

EXPERIMENTAL<sup>5</sup>

**Compounds of I<sub>A-E</sub> series.** In a wash bottle—tall form—fitted with a fritted aspirator plate was placed 0.15 mole of the pyrone with 30 ml. of trifluoroacetic acid. A 50–50 mixture of carbon monoxide and dry hydrogen chloride from a tank was bubbled fairly rapidly through the solution at room temperature for not less than 3 hr. Usually during the initial portion of the reaction period the mixture warmed up somewhat but as the pyrone dissolved the temperature decreased and the viscosity of the material increased to a thick sirup. At the termination of the reaction period the product was diluted with 100 ml. of water and chilled overnight in the freezing compartment of the refrigerator. The precipitate was suctioned off and dried in air. With compounds I<sub>A-C</sub> the crude material was recrystallized twice from absolute ethanol. However, for I<sub>D</sub> three recrystallizations from distilled water was necessary and I<sub>E</sub> was purified by recrystallizing it twice from heptane.

**Compounds of II<sub>A-D</sub> series.** A mixture consisting of 0.01 mole of the pyrone aldehyde, 0.01 mole of malonic acid, 5 drops of piperidine in 30 ml. of absolute ethanol was placed in a flask, protected from moisture, then immersed in a water bath at 80° for at least 5 hr. The solutions were then acidified with 10–15 drops of concentrated hydrochloric acid and chilled. The precipitates were recrystallized once from absolute ethanol. In the case of sample II<sub>D</sub> the alcoholic solution was acidified, 50 ml. of water added, and then heated to drive off some of the ethanol. Upon chilling, a chocolate-colored precipitate was obtained which was taken up in distilled water, decolorized with Norite, and then chilled to give colorless crystals.

(5) All analyses were by Dr. Carl Tiedeke and all melting points were determined on a Fisher-Johns melting point assembly.

**Reduction of I<sub>C</sub>.** Two grams of I<sub>C</sub> was dissolved in 50 ml. of ethanol and 4 g. of potassium borohydride was added. The reaction flask was stoppered with cotton and allowed to stand overnight, following which 10 ml. of concentrated hydrochloric acid was added and an additional 40 ml. of ethanol. The solution was heated, filtered while warm, and the solution evaporated to dryness over a steam bath to give a brown compound which was 2,3-bis(hydroxy-methyl)-5-hydroxy-4-pyrone, crude yield 1.4 g.

The material was recrystallized twice from ethanol; it softened above 164° and melted at 167°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>O<sub>5</sub>: C, 51.61; H, 5.42. Found: C, 51.90; H, 5.19.

**Bisformylation of  $\alpha$ -chloro- $\alpha$ -deoxykojic acid.** To 30 g. of  $\alpha$ -chloro- $\alpha$ -deoxy kojic acid in a wash bottle, described previously, 40 ml. of trifluoroacetic acid was added and the mixture of carbon monoxide–hydrogen chloride was bubbled in at a rapid rate for 6.5 hr. The solution was diluted with 200 ml. of water and chilled as previously stated; crude yield 21.3 g. Recrystallization of the compound three times from absolute ethanol gave a tan substance m.p. 165–166.5°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>7</sub>ClO<sub>5</sub>: C, 44.65; H, 2.32; Cl, 16.37. Found: C, 44.82; H, 2.52; Cl, 16.22.

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HOUSTON 4, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

## Acylation of Bisacetylferrocene with Esters by Potassium Amide to Form Bis- $\beta$ -diketones. Consideration of Mechanism<sup>1</sup>

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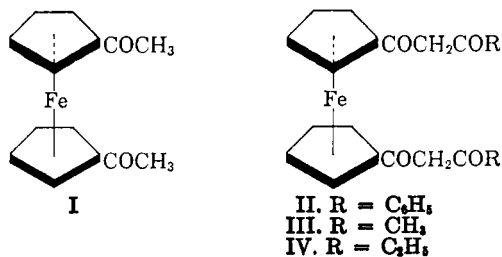
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Acylation at both of the methyl groups of bisacetylferrocene with esters by potassium amide in liquid ammonia to form bis- $\beta$ -diketones appears to be quite general. Unsuccessful attempts were made to isolate the corresponding mono- $\beta$ -diketones, which might be expected as intermediates. The bis- $\beta$ -diketones were allowed to react with an excess of hydrazine to form bis-pyrazoles. A mechanism for the diacylations is suggested.

