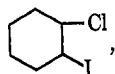


copper(II) chloride and the indicated quantity of iodine donor. The reaction mixture was worked up in the usual manner. The results are summarized in Table II.

TABLE II

Diluent	Iodine donor ^a	Temp, °C	Time, hr	yield, %
C ₆ H ₁₂	I ₂	60	0.3	88
C ₆ H ₆	I ₂	80	0.1	91
CCl ₄	I ₂	80	0.1	90
C ₆ H ₁₀ ^b	CuI	80	1	83
C ₆ H ₁₀	KI	80	2	0
C ₆ H ₁₀	LiI	80	4	92
C ₆ H ₁₀	BiI ₃ ^c	80	2	93
CCl ₄	CuI	80	2	0
C ₇ H ₁₆	CuI	98	2	66

^a 0.1 mol. ^b 100 ml of cyclohexene as diluent. ^c 0.02 mol.



Reaction of Conjugated Olefins. Butadiene.—A Parr reactor was charged with 100 ml of benzene, 26.6 g (0.2 mol) of copper(II) chloride, 25.4 g (0.1 mol) of iodine, and 0.2 mol of butadiene. The reaction was stirred at 70° for 2 hr. The reaction mixture was filtered to give 37 g of copper(I) iodide. The benzene was removed from the filtrate on a rotary evaporator, and the residue was distilled to give 19.4 g (78%) of isomeric dichlorobutenes, bp 48–53° (14 mm). Vpc analysis (5 ft × 0.25 in. 20% diethylene glycol succinate column, 125°, 48 ml/min) gave the following isomer distribution: 3,4-dichlorobutene-1, 16% (*r_t* 3.7 min); *cis*-1,4-dichlorobutene-2, 3% (*r_t* 10.0 min); *trans*-1,4-dichlorobutene-2, 81% (*r_t* 12.0 min). The products were identified by comparison with authentic samples.

If 0.1 mol of copper(I) iodide was used as the iodine source, a 23% yield of dichlorobutenes was realized after 3 hr at 70°. When carbon tetrachloride was used as a reaction diluent, no reaction occurred with copper(I) iodide. This diluent in combination with molecular iodine gave a 90% yield of dichlorobutenes in 90 min.

In a control experiment 1 g (4.6 mmol) of 1-chloro-4-iodobutene-2^{3c} and 1 g (10.2 mmol) of copper(I) chloride were stirred at 70° for 90 min in 10 ml of benzene. The benzene solution was analyzed by vpc and was shown to contain the three isomeric dichlorobutenes; the isomer distribution was comparable with that described above.

Styrene.—To a mixture of 13 g (0.05 mol) of iodine, 13.3 g (0.1 mol) of copper(II) chloride, and 60 ml of *n*-octane at reflux was added dropwise a solution of 10.4 g (0.1 mol) of styrene in 40 ml of *n*-octane. The addition required ~40 min.; the reaction was maintained at reflux for an additional 10 min. The reaction mixture was cooled and filtered to give 17.6 g of copper(I) iodide (theory, 19.0 g). The filtrate was washed with 20% sodium thiosulfate solution and was dried over magnesium sulfate. The *n*-octane was removed on a rotary evaporator [60° (15 min)] to give 17.4 g of crude product. Distillation gave 13.8 g (79%) of 1,2-dichloro-1-phenylethane: bp 67–73° (0.2 mm); nmr (neat) δ 7.2 (s, 5, C₆H₅), 4.85 (t, 1, >CHCl), 3.75 (d, 2, -CH₂Cl). Vpc analysis [2 m × 0.25 in. 20% silicone (DC-200) column, 150°, 105 ml/min] showed a single peak, *r_t* 16.0 min; a small amount of styrene, *r_t* 2.6 min, was present as an impurity (~3–5%). *Anal.* Calcd for C₈H₈Cl₂: C, 54.89; H, 4.60; Cl, 40.51. Found: C, 54.92; H, 4.47; Cl, 39.67.

A sample of the dichlorophenylethane was dehydrochlorinated with methanolic sodium hydroxide to give *α*-chlorostyrene: bp 74–77° (14 mm); *n_D²⁰* 1.5561 (lit.²¹ *n_D²⁰* 1.5590); nmr (neat) δ 7.1–7.5 (m, 5, C₆H₅), 5.43 (q, 2, =CH₂).

The reaction of styrene was repeated at room temperature for a period of 20 hr. The reaction produced 4.5 g (26%) of dichlorophenylethane and 8.6 g (0.083 mol) of polystyrene. The inorganic by-product was a mixture of unreacted copper(II) chloride (6.0 g) and copper(I) iodide (11.8 g); unreacted iodine (0.02 mol) was determined by titration with thiosulfate.

Registry No.—Copper(II) chloride, 7447-39-4; 1-chloro-2-iodoethane, 624-70-4; 1-iodo-2-chloropropane, 29568-69-2; 1-chloro-2-iodopropane, 29568-70-5; 1-chloro-2-iodocyclohexane, 29641-86-9; 1-chloro-2-iodoethylacetate, 29568-71-6; 1,2-dichloro-1-phenylethane, 1074-11-9.

Paramagnetic Metallocenes. Oxidation of Ferrocenyl Ketones¹

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Ferrocenyl ketones which have an *α*-methylene group were oxidized to the stable paramagnetic semidiones. An excess of oxygen resulted in ortho oxygenation of the metallocene ring. The esr spectra indicated a remarkably small amount of electron spin delocalization into the metallocene ring. The simplicity of the esr spectra permitted the elucidation of the relative rates of semidione formation as a function of substituent on metal ion. Interannular substituent effects on electron distribution were shown to be primarily inductive in nature. Hydrogen-deuterium exchange of alkyl hydrogens *α* to the semidione when the oxidation was conducted in DMSO-*d*₆ was very slow; this observation was interpreted in terms of a dianion in the exchange reaction.

Ketones with an *α*-methylene group can be oxidized with molecular oxygen to the corresponding semidiones in dimethyl sulfoxide (DMSO) solution containing an excess of potassium *tert*-butoxide. The reaction is quite general and many semidiones prepared by this technique have been observed by esr spectroscopy.² Since our initial report on the conveniently prepared and stable semidione derivatives of metallocenes,³ other stable metallocene radicals have been observed

by esr.^{4–7} These species are of interest from a viewpoint of electron spin delocalization, metal ligand interaction, and chemical reactivity. Despite the application of metallocenes as antioxidants, combustion control additives, photoprotecting uv absorbers, and medicinals (areas which clearly involve radical chemistry), the chemical and physical properties of stable metallocene radicals have been almost uninvestigated⁸ until very recently. Most of the previous studies concerning radi-

(1) Supported by the Petroleum Research Fund administered by the American Chemical Society (Grant 1375-G1).

(2) G. A. Russell, *et al.*, *Rec. Chem. Progr.*, **27**, 3 (1969); and E. I. Kaiser and L. Kevan, Ed., "Radical Ions," Wiley, New York, N. Y., 1969, Chapter 8.

(3) J. J. McDonnell, *Tetrahedron Lett.*, 2039 (1969).

