

p.p.m., while the other set of three occurred as a multiplet at 5.34 p.p.m. The methyl group occurred as a triplet (J 2.0 c.p.s.) at 2.11 p.p.m.

Anal. Calcd. for $C_{15}H_{20}Sn$: C, 56.47; H, 6.32. Found: C, 56.43; H, 6.57.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, W. LAFAYETTE, IND.]

Factors Governing Orientation in Metalation Reactions. III. The Metalation of Alkylferrocenes¹

BY ROBERT A. BENKESER AND JOSEPH L. BACH

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A systematic study of the metalation of methyl-, ethyl-, isopropyl-, and *t*-butylferrocene by *n*-amylsodium and *n*-amylpotassium has been made. The monometalation products in these reactions consisted of a mixture of 3- and 1'-metalloalkylferrocenes in an approximate ratio of 1:2.6. A statistical distribution would be 1:2.5. Despite a 1:1 molar ratio of alkylferrocene to metalating agent, dimetalation was predominant in these reactions. It was established by n.m.r. spectroscopy that the major dimetalation product in each case was the 3,1'-dimetalloalkylferrocene. The suggestion is made that the dianion is more thermodynamically stable than the monoanion, which would account for its preferential formation. Even in metalations of ferrocene and alkylferrocenes with *n*-butyllithium (1:1 molar ratio), which were knowingly carried out in a homogeneous fashion, there was produced about a 3:2 mixture of mono- to dimetalation products. There was no observable tendency for the metal atom in any of these metalations to revert from the ring to the side chain in contradistinction to results with alkylbenzenes. Apparently the ring carbanions are more stable than the corresponding α -carbanions in the ferrocene system.

In the first two papers in this series,² a detailed study was made of the metalation of ethyl- and isopropylbenzene by *n*-amylsodium and *n*-amylpotassium. It was found that, in the early stages of reaction, the aromatic ring was metalated principally in the *meta* and *para* positions to the alkyl group. As reaction progressed, the ring isomers were converted, *via* a transmetalation process, to the more thermodynamically stable α -isomers.

It has been known for some time that ferrocene,³ as well as its alkyl derivatives,⁴ can be metalated in a similar fashion to benzene. No systematic study of orientation has been made, however, in the alkylferrocene series. One of the difficulties inherent in such a study is the quantitative separation of many closely related isomer structures, which, in the case of ferrocene compounds, often possess very similar solubilities. Another difficulty is the problem of identifying the ferrocene isomers once they have been separated from the mixture. Up to this time, principal reliance for structure determination in substituted ferrocenes has been placed on infrared spectroscopy.⁵ However useful this tool has been, it has very definite limitations, and, in some instances, structural assignments have been based solely on subtle spectral differences.⁶

With our recent discovery⁷ of the usefulness of n.m.r. spectroscopy in the determination of ferrocene structures, one of the principal difficulties connected with

metalation studies in the ferrocene series has been removed. Likewise, as is reported in this paper, we have found that vapor phase chromatography can be applied very profitably to a variety of ferrocene compounds. Thus, the perennial problems of separation which have plagued chemists working in this area have now been alleviated considerably.

It was the purpose of this present work to make a systematic study of the metalation of alkylferrocenes with *n*-amylsodium and *n*-amylpotassium, and to contrast these results with those reported for the alkylbenzenes.² We were particularly interested in the directive effects of the alkyl groups on the ferrocene nucleus toward metalation and whether there was any tendency for side chain reversion of the metal atom with time as was the case with the alkylbenzenes.²

Results.—Methyl-, ethyl-, isopropyl-, and *t*-butylferrocene were metalated with *n*-amylsodium in decane in duplicate runs. Methyl- and ethylferrocene were also metalated by *n*-amylpotassium under identical conditions. In the case of the *n*-amylsodium metalations, a 1:1 mole ratio of metalating agent to alkylferrocene was employed throughout.⁸ The reaction time (30–40 hr.), quantity of solvent, and temperature were held constant in all runs.

Initially, all metalation products were carbonated and esterified with diazomethane to convert the products to methyl esters. It was hoped that these could be analyzed by vapor phase chromatography. This analytical procedure had proved quite successful in our earlier metalation work.² It became apparent immediately that the dimetalation products which were forming in considerable quantities (despite a 1:1 mole ratio of reactants) could be nicely separated and analyzed by this technique. Unfortunately, the monoesters thus produced resisted separation by v.p.c. despite our use of eight different column packings. An attempt was made to reduce the methyl esters with lithium aluminum hydride–aluminum chloride to a mixture of completely alkylated ferrocenes. The hope was that a v.p.c. separation of the dialkylferrocenes (arising from the monometalated products) could be effected. As

(8) It was established through carbonation and esterification with diazomethane that a 70% yield of *n*-amylsodium from *n*-amyl chloride could be obtained. We used this value in each case as a basis for calculating the amount of *n*-amylsodium necessary to attain the 1:1 mole ratio.

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. A.F. 49 (638)-297. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *J. Am. Chem. Soc.*, **84**, 4971 (1962); R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *ibid.*, **85**, 3984 (1963).

(3) R. A. Benkeser, I. Goggin, and G. Schroll, *ibid.*, **76**, 4025 (1954); A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954).

(4) A. N. Nesmeyanov, E. G. Perevalova, Z. A. Beynoravichute, and I. L. Malygina, *Proc. Acad. Sci., U.S.S.R., Chem. Sect., Engl. Transl.*, **120**, 499 (1958).

(5) K. L. Rinehart, K. L. Motz, and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957); M. Rosenblum and W. G. Howells, *ibid.*, **84**, 1167 (1962).

(6) A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin, and V. D. Vil'chevskaya, *Doklady Akad. Nauk S.S.S.R.*, **126**, 1037 (1959); K. Schlägl and H. Seiler, *Tetrahedron Letters*, **7**, 4 (1960).