It has recently been observed<sup>3</sup> that both of the methyl groups of bisacetylferrocene (I) can be benzoylated readily with methyl benzoate by means of potassium amide to form the bis- $\beta$ -diketone II in good yield.

It has now been found that I can similarly be acylated with ethyl acetate and ethyl propionate to form the bis- $\beta$ -diketones III and IV respectively.

Although mono- $\beta$ -diketones of type V might be expected to be formed as intermediates, no such



compound could be isolated either in the previous work or in the present investigation.

That the products isolated were the bis- $\beta$ -diketones II, III, and IV was supported not only by their analyses and molecular weight (for II),<sup>4</sup> but also by their infrared spectra, which showed

(1) Supported in part by the Office of Ordnance Research, U. S. Army.

(2) Esso Research and Engineering Company Fellow, 1957–1958.

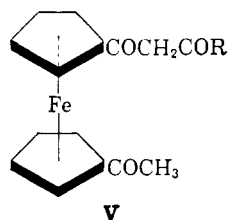
(3) C. R. Hauser and C. E. Cain, *J. Org. Chem.*, **23**, 1142 (1958).

TABLE I

YIELDS OF  $\beta$ -DIKETONES FROM BIS- AND MONOACETYLFERROCENES WITH ESTERS BY VARIOUS EQUIVALENTS OF POTASSIUM AMIDE

Expt. No.	Acetyl Ferrocene	$\text{KNH}_3$ Equiv.	Ester	Equiv.	Medium	Time, hr.	$\beta$ -Diketone	Yield, %	Recov., I or IX, %
1	Bis (I)	1	Methyl benzoate	1	Liq. $\text{NH}_3$ , then ether	5.5 <sup>a</sup>	II	0	95
2	Bis (I)	1	Ethyl acetate	1	Liq. $\text{NH}_3$ , then ether	3.5 <sup>a</sup>	III	0	88
3	Bis (I)	2	Methyl benzoate	1	Liq. $\text{NH}_3$ , then ether	8.5 <sup>a,d</sup>	II	20	67
4	Bis (I)	2	Methyl benzoate	2	Liq. $\text{NH}_3$ , then ether	6.5 <sup>a,d</sup>	II	46	45
5	Bis (I)	2	Methyl benzoate	2	Liq. $\text{NH}_3$	0.33	II	—	83
6	Bis (I)	2	Ethyl acetate	1	Liq. $\text{NH}_3$ , then ether <sup>b</sup>	4.5 <sup>a</sup>	III	45-50	—
7	Bis (I)	4	Methyl benzoate	4	Liq. $\text{NH}_3$	0.33	II	10	82
8	Bis (I)	4	Methyl benzoate	4	Liq. $\text{NH}_3$	1.0	II	35	39
9	Bis (I)	4	Methyl benzoate	4	Liq. $\text{NH}_3$	5.0	II	72	—
10	Bis (I)	4	Methyl benzoate	4	Liq. $\text{NH}_3$ , then ether	4.5 <sup>a,d</sup>	II	62	20
11	Bis (I)	4	Ethyl acetate	4	Liq. $\text{NH}_3$	0.33	III	—	85
12	Bis (I)	4	Ethyl acetate	4	Liq. $\text{NH}_3$ , then ether	1.25 <sup>a,c</sup>	III	72	9
13	Bis (I)	4	Ethyl propionate	4	Liq. $\text{NH}_3$ , then ether	1.25 <sup>a,c</sup>	IV	50	23
14	Mono (IX)	1	Methyl benzoate	1	Liq. $\text{NH}_3$	—	X	29	—
15	Mono (IX)	1	Ethyl acetate	1	Liq. $\text{NH}_3$	1.5	XI	25	—
16	Mono (IX)	2	Methyl benzoate	2	Liq. $\text{NH}_3$ , then ether	1.5 <sup>a,e</sup>	X	58-63	—
17	Mono (IX)	2	Ethyl acetate	2	Liq. $\text{NH}_3$ , then ether	1.5 <sup>a</sup>	XI	54-66	—
18	Mono (IX)	2	Methyl benzoate	2	Liq. $\text{NH}_3$	1.0	X	45	—

