, 27 mmol) in methanol (375 ml). The mixture was stirred for 1.25 hr at room temperature; it was then worked up in the usual manner. The crude product was chromatographed on a column of basic alumina (3 \times 30 cm) that had been deactivated by the addition of water (4.6% by weight). Traces of acetylferrocene (impurity in the starting material) and methylferrocenylcarbinol were eluted first with benzene. An undetermined amount of diacetylferrocene was eluted next with 10% ether in benzene. Methyl(1'-acetylferrocenyl)carbinol (1.80 g, 30% yield) was eluted just after the diacetylferrocene band; it was collected in seven fractions (total volume 6 l.). An undetermined amount of bis(1'-hydroxyethyl)cyclopentadienyliron contaminated with an orange oil (probably the ether) was eluted last with 20% ether in benzene. The infrared spectrum (carbon tetrachloride) of methyl(1'-acetylferrocenyl)carbinol possessed a fairly well-resolved doublet carbonyl absorption at 1667 and 1677 cm^{-1} . A strong aromatic ketone band occurred at 1282 cm^{-1} .

Methyl(1'-acetylferrocenyl)carbinyl acetate was prepared from the alcohol in the usual manner. The yield was approximately 90% of theory after molecular distillation (apparatus with a conventional oil bath attached to the heating chamber) at 60° and approximately 5 μ . The product was a clear red-orange oil, n_D^{25} 1.5850. The infrared spectrum was determined from a liquid smear and in carbon tetrachloride. The ultraviolet spectrum was determined in methanol (maxima at 226 (17,480), 269 (6220), and 337 $\text{m}\mu$ (ϵ 1222)) and in cyclohexane (maxima at 223 (23,200) and 269 $\text{m}\mu$ (ϵ 5280); shoulder at 325 $\text{m}\mu$ (ϵ 884)).

Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Fe}$: C, 61.19; H, 5.74. Found (Elek): C, 61.10; H, 5.84.

Methyl(1'-methylferrocenyl)carbinyl acetate was prepared by first reducing 1'-methylacetylferrocene^{8a} with lithium aluminum hydride according to the previously published procedure,^{2b} and then treating the chromatographed alcohol with acetic anhydride in pyridine. Distillation of the crude acetate gave a clear red-orange oil.

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{Fe}$: C, 62.96; H, 6.34; Fe, 19.52. Found (Spang): C, 63.17; H, 6.51; Fe, 19.78.

Kinetic Procedure. The procedures used in these experiments were similar to those reported in an earlier paper.^{2b} Preparation of the "80% acetone" solvent used in all these solvolyses was also described in the above reference. In the case of several of the more slowly reacting acetates it was necessary to use the theoretical infinity titers because of apparent decomposition after several half-lives. Results are summarized in Table I.

Results

Methylferrocenylcarbinols with substituents in the 1' position were prepared by lithium aluminum hydride or sodium borohydride reduction of the corresponding acetylferrocenes. Acetates of the carbinols were prepared with acetic anhydride in pyridine and purified by molecular distillation. Solvolysis rates were determined for acetates having acetyl, bromo, carbomethoxy, chloro, cyano, hydrogen, and methyl groups in the 1' position (Figure 1). Table II lists the relative rates of solvolysis of these acetates at 45° in "80% acetone." Also listed in Table II are activation parameters, when determined, and quarter-wave potentials for the ferrocene derivatives corresponding to the acetates.

(9) F. S. Arimoto and A. C. Haven, Jr., *J. Amer. Chem. Soc.*, **77**, 6295 (1955).

(10) M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

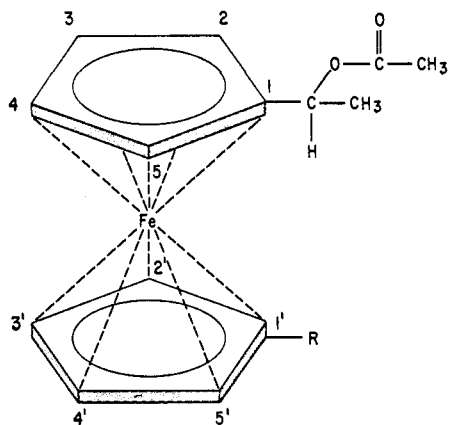


Figure 1. Structure of heteroannularly substituted methylferrocenylcarbinyl acetates.