(7) (a) R. A. Benkeser, Y. Nagai, and J. Hooz, *Bull. Chem. Soc. Japan*, **36**, 482 (1963); (b) Y. Nagai, J. Hooz, and R. A. Benkeser *ibid.*, in press.

shown in Table II (columns A and B) this reduction proceeded quite quantitatively. Again the trialkylferrocenes (arising from dimetalation) could be separated by v.p.c., but the dialkylferrocenes thus produced generally resisted separation⁹ although twelve different column packings were tried. Finally it was found that the monometalated products could be separated by v.p.c. if they were first coupled with trimethylchlorosilane or triethylbromosilane. In the case of methyl- and ethylferrocene, separation was achieved by coupling with triethylbromosilane. With isopropyl- and *t*-butylferrocene, coupling with trimethylchlorosilane afforded products which were very amenable to v.p.c. analysis (see Table I). Again, the dimetalation products were easily separated by coupling with either of the trialkylhalosilanes (see Table II).

TABLE I
MONOMETALATION OF ALKYLFERROCENES WITH *n*-AMYLSDIUM.
ISOMER RATIOS DETERMINED BY COUPLING WITH TRIMETHYL-
CHLOROSILANE AND TRIETHYLBROMOSILANE^a

Alkylferrocene	1,3-Product, %	1,1'-Product, %
Me- ^b	29	71
Et- ^b	30	70
<i>i</i> -Pr- ^{c,d}	27(30)	73(70)
<i>t</i> -Bu- ^c	25	75

^a The values given in this table are not yields, but rather isomer distributions. ^b The values listed were obtained by coupling the metalated products with triethylbromosilane. ^c The values listed were obtained by coupling the metalated products with trimethylchlorosilane. ^d The values in parentheses were obtained in a completely homogeneous metalation of isopropylferrocene with *n*-butyllithium in diethyl ether.

TABLE II
DIMETALATION OF ALKYLFERROCENES WITH *n*-AMYLSDIUM.
ISOMER RATIOS DETERMINED BY CARBONATION AND BY COUPLING
WITH TRIALKYLCHLORO- AND -BROMOSILANES^a

Alkyl- ferro- cene	2-Alkyl-1,1'-disubstituted product, %				3-Alkyl-1,1'-disubstituted product, %			
	Methods				Methods			
	A ^b	B ^c	C ^d	D ^e	A ^b	B ^c	C ^d	D ^e
Me-	12	10	11	11	88	90	89	89
Et-	7	6	8	7	93	94	92	93
<i>i</i> -Pr- ^f	3	3	3(3)	..	97	97	97(97)	..
<i>t</i> -Bu-	<2	<2	<2	..	98	..	98	..

^a The values listed in this table are not yields but isomer distributions. ^b This column lists the isomer distributions obtained by carbonation of metalated products and treatment with diazomethane. ^c This column lists the isomer distribution obtained by reducing the methyl ester mixtures with lithium aluminum hydride-aluminum chloride. ^d Values obtained by treating metalated products with trimethylchlorosilane. ^e Metalated products were treated with triethylbromosilane. ^f The values in parentheses were obtained in a completely homogeneous metalation of isopropylferrocene with *n*-butyllithium in diethyl ether.

The variety of analytical procedures which were tried and the very consistent results which were obtained (Table II) provides assurance for the accuracy of the results. They also tend to confirm an earlier assumption made consistently by us² and other workers—that carbonation provides an accurate probe for the position of the metal atom in an organic molecule.

Identification of Products.—The major monometalation products from methylferrocene were identified as the 1,1'-products by the use of a 150-ft. capillary v.p.c. column and by a comparison of retention times with authentic samples.

In the case of *t*-butylferrocene, 1-*t*-butyl-1'-trimethylsilylferrocene was actually isolated as the major component of the monometalation products. Since it was

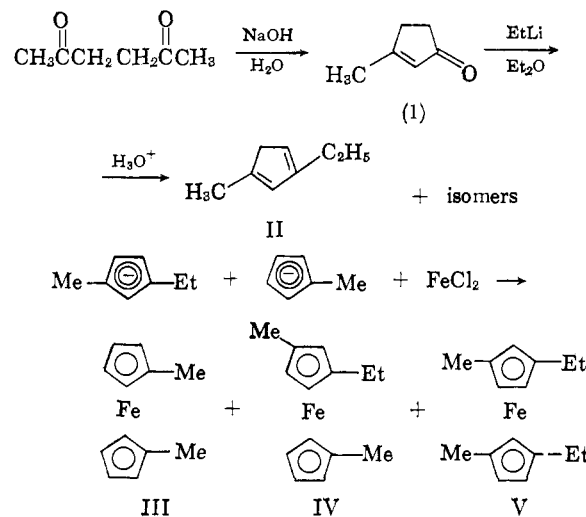
devoid of 9,10 μ absorption¹⁰ (infrared), this material, of necessity, had the 1,1'-structure.

It was shown in the case of ethylferrocene that only trace amounts of a 1,2-disubstitution product were present in the monometalation mixture. This was done by comparing the retention time of an authentic sample of 1-methyl-2-ethylferrocene^{7b} with the reduction products obtained by treating the ethylcarbo-methoxyferrocenes with lithium aluminum hydride-aluminum chloride. There was an insignificant peak in the latter reduction product which compared in retention time with that of an authentic sample of 1-methyl-2-ethylferrocene.

In summary, all four alkylferrocenes showed only two monometalation products, one of which in each case was only a minor constituent. In three of the four cases, the major constituent was shown to have the 1,1'-structure. In the fourth case (ethylferrocene), the 1,2-disubstituted product was shown to be absent. Hence, it can be concluded that the monometalation products possessed the 1,1'- (major product) and the 1,3-structures.

The dimetalation products shown in Table IV were isolated by v.p.c. and their structures established unequivocally by n.m.r. spectroscopy. We had shown in previous work⁷ that a strong electron-withdrawing group on a ferrocene ring like acetyl causes a definite shift to lower fields of the two hydrogen atoms located in the 2- and 5-positions relative to acetyl. Likewise, the ring hydrogens located in the 3- and 4-positions were similarly shifted to lower field, albeit to a lesser extent. It was reasoned that the same phenomenon should also be observed in the case of an electron withdrawer like a carbomethoxy group. That this turns out to be true is apparent from entries 1 and 2 in Table IV. From the shielding effect of the carbomethoxy group and the relative proton intensities involved, it was a simple matter to make the structural assignments^{7b} for the dimetalated products shown in Table IV.