(4) J. J. McDonnell, G. Capen, and R. Michealson, *ibid.*, 4251 (1969).

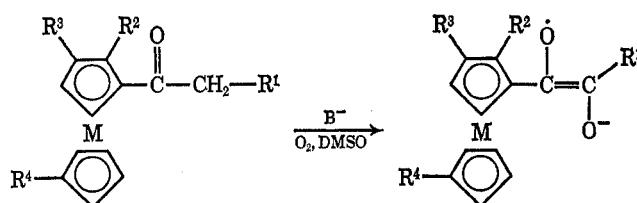
(5) A. R. Forrester, S. P. Hepburn, R. S. Dunlop, and H. H. Mills, *Chem. Commun.*, 698 (1969).

(6) C. Elschenbroich and M. Cais, *J. Organometal. Chem.*, **18**, 135 (1969).

(7) W. C. Danen and C. T. West, *Tetrahedron Lett.*, 219 (1970).

(8) V. M. Kazakava and Y. K. Syrkin, *Zh. Strukt. Khim.*, **3**, 536 (1962).

TABLE I
HYPERFINE SPLITTING CONSTANTS OF RADICALS OBSERVED ON INITIAL OXIDATION



X	M	R ¹	R ²	R ³	R ⁴	X _a	a ^H , gauss	g
1	Ru	CH ₃	H	H	H	1a	4.25 (3 H), 0.54 (2 H)	2.00642
2	Fe	CH ₃	H	H	H	2a	4.20 (3 H), 0.50 (2 H)	2.00706
2'	Fe	CH ₃	2,5-Dideuteriopropionylferrocene			2'a	4.20 (3 H), D not observed	2.00706
2''	Fe	CH ₃	Propionylferrocene-d ₃			2''a	4.20 (3 H), D not observed	2.00706
3	Fe	CH ₂ CH ₃	H	H	H	3a	3.80 (2 H), 0.50 (2 H)	2.00703
4	Fe	CH(CH ₃) ₂	H	H	H	4a	1.75 (1 H), 0.50 (2 H)	2.00699
5	Fe	CH ₂ CH(CH ₃) ₂	H	H	H	5a	3.40 (2 H), 0.50 (2 H)	2.00696
6	Fe	C ₆ H ₅	H	H	H	6a	1.70 (3 H), 0.50 (4 H)	2.00666
7a	Fe	CH ₃	COCH ₃	H	H	7a ^a	4.38 (3 H)	2.01604
							3.47 (4 H), 0.43 (2 H)	2.00790
8	Fe	CH ₃	CH ₂ CH ₂ CH ₂ CH ₃	H	CH ₂ CH ₂ CH ₂ CH ₃	8a	4.35 (3 H), 0.42 (3 H)	2.00714
9	Fe	CH ₃	CH ₃	H	CH ₃	9a	4.30 (3 H), 0.45 (4 H)	2.00717
10	Fe	CH ₃	<i>p</i> -C ₆ H ₄ Cl	H	H	10a	4.17 (3 H), 0.50 (1 H)	2.00694
11	Fe	CH ₃	H	CH ₂ CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₂ CH ₃	11a	4.25 (3 H), 0.50 (2 H)	2.00737
12	Fe	CH ₃	H	CH ₃	CH ₃	12a	4.25 (3 H), 0.50 (2 H)	2.00742
13	Fe	CH ₃	H	<i>p</i> -C ₆ H ₄ Cl	H	13a	4.20 (3 H), 0.50 (2 H)	2.00680
14	Fe	CH ₃	H	H	C(CH ₃) ₃	14a	4.20 (3 H), 0.50 (2 H)	2.00706
15	Fe	CH ₃	H	H	<i>p</i> -C ₆ H ₄ Cl	15a	4.00 (3 H), 0.52 (2 H)	2.00749
16	Fe	CH ₃	H	H	Br	16a	3.95 (3 H), 0.55 (2 H)	2.00700
17	Fe	CH ₃	H	H	Adamantyl ketone	17a	3.85 (3 H), 0.52 (2 H)	2.00728
18	Fe	CH ₃	H	H	COC(CH ₃) ₃	18a	3.83 (3 H), 0.52 (2 H)	2.00728
19	Fe	CH ₃	H	H	COCH ₂ CH(CH ₃) ₂	19a	3.82 (3 H), 0.55 (2 H)	2.00728
							1.55 (1 H), 0.55 (2 H)	2.00729
20	Fe	CH ₃	H	H	COOCH ₃	20a	3.82 (3 H), 0.55 (2 H)	2.00728
21	Fe	CH ₃	H	H	COCH ₂ CH ₂ CH ₃	21a	3.80 (3 H), 0.55 (2 H)	2.00728
							3.55 (2 H), 0.55 (2 H)	2.00729
22	Fe	CH ₃	H	H	COCH ₃	22a	3.80 (3 H), 0.55 (2 H)	2.00728
23	Fe	CH ₃	H	H	<i>p</i> -COC ₆ H ₄ CH ₃	23a	3.72 (3 H), 0.55 (2 H)	2.00739
24	Fe	CH ₃	H	H	CN	24a	3.72 (3 H), 0.55 (2 H)	2.00709

^a 7 gives anomalous esr signals believed to arise from intramolecular condensation to form the *p*-benzoquinone type radical anions.

cal chemistry of metallocenes have been in the area of synthetic intermediates and one-electron oxidation of Fe²⁺ to Fe³⁺.⁹ In this paper some aspects of metallocene chemistry are discussed in terms of the stable paramagnetic semidione intermediate.

Results and Discussion

Ketones 1–24 (Table I) are oxidized initially to semidiones under conditions described in the Experimental Section. The experimental data shown in Table I provide an unambiguous assignment of the hyperfine splitting constants to the individual hydrogen atoms.

The quartet splitting of 4.20 G for entry 2 in Table I is assigned to the methyl hydrogens α to the semidione. As CH₃ is replaced by CH₂CH₃ and CH(CH₃)₂, the quartet splitting is respectively replaced by a triplet splitting from 2 H of 3.80 G and a doublet splitting from 1 H of 1.75 G.¹⁰ When the ortho metallocene hydrogens are replaced with deuterium, the two 0.5-G hydrogen hyperfine splittings (Figure 1A) are replaced with deuterium hyperfine splittings of 0.50/6.5 G

which are observed only as line broadening (Figure 1B). The replacement of an ortho hydrogen by CH₃ (entry 9 of Table I) results in the appearance of a hyperfine splitting pattern which requires the interaction of 4 H, $a^H = 0.45$ G, indicating that the CH₃ hyperfine splittings are the same as the hydrogen they replace. This is taken as evidence for a π delocalization mechanism into the metallocene ring in which a spin polarization mechanism places the same amount of spin density on the ortho hydrogen as a hyperconjugative mechanism places on each of the ortho methyl hydrogens.¹¹

Protons in the interannular ring do not interact with unpaired spin. Yet, polar substituent effects are conducted through the metallocene ring with facility. In fact, the methyl hyperfine splitting constants of ferrocenyl methyl semidiones (Figure 2A) are as sensitive to 1' substituents as phenyl methyl semidiones (Figure 2B) are to meta substituents; the ρ value for the plot of meta CH₃, Br, H, and CN values *vs.* $a_H^{CH_3}$ for both radical series are identical. These results indicate that the interannular substituent effects are primarily inductive in nature and that inductive effects are rather efficiently transferred between metallocene rings. Fig-

(9) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Wiley, New York, N. Y., 1965.

