Journal of Organometallic Chemistry, 168 (1979) 203—214

THE COMPETING METHOXYMERCURATION AND RING-MERCURATION REACTIONS OF SOME ALKYLVINYL-SUBSTITUTED FERROCENES

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(Received September 11th, 1978)

Summary

Product analysis and kinetic data for the reaction of some alkylvinylferrocenes with mercuric acetate in methanol are reported. Depending on the location and nature of the alkyl group(s), exclusive addition or ring-substitution reactions are observed as well as both reactions together. This behaviour is interpreted in terms of the relative polar and steric effects. Styrene has also been investigated under similar conditions to provide comparisons of mechanistic significance. The methoxymercuration reaction seems to proceed via a slowly formed, possibly bridged intermediate, with weak carbonium ion character; with the ferrocene derivatives as substrates it appears to be a complex process as suggested by an anomalous temperature-dependence behavior.

Introduction

In the field of metallocene chemistry, vinyl-substituted derivatives have received considerable attention with regard to polymerization reactions [1] but their primary interactions with electron-deficient reagents have been less extensively studied [2—6]. Our introductory work [7] on the reaction of vinylferrocene with mercuric acetate has revealed a number of factors worthy of investigation, such as the steric requirements of the methoxymercuration reaction and the competition between electrophilic addition and electrophilic substitution due to the strongly electron-donating ability of the ferrocenyl system. Furthermore, since some aspects of the methoxymercuration of olefinic linkages have not yet been elucidated, we hoped to obtain some useful information through the behavior of such a special system as vinylferrocene.

In continuation of our previous work we now report on the product analysis for the reaction of β-methylvinyl- and β,β-dimethylvinyl-ferrocenes with mercuric acetate, and on the reaction kinetics for a number of alkylvinyl-substituted ferrocenes and of styrene at various temperatures.

Results and discussion

The reaction of the substrates with mercuric acetate was carried out in methanol at concentrations of the order of 1×10^{-2}—3×10^{-2} M for the product analyses and 2×10^{-2}—1×10^{-5} M for the rate measurements.

Product analyses show that two reactions may occur, addition to the olefinic linkage (methoxymercuration) and aromatic substitution at the Cp ring. Addition is found to be the sole reaction for vinyl- and α-methylvinyl-ferrocenes [7], whereas ring-substitution is the sole reaction for α-t-butylvinyl [7] and β,β-dimethylvinyl-ferrocenes. Both reactions occur together in the case of the *trans*-β-methylvinyl derivative, for which 64% addition and 36% substitution at 25°C were obtained. In all cases the addition was of the Markownikov type, and substitution occurred at the Cp ring other than that bearing the vinyl chain.

For an interpretation of these results, the study was complemented by rate measurements. Both reactions were found to be first order in each reactant. The rate constants at 25°C are listed in Table 1. The k values for the competing reactions of the *trans*-β-methylvinyl derivative were calculated from the overall rate constants and the isomeric composition of the reaction products.

The ring-mercuration rates for α-t-butylvinyl-, β-methylvinyl-, and β,β-dimethylvinyl-ferrocenes were found to be closely similar to each other and higher by a factor of about 2 than that of ferrocene itself after allowances for the statistical factor 2.

The addition reaction can be assumed to be a two-step process [8—11]. In some cases [12,13] the second step, i.e., the reaction of the cationic intermediate with the nucleophilic solvent, has been suggested to be the slow step. However, the lack of any evidence for the accumulation of the reaction intermediate under the investigated experimental conditions and the effects of the alkyl substituents at the vinyl chain are consistent with the assumption that the formation of the cationic intermediate is the slow step of the process. Since the addition is of the Markownikov type and the electrophile attacks the β-position of the vinyl chain, the effect of the α-methyl group can be regarded as essentially polar, whereas that of the β-methyl group is expected to reflect a

TABLE 1

SECOND ORDER RATE CONSTANTS FOR THE REACTION OF MERCURIC ACETATE WITH SOME VINYLFERROCENES AND STYRENE IN METHANOL, AT 25°C