One chemical proof of structure was carried out on the major dimetalation product obtained from ethylferrocene. This product had been characterized by n.m.r. as 3-ethyl-1,1'-dicarbomethoxyferrocene (Table IV, entry 6). Reduction of this material with lithium aluminum hydride-aluminum chloride produced 3-ethyl-1,1'-dimethylferrocene in nearly quantitative yield as shown in Table II. An authentic sample of the latter was prepared by the sequence



(9) The mixture of 1,1'- and 1,3-dimethylferrocene was analyzed successfully with a 150-ft. capillary column (see Experimental).

(10) (a) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953; (b) P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954).

TABLE III
SUMMARY OF ALKYLFERROCENE METALATIONS

Alkylferrocene	Monosubstn. ^a	Disubstn. ^b	Dimetalation/ monometalation
	product ratio (1,1'/1,3)	product ratio (3,1,1'/2,1,1')	
Me-	2.4	8	2.2
Et-	2.3	13	3
<i>i</i> -Pr-	2.7	32	2.2
<i>t</i> -Bu-	3	98	2.7

^a The ratio listed in this column is calculated from the values given in Table I. ^b These values are calculated from Table II, taking the average value for the analytical methods A, B, C, and D in each case.

TABLE IV
CHEMICAL SHIFTS FOR THE PROTONS OF SOME FERROCENE ESTERS^{a,b}

Substituent	ESTERS ^{a,b}			
	a ^c	b ^d	c ^e	d ^f
1 Carbomethoxy ^g	5.28 (2)	5.73 (2)
2 1,1'-Dicarbomethoxy	5.20 (4)	5.60 (4)
3 2-Methyl-1,1'-dicarbomethoxy	5.35 (3)	5.74 (4)	7.82 (3)	..
4 3-Methyl-1,1'-dicarbomethoxy	5.31 (4)	5.74 (3)	8.05 (3)	..
5 2-Ethyl-1,1'-dicarbomethoxy	5.33 (3)	5.78 (4)	7.36 (2)	8.80 (3)
6 3-Ethyl-1,1'-dicarbomethoxy	5.30 (4)	5.74 (3)	7.70 (2)	8.82 (3)
7 3-Isopropyl-1,1'-dicarbomethoxy	5.35 (4)	5.76 (3)	7.40 (1)	8.84 (6)
8 3- <i>t</i> -Butyl-1,1'-dicarbomethoxy	5.31 (4)	5.75 (3)	..	8.77 (9)

^a The data listed are " τ " values using tetramethylsilane as an internal standard in a solvent of carbon tetrachloride. ^b The values in parentheses are relative intensities. All measurements were made on a Varian A-60 analytical spectrometer. ^c Column "a" values refer to the H in the 2- and 5-positions relative to the carbomethoxy group. ^d Column "b" refers to the H in the 3- and 4-position relative to the ester group. ^e Column "c" refers to H located on the α -carbon atom of the alkyl side chain. ^f Column "d" refers to H located on the β -carbon atom of the alkyl side chain. The methyl of the carbomethoxy group has been omitted from the table since it exhibits a fairly constant τ -value of 6.21-6.25. ^g The unsubstituted ring protons of this compound absorb at 5.87 τ with a relative intensity of 5.

TABLE V
METALATION OF ISOPROPYLFERROCENE WITH *n*-AMYL SODIUM AT VARIOUS TIME INTERVALS^a

Time, hr.	Monosubstitution	Disubstitution	Dimetalation/ monometalation
	product ratio (1,1'/1,3)	product ratio (3,1,1'/2,1,1')	
1	72/28	96/4	78/22
3	73/27	97/3	85/15
5	70/30	95/5	79/21
10	72/28	97/3	77/23
20	72/28	98/2	73/27

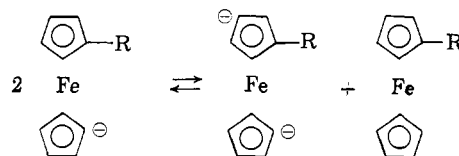
^a Analyses of all products were achieved by coupling with trimethylchlorosilane.

When the product of the last reaction was analyzed by v.p.c., it was shown to be a three-component mixture. The first peak was the major component (58%) and was shown to have the identical retention time as an authentic sample of 1,1'-dimethylferrocene (III). The second peak (35%) had a retention time identical with that of the supposed sample of 3-ethyl-1,1'-dimethylferrocene (IV) obtained from the metalation reaction. The third and last peak obtained from the synthesis must be 1,1',3,3'-dimethyldiethylferrocene (V). Hence the chemical structure proof nicely corroborated the n.m.r. results.

Conclusions.—In order to ascertain whether the orientations which were observed were the result of a kinetic rather than an equilibrium situation, five duplicate metalations of isopropylferrocene with *n*-amyl-

sodium were carried out with reaction times of 1, 3, 5, 10, and 20 hr., respectively. The isomer distributions observed in each run were quite constant (Table V) suggesting equilibrium rather than kinetic control.

It will be seen from Table III that the ratio of di- to monometalation products in all the metalations was of the order of 2.5:1 despite a 1:1 mole ratio of reactants. Presumably an equilibrium must exist between the mono- and dianion.



This equilibrium would be shifted to the right if the dianion species were less soluble than the monoanion. While conceivably this could be the sole reason for the preponderance of dimetalation, there are two observations which cast doubt on the validity of this explanation.

A metalation of ferrocene and isopropylferrocene by *n*-butyllithium in ether was carried out in a completely homogeneous system. In both cases, dimetalation and monometalation products were present in approximately a 3:2 ratio¹¹ despite a 1:1 ratio of reactants.