<sup>a</sup> The time in liquid ammonia was about 45 min., the remainder being in ether. <sup>b</sup> Ether at reflux for 4 hr. <sup>c</sup> Ether at reflux for 0.25 hr. <sup>d</sup> Ref. 3. <sup>e</sup> Ref. 10.



strong, broad bands in the region of 6.2–6.6  $\mu$  for their conjugate-chelate structures.<sup>5</sup> None of them gave a band in the region of 5.88–5.96  $\mu$  for a free carbonyl group,<sup>6</sup> which should have been present had the products been the mono- $\beta$ -diketones of type V. Bisacetylferrocene (I) shows such a band at 6.0  $\mu$ . Only II exhibited a band at 14.5  $\mu$  attributable to the monosubstituted benzene ring.<sup>7</sup>

Further support for the structures of the bis- $\beta$ -diketones II, III, and IV was their conversion to bispyrazoles VI, VII, and VIII respectively. The analyses of these products showed no oxygen,

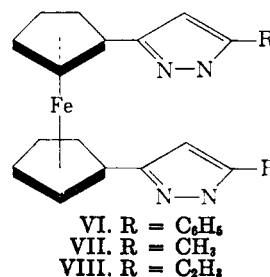
(4) This molecular weight, which was not reported in Ref. 3, was determined by Dr. Carl Tiedcke, Laboratory of Microchemistry, Teaneck, N. J. Calcd. for  $\text{C}_{28}\text{H}_{22}\text{FeO}_4$ , 478. Found: 440, 464, 458, 447. Average  $452 \pm 10\%$ .

(5) See L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley and Sons, New York, 1958, p. 142.

(6) See Ref. 5, page 137.

(7) See Ref. 8, page 76.

some of which would have been present had they been pyrazoles of mono- $\beta$ -diketones of type V.



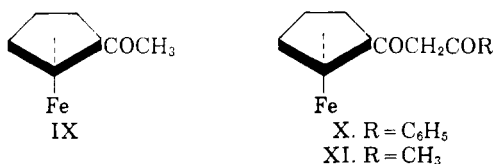
The infrared spectra of these products were very similar to one another. They showed bands in the regions considered characteristic of the pyrazole ring<sup>8</sup> except in the region of 10.7  $\mu$ .<sup>9</sup>

In Table I are summarized the yields of bis- $\beta$ -diketones II, III, and IV obtained from I under various conditions. Also in this table are given, for comparison, some results on the benzylation and acetylation of mono-acetylferrocene (IX) to form mono- $\beta$ -diketones X and XI respectively. While the benzylation of IX with potassium amide has

(8) See C. S. Rondestvedt and P. K. Chang, *J. Am. Chem. Soc.*, **77**, 6532 (1955).

(9) See P. Mirone and M. Vampiri, *Atti. acad. nazl. Lincei., Rend., Classe sci. fis., mat. e nat.*, **12**, 583 (1952); *Chem. Abstr.*, **46**, 9423 (1952).

previously been described<sup>10</sup> the acetylation with this reagent has apparently not been reported earlier.



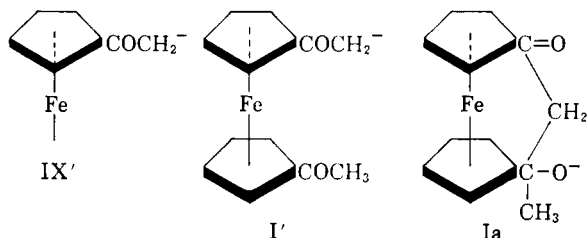
It can be seen from Table I that the best yields of bis- $\beta$ -diketones II, III, and IV were obtained employing four molecular equivalents each of potassium amide and appropriate ester to one of bisacetylferrocene (I) (Experiments 8, 10, 12, and 13). These proportions of reactants correspond to the use of two molecular equivalents each of an alkali amide and ester to one of a monoketone such as IX as recommended when the yield is to be based on the ketone.<sup>11</sup>

Whereas the acylation of ordinary monoketones have generally been effected in ether,<sup>11</sup> those of bis- and monoacetylferrocenes were initiated in a mixture of liquid ammonia and ether, and completed either in this medium or in ether after replacing the ammonia by the latter solvent (see Table I).