Compound	k_{addition} (M^{-1} s^{-1})	$k_{\text{substitution}}$ (M^{-1} s^{-1})	Ref.
Fc—CH=CH$_2$	230 ± 30		7
Fc—C(CH$_3$)=CH$_2$	910 ± 80		This work [a]
Fc—C(t-Bu)=CH$_2$		0.24 ± 0.02	This work
Fc—CH=CH-CH$_3$	0.67 ± 0.04	0.37 ± 0.02	This work
Fc—CH=C(CH$_3$)$_2$		0.26 ± 0.02	This work
Ph—CH=CH$_2$	10.4 ± 0.5		This work
FcH		0.25 ± 0.02	7

[a] This value confirms the preliminary value reported in ref. 7.

combination of polar and steric effects. In the former case, the higher rate for the α-methyl derivative relative to hydrogen by a factor of about 4 is a clear evidence in favor of a slow attack of the electrophile in the reactions under examination. In the latter case, in view of the expectedly large steric requirements of the mercury reagent in this reaction, the reactivity order H > β-methyl > β,β-dimethyl undoubtedly reflects a steric order, and can be interpreted as resulting from a steric effect which more than offsets the assumed rate-enhancing polar effect of the methyl group located at the site of attack.

If the above interpretation is correct, one would expect steric effects eventually to become important on increasing the steric requirements of an alkyl group even when located at one position away from the site of attack. This is what is found for the α-t-butylvinyl derivative, for which the reaction is completely diverted from addition to ring-substitution. Our previous tentative interpretation [7] thus appears to be confirmed.

Finally, it is worth noting that inspection of molecular models indicates that of the investigated compounds, the β,β-dimethylvinyl and the α-t-butylvinyl derivatives appear to be the most hindered towards the approach of a bulky electrophile to the double bond.

A major problem for the elucidation of the mechanism of the methoxymercuration concerns the structure of the cationic intermediate. The subject has been recently reviewed by Ambidge et al. [14]. Evidence has been brought forth in support of a free carbocation [15,16], as well as of symmetrically [17,18] and unsymmetrically [19] bridged mercurinium ions for the structure of the intermediate. It is possible that of the proposed alternatives each may play a role depending on the nature of the reacting systems.

The present data may have a bearing on this problem. The reactivity of styrene (Table 1) shows that the substrate selectivity of the reaction is small, vinylferrocene being about 25 times as reactive as styrene. Furthermore, the absolute rates are quite high, i.e., 230 and 10.4 $M^{-1}s^{-1}$, and indicate that markedly stabilized intermediates are involved. The variation in the substrate selectivity is clearly small when considered along with the relative stabilities of the relevant non-mercurated carbonium ions. The pK_{R^+} value for the protonation of ferrocenylethanol leading to 1-ferrocenylethyl cation is −0.64 [20]. Although the pK_{R^+} value for the 1-phenylethyl cation is not available, it can be estimated from data for similar substrates * to be lower by about 12 pK units. That such huge difference in stability of the carbonium ion is reflected in the substrate selectivity of the methoxymercuration only to a minor extent supports the view that the reaction intermediate has little carbonium ion character. This is consistent with the hypothesis that the structure of the reaction intermediate is a bridged species ** [14].

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* This conclusion is reached on the basis of the following data for the pK_{R^+}'s for formation of the carbonium ions from the alcohols. 1-Ferrocenylethyl, −0.64 [20]; 2,4,6-trimethyl, −17.3 [21]. The latter value must be corrected to allow for the lack of a methyl group on the charged carbon and we note the following pK_{R^+} values: 2,4,6-trimethylisopropyl cation, −12.2 [21]; 1,1-diphenylethyl cation, −10.4 [22]; diphenylmethyl cation, −13.3 [23], indicating that a methyl group on the charged carbon brings about a pK_{R^+} increase of ca. 3 pK units.

** For other possible stabilizing factors, such as σ—π conjugation [15,24,25], see a recent discussion by Olah [26].

Substituents effects are known to be relatively small in the ferrocenyl system because of a "saturation" effect associated with the very large electron-donating ability of the ferrocenyl group [27]. Thus the 1-ferrocenylethyl cation is more stable than the ferrocenylmethyl cation by a factor of 8. Again, the methoxymercuration reaction is less selective and involves a factor of 4. Although the selectivity scale is markedly flattened out here, it does show the same qualitative order and indicate again a weak carbonium ion character for the mercurated charged intermediate.