In several of the amylsodium metalations, we attempted to detect the presence of organometallic in the supernatant liquid before carbonation or treatment with trialkylhalosilanes. Practically no activity could be detected, which permits the conclusion that both the mono- and dianion are quite insoluble species. We favor the view that the dianion is more thermodynamically stable¹² than the monoanion, which would cause the above equilibrium to lie to the right. This remains a moot point, however.

It can be seen in Table III that the isomer ratios of 1,1'- to 1,3-products are, on the average, about 2.6:1. Statistically one would expect a ratio of 2.5:1, since there are five available positions for attack in the unsubstituted ring and only two such positions in the ring bearing the alkyl group. Hence, electrical effects operating at the 3-position seem quite comparable to the electrical effects in the unsubstituted ring.¹³

It becomes quite apparent from Table II, that, as the steric bulk of the alkyl group is increased, the quantity of 2,1,1'-isomer falls off relative to the 3,1,1'-as would be predicted. We are inclined to view this as a steric rather than electronic effect.

Perhaps most significant of all is the observation that there was no detectable tendency for the ring-substituted metalation products to revert to the side chain as was noted in the case of the alkylbenzenes.² Even in the metalations where *n*-amylpotassium was employed, side chain products could not be detected. Presumably, the ring-substituted isomers are more thermodynamically stable in the case of alkylferrocenes than those in which the metal atom is bonded to the α -carbon atom of the alkyl side chain.

Experimental

Preparation of Alkylferrocenes. (a) **Methylferrocene.**—To a mixture of 6.2 g. (0.16 mole) of lithium aluminum hydride in 300

(11) Interestingly, the isomer ratios obtained in the case of isopropylferrocene were almost identical with those obtained when *n*-amylsodium was used as the metalating agent (see Table I and II).

(12) It seems highly improbable that a rate effect can explain the preference for dimetalation. Removal of a proton from the monoanion to form the dianion species should be slower than attack on the neutral molecule. See P. L. Pauson in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 127.

(13) This conclusion receives further support from n.m.r. data. The τ -values for the H atoms on the substituted and unsubstituted rings of alkylferrocenes are quite similar (see ref. 7).

ml. of ethyl ether was added 35.2 g. (0.16 mole) of hydroxymethylferrocene.¹⁴ The reaction vessel was immersed in an ice bath during this and subsequent additions. An ethereal solution of 21.7 g. (0.16 mole) of aluminum chloride was then introduced. Water was added to destroy the excess hydride and the ethereal solution was separated and dried.

The residue was chromatographed on a short column of Alcoa alumina with petroleum ether (35–37°) as both developer and eluent. There was obtained 32 g. (100%) of methylferrocene¹⁵ (m.p. 36–38°) which gave a single peak when subjected to vapor phase chromatography.

When carbomethoxyferrocene was substituted for hydroxymethylferrocene and the above procedure repeated, the yield of methylferrocene was again quantitative.

(b) **Ethylferrocene.**—Prepared in essentially the same fashion as described above for methylferrocene. A 97% yield of ethylferrocene was obtained (b.p. 112° (5 mm.)) starting with 125 g. (0.55 mole) of acetylferrocene.¹⁶

(c) **Isopropylferrocene.**—To a cooled solution of methyl-lithium (0.6 mole) in ether was added 91.2 g. (0.4 mole) of acetylferrocene in 700 ml. of anhydrous ether. After the addition was complete, a sufficient quantity of water was added to destroy the excess methyl-lithium. Lithium aluminum hydride (15.2 g., 0.4 mole) was added next, followed by an ethereal solution of 53.2 g. (0.4 mole) of aluminum chloride. Water was then used to destroy the excess hydride and also to dissolve the aluminum salts. The ethereal layer was then separated and dried. After column chromatography treatment (exactly as described above for methylferrocene), there was collected 89.4 g. (94%) of isopropylferrocene¹⁷ boiling at 118–119° (5 mm.). This dark red liquid showed only a single peak by v.p.c.

(d) ***t*-Butylferrocene.**—To a mixture of 186 g. (1.0 mole) of ferrocene and 93 g. (1.0 mole) of *t*-butyl chloride in 1 l. of olefin-free petroleum ether (b.p. 65–67°) was added 213 g. (1.5 moles) of boron trifluoride etherate. The mixture was heated to reflux for 24 hr. with stirring and was then poured into ice water containing potassium carbonate. The ethereal layer was separated and dried.

After the solvent was removed, the residue was chromatographed on a short column of Alcoa alumina with petroleum ether (35–37°) as solvent in order to remove some decomposition products. Analysis of this material by v.p.c. showed that it contained the four materials: ferrocene (30%), *t*-butylferrocene (45%), and two unknowns in 18 and 7% quantities, respectively. The latter two materials may well be di-*t*-butylferrocenes and tri-*t*-butylferrocenes, respectively, although no attempt was made to establish their identity. This mixture was dissolved in 100 ml. of petroleum ether (35–37°) and placed in a refrigerator. After a few hours, ferrocene precipitated and was collected by filtration. This technique was repeated until only 5% of the original ferrocene remained.

The red oil which remained was purified by repeated passes through a 4-ft. column of Merck alumina. Petroleum ether was used (35–37°) as both developer and eluent. Final purification was effected by distillation through a Todd column. A red liquid (97 g., 40%) boiling at 99–100° (0.5 mm.)¹⁸ was collected. This was shown by v.p.c. to be pure *t*-butylferrocene.

Metalation of Alkylferrocenes.—The metalation procedure for all the alkylferrocenes was essentially identical. Duplicate runs were made in every case. The agreement was excellent. Only details for the metalation of methylferrocene will be given here.