(10) The decrease in the magnitude of the 2-hydrogen splitting constants is a result of a time-averaged decrease in the C–H bond–semidione π system angle.

(11) For a discussion of spin delocalization mechanisms, see P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen and Co., London, 1967, p 74.

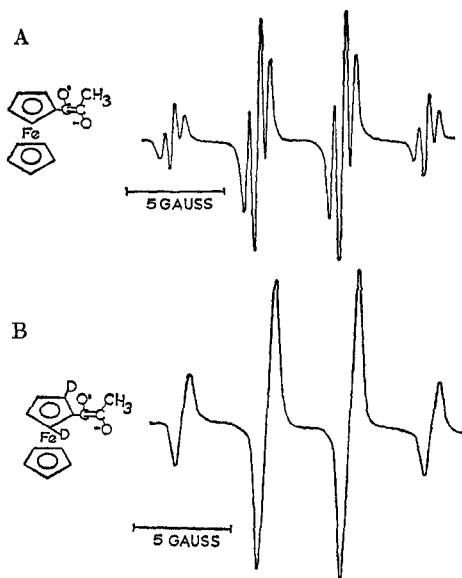


Figure 1.—Esr spectrum resulting from the oxidation of ketones 2 (A) and 2' (B) in Table I.

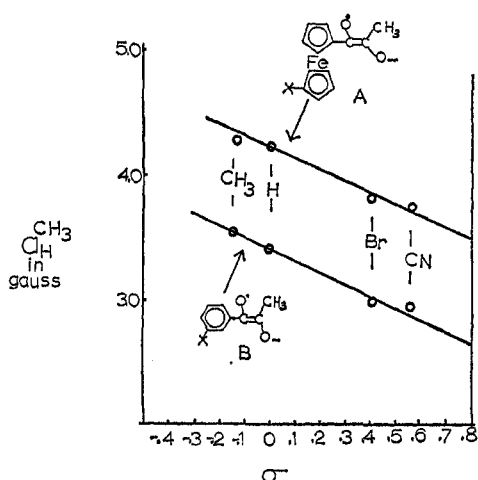


Figure 2.—A: Plot of methyl hyperfine splitting constants of methyl 1'-substituted ferrocenyl semidione vs. σ_m value of the interannular substituent. B: The corresponding plot for meta-substituted phenyl methyl semidiones. The latter data taken from a study by E. T. Strom, *J. Amer. Chem. Soc.*, **88**, 2065 (1966).

ure 3 illustrates excellent correlation between the relative rates of solvolysis of 1'-substituted methyl ferrocenyl carbinyl acetates¹² and the hyperfine splitting constants of methyl 1'-substituted ferrocenyl semidiones. The least-squares analysis shows a correlation coefficient of 0.9906 and standard deviation of 0.19. Statistical analysis of the solvolysis data by Hall, Hill, and Richards¹³ showed the best agreement when the rate data was plotted against inductive parameters σ_p^0 and σ_m^0 and they proposed an inductive mechanism in which resonance effects are not effectively transmitted by ring-metal bonds.¹⁴

The ferrocene and ruthenocene nuclei are remarkably ineffective in delocalizing unpaired spin. The cyman-

(12) D. W. Hall, E. A. Hill, and J. H. Richards, *J. Amer. Chem. Soc.*, **90**, 4972 (1968).

(13) The authors of ref 12 define an arbitrary parameter $(\sigma_m + 2\sigma_p)/2$ which fits better than σ_m^0 or σ_p^0 . This parameter is not considered in the present work.

(14) Uv absorption data show very little interannular interaction. See ref 9, p 214.

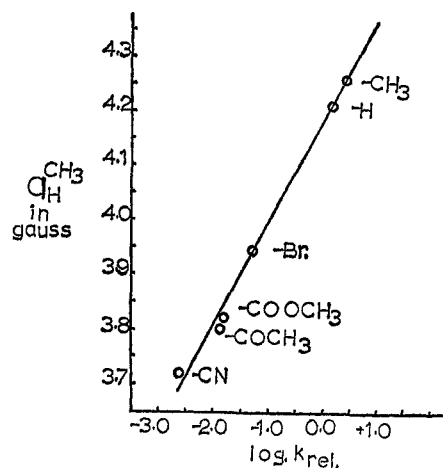


Figure 3.—Methyl hyperfine splitting constants of methyl 1'-substituted ferrocenyl semidiones vs. the relative rates of solvolysis of 1'-substituted methyl ferrocenyl carbinyl acetates.

trene¹⁵ nucleus is somewhat more efficient in delocalizing electron spin and this behavior most likely reflects in the differences in the electron availability of the cyclopentadienyl anion ligands. For example, ferrocene > ruthenocene > cymantrene > benzene is the order of electrophilic attack; these nuclei have the opposite tendency to delocalize an odd electron. Electron availability facilitates electrophilic attack and appears to inhibit electron spin delocalization.

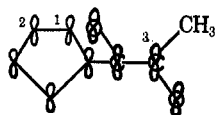
These semidiones have somewhat high g values. An interesting observation is that $g^1 < g^2$, an order opposite to that of the spin-orbit, LS, coupling constants for the metal ions involved (ζ Ru²⁺ = 1140 cm⁻¹, Fe²⁺ = 410 cm⁻¹). These results imply very little free electron density at the metal atom itself and this conclusion is supported by the absence of metal hyperfine splitting (Fe⁵⁷, spin = $1/2$, 2.245% natural abundance, Ru⁹⁹, spin = $5/2$, 12.81% natural abundance, or Ru¹⁰¹, spin = $5/2$, 16.98% natural abundance). The metal apparently plays a more subtle role in its effect on the g value, perhaps by altering molecular orbital energy levels through $E1g$ (ring $E1g$ -metal $d_{xy, yz}$) or $E2g$ (ring $E2g$ - d_{xy, z^2-y^2}) ring-metal interaction so that the odd electron of ferrocene is in a higher energy orbital.¹⁶ This difference in g value between entries 1 and 2 of Table I, as well as the interannular substituent effect on g values and hyperfine splitting constants, is clear evidence that the metallocene moiety remains intact during the oxidation procedure.

Spin density calculations of the Hückel-McLachlan type on π system I are in reasonable agreement with experimental values. In these calculations the effect of the metal ion is accommodated by altering the columbic integral of the cyclopentadienyl ring carbons to $\alpha = \alpha + hB$ where $h = -0.3$. This procedure makes the carbon atomic orbitals less electronegative and has the net effect of preventing spin delocalization into the cyclopentadienyl ring. The experimental values for the spin density, ρ , in position 1 and w were obtained by using the equation $a^H = Q\rho$. A Q value of 30 was chosen from the sum of the hydrogen hyperfine splitting constants of the cyclopentadiene radical. The experi-

(15) The ring protons of cymantrene (cyclopentadienylmanganese tricarbonyl) semidione have hyperfine splittings of 2.1 G ortho and 0.6 G meta; unpublished data from present authors.