Temperature-dependence of reaction rates

Surprising results were obtained for the rates for vinylferrocene and its α-methyl derivative at diverse temperatures (Table 2). Over a temperature range of 33°C the methoxymercuration rates for vinylferrocene were practically unaffected by temperature, while those of α-methylvinylferrocene appeared to fall slightly with increasing temperature. In the latter case the Arrhenius plot was linear with slope —0.9. This behavior indicates that the reaction is complex.

In the literature the only data for oxymercuration rates at different temperatures are those reported by Halpern [28] for hydroxymercuration; and they showed a regular dependence on temperature and the activation parameters were determined for a number of alkenes. Styrene also displays normal behavior (Table 3). Thus, it is reasonable to suppose that the observed anomalous dependence is to be associated with the ferrocenyl system.

Examples of anomalous temperature dependence, though infrequent, have been reported in the literature. They include certain aromatic halogenations and addition reactions of halogens to olefins in non-polar solvents [29—33]. Zero or "negative" activation energies have been accounted for in terms of the mildly exothermic formation of molecular complexes between the substrate and the electrophile before the rate-determining step. Similarly, in view of the strong electron-donating ability of the Cp rings of ferrocene, a fast pre-equilibrium leading to a π-complex [34] between the alkenylferrocene and the electrophile can be assumed to precede the rate-determining attack of electrophile on the double bond. The two consecutive processes would depend on tempera-

TABLE 2

SECOND ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES FOR THE METHOXYMERCURATION OF VINYLFERROCENE AND α-METHYLVINYLFERROCENE

T (°C)	$k(\text{Fc—CH=CH}_2)$ $(M^{-1}\ s^{-1})^a$	$k(\text{Fc—C(CH}_3\text{)=CH}_2)$ $(M^{-1}\ s^{-1})^b$
17.2	292	1024
20.7	261	1068
22.2	248	861
25.3	230	910
27.8	263	931
41.6	280	750
50.5	233	681

[a] $[\text{Fc—CH=CH}_2] = 1.12 \times 10^{-4}\ M$, $[\text{Hg(OAc)}_2] = 8.20 \times 10^{-5}\ M$. [b] $[\text{Fc—C(CH}_3\text{)=CH}_2] = 1.32 \times 10^{-4}\ M$, $[\text{Hg(OAc)}_2] = 1.20 \times 10^{-4}\ M$.

TABLE 3

SECOND ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES AND ACTIVATION PARAMETERS FOR THE METHOXYMERCURATION OF STYRENE

T (°C)	k (M^{-1} s^{-1}) [a]
15.5	6.0
18.0	7.4
21.2	8.9
25.0	10.4
33.3	15.6

$E_a = 10.6 \pm 0.5$ kcal/mol
$\Delta S^{\ddagger} = -20.0 \pm 1.5$ e.u.

[a] [Ph—CH=CH$_2$] = 1.15×10^{-4} M, [Hg(OAc)$_2$] = 1.54×10^{-3} M.

ture in opposite ways and give rise to somewhat different effects for vinylferrocene and for its α-methyl derivative. The system does not permit a detailed study of the process because of the relatively high reaction rates. Further information could be sought from reactions in other media.

It is noteworthy that the ring-mercuration of α-t-butylvinyl- and β,β-dimethylvinyl-ferrocenes obey the Arrhenius equation normally, the activation parameters being quite close to those found for the unsubstituted ferrocene (E_a 12.6 kcal/mol, $\Delta S^{\neq}$ —21 e.u. [35]). The relevant data are listed in Table 3. These results indicate that the role of the pre-equilibrium is probably different in the two reactions.

Experimental

Materials

The alkenes were prepared by the dehydration of the corresponding alcohols, in a modification of the methods reported in the literature [36—38]. A typical experiment is reported below for the preparation of vinylferrocene.