To 0.08 mole of *n*-amylsodium prepared from 12.2 g. (0.114 mole) of *n*-amyl chloride and 7.9 g. (0.342 g.-atom) of dispersed sodium¹⁹ in 130 ml. of decane was added 16 g. (0.08 mole) of methylferrocene in 50 ml. of decane. The reaction was allowed to proceed at room temperature for 40 hr. with high speed stirring. After carbonation and esterification with diazomethane, a sample was analyzed by v.p.c. (Craig polyester succinate column, 228°, 20 p.s.i. He). Three peaks appeared (retention times of 5.5, 26.5, and 29.5 min.). The first peak was shown to be a mixture of 1-methyl-1'-carbomethoxyferrocene and 3-methyl-1-carbomethoxyferrocene. The next two peaks were an isomeric mixture of 2-methyl-1,1'-dicarbomethoxyferrocene and 3-methyl-1,1'-dicarbomethoxyferrocene. A total of 6 g. of the mixed esters was obtained. In addition, methylferrocene was recovered from the neutral layer, such that a 90% material balance was realized. Tables II and III list the analytical results for all the metalation runs.

The monometalation products could be separated from the di-products by chromatography on a 3-ft. column of Alcoa alumina

with petroleum ether (35–37°) as the developer. Benzene was used to elute the monocarbomethoxy fraction, while ethyl ether was used to elute the dicarbomethoxy fractions. The isomeric monocarbomethoxy compounds could not be separated successfully by v.p.c. even though eight different column packings were tried.

Anal. Calcd. for C₁₃H₁₄O₂Fe (isomeric mixture of 1-methyl-1'-carbomethoxyferrocene and 3-methyl-1-carbomethoxyferrocene): C, 60.48; H, 5.48; Fe, 21.64. Found: C, 60.23; H, 5.47; Fe, 21.34. Calcd. for C₁₈H₁₈O₄Fe (isomeric mixture of 2- and 3-methyl-1,1'-dicarbomethoxyferrocene): C, 56.99; H, 5.10; Fe, 17.67. Found: C, 57.21; H, 5.32; Fe, 17.50.

Metalation of Methylferrocene with *n*-Amylpotassium.—The procedure employed for this metalation was identical in every detail with the run described above which utilized *n*-amylsodium. The isomer distributions and ratio of mono- to dimetalation products were identical to the *n*-amylsodium run. The yield of metalation product was considerably lower, however (19%).²⁰

In order to ascertain that no side chain metalation had occurred in either the *n*-amylsodium or *n*-amylpotassium metalations of methylferrocene, the following procedure was employed.

The isomeric methylcarbomethoxyferrocenes (monometalation products) obtained from the two above metalations were reduced to the isomeric dimethylferrocenes with lithium aluminum hydride-aluminum chloride. After reduction, the product was chromatographed on a short column of Merck alumina with petroleum ether (35–37°) as the developer and eluent. The ferrocene compounds eluted quickly as a single orange-red band. An infrared spectrum of this material *did not* show OH absorption. If side chain metalation had occurred, methylferrocenyl acetate would have formed and reduction with lithium aluminum hydride would yield either 2-ferrocenylethanol or ethylferrocene.

It was further demonstrated by v.p.c. (18-ft. Craig polyester succinate column, 160°, 15 p.s.i. He) that ethylferrocene was *absent* in the mixture by the use of an authentic sample of the latter compound for retention time purposes.

In a similar way it was demonstrated that no side chain metalation had occurred in the metalation of ethylferrocene with either *n*-amylsodium or *n*-amylpotassium.

Reduction of an Isomeric Mixture of 1'- and 3-Methyl-1-carbomethoxyferrocenes.—To a mixture of 0.57 g. (0.015 mole) of lithium aluminum hydride in 50 ml. of ethyl ether was added 4 g. (0.015 mole) of an isomeric mixture of 1'- and 3-methyl-1-carbomethoxyferrocene. After the addition was complete, an ethereal solution of 2 g. (0.015 mole) of aluminum chloride was introduced into the reaction mixture. This reduction yielded 3.15 g. (98%) of a mixture of 1,3- and 1-1'-dimethylferrocenes which resisted resolution by v.p.c. even though twelve different columns were tried. Likewise the attempted separation of the other methylalkylferrocenes also failed at this point.

Anal. Calcd. for C₁₂H₁₄Fe (isomeric mixture of 1,3- and 1,1'-dimethylferrocenes): C, 67.32; H, 6.59; Fe, 26.09. Found: C, 67.32; H, 6.47; Fe, 25.90.

Reduction of an Isomeric Mixture of 2- and 3-Methyl-1,1'-dicarbomethoxyferrocene.—The details of this reduction are essentially identical with those described above for the reduction of the monoesters. From 4.8 g. (0.015 mole) of a mixture of 2- and 3-methyl-1,1'-dicarbomethoxyferrocene was obtained 3.35 g. (98%) of isomeric trimethylferrocenes. This mixture was shown by v.p.c. (18-ft. Craig polyester succinate column, 180°, 20 p.s.i. He) to be composed of 1,3,1'-trimethylferrocene (90%) and 1,2,1'-trimethylferrocene (10%). Separation of all dimetalated products could be achieved this way.²¹ These results are listed in Table II under the heading of analytical method "B".

Anal. Calcd. for C₁₃H₁₆Fe (mixture of trimethylferrocenes): C, 68.44; H, 7.07; Fe, 24.49. Found: C, 68.59; H, 7.30; Fe, 24.51.

Metalation of Methylferrocene by *n*-Amyl-sodium Followed by Treatment with Trimethylchlorosilane or Triethylbromosilane.—To a mixture of 0.15 mole of *n*-amylsodium prepared from 22.9 g. (0.21 mole) of *n*-amyl chloride and 9.7 g. (0.42 g.-atom) of sodium in 130 ml. of decane was added 30 g. (0.15 mole) of methylferrocene in 50 ml. of decane. The metalation was carried out for 30 hr. with high speed stirring. There was then added 19.5 g.

(20) We have shown in paper I in this series that the yield of *n*-amylpotassium from *n*-amyl chloride is lowered by the incursion of side reactions like dehydrohalogenation.