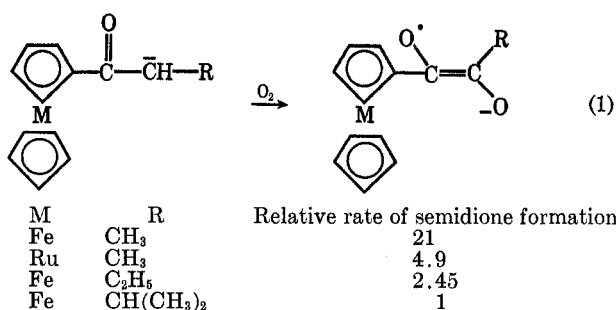
(16) A. F. Stone, *Mol. Phys.*, **6**, 509 (1963).

mental spin density at 3 was calculated from the methyl hyperfine splitting constant $a_{\text{H}}^{\text{CH}_3} = Q_{\text{C}-\text{CH}_3}\rho$ (carbon 3), where $Q_{\text{C}-\text{CH}_3}$ equals 23. A more complete treatment of spin density calculations involving the cyclopentadienyl ring will appear elsewhere. It is also interesting to point out that the odd electron may occupy a ligand orbital which is not significantly involved in the metal ligand bonding.

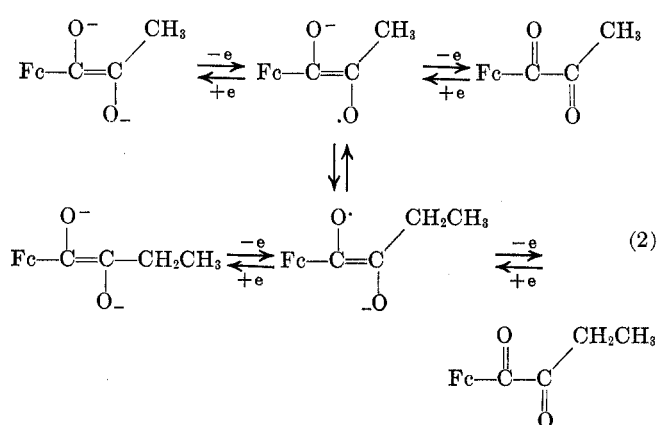


Position	Calcd	Expt
1	0.015	0.0165
2	0.005	0.000
3	0.21	0.18

Oxidation Chemistry.—Steric and electronic factors control the rate of enolate anion oxidation (eq 1).



When equimolar concentrations of propionyl-, R = CH₃, and butyryl-, R = C₂H₅, ferrocene are oxidized competitively, the esr signal shows the relative intensity of the resulting semidiones to be 8.6:1, respectively. When the ketones are oxidized in base independently and then mixed in the absence of oxygen, the relative signal levels are approximately the same as before mixing. For example, the mixed signals with the R = CH₃ semidione are only twice the concentration as the R = Et semidione and this ratio is constant for the lifetime of the signal. These results indicate that equilibrium (eq 2) is not controlling the concentration



Fc = ferrocene

of the radicals and that the intensities of the signals observed represent the kinetic rate of semidione formation. The oxidation rate of propionylruthenocene is one-fourth that of the ferrocene analog. This difference is probably the result of ground-state stabilization of the enolate anion by the more electronegative

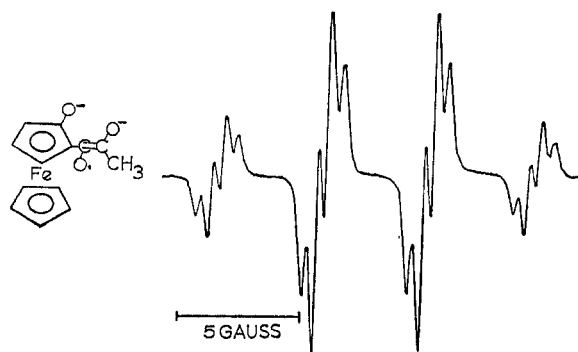


Figure 4.—Esr spectrum resulting from overoxidation of ferrocenyl methyl semidione.

Ru²⁺ ion. These reaction mechanisms are envisioned as the formation of equivalent amounts of each secondary anion in the large excess of very strong base followed by competition for a deficiency of oxygen. The detailed reaction mechanism is obscured by many competing reaction pathways.

The propionyl and butyryl moiety of 1,1'-propinylbutyrylferrocene (II) oxidize to the 1'-substituted semidiones III and IV in a 8.6 to 1 ratio as did the monosubstituted ketones. The former reaction requires a larger amount of potassium *tert*-butoxide and is also facilitated by the stronger base, cesium *tert*-butoxide. This effect of base implicates oxidation of the 1,1' dianion V. The equilibrium VI \rightleftharpoons VII can be envisioned as lying in the direction of VI (Scheme I). In this regard, it is noteworthy that 1,1'-diferochenyl ketones dialkylate¹⁷ without monoalkylation, also implicating the dianion intermediate.

An excess of oxygen results in the disappearance of the original semidione and the appearance of a new paramagnetic species (Figure 4). These new paramagnetic species evidently result from ortho oxygenation of the metallocene ring. The data in Table II as-

TABLE II
HYPERFINE SPLITTING CONSTANTS OF RADICALS
OBSERVED ON OVEROXIDATION

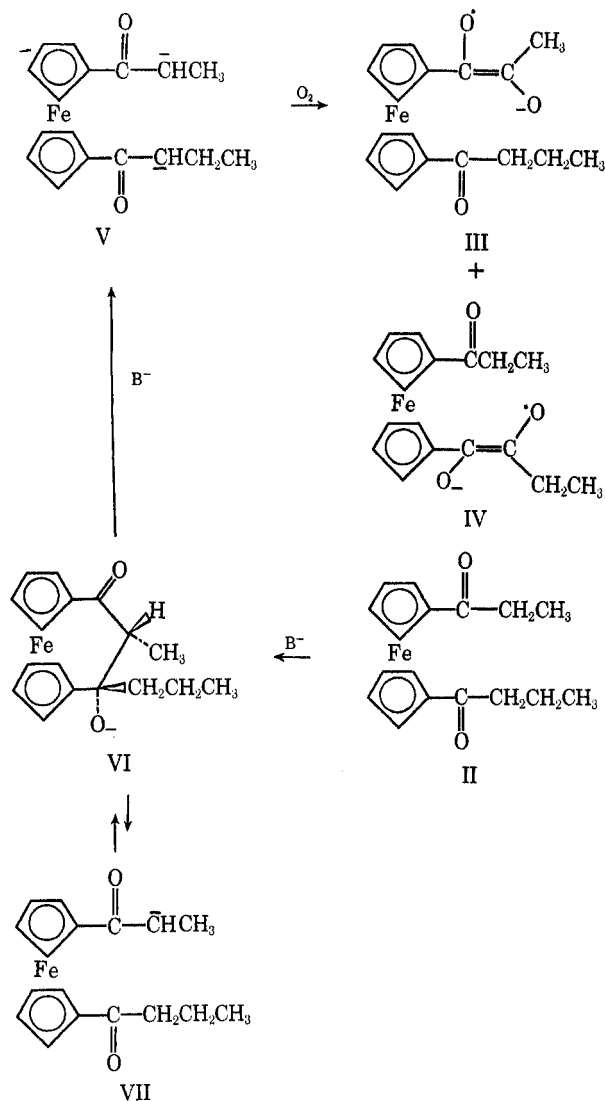
	a_{H} , gauss	a
1a \rightarrow 1b	4.30 (3 H), 0.55 (3 H)	2.00644
2a \rightarrow 2b	4.25 (3 H), 0.5 (3 H)	2.00708
3a \rightarrow 3b	3.70 (2 H), 0.5 (3 H)	2.00708
4a \rightarrow 4b	1.71 (2 H), 0.5 (3 H)	2.00708
2'a \rightarrow 2'b	4.25 (3 H), 0.5 (2 H)	2.00708
2''a \rightarrow 2''b	4.25 (3 H)	2.00708
11a \rightarrow 11b	4.25 (3 H), 0.5 (4 H)	2.00740