TABLE 4

SECOND ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES AND ACTIVATION PARAMETERS FOR THE MERCURATION OF α-t-BUTYLVINYLFERROCENE AND β,β-DIMETHYLVINYLFERROCENE

T (°C)	k(Fc—C(t-Bu)=CH$_2$) (M^{-1} s^{-1}) [a]	T (°C)	k(Fc—CH=C(CH$_3$)$_2$) (M^{-1} s^{-1}) [b]
24.8	0.24	16.4	0.15
31.5	0.37	20.7	0.20
34.4	0.42	25.0	0.26
40.0	0.58	31.3	0.37
45.3	0.74	36.0	0.46
		40.9	0.62
$E_a = 10.3 \pm 0.5$ kcal/mol $\Delta S^{\ddagger} = -28.8 \pm 1.5$ e.u.		$E_a = 10.3 \pm 0.5$ kcal/mol $\Delta S^{\ddagger} = -28.7 \pm 1.5$ e.u.	

[a] [Fc—C(t-Bu)=CH$_2$] = 1.21×10^{-2} M, [Hg(OAc)$_2$] = 6.40×10^{-4} M. [b] [Fc—CH=C(CH$_3$)$_2$] = 1.58×10^{-2} M, [Hg(OAc)$_2$] = 1.21×10^{-3} M.

Commercially available styrene was used without further purification. The purity of the compounds was checked by VPC with a Fractovap Carlo Erba instrument, equipped with a 1 meter column of 5% methylsilicone SE-30 on Chromosorb W 60—80 with 0.5 ATPET. The structure of the alkenes was confirmed by the PMR spectra, which were recorded on a Jeol C-60 spectrometer, using TMS as an internal standard. All the alkenes decompose slowly in bulk and more rapidly in solution, yielding a residue insoluble in organic solvents.

Vinylferrocene. An intimate mixture of 1-ferrocenylethanol [36] (2.3 g, 0.01 mol) with 50 g of alumina (neutral, Brockman II-III) was heated in a round-bottomed flask until water drops appeared in the reflux condenser (ca. 20—30 min). After cooling, the mixture was transferred to an alumina column and eluted with 40—70°C petroleum ether. The first, yellow band was collected and evaporated. Vinylferrocene was obtained in 76% yield (1.6 g, 0.075 mol); m.p. 50—51°C (lit. 56°C [36]).

α-Methylvinylferrocene. 2-Ferrocenyl-2-propanol was first prepared by adding 0.025 mol of methyllithium in 25 ml of anhydrous diethyl ether dropwise to a stirred solution of acetylferrocene [39] (4.5 g, 0.02 mol) under nitrogen. The mixture was stirred overnight and then added to an ice-cold 10% NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted repeatedly with benzene. The organic extracts were combined, washed with water, and dried over Na_2SO_4. The PMR spectrum of the solid obtained after evaporation of the solvent, showed the presence of some unreacted acetylferrocene. The product was used without further purification for the subsequent dehydration. After dehydration and elution on alumina with 40—70°C petroleum ether, the α-methylvinyl derivative was obtained as an orange yellow solid, m.p. 65.0—66.5°C (lit. 77.5—78.5°C [40]).

α-t-Butylvinylferrocene. Pivaloylferrocene was prepared in a 60% yield by Friedel—Crafts acylation of ferrocene with pivaloyl chloride and aluminum chloride in CH_2Cl_2 [41]. 2-Ferrocenyl-3,3-dimethyl-2-butanol was obtained in a 100% yield by treating 2.7 g (0.01 mol) of pivaloylferrocene with the equivalent amount of methyllithium in anhydrous diethyl ether, and α-t-butylvinylferrocene was prepared by dehydration of this alcohol.