(21) The v.p.c. retention times of all the substituted ferrocenes reported in this paper followed a uniform pattern. Thus, the retention time of all 1,3,1'-trialkylferrocenes was shorter than the corresponding 1,2,1'-isomers (Craig polyester succinate column). Likewise, in the bis-trialkylsilylalkylferrocene series (Apiezon L column), the 1,3,1'-isomers eluted before the 1,2,1'. The 1,3-trialkylsilylalkylferrocenes eluted before the corresponding 1,1'-isomers (Apiezon L). In the alkyl-dicarbomethoxyferrocene series (Craig polyester succinate or diethylene glycol succinate columns) the 1,2,1' isomers eluted before the 1,3,1'.

(14) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 355 (1957).

(15) K. Schlögl, A. Mohar, and M. Peterlik, *Monatsh.*, **92**, 921 (1961).

(16) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

(17) A. N. Nesmeyanov and H. C. Kochetkova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 242 (1958).

(18) A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk S.S.S.R.*, **117**, 92 (1957).

(19) See paper I of this series (ref. 2) for details of the preparation of metal dispersions, diazomethane, carbonation, and esterification procedures.

(0.18 mole) of trimethylchlorosilane (or an equivalent amount of triethylbromosilane) at 0°. Excess sodium was then destroyed by the addition of a 70% aqueous ethanol solution. Water was added to dissolve all of the salts and the colorless aqueous layer was discarded. After the organic layer was dried, the solvent was removed under vacuum and the residue was chromatographed on a short Alcoa alumina column to rid the mixture of decomposition products. Analysis of the product by v.p.c. (16-ft. Apiezon L column, 240°, 60 ml./min. He) showed only one peak for monometalated products and two peaks for dimetalated products in the run in which trimethylchlorosilane was used. However, in the run in which triethylbromosilane was used, the peak for the mono products could be resolved. The analytical results obtained in both of these runs are listed in Table I and II.

Anal. Calcd. for $C_{17}H_{26}FeSi$ (isomeric mixture of 1'- and 3-methyl-1-triethylsilylferrocene): C, 64.96; H, 8.35; Fe, 17.76. Found: C, 64.91; H, 8.51; Fe, 17.65. Calcd. for $C_{23}H_{40}FeSi_2$ (isomeric mixture of 2- and 3-methyl-1,1'-ditriethylsilylferrocene): C, 64.46; H, 9.41; Fe, 13.03. Found: C, 64.33; H, 9.41; Fe, 13.00.

Essentially the same results as described above were obtained when ethylferrocene was metalated with *n*-amylsodium and the product was coupled with trimethylchlorosilane and triethylbromosilane. The isomeric mixture of 1'- and 3-ethyl-1-trimethylsilylferrocene could again not be resolved by v.p.c. On the other hand, complete resolution of all isomers was achieved by coupling the metalated products with triethylbromosilane (see Tables I and II for these results).

In the case of the metalated products derived from isopropyl-²² and *t*-butylferrocene, complete separation of all isomers could be achieved by coupling with trimethylchlorosilane (see Tables I and II).

Identification of Monometalation Products (Table I).—The isomeric dimethylferrocenes obtained as described above from the reduction of the isomeric methylcarbomethoxyferrocenes were analyzed by v.p.c. (150-ft. column "R" capillary column, 132°, H_2 flame detector) and two peaks were obtained. The first peak (major) was identical in retention time with an authentic sample of 1,1'-dimethylferrocene (m.p. 37–38°) which had been prepared by the lithium aluminum hydride–aluminum chloride reduction of 1,1'-dicarbomethoxyferrocene.

When the monometalation products derived from ethylferrocene were coupled with triethylbromosilane, v.p.c. analysis indicated a two-component mixture which analyzed well for ethyl-triethylsilylferrocenes.

Anal. Calcd. for $C_{18}H_{28}FeSi$: C, 65.85; H, 8.60; Fe, 17.01. Found: C, 65.91; H, 8.79; Fe, 17.21.

The ethylcarbomethoxyferrocenes were reduced to an isomeric mixture of ethylmethylferrocenes by the method already described. Likewise, an authentic sample of 1-methyl-2-ethylferrocene was prepared by a similar reduction of methyl-2-acetylferrocene.²³ It was shown by v.p.c. (18-ft. Craig polyester succinate column, 160°, 15 p.s.i.) that 1-methyl-2-ethylferrocene was *not* present in the isomeric mixture obtained from the metalation. Hence, the two-component mixture was composed of 1,3- and 1,1'-isomers.

When the metalation product of *t*-butylferrocene was coupled with trimethylchlorosilane, a two-component mixture, constituting the monometalation products, could be detected and isolated by v.p.c.

Anal. Calcd. for $C_{17}H_{26}FeSi$: C, 64.96; H, 8.34; Fe, 17.77. Found: C, 65.11; H, 8.36; Fe, 17.55.

The material responsible for the major peak of this two-component mixture was isolated also by v.p.c. (16-ft. Apiezon "L" column, 240°, 60 cc./min. He). The infrared spectrum of this material was devoid of 9,10 μ absorption indicating the structure of this material to be 1-*t*-butyl-1'-trimethylsilylferrocene. The other peak must therefore be caused by 1-*t*-butyl-3-trimethylsilylferrocene.

Identification of Dimetalation Products (Table II).—The structures of the alkylcarbomethoxyferrocenes were determined principally by n.m.r. spectroscopy (see Table IV). Small samples of each of the compounds listed in Table IV were isolated by column chromatography (3-ft. Merck alumina) and submitted for n.m.r. determinations.

(22) In some earlier unpublished studies from this laboratory, Dr. Yoichiro Nagai identified the major monometalation product (using *n*-amylsodium as metalating agent) of isopropylferrocene as the 1,1'-product. The metalation product was coupled with triethylchlorosilane and the 1-isopropyl-1'-triethylsilylferrocene was separated by v.p.c. (Apiezon L column, 16 ft., 280°). It boiled at 140° (0.8 mm.), n_D^{20} 1.5534. *Anal.* Calcd. for $C_{18}H_{30}FeSi$: C, 66.65; H, 8.83; Fe, 16.31. Found: C, 67.06; H, 8.88; Fe, 16.17. The compound showed no absorption at 9 and 10 μ , clearly identifying it as the 1,1'-structure.