sure that substitution is occurring in the ortho position and that the additional hydrogen hyperfine splitting originate in the metallocene ring. Homoannular electrophilic substitution of acetylferrocenes occurs exclusively in the ortho position¹⁸ but the yield in the

(17) C. R. Hanser and T. A. Mashburn, *J. Org. Chem.*, **26**, 1795 (1965).

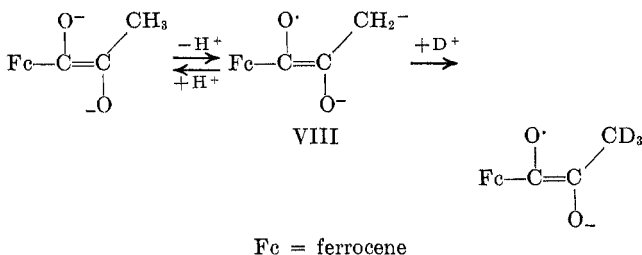
(18) J. H. Richards and T. J. Curphey, *Chem. Ind. (London)*, 1456 (1965).

SCHEME I



reaction is extremely low. The overoxidation is a fairly efficient process and it is therefore reasonable to propose that the oxygen directly attacks what should be a more nucleophilic semidione as opposed to the ketone or α diketone.

Another unusual property of this class of semidione is the remarkably slow rate of hydrogen-deuterium exchange of the alkyl hydrogens α to the semidione when the oxidation is conducted in $\text{DMSO-}d_6$. This slow exchange rate is an indication that exchange is occurring from the dianion intermediate VIII. The powerful



electron-supplying property of the metallocene ring also serves to retard the formation of the dianion. Table III list the times for complete $\text{H} \rightarrow \text{D}$ exchange. In general, the times of exchange are not affected by the

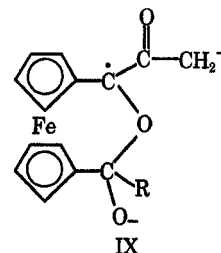
TABLE III

HYDROGEN-DEUTERIUM EXCHANGE

X	Time for complete exchange, min
1. H	40 \pm 5
2. <i>p</i> -C ₆ H ₄ Cl	40 \pm 5
3. COCH ₂ CH ₂ CH ₃	15 \pm 5
4. COC(CH ₃) ₃	15 \pm 5
5. CN	40 \pm 5
6. Adamantyl ketone	15 \pm 5
7. ^a H, CH ₂ CH ₃ \rightarrow CD ₂ CH ₃	10 hr
8. ^a H, CH(CH ₃) ₂ \rightarrow CD(CH ₃) ₂	72 hr

^a Entries 7 and 8 represent the times for complete exchange of the α protons when the methyl group adjacent to the semidione is replaced by ethyl and isopropyl, respectively.

transannular substituent unless the substituent is a ketone, in which case the rate of exchange is substantially increased as in entries of 3, 4, and 6 (Table III). Interannular stabilization of the dianion IX is most



likely responsible for this effect. The protons α to the semidione in entry 7 and 8 of Table III were, as expected, much slower to exchange because the exchange respectively requires the formation of a secondary and a tertiary anion.

Experimental Section

Esr Spectra.—The esr spectra were obtained on a Varian 4502 Model spectrometer with field dial control.

General Procedure for the Preparation of the Semidione.—To 10–15 mg of the ferrocenyl ketone in one side of an H cell was added 0.9 cc of dry DMSO; to a 3–4 molar excess of potassium *tert*-butoxide in the other half of the H cell was added 0.5 cc of dry DMSO. After thoroughly degassing both the solutions with N₂ (5 min), the sealed H cell was inverted and the solutions were thoroughly mixed. Unstopping the H cell for a second allowed sufficient oxygen to enter to form the semidione. The procedure has previously been described.¹⁹

General Procedure for the Mixing of Semidione Solution.—The propionyl and butyryl semidiones were each prepared as described above in individual H cells and their approximate relative radical concentration was determined by instrumental settings. One of the radical-containing solutions was transferred to the other cell by means of a hypodermic syringe in a dry bag filled with nitrogen. The esr spectrum was observed after thorough mixing.

General Procedure for Hydrogen-Deuterium Exchange.—The semidione was prepared in the usual manner except that $\text{DMSO-}d_6$ (99.9%) was used in place of ordinary DMSO. The esr spectra was monitored as a function of time where t_0 was recorded at the addition of oxygen.

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Propionylruthenocene (1).—To 3.0 g (0.023 mol) of anhydrous AlCl_3 in 75 ml of dry CH_2Cl_2 (MgSO_4) was added dropwise, with stirring, under N_2 , 2.32 g (0.010 mol) of ruthenocene and 1.30 g (0.010 mol) of propionic anhydride. After refluxing for 3 hr the solution was hydrolyzed with H_2O and washed with water, and the layers were separated. The combined organic layer and the ether extract of the aqueous layer were dried (MgSO_4), concentrated to an oil, and chromatographed on alumina. Elution with 10% ether in Skelly B produced two bands. The first band (pale yellow) was starting material. The second band (yellow) contained 1.18 g (41%) of 1: mp 70–71°; nmr (CDCl_3) δ 1.14 (t, 3, CH_3), 2.63 (d, 2, CH_2), 4.57 (s, 5, Fe), 4.65 (t, 2, Fe), and 5.11 (t, 2, Fe).

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{ORu}$: C, 54.36; H, 4.88. Found: C, 54.24; H, 4.95.

Propionylferrocene (2).—2 was prepared by the method of Rinehardt²⁰ in 50% yield: mp 37.5–38° (lit.²⁰ 38–39°); nmr (C_6D_6) δ 1.12 (t, 3, CH_3), 2.45 (m, 2, CH_2), 3.90 (s, 5, Fe), and 4.10 (t, 2, Fe).

