

methyl ether of phenylferrocenylmethanol (III, R = CH<sub>3</sub>) was obtained, m.p. 111–112°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>OFe: C, 70.59; H, 5.88; active H, 0.0. Found: C, 70.26; H, 5.20; active H, 0.0.

The infrared spectrum showed absorption of aliphatic C–H at 2880, 2930 and 2970, phenyl absorption at 1492 and 1559, absorption of unsubstituted ferrocene rings at 1104 and very strong ether absorption at 1063 cm.<sup>-1</sup>.

**Isopropyl Ether of Phenylferrocenylmethanol (III, R = *i*-Pr).**—Benzoylferrocene (1 g.) was reduced by the method of Meerwein-Ponndorf-Verley.<sup>17</sup> The hydrolyzed reaction mixture was extracted with benzene, the solvent removed and the mixture extracted with Skellysolve B and chromatographed on alumina with methanol. In addition to a small amount of the methyl ether of phenylferrocenylmethanol, there was isolated 0.35 g. (33%) of yellow crystals of the isopropyl ether, m.p. 74–75°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>20</sub>OFe: C, 72.07; H, 6.31. Found: C, 71.24; H, 6.81.

The infrared spectrum showed absorption in the aliphatic C–H region at 2880, 2930 and 2970, phenyl absorption at 1492, 1540 and 1559, absorption of unsubstituted ferrocene rings at 1104 and very strong ether absorption at 1063 cm.<sup>-1</sup>.

Like the carbinol and the methyl ether, the isopropyl ether is soluble in concentrated hydrochloric acid.

**Reduction of Monobenzoylferrocene by Sodium.**—To 0.25 g. of monobenzoylferrocene in 3 ml. of benzene was added 2.5 g. of 5% sodium amalgam. The mixture was

(17) A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

refluxed 2 hr., poured into water and filtered. The organic layer was washed, dried and chromatographed on alumina. Evaporation of solvent from the eluted yellow band, just preceding the large red band of unreacted monobenzoylferrocene, left 35 mg. of orange yellow powder, 150–170° dec. (180–185° red droplets). This substance is believed to be phenyldiferrocenylmethanol (IX). Infrared absorption was found at 3520 (OH), 1492 and 1600 (phenyl) and 1107 cm.<sup>-1</sup> (ferrocenyl).

*Anal.* Calcd. for C<sub>27</sub>H<sub>24</sub>OFe<sub>2</sub>: C, 68.05; H, 5.04; active H, 0.21. Found: C, 68.44; H, 5.11; active H, 0.36.

This compound was dissolved in 95% ethanol by refluxing for 15 min. Excess zinc dust was added, then alternately, small amounts of hydrochloric acid and zinc dust till most of the color was gone from the solution. The mixture was filtered, washed, dried, extracted with benzene and the solvent evaporated. The residue was extracted with hexane and chromatographed on alumina in that solvent, yielding a yellow solid with an infrared spectrum identical to that of phenyldiferrocenylmethane (VI).

A 30-mg. sample of the hydroxy compound was refluxed with methanol for 7.5 hr. Evaporation of the methanol yielded crystals which were purified by chromatography on alumina. The resulting product 28 mg., m.p. 158° dec., is presumably the methyl ether of IX. Its infrared spectra showed peaks at 2920, 2820, 1554, 1494, 1106 and a high absorption, indicative of ethers, at 1076 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>28</sub>H<sub>26</sub>OFe<sub>2</sub>: C, 68.55; H, 5.31. Found: C, 69.41; H, 5.59.

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE PLASTICS LABORATORY, PRINCETON UNIVERSITY]

## Reductive Cleavage of Ferrocene<sup>1</sup>

BY DANIEL S. TRIFAN AND LOUIS NICHOLAS

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In contrast to the extreme resistance of ferrocene to catalytic reduction, this aromatic ring system is reduced readily by lithium in ethylamine with cleavage of the molecule to metallic iron and cyclopentadiene. The reaction of lithium with ferrocene in ethylamine is very rapid and may be stopped after several minutes with good conversion. Qualitative experiments have ascertained that other metal-amine, ammonia combinations also similarly reduce ferrocene.