(23) Kindly supplied by Dr. Y. Nagai of these laboratories. Its structure was unequivocally established by n.m.r. spectroscopy; see ref. 7.

3-Methylcyclopent-2-enone was prepared essentially by the method of Robinson²⁴ with a modification in the purification procedure of the product. There was obtained 115 g. of a colorless liquid boiling at 68–71° (15 mm.). Analysis by v.p.c. (8-ft. Ucon polar column, 125°, 60 cc./min. He) disclosed that the product was contaminated with about 30% of the starting material (acetylacetone). Distillation through a Pirox-Glover micro spinning band column (b.p. 108° (75 mm.)) yielded a product which, by v.p.c., was 99% pure. An n.m.r. determination on the purified sample disclosed 7 saturated and 1 vinyl H.

1-Methyl-3-ethylcyclopentadiene was prepared in accord with directions by Taylor²⁵ except that ethyllithium was used instead of ethylmagnesium bromide. Distillation of the product through a Todd column yielded 32 g. (50%) of a colorless liquid boiling at 63–65° (60 mm.). The ultraviolet absorption of this material agreed well with the literature²⁶ (λ_{max}^{hexane} 240 $\mu\mu$), although analysis by v.p.c. disclosed there was a 10% impurity present.

Reaction of Potassium Salts of Methylcyclopentadiene and 1-Methyl-3-ethylcyclopentadiene with Anhydrous Ferrous Chloride.

—A sodium-potassium alloy was prepared in dry *p*-xylene from 1.2 g. (0.05 g.-atom) of sodium and 9.8 g. (0.25 g.-atom) of potassium. The *p*-xylene was removed by a filter stick and replaced with 200 ml. of tetrahydrofuran.

Methylcyclopentadiene (12.0 g., 0.15 mole) was added to the alloy with stirring and cooling and a tetrahydrofuran solution of 16.2 g. (0.15 mole) of 1-methyl-3-ethylcyclopentadiene was introduced. After this addition was completed, the reaction mixture was stirred for 2 hr. at room temperature. The potassium salts thus formed were removed from the unreacted alkali metals by means of a filter stick. These salts were added slowly with stirring to anhydrous ferrous chloride²⁸ (from 16.2 g. of $FeCl_3$ and 2.2 g. of iron powder) in 150 ml. of tetrahydrofuran. The mixture was refluxed for 5 hr. and then the solvent was removed under vacuum leaving a red viscous liquid. The latter was extracted several times with petroleum ether (35–37°). After solvent removal, the residue was distilled to removed the unreacted cyclopentadienes. Analysis of the ferrocene compounds which remained by v.p.c. (18-ft. Craig polyester succinate, 180°, 15 p.s.i. He) disclosed three peaks. The first of these peaks (comprising 58% of the mixture) had an identical retention time with an authentic sample of 1,1'-dimethylferrocene. The second peak (35%) had an identical retention time with the principal peak obtained in the analysis of the dimethylethylferrocene isomers obtained from the dimetalation of ethylferrocene. The last peak (6%) was assumed to be 3,3'-diethyl-1,1'-dimethylferrocene. There was obtained a total of 10.2 g. (40%) of ferrocene products in this reaction.

Metalation of Isopropylferrocene with *n*-Amylsodium for Varying Periods of Time.—The procedure was the same as that described above. Five metalations were performed with reaction times of 1, 3, 5, 10, and 20 hr. Analyses of the metalated products were accomplished by coupling with trimethylchlorosilane. The results of these five experiments are listed in Table V.

Homogeneous Metalation of Ferrocene with *n*-Butyllithium.

(a) **Treatment with Trimethylchlorosilane.**—To a mixture of 0.2 mole of *n*-butyllithium (titer determined by Gilman double titration technique²⁷) in ethyl ether was added with stirring under a nitrogen atmosphere an ethereal solution of 37.2 g. (0.2 mole) of ferrocene. A total of 800 ml. of ethyl ether was used as the solvent. The reaction was stirred for 30 hr. at room temperature. The ether solution was then transferred (filter stick) to a dry flask and the gray solid remaining in the bottom of the original flask was washed with a small portion of ethyl ether and then treated with an ethereal solution of trimethylchlorosilane. The residue did *not* yield any ferrocene compounds upon work-up.

The ethereal solution of metalated ferrocene was then cooled to 0° and 24.0 g. (0.22 mole) of trimethylchlorosilane was added to it. The work-up was performed in the usual manner. A sample of the residue, after solvent removal, was used for v.p.c. analysis (4-ft. silicone rubber column, 160°, 60 cc./min. He) and showed two peaks in the ratio of 57:43. These two peaks had identical retention times to authentic samples of trimethylsilylferrocene and 1,1'-ditrimethylsilylferrocenes.²⁸

The above reaction was performed in triplicate and the results were in good agreement.

(b) **Carbonation and Treatment with Diazomethane.**—The metalation procedure with *n*-butyllithium was essentially identical with that described in a above. The metalated products were carbonated and treated with diazomethane in the usual manner.

Separation of the mono- and dicarbomethoxyferrocene was achieved by chromatography on a 3-ft. Merck alumina column. Petroleum ether (35–37°) was used as the developer, and after two distinct bands had formed, benzene was used to elute the monoester and ethyl ether to elute the diester. The melting

(24) R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1127 (1952).

(25) D. A. H. Taylor, *ibid.*, 4779 (1958).

(26) *Org. Syntheses*, **36**, 31 (1956).

(27) H. Gilman and A. H. Hauben, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(28) M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

point of each ester agreed with the literature value,^{3,20} and the ratio of carbomethoxyferrocene (5.8 g.) to 1,1'-dicarbomethoxyferrocene (5.0 g.) was 59:41.