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{OFe}$: C, 64.46; H, 5.78. Found: C, 64.20; H, 6.59.

2,5-Dideuteriopropionylferrocene (2').—2' was prepared by the method of Rausch²¹ employing ethyllithium instead of methyl-lithium in one step of the reaction: mp 36° (lit.²⁰ 38–39°); nmr (CDCl_3) δ 1.20 (t, 3, CH_3), 2.74 (m, 2, CH_2), 4.17 (s, 5, Fe), and 4.48 (s, 2, Fe); *m/e* 244, 243, and 242 show greater than 96% deuterium incorporation.

Propionylferrocene- d_9 (2'').—Ferrocene- d_{10} (1.0 g, 0.0051 mol), as prepared by the method of Pavlik,²² 0.72 g (0.0065 mol) of AlCl_3 , and 0.60 g (0.0046 mol) of propionic anhydride were reacted for 4 hr in the manner and under the conditions described for 4. Subsequent chromatography on silica gel produced two bands when eluting with Skelly B. The second band (orange) contained 0.5 g (38.5%) of 2'': mp 38° (lit.²⁰ 38–39°); nmr (CDCl_3) δ 1.20 (t, 3, CH_3) and 2.74 (m, 2, CH_2); *m/e* 251 to 242 showed greater than 96% d_9 incorporation.

Butyrylferrocene (3).—3 was prepared by the method of Schlogl²³ in 75% yield: mp 34–35° [lit.²³ bp 144–145° (1.5 mm)]; nmr (CDCl_3) δ 1.00 (t, 3, CH_3), 1.76 (m, 2, CH_2CH_2), 2.68 (t, 2, COCH_2), 4.17 (s, 5, Fe), 4.47 (t, 2, Fe), and 4.77 (t, 2, Fe).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{OFe}$: C, 65.63; H, 6.25. Found: C, 65.58; H, 6.35.

3-Methylbutyrylferrocene (4).— AlCl_3 (7.8 g, 0.0600 mol), 10.0 g (0.0535 mol) of ferrocene, and 5.95 g (0.0536 mol) of 3-methylbutyryl chloride were reacted and worked up according to the method described for 1 except that the reaction mixture was not refluxed. Chromatography on alumina produced two bands when eluting with 10% ether in Skelly B. Of the two bands obtained, the first band (yellow) contained ferrocene. The second band (red) contained 7.86 g (56.2%) of 4: mp 55–56°; nmr (CDCl_3) δ 1.0 (s, 6, CH_3), 2.28 (m, 1, CH), 2.58 (d, 2, CH_2), 4.17 (s, 5, Fe), 4.47 (t, 2, Fe), and 4.77 (t, 2, Fe).

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{OFe}$: C, 66.67; H, 6.67. Found: C, 66.53; H, 6.69.

4-Methylvalerylferrocene (5).— AlCl_3 (7.2 g, 0.0540 mol), 10 g (0.0535 mol) of ferrocene, and 7.2 g (0.0537 mol) of 4-methylvaleryl chloride were reacted and worked up as in the preparation of 4. Chromatography on silica gel produced two bands when eluting with 10% ether in Skelly B. The first band (yellow) contained ferrocene and the second band (red) contained 10.17 g (66.7%) of 5: mp 33–34°; nmr (CDCl_3) δ 0.97 (d, 6, CH_3), 1.55 (t, 2, CH_2), 2.06 (m, 1, CH), 2.69 (t, 2, COCH_2), 4.17 (s, 5, Fe), 4.47 (t, 2, Fe), and 4.77 (t, 2, Fe).

Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{OFe}$: C, 67.61; H, 7.04. Found: C, 67.60; H, 7.18.

Benzylferrocenyl Ketone (6).—6 was prepared according to the method of Dabard²⁴ in 78% yield: mp 129–130° (lit.²⁴ 130°); nmr (CDCl_3) δ 3.98 (s, 2, CH_2), 4.00 (s, 5, Fe), 4.50 (t, 2, Fe), 4.83 (t, 2, Fe), and 7.33 (s, 5, Ph).

Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O Fe}$: C, 71.05; H, 5.26. Found: C, 69.96; H, 5.35.

1-Propionyl-2-acetylferrocene (7) and 1-Propionyl-1-acetyl-

ferrocene (22).—22 was prepared by the method of Furdik²⁵ in 62.8%: mp 58.5–59° (lit.²⁶ 54–55°); nmr (CDCl_3) δ 1.19 (t, 3, CH_2CH_3), 2.35 (s, 3, COCH_3), 2.70 (m, 2, CH_2), 4.49 (t, 4, Fe), and 4.77 (m, 4 Fe). Also obtained by chromatography (on silica gel) was 7 in 5.3% yield when eluting with 25% ether in Skelly B: mp 46°; nmr (CDCl_3) δ 1.17 (t, 3, CH_2CH_3), 2.47 (s, 3, COCH_3), 2.86 (m, 2, CH_2), 4.25 (s, 5, Fe), 4.58 (t, 1, Fe), and 4.88 (d, 2, Fe).

Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Fe}$ (22): C, 63.38; H, 5.63. Found: C, 63.31; H, 5.69.

Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Fe}$ (7): C, 63.38; H, 5.63. Found: C, 63.28; H, 5.71.

1,1'-Di-*n*-butyl-2-propionylferrocene (8) and 1,1'-Di-*n*-butyl-3-propionylferrocene (11).— AlCl_3 (8.0 g, 0.0602 mol), 10 g (0.0334 mol) of 1,1'-di-*n*-butylferrocene, and 5 g (0.0385 mol) of propionic anhydride were reacted for 15 hr according to the preparation of 4. Chromatography on silica gel produced four bands when eluting with Skelly B. The first band (yellow) contained 0.5 g of starting material. The second band (orange) contained 2.0 g (16.8%) of 8: bp 170–172° (0.3 mm); nmr (CDCl_3) δ 1.17 (m, 17, $\text{CH}_2\text{CH}_2\text{CH}_3$, COCH_2CH_3), 2.22 (t, 4, Fe CH_2), 2.73 (m, 2, COCH_2), 3.96 (s, 4, Fe), 4.25 (m, 2, Fe), and 4.54 (m, 1, Fe). The third band contained 7.7 g (64.8%) of 11: bp 177–179° (0.3 mm); nmr (CDCl_3) δ 1.17 (m, 17, $\text{CH}_2\text{CH}_2\text{CH}_3$, COCH_2CH_3), 2.23 (t, 4 H, Fe CH_2), 2.68 (m, 2, COCH_2), 3.95 (s, 4, Fe), 4.28 (m, 1 H, Fe), and 4.58 (m, 2 H, Fe). The fourth band (red) was not characterized.

Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{OFe}$ (8): C, 71.19; H, 8.47. Found: C, 71.15; H, 8.63.

Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{OFe}$ (11): C, 71.19; H, 8.47. Found: C, 71.08; H, 8.62.