No method has yet been described for a mild controlled degradation of the ferrocene ring system (bis-cyclopentadienyl iron, Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>) suitable for structure assignments for isomeric substituted ferrocenes. In this investigation a convenient degradation procedure was sought which would effect cleavage of the ferrocene molecule into its component parts and permit separate examination of each of the resulting 5-carbon rings.

The catalytic hydrogenation route to dearomatization and collapse of the ferrocene molecule appears to be unsuccessful. The resistance of ferrocene to catalytic hydrogenation over platinum has been reported by Woodward, Rosenblum and Whiting.<sup>2</sup> Our own attempts to hydrogenate ferrocene using the more active 5% rhodium-on-alumina in acetic acid for periods up to several weeks have given similar negative results. Under these same conditions benzene is completely hy-

drogenated in 5 minutes. Fischer<sup>3</sup> also has reported failure to hydrogenate ferrocene with Raney nickel in alcohol at 150° and 150 atmospheres.<sup>4</sup>

As a means of transferring an electron to the ferrocene nucleus to dearomatize the molecule, the use of alkali metals was investigated. Lithium does not attack ferrocene in refluxing ether, benzene or toluene, although attack does occur at ca. 200° in mineral oil with formation of metallic iron. In contrast to these slow heterogeneous reactions, however, rapid cleavage of the ferrocene molecule into metallic iron and cyclopentadiene is obtained by use of lithium in ethylamine, the amine functioning as solvent for lithium atoms. This reducing system has been investigated by Benkeser and co-workers in connection with benzenoid aromatic compounds.<sup>5</sup>

(3) E. O. Fischer, *Angew. Chem.*, **67**, 475 (1955).

(4) ADDED IN PROOF.—We have recently noted the interesting publication of A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina and N. A. Simukova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 749 (1956), in which these investigators report the first successful catalytic hydrogenation of ferrocene and several of its derivatives using Raney nickel at 265–345° and 200–280 atmospheres.

(5) (a) R. A. Benkeser, R. E. Robinson, D. A. Sauve and O. H. Thomas, *THIS JOURNAL*, **76**, 631 (1954); **77**, 3230 (1955); (b) R. A. Benkeser, C. Arnold, R. F. Lambert and O. H. Thomas, *ibid.*, **77**, 6042 (1955).

(1) This research was supported jointly by the Army, Navy and Air Force under Signal Corps Contract No. DA-36-039SC-42633. Most of this material was submitted in preliminary form in August, 1955, and presented before the Division of Organic Chemistry, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(2) R. B. Woodward, M. Rosenblum and M. C. Whiting, *THIS JOURNAL*, **74**, 3458 (1952).

A series of qualitative experiments summarized in Table I has been carried out to indicate the generality of ferrocene reduction by other alkali and alkaline earth metal-amine, ammonia combinations. The progress of the reaction was followed by the rate of reflux and the appearance of black metallic iron. Rates are substantially lower with sodium than with lithium, and lower in *n*-hexylamine than in ethylamine. Calcium-amine combinations give no reaction. In liquid ammonia, however, reductions with calcium, lithium and sodium are all vigorous. The lithium-ethylamine combination appears to be the most convenient and has therefore been selected for use in quantitative studies.