β-Methylvinylferrocene. Propionylferrocene was obtained as a red solid (m.p. 30—31°C) in 83% yield by Friedel—Crafts acylation of ferrocene with propionyl chloride and aluminum chloride in CH_2Cl_2 [41]. 1-Ferrocenyl-1-propanol was obtained as an orange red oil in 88% yield by reducing propionylferrocene with lithium aluminum hydride in anhydrous diethyl ether. β-Methylvinylferrocene was prepared in the usual manner from 1-ferrocenyl-1-propanol and purified by distillation under vacuum (b.p. 83—85°C/0.45 mmHg); yield 50%; m.p. 34.5—35.5°C. A comparison of the PMR spectrum and melting point value with the literature data [3] indicates that β-methylvinylferrocene is essentially in the *trans* configuration (more than 90% based on GLC).

β,β-Dimethylvinylferrocene. Isobutyrylferrocene was synthesized by a Friedel—Crafts acylation of ferrocene with isobutyryl chloride and aluminum chloride in dichloromethane [41]. 1-Ferrocenyl-2-methyl-1-propanol was prepared in 90% yield by reduction of isobutyrylferrocene with $LiAlH_4$ in anhydrous diethyl ether. β,β-Dimethylvinylferrocene was obtained as a red oil in 100% yield by dehydrating 1-ferrocenyl-2-methyl-1-propanol in the usual manner.

Spectral characterization

The electronic spectra were recorded with a Beckman DB-GT spectrophotometer using silica cells, with methanol as solvent. All the alkenes show a maximum absorption around 275 nm, attributed to the double bond and a maximum around 450 nm, due to the transition of the non-bonding electrons of iron atom [42]. The wavelengths (nm) of the maxima are as follows (absorptivities given in parentheses): Fc—CH=CH$_2$: 276 (6900), 445 (260); Fc—C(CH$_3$)=CH$_2$: 274 (6400), 443 (200); Fc—C(t-Bu)=CH$_2$: 274 (3500), 448 (225); Fc—CH=CHCH$_3$: 275 (7800), 447 (220); Fc—CH=C(CH$_3$)$_2$: 276 (7400), 448 (215).

Infrared spectra were recorded with a Perkin-Elmer 257 spectrophotometer using NaCl cells and CCl$_4$ as a solvent, The bands at 1100 and 1005 cm^{-1} appear in all the spectra, following the "9—10 μ" rule [42] for a non-substituted cyclopentadienyl ring. Other main signals are the double bond C=C stretching (in the range 1635—1725 cm^{-1}) and the C—C stretching of the cyclopentadienyl ring (at 3100 cm^{-1}). The band of methyl C—H stretching appears at ca. 2900 cm^{-1} in the spectra of the alkyl-substituted vinylferrocenes.

PMR spectra were recorded on a Jeol C60-HL, spectrometer, with CCl$_4$ or CDCl$_3$ as solvent and TMS as an internal standard. The spectra obtained are in agreement with those reported for the known alkenes [3,6,43]. The PMR spectrum of α-t-butylvinylferrocene shows two doublets at δ 5.13 and 5.48 ppm (2 H, J 2 Hz) due to the vinyl protons, two complex signals centered at δ 4.10 and 4.20 ppm (4 H), due to the substituted ring protons, a singlet at δ 4.05 ppm (5 H), due to the unsubstituted ring, and a singlet at δ 1.02 ppm (9 H), due to the t-butyl group.

Product analysis

This was carried out by treating the alkenylferrocenes and styrene with mercuric acetate in methanol and isolating and identifying the reaction products. Since organomercurials of the type RHgX where R = alkyl are known to undergo reduction to RH when treated with NaBH$_4$ in basic aqueous solution [44], the analysis of the products of addition were confirmed by reductive cleavage of C—Hg bonds. Under these conditions the substitution products remain unaffected.

All the mercurated compounds decompose quite rapidly even in the solid state, yielding a residue insoluble in organic solvents. Sometimes decomposition occurred in the NMR tube, causing broadening of the spectrum. The ethers resulting from the reductive cleavage of the addition products also decompose slowly.