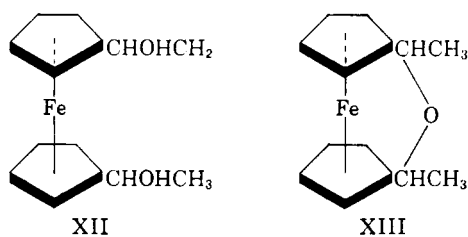
Attempts to stop the benzoylation and acetylation of bisacetylferrocene (I) at the monoacylation stage V were unsuccessful. These attempts included the neutralization of the reaction mixture before the acylation was complete and the use of less of the alkali amide and ester than that required for maximum yield. In all such experiments, only the bis- $\beta$ -diketone was isolated and/or the starting bisacetylferrocene was recovered (see experiments 1, 2, 3, 4, 5, 6, 7, 9, and 11). For example, when the reaction of I with four equivalents each of potassium amide and methyl benzoate in liquid ammonia was stopped after twenty minutes or one hour (experiments 7 and 8) the only product that could be isolated was the bis- $\beta$ -diketone II and much of the starting bisacetylferrocene (I) was recovered. Moreover, in experiment 8 the crude, recovered I appeared not to be contaminated with any  $\beta$ -diketone as determined by an infrared spectrum (no band in the 6.1–6.5  $\mu$  region). Similarly when the benzoylation of I was effected with two equivalents of the alkali amide and one or two equivalents of the methyl benzoate (experiments 3 and 4), the only product isolated was II, much of I being recovered. From these results it may be concluded that the second acyl group is introduced into the molecule more readily than the first.

It can further be seen from Table I that one equivalent of potassium amide failed to effect the benzoylation or acetylation of the diketone I (experiments 1 and 2), whereas this amount of reagent

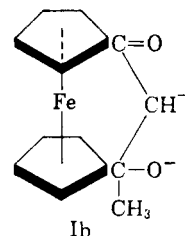
brought about considerable acylation of the monoketone IX (experiments 14 and 15). Even an excess of sodium methoxide has failed to effect the benzoylation of I<sup>3</sup>, although this reagent has been reported to bring about the acetylation of IX to form XI in 29% yield.<sup>12</sup> As the reactive intermediate of IX is presumably monocarbanion IX', the failure of I to be acylated by an equivalent of the alkali amide indicates that the corresponding monocarbanion I' is not present in appreciable concentration. Instead I' is suggested to undergo intramolecular cyclization to form the anion Ia, which might not be expected to be acylated under the conditions employed.



There is evidence that the two groups of certain bis derivatives of ferrocene have a "cis" configuration<sup>13</sup> as would be required for the formation of Ia. Moreover there is only a low energy barrier to rotation in this type of molecule.<sup>14,15</sup> In this connection, we have observed that the bisglycol XII readily undergoes an acid-catalyzed dehydration in refluxing ethanol-water to form cyclic ether XIII.<sup>16</sup>



As two or more equivalents of potassium amide effects the acylation of I (see Table I), this amount of reagent evidently produces an intermediate carbanion which, on the assumption that the monoanion has cyclic structure Ia, would presumably be Ib.



(12) V. Weinmayr, *Naturwiss*, **45**, 311 (1958).

(13) See D. A. Semenov and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 2741 (1957).

(14) See M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

(15) See Yu. T. Struchkov, *Zhur. Obschchei Khim.*, **27**, 2039 (1957).