Most of the quarter-wave potentials, expressed as $\Delta E_{1/4}$ values relative to the quarter-wave potential for ferrocene itself, were either taken directly from the tabulation given by Hall and Russell¹¹ or else calculated

Table I. Rate Data

Substituent	$T, ^\circ\text{C}$	$k \times 10^6, \text{sec}^{-1}$ ^a
1'-Methyl	0.00	1.032 ± 0.021^b
	10.00	3.54 ± 0.02^b
	20.00	11.3 ^c
	45.00	148.3 ^d
1'-Hydrogen	45.00	79.2 ^e
1'-Chloro	45.00	3.91 ± 0.11
1'-Bromo	30.00	0.636 ^c
	45.00	3.13 ± 0.01^b
1'-Carbomethoxy	35.00	0.438 ± 0.019^b
	45.00	1.39 ± 0.02
	63.50	10.0 ± 0.5^b
1'-Acetyl	45.00	1.242 ± 0.012
1'-Cyano	45.00	0.1814 ± 0.0051

^a Rate at a given temperature is based on an average of three runs unless otherwise noted. ^b Based on two runs. ^c Based on a single run. ^d Extrapolated from the data from lower temperatures. ^e Extrapolated from the data listed in ref 2b.

Table II. Relative Rates of Solvolysis of 1'-Substituted Methylferrocenylcarbinyl Acetates in "80% Acetone" at 45°

1' substituent	Rel k	$\Delta\Delta H, \text{kcal}$	$\Delta\Delta S, \text{eu}$	$\Delta E_{1/4}, \text{V}$
CH ₃	1.8725	-0.42 ± 0.38	0.0	-0.060
H	1.0000	0.0 ± 0.57	0.0	0.000
Cl	0.0494			0.172
Br	0.0395	$+0.78 \pm 1.5$	-2.15	0.155
COOCH ₃	0.0176	$+2.33 \pm 1.13$	+1.5	0.241
COCH ₃	0.0157			0.255
CN	0.0023			0.375

from the appropriate data listed by them. $\Delta E_{1/4}$ for carbomethoxyferrocene was taken from the compilation of Little and coworkers.¹² $\Delta E_{1/4}$ values for chloro- and bromoferrocenes have not been determined. The appropriate $\Delta E_{1/4}$ values were calculated, presuming additivity of substituent effects in the oxidation reaction,¹² from the values for acetylferrocene, 1'-acetyl-

(11) D. W. Hall and C. D. Russell, *J. Amer. Chem. Soc.*, **89**, 2316 (1967).

(12) W. F. Little, C. N. Reilly, J. D. Johnson, and A. P. Sanders, *ibid.*, **86**, 1382 (1964).

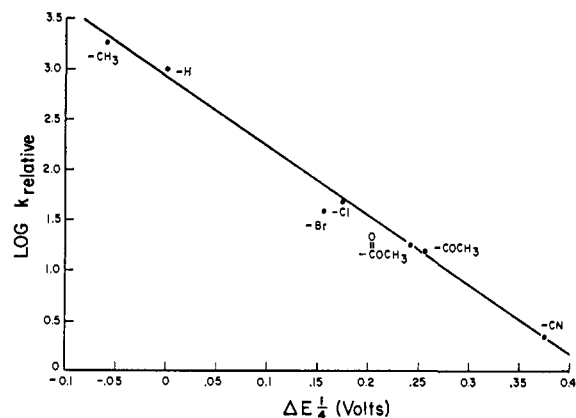


Figure 2. Relationship between the relative rates of solvolysis of 1'-substituted methylferrocenylcarbinyl acetates and the quarter-wave potentials of appropriately substituted ferrocenes.

chloroferrocene, 1'-acetylferrocene, and 1,1'-dibromoferrocene.

Figure 2 shows the linear correlation which results when the relative solvolysis rate data are plotted *vs.* the corresponding $\Delta E_{1/4}$ values.

Table III lists the results of least-squares analyses for the relative solvolysis rate data plotted *vs.* $\Delta E_{1/4}$, Hammett's σ_m and σ_p constants,¹³ Taft's σ_m and σ_p constants,¹⁴ and an arbitrary calculated constant, $(\sigma_m + 2\sigma_p)/3$. To obtain the data listed in Table III, the

Table III. Statistical Evaluation of the Correlation between the Relative Rates of Solvolysis and Various Selected Parameters

Computation no.	Parameter	Slope regression line	Correln coeff (r) ^a	Std dev(s) ^a
1	$\Delta E_{1/4}$	-6.937	0.995	0.115
2	σ_m	-4.460	0.976	0.249
3	σ_p	-3.524	0.977	0.244
4	σ_m^0	-4.277	0.976	0.248
5	σ_p^0	-3.608	0.989	0.169
6	$(\sigma_m + 2\sigma_p)/3$	-3.919	0.993	0.131

^a See discussion of statistical treatment of the Hammett equation in ref 13.