Vinylferrocene. Hg(OAc)$_2$ (0.6 g, 1.9 × 10^{-3} mol) in 75 ml of methanol added dropwise to a stirred solution of vinylferrocene (0.8 g, 3.8 × 10^{-3} mol) at 25°C. After a further 10 min stirring, the mixture was poured in water and extracted with CH$_2$Cl$_2$ repeatedly. The organic layer was washed with water, dried and evaporated to yield a product from which the excess of vinylferrocene was removed by washing with several portions of 30—50°C petroleum ether. The PMR of the viscous brown compound is consistent with an addition product (disappearance of the vinyl protons and appearance of signals due to the OCH$_3$ and HgOCOCH$_3$ protons, at δ 3.25 and 1.92 ppm, respectively).

The reaction was repeated under the same conditions but with a different work-up. 55 ml of 1 *N* NaOH were added to the reaction mixture and $NaBH_4$ (0.58 g, 1.0×10^{-2} mol) in 20 ml of 2.5 *M* NaOH was added dropwise to the stirred suspension, causing an immediate precipitation of a grey powder. After 5 min additional stirring the mixture was poured into CCl_4 and water was added. The organic layer was separated and the aqueous phase was extracted with several portions of CCl_4. The combined organic layers were washed with water, dried over anhydrous sodium sulfate and evaporated. The residue was chromatographed on a silica gel column. The first band was eluted with 30—50°C petroleum ether (unreacted vinylferrocene), while a second fraction was eluted with benzene. VPC analysis indicated the presence of a single compound, the PMR spectrum of which is in agreement with the structure Fc—CH-$(OCH_3)CH_3$ (δ 4.05 ppm, 10 H, singlet with broadened base due to the superposition of ferrocenyl protons and CH signals; δ 3.15 ppm, 3 H, singlet, due to the OCH_3 protons and δ 1.43 ppm, 3 H, doublet, *J* 6 Hz, due to the CH_3 protons).

To confirm this structure, α-methoxyethylferrocene was prepared independently by stirring 1.14 g (5.0×10^{-3} mol) of vinylferrocene in 10 ml of diethyl ether with 2 ml of 1.07×10^{-1} *N* HCl in methanol. After 15 min, TLC examination revealed the disappearance of the spot corresponding to 1-ferrocenylethanol and the appearance of a new spot with higher RF. After additional stirring for ten minutes, the solution was added to water and extracted with some portions of diethyl ether. The organic layer was washed with water, dried and evaporated, yielding an orange red oil (1.0 g, yield 82%) giving PMR spectrum and VPC analysis identical to those for the product obtained by reaction of 1-ferrocenyl-1-methoxy-2-acetoxymercuriethane.

α-Methylvinylferrocene. 1.0 g (3.0×10^{-3} mol) of mercuric acetate in 50 ml of methanol were added dropwise to a stirred solution of α-methylvinylferrocene (800 mg, 3.5×10^{-3} mol) in 50 ml of methanol at 25°C. After stirring for half an hour and evaporation of the solvent, the residue was chromatographed on an alumina column. The unreacted ferrocene was collected by elution with 40—70°C petroleum ether, and the product which was absorbed on the alumina was extracted with methanol in a Soxhlet apparatus. The PMR spectrum in $CDCl_3$ of the brown solid obtained after evaporation of the solvent was consistent with an addition product, since the vinyl protons signals had disappeared.

The reaction was repeated under the same conditions but 55 ml of 1 *M* aqueous NaOH was added to the mixture at the end of the reaction. Aqueous NaOH (40 ml, 2.5 *M*) containing, 0.76 g (2.0×10^{-3} mol) of $NaBH_4$ were added to the stirred suspension, causing the reductive cleavage of the C—Hg bond. After stirring a few minutes, the solution was poured into water and extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, and evaporated. GLC indicated that the resulting red oil was a single compound and the PMR spectrum in CCl_4 was consistent with a structure of the type Fc—$C(CH_3)_2OCH_3$ (δ 4.00 ppm, 9 H, a singlet with a broadened base, due to the superposition of the substituted and unsubstituted ring protons; δ 2.85 ppm, 3 H, singlet due to the OCH_3 protons, and δ 1.47 ppm, 6 H, singlet, due to the CH_3 protons).