1,1'-Dimethyl-2-propionylferrocene (9) and 1,1'-Dimethyl-3-propionylferrocene (12).— AlCl_3 (7.14 g, 0.0536 mol), 7.12 g (0.0331 mol) of 1,1'-dimethylferrocene, and 4.0 g (0.0307 mol) of propionic anhydride were reacted for 15 hr as in the preparation of 4. Chromatography on silica gel, eluting with 10% ether in Skelly B, produced three bands. The second band (orange) contained 1.62 g (18.1%) of 9: bp 138–141° (0.3 mm); nmr (CDCl_3) δ 1.17 (t, 3, CH_2CH_3), 1.87 (s, 3, Fe CH_3), 2.27 (s, 3, Fe CH_3), 2.73 (m, 2, COCH_2), 3.95 (s, 4, Fe), 4.27 (m, 2, Fe), and 4.54 (m, 1, Fe). The third band (red) contained 3.92 g (43.7%): bp 140–144° (0.3 mm); nmr (CDCl_3) δ 1.18 (t, 3, CH_2CH_3), 1.88 (s, 3, Fe CH_3), 2.02 (s, 3, Fe CH_3), 2.70 (m, 2, COCH_2), 3.96 (s, 4, Fe), 4.30 (m, 1, Fe), and 4.60 (m, 2, Fe).

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{OFe}$ (9): C, 66.42; H, 7.01. Found: C, 66.25; H, 7.05.

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{OFe}$ (12): C, 66.42; H, 7.01. Found: C, 66.37; H, 7.09.

1-Propionyl-2-*p*-chlorophenylferrocene (10), 1-Propionyl-3-*p*-chlorophenylferrocene (13), and 1-Propionyl-1'-*p*-chlorophenylferrocene (15).—*p*-Chloroferrocene (4.20 g, 0.0141 mol) as prepared by the method of Weinmayer,²⁶ 2.5 g (0.0187 mol) of AlCl_3 , and 2.0 g (0.0153 mol) of propionic anhydride were reacted for 4.5 hr in the manner and under the conditions described for 4.

After the starting material was separated by chromatography on silica gel when eluting with Skelly B, 15 was separated from the reaction mixture by selective recrystallization: 1.51 g (30.2%); mp 102–103°; nmr (CDCl_3) δ 1.07 (t, 3, CH_3), 2.47 (m, 2, CH_2), 4.33 (t, 4, Fe), 4.62 (m, 4, Fe), and 7.28 (s, 4, Ph). The remaining material was rechromatographed on silica gel eluting with 7% benzene in cyclohexane. Two major bands developed. The first band (orange) contained 0.93 g (18.6%) of 13: mp 113°; nmr (CDCl_3) δ 1.22 (t, 3, CH_3), 2.77 (m, 2, CH_2), 4.04 (s, 5, Fe), 4.90 (d, 2, Fe), 5.23 (m, 1, Fe), and 7.34 (m, 4, Ph). The second band (yellow) contained 0.77 g (15.4%) of 10: mp 103°; nmr (CDCl_3) δ 1.17 (t, 3, CH_3), 2.74 (m, 2, CH_2), 4.20 (s, 5, Fe), 4.60 (m, 2, Fe), 4.84 (m, 1, Fe), and 7.40 (m, 4, Ph).

Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{OClFe}$ (15): C, 64.59; H, 4.81. Found: C, 64.42; H, 4.92.

Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{CClFe}$ (10): C, 64.59; H, 4.81. Found: C, 64.61; H, 4.88.

Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{OClFe}$ (13): C, 64.59; H, 4.81. Found: C, 64.45; H, 4.92.

1-Propionyl-1'-*tert*-butylferrocene (14).—*tert*-Butylferrocene (2.3 g, 0.0093 mol), as prepared by the method of Neuse,²⁷ 1.25

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g (0.0094 mol) of AlCl_3 , and 1.20 g (0.0092 mol) of propionic anhydride were reacted according to the preparation of 4. Chromatography on alumina produced four bands. The second band (orange) contained 0.6 g (22.0%) of 14: nmr (CDCl_3) δ 1.17 (t, 3, CH_2CH_3), 1.22 (s, 9, $\text{C}(\text{CH}_3)_3$), 2.70 (m, 2, CH_2), 4.05 (m, 2, Fc), 4.15 (d, 2, Fc), 4.47 (m, 2, CH_2), 4.05 (m, 2, Fc), 4.15 (d, 2, Fc), 4.47 (m, 2, Fc), and 4.75 (m, 2, Fc).

Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{OFe}$: C, 73.28; H, 7.38. Found: C, 73.20; H, 7.47.

1-Propionyl-1'-bromoferrocene (16).—Bromoferrocene (2.44 g, 0.0067 mol), as prepared by the method of Fish,²⁸ 0.75 g (0.0057 mol) of propionic anhydride, and 0.92 g (0.0069 mol) of AlCl_3 were reacted as in the preparation of 4 but at 0°. Chromatography on silica gel produced two bands when eluting with Skelly B. The first band (yellow) contained 1.45 g of bromoferrocene (59.5%) and the second band (orange) contained 0.61 g (20.9%) of 16: mp 31°; nmr (CDCl_3) δ 1.19 (t, 3, CH_3), 2.78 (m, 2, CH_2), 4.12 (t, 2, Fc), 4.41 (t, 2, Fc), 4.52 (t, 2, Fc), and 4.82 (t, 2, Fc).

Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{OBrFe}$: C, 48.60; H, 5.04. Found: C, 48.52; H, 4.13.

1-Propionyl-1'-carboadamantylferrocene (17).—To 20 g (0.1504 mol) of AlCl_3 in 150 ml of dry CH_2Cl_2 (MgSO_4) was added with stirring, under N_2 , 9 g (0.0481 mol) of ferrocene and 11 g (0.0554 mol) of adamantancarboxyl chloride in 300 ml of dry CH_2Cl_2 . The solution was refluxed for 30 hr. After the usual work-up, the oil was chromatographed on alumina and three bands were obtained. The second band (orange) was brought down with CH_2Cl_2 to yield 7.0 g (38.4%) of adamantylferrocenyl ketone: mp 147–148°; nmr (CDCl_3) δ 1.80 (m, 5, Ad), 4.18 (s, 5, Fc), and 4.90 (t, 2, Fc).

Adamantylferrocenyl ketone (1.7 g, 0.0049 mol), 4.5 g (0.0338 mol) of AlCl_3 , and 3.5 g (0.0269 mol) of propionic anhydride were allowed to react for 4.5 hr in the manner and under the conditions described for 4. Chromatography on alumina produced two bands when eluting with 25% ether in Skelly B. The second band (orange brown) was brought down with ether and contained 1.4 g (71%) of 17: mp 89°; nmr (CDCl_3) δ 1.17 (t, 3, CH_3), 1.75 (m, 5, Ad), 2.00 (s, 10, Ad), 2.60 (m, 2, CH_2), 4.43 (m, 4, Fc), 4.77 (t, 2, Fc), and 4.87 (t, 2, Fc).

Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_2\text{Fe}$: C, 71.29; H, 6.93. Found: C, 71.17; H, 7.02.