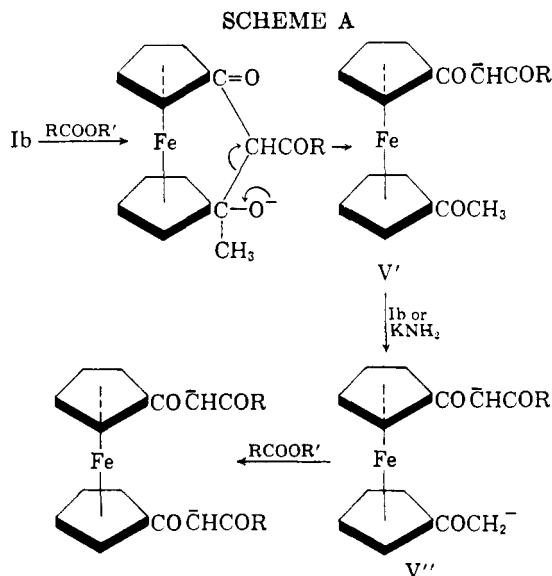
(16) The details of this reaction will be published later.

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

(11) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 114, 122 (1954).

Some support for the formation of such a carbanion with two equivalents of the reagent but not with one is the observation that the addition of one equivalent of the reagent to an orange-red suspension of I in liquid ammonia produced no color change, whereas the addition of a second equivalent gave a dark, brown-red mixture. Step-wise neutralization of the reaction mixture with ammonium chloride reversed these color changes, and 88% of I was recovered. On the other hand, the addition of one equivalent of the reagent to a brown-red solution of monoacetylferrocene (IX) in liquid ammonia produced a brown-yellow mixture indicating the formation of a carbanion. This color change was reversed on adding an equivalent of ammonium chloride.

The acylation of carbanion Ib with an ester to form the dianion of bis- $\beta$ -diketone II, III, or IV is suggested to follow the course outlined in Scheme A.



According to Scheme A, the first acylation occurs at a carbanion of a methylene ketone (Ib) and the second acylation, at the carbanion of a methyl ketone (V'). As methyl ketones are known to undergo acylation more readily than similar methylene ketones,<sup>17</sup> Scheme A is in line with the conclusion drawn above that the second acyl group is introduced into the bisacetylferrocene molecule more readily than the first. The more rapid introduction of the second acyl group might be favored by a greater solubility of the dipotassio salt of dicarbanion V'' compared to that of the dipotassio salt of dianion Ib and possibly also by the isomerization of "cis" dianion V'' to the "trans" configuration because of repulsion between the negative charges on the two side-chains.

(17) See Ref. 11, p. 69.

## EXPERIMENTAL<sup>18</sup>

*Acylation of bisacetylferrocene (I) to form bis- $\beta$ -diketones.* The results under various conditions are summarized in Table I, the yields of products being based on essentially pure compounds. The experiments employing 4 equivalents each of the reagent and ester, which produced the best yields, are described below.

*A. With methyl benzoate to form II.* This reaction has previously been initiated in a mixture of liquid ammonia and ether but completed in ether alone. It has now been effected entirely in a mixture of liquid ammonia and ether as described below.

To a stirred solution of 0.1 mole of potassium amide in 300 ml. of liquid ammonia<sup>19</sup> was added 6.8 g. (0.025 mole) of bisacetylferrocene (I). The resulting yellow suspension was stirred for 30 min., and 13.6 g. (0.1 mole) of methyl benzoate in 100 ml. of dry ether was added dropwise. The resulting red-brown suspension was stirred in liquid ammonia for 5 hr. and then neutralized with an excess of ammonium chloride. The ammonia was replaced with ether on the steam bath, and the resulting ethereal suspension was filtered. The dark red bis- $\beta$ -diketone II on the funnel was washed thoroughly with ether followed by water. It melted at 208–210° and, after recrystallization from acetone at 212–214°; reported m.p. 213.5–214°.<sup>3</sup> The yield was 8.7 g. (72%). Some infrared bands occurred at 6.2, 6.35, 6.75, 7.75, and 14.5  $\mu$ .