α-t-Butylvinylferrocene. $Hg(OAc)_2$ (340 mg, 1.1×10^{-3} mol) in 50 ml of methanol was added dropwise to a stirred solution of α-t-butylvinylferrocene (410 mg, 1.5×10^{-3} mol) in 50 ml of methanol at 25°C. The solution was stirred for two hours, the solvent was evaporated, and the crude residue was eluted on an alumina column with 40—70°C petroleum ether, yielding the unreacted alkene. The mercurated product was obtained by a Soxhlet extraction of the column alumina with methanol, followed by evaporation of the solvent. A brown tarry compound was isolated, the PMR spectrum of which in $CDCl_3$ showed signals due to the vinyl protons (the two doublets at δ 5.13 and 5.48 ppm of the alkene resulted shifted to δ 5.00 and 5.35 ppm, respectively), and the sharp peak due to the unsubstituted cyclopentadienyl ring protons was absent. This is consistent with substitution in the unsubstituted ring of the alkenylferrocene.

β,β-Dimethylvinylferrocene. $Hg(OAc)_2$ (680 mg, 2.1×10^{-3} mol) in 50 ml of methanol was added dropwise to a stirred solution of β,β-dimethylvinylferrocene (510 mg, 2.1×10^{-3} mol) in 50 ml of methanol at 25°C. The solution was stirred 2 h, then the solvent was evaporated, and the crude product was dissolved in the minimum amount of chloroform and precipitated with hexane, in which the unreacted substrate is soluble. The brown solid was filtered off, washed with hexane and dried, and gave a PMR spectrum consistent with a product of substitution on the unsubstituted cyclopentadienyl ring; the sharp signal due to the unsubstituted ring protons had disappeared, but the vinyl proton signal was present at δ 5.80 ppm.

β-Methylvinylferrocene. 2.5 g of mercuric acetate (7.8×10^{-3} mol) in 75 ml of methanol were added dropwise to a stirred solution of β-methylvinylferrocene (1.0 g, 4.4×10^{-3} mol) in 75 ml of methanol at 25°C. The solution was stirred for 24 h and then evaporated. The crude brown residue was eluted from a silica gel column. The first, yellow, band eluted with 40—70°C petroleum ether, gave the unreacted alkenylferrocene. A second red band was developed with chloroform, yielding 50 mg of a product, the PMR spectrum of which in $CDCl_3$ was in agreement with an addition product (a singlet at δ 4.27 ppm, 7 H, broadened at the base, due to the superposition of the unsubstituted ring protons and the two CH protons; two complex signals centered at δ 4.78 and 4.58 ppm, 4 H, due to the substituted ring protons; a singlet at δ 2.09 ppm, 3 H, due to the OCH_3 protons; a doublet at δ 1.77 ppm, 3 H, J 7 Hz, due to the CH_3 protons; and a singlet at δ 1.27 ppm, due to the $HgOCOCH_3$ protons). A third brown band was collected by elution with ethanol, and gave 300 mg of the substitution product (PMR spectrum in $CDCl_3$: a complex signal centered at δ 4.20 ppm, 8 H, due to the cyclopentadienyl ring protons; a complex signal centered at δ 6.10 ppm, 2 H, due to the vinyl protons; a doublet at δ 1.75 ppm, 3 H, due to the CH_3 protons, and a singlet at δ 1.25 ppm, 3 H, due to the $HgOCOCH_3$ protons).

Several attempts to carry out reductive cleavage of the C—Hg bond of the addition product with $NaBH_4$ failed, and the only product obtained was β-methylvinylferrocene. Probably the addition product undergoes deoxymercuration under these conditions [9].

The reaction was repeated under pseudo-first order conditions, in order to determine the proportion of substitution and addition products necessary for the determination of the corresponding rate constants, from the overall rate constant measured from kinetic experiments. Mercuric acetate (150 mg, 4.7×10^{-4} mol) in 50 ml of methanol were added to a stirred solution of β-methylvinylferrocene (1.0 g, 4.0×10^{-3} mol) in 40 ml of methanol at 25°C. After being stirred for 2 h the solution was poured into water and extracted with dichloromethane. After washing, drying, and evaporation of the organic solvent, the residue was chromatographed on a silica gel column. β-Methylvinylferrocene (900 mg) were recovered by evaporating the first band, eluted with 40—70°C petroleum ether; 87.7 mg of the addition product were obtained from the second fraction, eluted with diethyl ether/ethanol (1/1), and 45.9 mg of the susbtitution product were isolated by eluting the third band with ethanol/acetic acid (50/1), adding to water and extracting with CH_2Cl_2. The organic layer was washed repeatedly with water to remove the acetic acid (which might cause oxidation of iron during the heating necessary to remove the solvent). The ratio of addition to substitution product was 1.8/1, and the respective percentages of reaction were 64 and 36%. The reaction was repeated some times and gave similar results to within experimental error.