TABLE I

QUALITATIVE RATES OF REDUCTION OF FERROCENE		
Metal	Amine	Description of initial reaction
Li	Ethylamine	Vigorous reaction, black iron
Na	Ethylamine	Gradual appearance of black iron; much slower than Li
Ca	Ethylamine	No reaction
Mg	Ethylamine	No reaction
Li	<i>n</i> -Hexylamine	Gradual appearance of black iron; slower than Na-ethylamine
Na	<i>n</i> -Hexylamine	Some darkening only after ca. 0.5 hr.
Ca	<i>n</i> -Hexylamine	No reaction even at b.p.
Li	Liq. NH <sub>3</sub>	Vigorous reaction, black iron
Na	Liq. NH <sub>3</sub>	Vigorous reaction, black iron
Ca	Liq. NH <sub>3</sub>	Very vigorous reaction, black iron
Mg	Liq. NH <sub>3</sub>	No reaction

When these results are compared with data on the reaction of sodium with various aromatic hydrocarbons, it may be estimated that in the series of aromatic compounds of increasing electron affinity: benzene  $\ll$  phenanthrene  $<$  naphthalene  $<$  anthracene, etc.,<sup>6</sup> ferrocene is closer to benzene than to other members of this series, although in view of the very much more rapid reaction of lithium-ethylamine with ferrocene than with benzene it would seem to be higher. Reaction periods of 8-10 hours are employed for the latter<sup>4</sup> while reductions of ferrocene give good conversions in a few minutes.

A typical ferrocene reduction using lithium in ethylamine for a period of 4-6 minutes resulted in reduction of 73% of the initial ferrocene. The cyclopentadiene was isolated both by distillation (53%) and by its adduct with maleic anhydride (71%).

A reductive cleavage of ferrocene using the calcium-ammonia reducing system<sup>7</sup> in ether was also carried out for comparison purposes and a 30% yield of cyclopentadiene, corrected for recovered ferrocene, was obtained as the maleic anhydride adduct. This procedure is much less convenient than that using lithium-ethylamine and no attempt was made to improve this yield.

The elemental iron produced in these ferrocene reduction reactions is very finely divided and when allowed to dry in air spontaneously oxidizes to a mixture of oxides. The yield of iron (98%) was

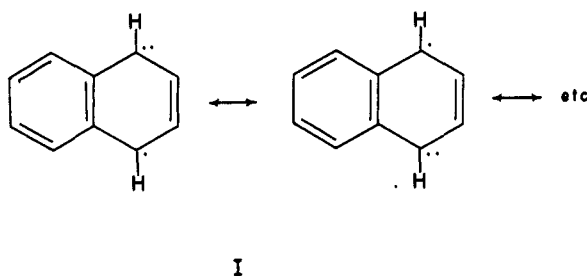
(6) D. E. Paul, D. Lipkin and S. I. Wiseman, *THIS JOURNAL*, **78**, 116 (1956).

(7) B. A. Kazanskii and N. F. Glushnev, *J. Gen. Chem. (U.S.S.R.)*, **8**, 642 (1938); *C. A.*, **33**, 1260 (1939).

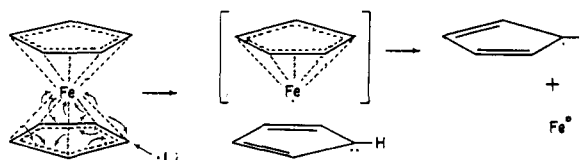
therefore determined by solution in dilute sulfuric acid and titration of ferrous ion. In a semi-quantitative run designed to verify the elemental state of the initial iron product, the volume of hydrogen produced from the acidification of the reaction mixture corresponded roughly to that calculated from the amount of ferrocene reduced.<sup>8</sup>

The finely divided iron obtained from a single run with sodium-ethylamine was pyrophoric and more reactive than that from lithium-ethylamine, probably because of a larger amount of adsorbed hydrogen in the former case due to the more rapid rate of hydrogen evolution.

The cleavage reaction proceeds by attack of lithium on carbon with transfer of an electron. Attack on the ferrocene aromatic system has different consequences from the parallel attack on benzenoid aromatic systems. In the latter case the  $\pi$ -electrons are displaced to give resonance-stabilized negative ion free radicals,<sup>5</sup> e.g., I, with no consequent molecular rupture.