Hammett equation was used in the form presented by Jaffé; therefore, the significance of the statistical parameters is the same as discussed in detail by Jaffé.¹³ The Hammett substituent constants employed were taken from the compilation of McDaniel and Brown.¹⁵ Insufficient data are available for the ionization constants of heteroannularly substituted ferrocenoic acids to make an evaluation of the degree of correlation of these with the solvolysis rate data in the present paper. Results of an attempted correlation of this type have been given elsewhere.^{1b}

Discussion

A substituent on one ring of the metallocene nucleus may alter the electron density on that ring through its inductive, field, or resonance interaction with the ring.

(13) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(14) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(15) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

This change in electron density may be relayed through the ring-metal bonds to a reaction center on the metal itself or on the second ring. Such transmission of effects will reflect the nature and polarizability of the ring-metal bonds. The π electrons of the cyclopentadienyl ring participate in bonding to the central metal atom, and as a result, some degree of contribution from a "resonance pattern" of substituent effects might be anticipated.¹⁶ In the extreme, it is at least conceivable that a resonance interaction between heteroannular groups might be transmitted by the ring-metal bonds quite efficiently. In that case, solvolysis of 1'-substituted methylferrocenylcarbonyl acetates might be correlated by a σ^+ relationship,¹⁷ and reactions involving smaller changes in conjugative interactions might be best correlated by σ_p or some similar blend of resonance and inductive effects. However, to the extent that the ring-metal bonds are incapable of transmitting such a resonance effect, the direct resonance contribution would be effectively screened out. Though a substituent could release electrons to the ring by resonance, this change in electron density would have to be transmitted to the metal or to the other ring by an inductive mechanism. Taft has considered similar situations for *meta*-substituted benzene derivatives or in systems of the type $\text{ArCH}_2\text{Y} \rightarrow \text{ArCH}_2\text{Y}'$, and has used such systems to define the σ^0 parameter.¹⁴

A reaction in the ferrocene series should not necessarily be expected to correlate precisely with any of the numerous substituent constants which have been derived for various aromatic and aliphatic systems. Each corresponds to a particular balance of electrical effects applicable with high precision only in a limited set of circumstances. However, the degree of correlation with a set of substituent constants may provide a semiquantitative evaluation of the types of electronic effects which prevail in the system, while the deviations observed from these plots may be suggestive of special interactions.

The direct field effect of a 1' substituent in reactions of ferrocene derivatives presents interesting possibilities for unusual types of behavior, since the magnitude and even the direction of the effect would depend on the rotational orientation of the two rings. Such field interactions might be strong enough to disturb the free rotation of the rings, and in extreme cases could lead to a situation where actual bonding occurs between the two heteroannular substituent groups; such interactions could limit the precision of any correlation obtainable for reactions of 1'-substituted ferrocenes. These possibilities are more nearly analogous to the situation with aliphatic and *ortho*-substituted aromatic compounds than to the *meta*- and *para*-substituted benzene derivatives for which linear free energy relations have found their greatest success.

Several previous studies have provided data for linear free energy correlations of heteroannular substituent effects in the ferrocene series. These include the ionization constants of substituted ferrocenoic acids studied

by Nesmeyanov and coworkers,¹⁸ Little and Eisenthal,¹⁹ and Benkeser and Hall;²⁰ rate constants for the reaction of substituted ferrocenoic acids with diphenyldiazomethane studied by Little and Eisenthal;²¹ and infrared carbonyl stretching frequencies of ferrocenoic acids and esters.²²

In order to place the earlier studies mentioned above on a consistent basis with the present work, the statistical treatments for the various correlations were recalculated leading to the conclusion, in contrast to the opinions expressed earlier, that there was little basis for deciding whether σ_m or σ_p gave better correlation with the reaction data.¹⁵ This was so either because too few substituents with well-defined σ constants were employed in a given study or, in the case of the carbonyl stretching frequencies, because the substituent effects were too small to make statistical analysis meaningful.¹³ In general, correlations with either σ_m or σ_p were fair to good according to Jaffé's arbitrary standards.¹³