1-Propionyl-1'-pivalylferrocene (18).—Pivalylferrocene (1.70 g, 0.0062 mol), as prepared by the method of Stephenson,²⁹ 4.5 g (0.0338 mol) of AlCl_3 , and 3.5 g (0.0269 mol) of propionic anhydride were reacted for 4.5 hr in the manner and under the conditions prescribed for 4. Chromatography on alumina produced two bands when eluting with 10% ether in Skelly B. The second band (red) contained 1.67 g (81.4%) of 18: mp 32°; nmr (CDCl_3) δ 1.20 (t, 3, CH_2CH_3), 1.32 (s, 9, $\text{C}(\text{CH}_3)_3$), 2.75 (m, 2, CH_2), 4.48 (t, 4, Fc), 4.78 (t, 2, Fc), and 4.84 (t, 2, Fc).

Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Fe}$: C, 66.26; H, 6.75. Found: C, 66.19; H, 6.77.

1-Propionyl-1'-3-methylbutylferrocene (19).—4 (3.65 g, 0.0135 mol), 8.1 g (0.0609 mol) of AlCl_3 , and 3.83 g (0.0294 mol) of propionic anhydride were reacted for 4.5 hr in the manner and under the conditions prescribed for 4. Chromatography on silica gel produced two bands when eluting with 10% ether in Skelly B. The one band which developed yielded 3.52 g (79.5%) of 19: mp 42°; bp 193–194° (0.3 mm); nmr (CDCl_3) δ 1.00 (d, 5, $\text{CH}(\text{CH}_3)_2$), 1.19 (t, 3, CH_2CH_3), 2.25 (m, 1, CH), 2.54 (d, 2, CH_2CH), 2.70 (m, 2, CH_2CH_3), 4.47 (m, 4, Fc), and 4.77 (m, 4, Fc).

Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Fe}$: C, 66.26; H, 6.75. Found: C, 66.18; H, 6.79.

1-Propionyl-1'-carbomethoxyferrocene (20).—20 was prepared by the method of Perevalova:³⁰ mp 64° (lit. 64–65°); nmr (CDCl_3) δ 1.18 (t, 3, CH_2CH_3), 2.73 (m, 2, CH_2), 3.80 (s, 3, OCH_3), 4.38 (t, 2, Fc), 4.48 (t, 2, Fc), and 4.79 (t, 4, Fc).

Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Fe}$: C, 60.00; H, 5.33. Found: C, 60.06; H, 5.44.

1-Propionyl-1-butylferrocene (21).—3 (2.35 g, 0.0087 mol), 5.41 g, 0.0407 mol) of AlCl_3 , and 2.50 g (0.0324 mol) of propionic anhydride were reacted for 4.5 hr in the manner and under the conditions prescribed for 4. Chromatography on silica gel produced two bands when eluting with 10% ether in Skelly B. The second band (red) contained 2.0 g (73.2%) of 21: mp 39.5°; bp 180–182° (0.3 mm); nmr (CDCl_3) δ 1.00 (t, 3, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.17 (t, 3, COCH_2CH_3), 1.73 (m, 2, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.63 (t, 2, COCH_2CH_2), 2.69 (m, 2, COCH_2CH_3), 4.45 (t, 4, Fc), and 4.76 (t, 4, Fc).

Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Fe}$: C, 65.38; H, 6.41. Found: C, 65.19; H, 6.50.

1-Propionyl-1'-p-tolylferrocene (23).—*p*-Tolylferrocene (0.85 g, 0.0028 mol), as prepared by the method of Dabard,²⁴ 3.0 g (0.0226 mol) of AlCl_3 , and 1.5 g (0.0115 mol) of propionic anhydride were reacted for 4.0 hr in the manner and under the conditions prescribed for 4. Chromatography on silica gel produced a single band, when eluting with 10% ether in Skelly B, which yielded 0.91 g (90%) of 23: mp 103°; nmr (CDCl_3) δ 1.10 (t, 3, CH_2CH_3), 2.43 (s, 5, Ph CH_3), 2.60 (m, 2, CH_2), 4.46 (t, 2, Fc), 4.53 (t, 2, Fc), 4.75 (t, 2, Fc), 4.89 (t, 2, Fc), and 7.51 (m, 4, Ph).

Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2\text{Fe}$: C, 70.00; H, 5.56. Found: C, 69.88; H, 5.69.

1-Propionyl-1'-cyanoferrocene (24).—Cyanoferrocene (0.85 g, 0.0040 mol), as prepared by the method of Broadhead,³¹ 2.0 g (0.0150 mol) of AlCl_3 , and 1.56 g (0.0120 mol) of propionic anhydride were reacted for 4 hr in the manner and under the conditions prescribed for 4. Chromatography on alumina produced two bands when eluting with 10% ether in Skelly B. The second band (orange) contained 1.00 g (93.3%) of 24: mp 53°; nmr (CDCl_3) δ 1.20 (t, 3, CH_3), 2.78 (m, 2, CH_2), 4.40 (t, 4, Fc), and 4.93 (t, 2, Fc); ir (neat) 2220 cm^{-1} ($\text{C}\equiv\text{N}$).

Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{ONFe}$: C, 62.72; H, 4.87; N, 5.24. Found: C, 62.81; H, 4.92; N, 5.36.

Registry No.—1, 12512-44-6; 1a, 12512-42-4; 1b, 12512-39-9; 2, 1271-79-0; 2a, 12512-41-3; 2b, 12512-38-8; 2', 12512-40-2; 2'a, 12512-36-6; 2'b, 12512-35-5; 2'', 12512-34-4; 2''a, 12512-33-3; 2''b, 12512-32-2; 3, 1271-94-9; 3a, 12512-49-1; 3b, 12512-48-0; 4, 12512-59-3; 4a, 12512-57-1; 4b, 12512-53-7; 5, 12512-63-9; 5a, 12512-62-8; 6, 12512-69-5; 6a, 12512-68-4; 7, 12512-56-0; 7a, 12512-51-5; 8, 12512-86-6; 8a, 12512-85-5; 9, 12512-60-6; 9a, 12512-55-9; 10, 12512-77-5; 10a, 12512-76-4; 11, 12512-87-7; 11a, 12512-84-4; 11b, 12512-83-3; 12, 12512-61-7; 12a, 12512-58-2; 13, 12512-78-6; 13a, 12512-75-3; 14, 12512-67-3; 14a, 12512-66-2; 15, 12512-79-7; 15a, 12512-74-2; 16, 12512-43-5; 16a, 12512-37-7; 17, 12512-89-9; 17a, 12512-88-8; 18, 12512-72-0; 18a, 12512-70-8; 19, 12512-73-1; 19a, 12512-71-9; 20, 1272-28-2; 20a, 12512-52-6; 21, 12512-65-1; 21a, 12512-64-0; 22, 12512-54-8; 22a, 12512-50-4; 23, 12512-81-1; 23a, 12512-80-0; 24, 12512-47-9; 24a, 12512-46-8; adamantylferrocene ketone, 12512-82-2.

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