Similarly, it seems reasonable to suggest that in the analogous instance of the attack of lithium on one of the 5-carbon rings of ferrocene, the  $\pi$ -electrons are displaced to the conjugated double bond orbitals, or more precisely directly to the resonance hybrid orbitals, of the cyclopentadienide ion with resulting detachment from the iron atom. The remaining radical fragment presumably separates into free iron and cyclopentadienyl radical, which in turn may abstract hydrogen from solvent or an electron from lithium.



It is interesting to note that the mass spectrograms of ferrocene<sup>9</sup> and ferrocene derivatives<sup>10</sup> exhibit a very strong peak at mass number 121, corresponding to the C<sub>5</sub>H<sub>5</sub>Fe fragment, which may be interpreted as evidence of some appreciable degree of stability of this cyclopentadienyl-iron entity.

The instability of the [(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> anion may be contrasted with the stability of the [(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>5</sub>)R]<sup>+</sup> cation which presumably is an intermediate in the Friedel-Crafts acylation reac-

(8) We are indebted to Alan R. Glueck of this Laboratory for these results.

(9) L. Friedman, A. P. Irsa and G. Wilkinson, *THIS JOURNAL*, **77** 3689 (1955).

(10) Unpublished results from this Laboratory.

tion. It may also be mentioned that the  $[(C_5H_5)_2Fe(C_6H_4)]^-$  anion, which readily is obtained<sup>11,12</sup> by exchange reaction with, *e.g.*, *n*-butyllithium, is an obviously stable system since the  $\pi$ -electrons are not involved, and may be utilized in synthesis of corresponding ferrocene derivatives.

This reductive cleavage reaction should prove general for analogous metallocene systems. In addition to degradative structure applications, the reaction also provides a novel approach to the preparation of certain substituted cyclopentadienes from the correspondingly substituted ferrocene derivatives. Some experiments directed toward this end are currently in progress.

### Experimental

**Ferrocene Reduction with Lithium in Ethylamine.**—Ferrocene cleavage runs were conducted in flasks with an 8 mm. bore stopcock at the bottom. Lithium wire (2 mm. diam.) was freshly extruded into the flask containing anhydrous ether which was drained through the stopcock just before the reaction was started. The flask was fitted with stirrer and a large capacity Dry Ice reflux condenser.

In a typical run, 29.39 g. of ferrocene was dissolved in 500 ml. of ethylamine (Matheson cylinder) and added to 21 g. of lithium wire from a dropping funnel. The reaction is very vigorous and a black suspension of iron immediately appears. A minimum addition period of *ca.* 2 min. was required to prevent flooding and after a total of 4–6 minutes, at the end of which time the vigorous refluxing abates, the reaction mixture and ethylamine rinse were drained from the excess lithium wire through the stopcock into 1500 ml. of ice-water mixture, diluted with benzene and filtered through Celite to remove iron. The aqueous phase was separated and extracted with numerous portions of benzene, followed by thorough washing of the benzene phase with water to remove ethylamine. The benzene solution was dried with magnesium sulfate and refluxed with 26.3 g. of maleic anhydride overnight. After the solution was concentrated and evaporated to dryness, the Diels–Alder adduct and excess maleic anhydride were hydrolyzed and extracted from unreduced ferrocene by treatment with portions of hot water. Fractional crystallization of the adduct acid, *endo-cis*-bicyclo[2,2,1]-5-heptene-2,3-dicarboxylic acid, from water yielded 25.78 g. (71% based on ferrocene reduced), m.p. 177.5–179°, lit.<sup>13</sup> 177–179°, mixed m.p. undepressed. A control run using cyclopentadiene and the same extraction and work-up procedure gave no better recovery.