Metalation of Ferrocene with *n*-Amylsodium (1:1 Ratio).—The metalation of ferrocene with *n*-amylsodium (1:1 ratio) followed by carbonation and esterification with diazomethane showed a ratio of carbomethoxyferrocene to 1,1'-dicarbomethoxyferrocene of 30:70. Thus dimetalation was favored.

Homogeneous Metalation of Isopropylferrocene with *n*-Butyllithium and Coupling with Trimethylchlorosilane.—The metalation

(29) R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

and coupling procedure with trimethylchlorosilane were identical with that described in (a) above for the metalation of ferrocene. Again the filtration technique followed by treatment of the solid residue with trimethylchlorosilane did not result in the isolation of any ferrocene derivative. When the ethereal solution was treated with trimethylchlorosilane, a v.p.c. analysis (16-ft. Apiezon L column, 240°, 60 cc./min. He) indicated a ratio 3-isopropyl- to 1'-isopropyl-1-trimethylsilylferrocene of 30:70. It also indicated a ratio of 3-isopropyl- to 2-isopropyl-1,1'-ditrimethylsilylferrocene of 97:3. The ratio of mono- to dimetalated products was 60:40. These results have been included in Table I and II.

[CONTRIBUTION FROM DOW CORNING CORPORATION, MIDLAND, MICH.]

The Addition of Silicon Hydrides to Olefinic Double Bonds. VIII. The Addition of Trichlorosilane-*d*

BY JOHN W. RYAN AND JOHN L. SPEIER

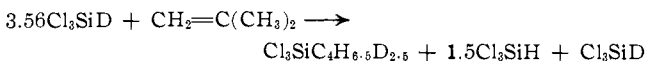
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The products formed by the addition of trichlorosilane-*d* (Cl_3SiD) to olefins are not usually monodeuterioalkylsilanes as might be expected. During the addition in the presence of a platinum catalyst extensive exchange occurs between the Si-D and C-H of the olefin. The adducts have deuterium distributed widely in their structures in a random manner. Certain olefins and diphenylacetylene add trichlorosilane-*d* without exchange and in an apparently simple manner. These exceptional compounds include allyl and methallyl chlorides and α -methylstyrene. Isomerization of olefins accompanies the exchange reaction. A mechanism to explain these data is postulated.

From the addition of silicon hydrides to olefins in the presence of platinum catalysts unexpected adducts were recognized¹ when methyl-*n*-pentylchlorosilane was the only adduct of methylchlorosilane to pentene-2. A tendency to form primary alkylsilanes from non-terminal olefins is common to a variety of silicon hydrides.² Isomerization of olefins occurred during these reactions. Each of the methylbutenes² and methylcyclohexenes^{3,4} form more than one adduct. Recent work⁵ indicates that olefins tend to form thermodynamic mixtures of isomers without change in their carbon skeletons during these addition reactions.

Benkeser⁶ and co-workers showed that the addition of trichlorosilane to acetylenes is a *cis* addition in the presence of either platinum-on-carbon or chloroplatinic acid, and more recently Selin and West⁴ found that addition of trichlorosilane to the ring of 1-methylcyclohexene proceeded in a stereospecific *cis* manner in the presence of chloroplatinic acid. In an effort to determine how these phenomena are the result of the catalyzed addition of silicon hydrides to olefins, a series of experiments was undertaken in which trichlorosilane-*d* was added to a variety of olefins in the presence of chloroplatinic acid.

Isobutylene was the chosen olefin because both it and isobutyltrichlorosilane have H^1 n.m.r. spectra that are easy to interpret. The reaction proceeded readily at room temperature and made no by-products. Excess trichlorosilane-*d*, with isobutylene and chloroplatinic acid, was sealed into a glass tube and held at 25° overnight. A noticeable shrinkage of the liquid volume in the tube indicated that the reaction was complete within an hour. Analysis indicated changes summed up by the equation



(1) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(2) J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

(3) J. C. Saam and J. L. Speier, *ibid.*, **83**, 1351 (1961).

(4) T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

(5) M. C. Musolf, work to be forthcoming from this laboratory.

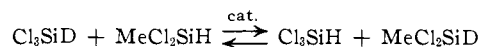
(6) R. A. Benkeser, M. L. Burruss, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).

The excess trichlorosilane was removed by distillation and analyzed by infrared. Both the Si-H and the Si-D bonds have very strong absorption maxima, the former at 2258 cm^{-1} and the latter at 1645 cm^{-1} . The recovered silane was approximately 60% Cl_3SiH and 40% Cl_3SiD . The adduct was examined by comparison of its H^1 n.m.r. spectrum with that of undeuterated isobutyltrichlorosilane. The tertiary position in the isobutyl group was more than 70% deuterated and deuterium was also found in every other possible position so that an average of 2.5 D's per molecule was present.

This deuterated product was sealed into a tube with octene-1, excess trichlorosilane, and catalyst and heated 4 hr. at 100°. Octyltrichlorosilane was made as expected, but the recovered trichlorosilane was entirely free of deuterium. No Si-H, C-D exchange had occurred. From this we conclude that the result of the first experiment could not be due to exchange between trichlorosilane-*d* and isobutyltrichlorosilane, but that exchange occurred before the latter compound was made. Excess isobutylene, trichlorosilane-*d*, and catalyst were heated in a sealed tube. In this case isobutylene was recovered, passed through a tube of pellets of sodium hydroxide to remove traces of silanes, and analyzed by infrared, which revealed an absorption maximum at 2200 cm^{-1} assigned to a C-D bond.

A series of olefins was studied in the same manner and the results are found in Table I.

A separate experiment is of pertinence with these data. Chloroplatinic acid was found to be an efficient catalyst for exchange between trichlorosilane-*d* and methylchlorosilane.



In the absence of the catalyst there was no exchange during many hours at 100°, but a trace of chloroplatinic acid caused exchange at room temperature.

These data can be rationalized as being the results of a series of reactions differing somewhat from previous schemes^{3,6} but nevertheless having much in common with them. All of these reactions appear to be examples of homogeneous catalysis. No precipitates were observable. The catalyst responsible for the reactions may plausibly be a lower valence form of platinum