*B. With ethyl acetate to form III.* To a rapidly stirred solution of 0.1 mole of potassium amide in 250 ml. of liquid ammonia<sup>19</sup> was added 6.8 g. (0.025 mole) of I, followed after 30 min., by 8.8 (0.1 mole) of ethyl acetate in 150 ml. of anhydrous ether. The resulting red suspension was stirred for 1 hr., and the ammonia was then evaporated as 300 ml. of anhydrous ether was added. After stirring for about 25 min., the ethereal suspension was filtered, and the red solid on the funnel was washed thoroughly with ether. The solid (presumably the dipotassio salt of bis- $\beta$ -diketone III) was dissolved in 150 ml. of water, and the solution was acidified with concentrated hydrochloric acid to pH 4. The resulting precipitate was collected and recrystallized from chloroform-hexane to give 6.3 g. (72%) of bis-acetyl- $\beta$ -diketone III as small red crystals, m.p. 142.5–144°. Some infrared bands occurred at 6.2, 6.4, 6.5, 6.8, 7.4, and 7.75  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{Fe}$ : C, 61.04; H, 5.12; Fe, 15.77. Found: C, 60.94; H, 4.87; Fe, 15.99.

*C. With ethyl propionate to form IV.* This acylation was effected essentially as described above for III, employing 0.2 mole of potassium amide<sup>19</sup> in 250 ml. of liquid ammonia, 0.05 mole of I, and 0.2 mole of ethyl propionate in 100 ml. of ether. There was obtained 9.5 g. (50%) of bis-propionyl- $\beta$ -diketone IV as fine, red crystals, m.p. 114–115.5°. Some infrared bands occurred at 6.3, 6.6, 6.8, and 7.4  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{22}\text{O}_4\text{Fe}$ : C, 62.84; H, 5.80; Fe, 14.62. Found: C, 62.89; H, 5.82; Fe, 15.37.

*Acylation of monoacetylferrocene (IX) to form mono- $\beta$ -diketones.* The results of the benzoylation are reported in Table I. The acetylation was carried out as described below.

To a rapidly stirred solution of 0.11 mole of potassium amide<sup>19</sup> in 300 ml. of liquid ammonia was added 12.5 g. (0.055 mole) of monoacetylferrocene. The resulting yellow suspension was stirred for 15 minutes and 9.7 g. (0.11 mole) of ethyl acetate in 150 ml. of dry ether was added dropwise to produce a red suspension. After 1 hr. an excess of ammonium chloride was added, and the ammonia replaced with dry ether. The mixture was filtered and the ethereal filtrate was shaken with an excess of saturated copper acetate solution to produce an orange-red solid. The mixture was

(18) Melting points are uncorrected. Analyses are by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Model 21 recording spectrophotometer.

(19) See C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

filtered, and the solid was washed well with water followed by ether. This solid was shaken with 15% hydrochloric acid to give 9.6 g. (60%) of monoacetyl- $\beta$ -diketone XI as red crystals; after recrystallization from hexane the compound melted at 97–97.5°, reported<sup>13,20</sup> m.p. 96–97°.

*Anal.* Calcd. for  $C_{14}H_{14}FeO_2$ : C, 62.25; H, 5.22. Found: C, 62.67; H, 5.30.

*Cyclizations of bis- $\beta$ -diketones with hydrazine to form pyrazoles.* Pyrazole VI was prepared as previously described.<sup>3</sup>

To a solution of 1 g. of bis- $\beta$ -diketones III or IV in 200 ml. of absolute ethanol was added 10 g. of 95% hydrazine in 20 ml. of absolute ethanol to produce a deep red color. After

adding 1 drop of glacial acetic acid, the solution was boiled for a few minutes. The resulting bright-red solution was cooled overnight in the refrigerator.

Pyrazole VII was obtained in 89% yield as a pink powder, m.p. 300° dec. Some infrared bands occurred at 6.3, 6.85, 7.28, 7.7, and 8.65  $\mu$ .

*Anal.* Calcd. for  $C_{18}H_{18}N_4Fe$ : C, 62.44; H, 5.24; N, 16.18; Fe, 16.13. Found: C, 62.04; H, 5.41; N, 16.16; Fe, 16.38.

Pyrazole VIII was obtained in 99% yield as a pink powder, m.p. 300° dec. Some infrared bands occurred at 6.25, 6.35, 6.85, 7.25, 7.7, and 8.62  $\mu$ .

*Anal.* Calcd. for  $C_{20}H_{22}N_4Fe$ : C, 64.18; H, 5.93; N, 14.97; Fe, 14.92. Found: C, 64.18; N, 15.01; Fe, 14.96.