A similar reduction was carried out using a reaction period of 6.5 hours during which time almost all of the lithium wire dissolved. However, only 32.8% (12.19 g.) of the theoretical amount of adduct acid was obtained under these conditions, possibly because of further reduction of the cyclopentadiene initial product.<sup>4</sup>

From a typical rapid reduction of ferrocene, as described above, cyclopentadiene also was isolated directly, although in poorer yield. Ferrocene (37.2 g.) in 300 ml. of ethylamine was allowed to react with 18 g. of lithium strips for 3 minutes and the black mixture was poured into ice. The volatile material was condensed into receivers cooled in Dry Ice at aspirator pressure and distilled. A hydrocarbon layer was separated from ethylamine by addition of water to several combined fractions and dried over CaSO<sub>4</sub> (11.2 g. of cyclopentadiene, 53% corrected for 7.4 g. of recovered ferrocene). The cyclopentadiene was identified as the maleic anhydride adduct, a 1.0-g. sample yielding 1.8 g. (72%) of the crude adduct, m.p. 161–163.5° unrecrystallized, lit.<sup>11</sup> 164–165°.

Delayed addition of the ferrocene after the lithium has entirely reacted with the ethylamine results in complete recovery of the ferrocene.

**Characterization of Iron from Ferrocene Reductions.**—Because of the spontaneous oxidation of the finely divided iron when dry, the yield of iron obtained from a ferrocene

reduction was determined by adding the product of a reaction to a mixture of dilute sulfuric acid and ice. Titration of the aqueous phase with 0.1 *N* KMnO<sub>4</sub>, after extraction with CCl<sub>4</sub> to remove cyclopentadiene, indicated 98% of the theoretical amount of ferrous ion.

The elementary state of the iron was verified by a semi-quantitative determination of hydrogen evolved from acidification of a reaction mixture.<sup>7</sup> The product from a typical reduction was transferred to an empty flask and most of the ethylamine swept out in a stream of helium. Dilute sulfuric acid was then added through a dropping funnel and the hydrogen collected in an inverted graduate, the estimated corrected volume corresponding to *ca.* 90% of the calculated amount.

The finely divided iron can be collected and rinsed with solvent but it immediately begins to oxidize to FeO, Fe<sub>2</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, turning from black to brown. Both the moist black and brown materials are characteristically magnetic.

In a single ferrocene cleavage (15 g.) the sodium–ethylamine combination was employed and the slower reaction allowed to continue for 50 minutes. The cyclopentadiene was not isolated, but the iron produced under these conditions was more reactive upon drying and oxidized in air with incandescence. Extreme precautions were required to avoid explosion.

X-Ray diffraction using a North American Philips Geiger-counter spectrometer was employed in the characterization of the iron and iron oxides obtained from this reaction. Freshly prepared iron samples were protected as well as possible from oxygen with either mineral oil (Nujol) or 2% Duco cement in acetone during filtration and measurement but it was still not possible because of the highly active surface to avoid the appearance of peaks corresponding to FeO, Fe<sub>2</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, *e.g.*, using Fe K $\alpha$  radiation,  $2\theta = 45.9^\circ, 53.5^\circ; 38.1^\circ, 54.9^\circ, 73.6^\circ; 45.2^\circ, 52.2^\circ$ , respectively. Of those samples most carefully protected the FeO peak at 45.9° was the most prominent oxide peak, while a sample which had been allowed to oxidize as completely as possible in air had its strongest peak at 45.2° (Fe<sub>2</sub>O<sub>3</sub>).

Although very weak Fe peaks at 57.0°, 85.4° and 102.2° could sometimes be detected with carefully protected samples, the results were not analytically satisfactory and the weak peaks may be due either to amorphous structure or particle size of the iron, where the oxides are either less critically dependent on particle size or have aggregated during oxidation. Finely divided iron similarly prepared by ferric chloride reduction with lithium in ethylamine showed the same weak Fe and various oxide peaks.