Styrene. $Hg(OAc)_2$ (17.0 g, 0.053 mol) in 100 ml of methanol were added dropwise to a stirred solution of styrene (5.5 g, 0.053 mol) in 50 ml of methanol. After stirring (30 min) the mixture was poured into water and CH_2Cl_2, and worked-up in the usual manner. On removal of CH_2Cl_2, a viscous oil was obtained, which crystallized to yield 16.8 g (80%) of a white solid, m.p. 155—157°C. The PMR spectrum was in agreement with the structure $PhCH(OCH_3)$-$CH_2HgOCOCH_3$, reported in the literature as prepared, but not isolated [45]. Reductive cleavage with $NaBH_4$ yielded a liquid, pure to VPC analysis, the PMR spectrum of which confirms the structure to be 1-phenyl-1-methoxyethane, $PhCH(OCH_3)CH_3$.

Kinetic measurements

The determination of the reaction rates was carried out spectrophotometrically in silica cells with septum in a thermostatted Beckman DB-GT self-recording spectrophotometer, with zero suppression and a twofold or tenfold expansion scale, depending on the overall spectral change.

As to methoxymercuration of vinylferrocene and α-methylvinylferrocene, the rate measurements were made in recording the absorbance decrease of the rate solutions at 276 nm due to the disappearance of the double bond. The reactions were carried out under second order conditions. The possible oxidation of the substrates by mercuric species was avoided by keeping the substrate concentration higher than that of mercuric acetate.

For mercuration of α-t-butylvinyl-, β-methylvinyl-, and β,β-dimethylvinylferrocenes, the rate measurements were made by recording the absorbance increase of the reaction solutions in the 370—380 nm minimum region. The kinetics were carried out under pseudo-first order conditions by keeping the substrate concentration at least 10 times higher than that of mercuric acetate.

The rate constants for the concurrent addition and substitution reactions of β-methylvinylferrocene were calculated by multiplying the overall pseudo-first order rate constant by the fraction of addition and substitution.

The kinetics of styrene methoxymercuration were followed at 250 nm, under pseudo-first order conditions, by keeping the mercuric acetate concentration at least 10 times higher than that of styrene.

The rate constants reported in Table 1 are mean values of several runs carried out with substrate and mercuric acetate concentrations in the following ranges: Fc—CH=CH$_2$: 2.33×10^{-5}—1.07×10^{-4} M, Hg(OAc)$_2$: 1.38×10^{-5}—1.12×10^{-4} M; Fc—C(CH$_3$)=CH$_2$: 4.03×10^{-5}—1.10×10^{-4} M, Hg(OAc)$_2$: 2.40×10^{-5}—7.39×10^{-5} M; Fc—C(t-Bu)=CH$_2$: 3.06×10^{-3}—1.57×10^{-2} M, Hg(OAc)$_2$: 1.98×10^{-4}—1.26×10^{-3} M; Fc—CH=CHCH$_3$: 2.23×10^{-3}—1.56×10^{-2} M, Hg(OAc)$_2$: 1.76×10^{-4}—1.26×10^{-3} M; Fc—CH=C(CH$_3$)$_2$: 1.26×10^{-3}—2.09×10^{-2} M, Hg(OAc)$_2$: 1.26×10^{-4}—1.26×10^{-3} M; PhCH=CH$_2$: 4.76×10^{-5}—1.48×10^{-4} M, Hg(OAc)$_2$: 8.35×10^{-4}—2.78×10^{-3} M.

The measurements at various temperatures were duplicated.

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