(20) See L. Wolf and M. Beer, *Naturwiss.*, **44**, 442 (1957).

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

## Ferrocenyl and 1,1'-Ferrocenylene Grignard Reagents<sup>1a</sup>

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Grignard reagents have been prepared by controlled reactions of magnesium with chloroferrocene, bromoferrocene, iodoferrocene, and 1,1'-dibromoferrocene, respectively, in tetrahydrofuran. Advantageous techniques involving methyl iodide and ethylene bromide have been developed. Ferrocenyl Grignard reagents decompose at elevated temperatures to give ferrocene and biferrocenyl; in the presence of cobaltous chloride, ferrocenylmagnesium bromide gives biferrocenyl in 80% conversion. These abnormal Grignard reactions apparently involve ferrocenyl radicals.

Lithio and sodioferrocenes are obtained by exchange of ferrocene with butyllithium<sup>2</sup> and phenyl- or amyl sodium,<sup>3</sup> respectively. These preparations often have disadvantages that mixtures of mono and dimetalloferrocenes are formed, and the excess metal alkyls or aryls required compete undesirably in many preparative sequences. Ferrocenyl Grignard reagents have not been previously described; efforts to prepare ferrocenylmagnesium iodide from iodoferrocene and magnesium in ethyl ether have been unsuccessful.<sup>4</sup> It is now reported that chloroferrocene, bromoferrocene, and iodoferrocene (Table I) react with magnesium powder in tetrahydrofuran under controlled conditions to give Grignard reagents in satisfactory yields. 1,1'-Dibromoferrocene has been converted to its di-Grignard reagent (59%). The yields of these reagents were determined by

carbonation and isolation of the resultant carboxylic acids. The potential utility of ferrocenyl Grignard reagents in synthesis is indicated by the present results in conjunction with the elegant methods for preparing bromo- and chloroferrocenes from lithioferrocenes and butyl borate and subsequent reaction of ferrocenylboronic acids with cupric halides.<sup>5</sup>

Reactions of haloferrocenes and magnesium to give Grignard reagents occur under oxygen-free nitrogen when initiated with methyl iodide; an attempt to use iodine as an initiator was unsuccessful. The relative reactivities of haloferrocenes are typical: iodo > bromo > chloro. The rates of reaction and conversions to Grignard reagents are increased by use of methyl iodide or ethylene bromide as entrainers (Table I). Methylmagnesium iodide does not undergo exchange with bromoferrocene under conditions for preparing the ferrocenyl Grignard reagent.

Haloferrocenes also react with magnesium in tetrahydrofuran to give biferrocenyl and ferrocene. Thus, reaction of iodoferrocene and magnesium at 25–30° for three hours in the presence of ethylene

(1)(a) Abstracted from a portion of the Ph.D. Dissertation of J. F. Helling, The Ohio State University, 1960.

(b) DuPont Company Fellow, 1958–1959; National Science Foundation Cooperative Fellow, 1959–1960. Present address, Chemistry Department, Massachusetts Institute of Technology, Cambridge, Mass.

(2)(a) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954). (b) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954).

(3)(a) A. N. Nesmeyanov, E. G. Perevalova, and Z. A. Beinoravichute, *Doklady Akad. Nauk S.S.S.R.*, **112**, 439 (1957). (b) A. N. Nesmeyanov, E. G. Perevalova, Z. A. Beinoravichute, and I. L. Malygina, *Doklady Akad. Nauk S.S.S.R.*, **120**, 1263 (1958).

(4) A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **100**, 1099 (1955).

(5)(a) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Doklady Akad. Nauk S.S.S.R.*, **126**, 1004 (1959).

(b) In the present research (see Experimental) preparation of lithioferrocenes in 1:1 tetrahydrofuran-ethyl ether and subsequent reaction with butyl borate in ethyl ether resulted in 44% conversion to ferrocenylboronic acid and 18% conversion to 1,1'-ferrocenylenediboronic acid; 29% ferrocene was recovered. (c) Iodoferrocene is prepared by reaction of chloromercuriferrocene and iodine (see Experimental).