**Ferrocene Reduction with Calcium in Ammonia.**—Several preliminary qualitative tests showed that the reaction of ferrocene with calcium in ammonia was very vigorous and required caution. Ferrocene (30 g.) was dissolved in 500 ml. of anhydrous ether in a flask fitted with a large Dry Ice condenser. Calcium turnings (50 g.) were added and anhydrous ammonia was introduced very slowly with stirring until *ca.* 200–300 ml. of ammonia had been condensed, the addition being interrupted several times when the reaction appeared to increase in rate. Evidence of reaction appeared shortly after introduction of ammonia by the darkening of the calcium and appearance of black iron particles. Additional ether (200 ml.) was added to the cold reaction flask to further dissolve some of the precipitated ferrocene. After 5 hours, during which time a considerable increase in the amount of black suspension had developed, the condenser was filled with ice and the flask was warmed with tap water to allow escape of ammonia.

When the contents were at room temperature, 150 ml. of water was added cautiously from a dropping funnel. The ether phase was decanted from the calcium hydroxide–iron residue and the latter was extracted with numerous portions of benzene until colorless. The combined ether–benzene layer was washed with water to remove ammonia, dried with magnesium sulfate and refluxed with 26.3 g. of maleic anhydride overnight. After the solution was concentrated and evaporated to dryness, the adduct acid was separated from unreduced ferrocene (22.17 g.) by crystallization from water to yield 4.79 g. (30.3%) of recrystallized adduct acid. The presence of iron in the extracted residue was confirmed with a magnet test.

**Ferrocene Reduction with Lithium in Mineral Oil.**—Lithium sand was prepared by melting 10 g. of lithium in 150 ml. of mineral oil (Nujol) and cooling below the melting

(11) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and G. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954).

(12) R. A. Benkeser, D. Goggin and G. Schroll, *This Journal*, **76**, 4925 (1954).

(13) O. Diels and K. Alder, *Ann.*, **460**, 112 (1925).

point while stirring at high speed. When the contents were at 100°, 3.0 g. of ferrocene was added and gradual heating resumed, using a protective helium atmosphere. Careful visual examination indicated no appreciable reaction until the temperature had reached ca. 190° at which time the lithium surface appeared to darken slightly and the presence of iron particles could be discerned by testing with a magnet. Heating was resumed and the temperature raised to 220° over a 10-minute period and then the mixture was allowed

to cool. By this time the lithium particles were very much darker and ca. 0.1 g. of magnetic black precipitate had settled to the bottom of the flask. After rinsing with solvent, the Fe-coated lithium sand adhered readily to the magnet. In the absence of lithium at these temperatures and in contact with air, no evidence of degradation could be observed.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Organic Chemistry of Ferrocene. I. The Acetylation of Dialkylferrocenes<sup>1</sup>

BY KENNETH L. RINEHART, JR., KAYE L. MOTZ AND SUNG MOON

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Acetylation of 1,1'-dimethylferrocene gives a 7 to 3 ratio of the 3- or  $\beta$ -acetyldialkylferrocene to the 2- or  $\alpha$ -acetyl isomer, while the ratio of the corresponding acetyldiisopropyl isomers obtained from acetylation of 1,1'-diisopropylferrocene is 9 to 2. The isomeric acetyldialkylferrocenes have been isolated, characterized by infrared and ultraviolet spectra and converted by oxidation to the corresponding carboxylic acids and by reduction to the corresponding alkyl derivatives. Dissociation constants of the isomeric dimethylferrocenecarboxylic acids and infrared spectra of the isomeric ethyldimethylferrocenes have been presented and discussed.