Hall and Russell recently reported a similar situation for the effects of substituents on the chronopotentiometric oxidation of ferrocene derivatives in anhydrous acetonitrile.¹¹ These authors demonstrated that $\Delta E_{1/4}$ data for a selected group of 20 ferrocene derivatives could be correlated quite well with either σ_m or σ_p . Only when data for ferrocene derivatives bearing substituents differing greatly in electronic effects, such as methoxy, the halogens, and cyano, were included in the Hammett treatment did σ_p give a correlation superior to that obtained using σ_m . Hall and Russell concluded that substituent effects in the oxidation reaction were best correlated by using a calculated constant, $(\sigma_m + 2\sigma_p)/3$, which weights resonance effects intermediately between that expressed by either σ_m or σ_p . Nesmeyanov also reached the conclusion that resonance effects in the oxidation of ferrocene derivatives were overemphasized by σ_p and stated that a better correlation was found when the data were plotted *vs.* σ_p^0 .²³

The present study leads to conclusions similar to those in the oxidation of ferrocene derivatives. Comparison of computations 2 and 3 in Table III shows that the relative rates of solvolysis of the acetates studied can be correlated equally well with σ_m or σ_p and that the correlations are "good" according to Jaffé's standards.¹³ Computation 4 shows that the correlation of the rate data with σ_m^0 gives a result little different from that using σ_m . This is not unexpected, considering the relatively small differences between the corresponding values for σ_m^0 and σ_m .

Computations 5 and 6 show that considerable improvement is obtained when the solvolysis relative rate data are plotted *vs.* either σ_p^0 or $(\sigma_m + 2\sigma_p)/3$. Thus, the present results show quite clearly that the ring-metal bonds must transmit electronic effects by a mechanism that is primarily inductive in nature. The reaction studied is one with a large ρ value and a very strong

(18) (a) A. N. Nesmeyanov and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **115**, 518 (1957); (b) A. N. Nesmeyanov and O. A. Reutov, *Izv. Akad. Nauk SSSR*, 926 (1959); *Chem. Abstr.*, **54**, 469c (1960).

(19) W. F. Little and R. Eisenthal, *J. Org. Chem.*, **26**, 3609 (1961).

(20) R. A. Benkeser and L. W. Hall, Jr., *U. S. Govt. Res. Rept.*, **32**, 165 (1959); *Chem. Abstr.*, **54**, 21025b (1960).

(21) W. F. Little and R. Eisenthal, *J. Amer. Chem. Soc.*, **83**, 4936 (1961).

(22) L. A. Kazitsnya, B. V. Lokshin, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **127**, 333 (1959).

(23) A. N. Nesmeyanov and E. G. Pervalova, *Ann. N. Y. Acad. Sci.*, **125**, 67 (1965).

(16) For a discussion of linear free energy correlations, see (a) ref 13; (b) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184; (c) R. W. Taft, in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 556-665; (d) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(17) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

electron demand, which might be correlated by σ^+ in the benzene series. However, the various $\sigma\rho$ correlations suggest that the resonance interaction is probably intermediate between those from the *meta* and *para* positions of a benzene ring in reactions which do not have a strong electron demand, and a model allowing for only inductive transmission through the ring-metal bonds correlates the data quite well. Singer and Cram²⁴ reached a similar conclusion for electron-withdrawing, transannular substituent effects in π - π complexes of paracyclophanes.

The excellent correlation between the solvolysis rate data and the $\Delta E_{1/4}$ values for the corresponding substituted ferrocenes depicted in Figure 2 is especially noteworthy. Computation 1 in Table III shows the rate data correlate better with $\Delta E_{1/4}$ than they do with any of the other parameters tested. Thus, at least for the case of the solvolysis reaction, the quarter-wave potentials constitute a standard reference for substituent effects, much as the ionization constants of benzoic acids do for side-chain reactions in the benzene series. This correlation implies that considerable positive charge is probably carried by the metal atom in α -

(24) L. A. Singer and D. J. Cram, *J. Amer. Chem. Soc.*, **85**, 1082 (1963).

metallocenylcarbonium ions, a situation which is predicted by both theoretical models²⁻⁴ for these ions. Whether or not quarter-wave potentials would accurately predict substituent effects in other side-chain reactions of ferrocene remains an open question.