Since the initial report in 1951 of the isolation of ferrocene<sup>2,3</sup> and the discovery that the compound is, in many respects, an aromatic system,<sup>4</sup> there have been numerous chemical confirmations of the similarity of its chemistry to that of the classical benzenoid compounds and, indeed, the name ferrocene was chosen to indicate the compound's aromatic character.<sup>4</sup> Thus, for example, ferrocene may be acylated,<sup>4,5</sup> sulfonated,<sup>5,6</sup> metalated<sup>7,8</sup> and arylated by other aromatic nuclei.<sup>7,9-12</sup> On the other hand, in its resistance to alkylation<sup>5,13</sup> and its behavior toward oxidizing media<sup>14</sup> ferrocene shows marked differences from benzene. The present study has been undertaken as part of a general investigation of substituted ferrocenes and to investigate to what extent the normal directive effects of alkyl groups<sup>15</sup> are observed in the ferrocene system.

For this purpose the acylation reaction is particularly well adapted since it has been studied ex-

tensively in benzenoid systems and found to be highly selective in substitution at ring positions.<sup>16</sup> Further, acylation of ferrocenes leads to little or no degradation of the ring system and often gives products in high yields.<sup>5,17</sup> Previous investigations of acylations have shown similarities between ferrocene and benzene in that acylation may be accomplished under conditions employed for benzene<sup>4,5</sup> and also in that the presence of one acyl group on the ferrocene nucleus strongly deactivates the substituted ring toward further acylation<sup>4,18</sup> and to a certain extent deactivates the other ring as well.<sup>5,13,18</sup> By contrast, the presence of an alkyl group might be expected to activate somewhat the substituted ring toward acylation.<sup>19</sup>

In the present study the compounds investigated have been the 1,1'-dialkylferrocenes,<sup>20</sup> in which each ring bears a substituent alkyl group. Both 1,1'-dimethyl- (Ia) and 1,1'-diisopropylferrocene (Ib) have been examined in order to observe the differing effects of the methyl and isopropyl substituents and the response of acylation of the system toward increasing steric bulk on the rings.

Acetylation of either of these compounds can give substitution in the 2- or 3- ( $\alpha$ - or  $\beta$ -)<sup>21</sup> positions. If care is taken to prevent disubstitution, only two isomers are formed, 2-acetyl- (IIa,b) and 3-acetyl-1,1'-dialkylferrocenes (IIIa,b); measurement of the proportion of the two isomers leads to

(1) Presented in part at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 8 to 13, 1956; see Abstracts of Papers, p. 12-N.

(2) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(3) S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(4) R. B. Woodward, M. Rosenblum and M. C. Whiting, *THIS JOURNAL*, **74**, 3458 (1952).

(5) V. Weinmayr, *ibid.*, **77**, 3009 (1955).

(6) A. N. Nesmeyanov, XIVth International Congress of Pure and Applied Chemistry, Zurich, July 21-27, 1955; *cf.* Abstracts of Papers, p. 193.

(7) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk SSSR*, **97**, 459 (1954).

(8) R. A. Benkeser, D. Goggin and G. Schroll, *THIS JOURNAL*, **76**, 4025 (1954).

(9) A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *Doklady Akad. Nauk SSSR*, **99**, 539 (1954).

(10) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, *ibid.*, **102**, 535 (1955).

(11) G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

(12) V. Weinmayr, *THIS JOURNAL*, **77**, 3012 (1955).

(13) P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).

(14) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *THIS JOURNAL*, **74**, 2125 (1952).

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 236.

(16) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 333; H. C. Brown and W. H. Bonner, *THIS JOURNAL*, **76**, 605 (1954); R. Pajeau, *Bull. soc. chim. France*, 544 (1946).

(17) R. Riemschneider and D. Helm, *Chem. Ber.*, **89**, 155 (1956).

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

(19) Reference 15, pp. 245-256.

(20) K. L. Rinehart, Jr., Sung Moon and K. L. Motz, in preparation.

(21) The  $\alpha$ - $\beta$  nomenclature commonly employed in heterocyclic and condensed ring aromatic compounds seems preferable to any system based on an *ortho-meta-para* scheme. Confusion arises in the five-membered ring series since electronically there are probably two "para" positions and no "meta" position (*cf.*, below).<sup>11</sup>