Hall and Russell¹¹ reported that ferrocenes bearing acetamido or urethano substituents possessed unusually low quarter-wave phenomenon, *i.e.*, the carbonyl oxygen atom of these groups coordinated with the positively charged iron atom in the oxidized species. Even if the iron atom does acquire a significant positive charge in the solvolysis of methylferrocenylcarbonyl acetates, it seems unlikely that appropriate substituents would lead to an unusually high solvolysis rate because of an internal solvation effect. This is so because the aqueous acetone solvent employed in these studies would likely compete with the substituent for coordination sites on the metal atom. Komenda and Tirouflet²⁵ observed no unusual effect when acetamidoferrocene was oxidized polarographically in ethanol-water.

Acknowledgment. This investigation was supported by a grant from the National Science Foundation (NSF-CP 5190) and the Paint Research Institute.

(25) J. Komenda and J. Tirouflet, *Compt. Rend.*, **254**, 3093 (1962).

Reaction of Nickelocene with Diazoalkanes^{1,2}

Helmut Werner³ and John H. Richards

Contribution No. 3541 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

Received January 25, 1968

Abstract: Nickelocene catalyzes the reaction of diazomethane to produce polymethylene; even in the presence of carbene acceptors polymethylene is the only product formed. Nickelocene catalyzes the reaction of ethyl diazoacetate, giving diethyl maleate and diethyl fumarate. In the presence of cyclohexene, ethyl norcaranecarboxylate is also formed. Nickelocene is recovered unchanged from these reactions. The catalytic effects of nickelocene seem to be unique to it; for example, neither ferrocene nor dicyclopentadienylchromium have similar properties. A mechanism for these reactions is proposed.

In continuing our studies on reactions and properties of electron-deficient metallocene derivatives (for example, carbonium ions⁴) we have studied the interaction of potential carbenoid reagents, for example, diazomethane, with metallocenes such as nickelocene. We were particularly attracted to nickelocene because it is a paramagnetic substance with two unpaired electrons⁵ and might have a novel interaction with a carbene, which in the triplet state would also have two unpaired electrons.

(1) Supported by the National Science Foundation, Grant No. GP-5190, and the Paint Research Institute.

(2) Reported at the Cincinnati Symposium on Organometallic Chemistry, June 12-15, 1963; see also *Off. Dig. Federation Soc. Paint Technol.*, **36**, 1433 (1964).

(3) Anorganisch-Chemisches Laboratorium der Technischen Hochschule München, 8 München 2, Germany.

(4) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961).

(5) G. Wilkinson, P. L. Pauson, J. M. Birmingham, and F. A. Cotton, *ibid.*, **75**, 1011 (1953); E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8b**, 217 (1953).

A great many substances have been previously investigated as catalysts for the decomposition of diazomethane, *e.g.*, Cu,⁶⁻⁹ CuX (Br, Cl, I),^{7,10} CuCl₂,^{7,10} CuSO₄,⁷ copper(II) stearate,^{7,9,11} BF₃,⁹⁻¹² B(OCH₃)₃,^{9,13} AlCl₃,^{7,9,10,14} Et₂AlCl,^{7,14} GaI₃,¹⁰ BeCl₂,¹⁰ MgCl₂,¹⁰ FeCl₃,^{9,10} Fe(DPM)₃,⁶ AgNO₃,⁷ Ag,⁷ PtCl₄,⁷ ZnI₂,^{7,10} and Ni(CO)₄.¹⁵ In addition, the photolysis of diazomethane has been extensively studied and both singlet

(6) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **83**, 2397 (1961); **84**, 1015 (1962).

(7) E. Müller and H. Fricke, *Ann.*, **661**, 38 (1963).

(8) G. D. Buckley, L. H. Cross, and N. H. Ray, *J. Chem. Soc.*, 2714 (1950).

(9) C. E. H. Bawn and T. B. Rhodes, *Trans. Faraday Soc.*, **50**, 934 (1954).

(10) G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).

(11) J. Feltzin, A. J. Restaino, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **77**, 206 (1955).

(12) S. W. Kantor and R. C. Osthoff, *ibid.*, **75**, 931 (1953).

(13) G. D. Buckley and N. H. Ray, *J. Chem. Soc.*, 3701 (1952).

(14) H. Hoberg, *Ann.*, **656**, 1 (1962).

(15) C. Ruechardt and G. S. Schrauzer, *Chem. Ber.*, **93**, 1840 (1960).