(0.098 mole) of crotonylpiperidine[13] in ether and the mixture was stirred for 30 min. Hydrolysis with dilute HCl, followed by fractionation yielded 11.6 g. (51%) of β-phenylbutyryl piperidine, b.p. 145–50° (0.3 mm.), n_D^{25} 1.5399.

Anal. Calcd. for $C_{15}H_{21}ON$: C, 77.88; H, 9.16. Found: C, 78.24; H, 8.95.

The ultraviolet absorption spectrum of the crude reaction product showed no peak in the region expected for phenyl propenyl ketone.

MADISON, WIS.

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[13] H. Staudinger and H. Schneider, *Ber.*, **56**, 699 (1923).

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Derivatives of Ferrocene. III. The Preparation of Some Acylferrocenes and Alkylferrocenes[1]

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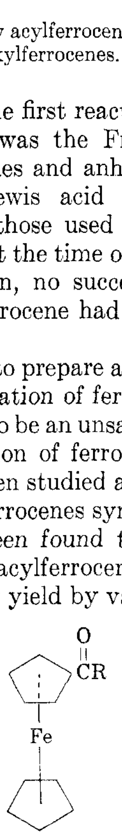
Several new acylferrocenes and 1,1′-diacylferrocenes have been prepared and reduced to the corresponding alkylferrocenes and 1,1′-dialkylferrocenes. Attempts to directly alkylate ferrocene resulted in mixtures of polyalkylated products.

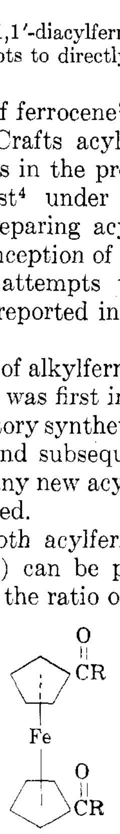
One of the first reactions of ferrocene[2,3] to be investigated was the Friedel-Crafts acylation with acid chlorides and anhydrides in the presence of a suitable Lewis acid catalyst[4] under conditions similar to those used for preparing acylbenzenes. However, at the time of the inception of the present investigation, no successful attempts to directly alkylate ferrocene had been reported in the literature.[5,6]

In order to prepare a series of alkylferrocenes, the direct alkylation of ferrocene was first investigated and found to be an unsatisfactory synthetic method. The acylation of ferrocene and subsequent reduction was then studied and many new acylferrocenes and alkylferrocenes synthesized.

It has been found that both acylferrocenes (I) and 1,1′-diacylferrocenes (II) can be prepared in satisfactory yield by varying the ratio of ferrocene, acid chloride, and aluminum chloride, and also the mode of addition. Compounds of type I were prepared by the dropwise addition of the acid chloride-aluminum chloride complex to the ferrocene solution, using equimolar amounts of acid chloride, catalyst, and ferrocene. The disubstituted derivatives, II, were prepared by adding the ferrocene solution to the complex, using a molar ratio of both the acid chloride and the aluminum chloride to ferrocene of greater than 2:1.



I



II

The preparation of both I and II by these procedures appears to be a very satisfactory synthetic method. Using the appropriate procedure, either was obtained uncontaminated by the other or by unreacted ferrocene. The unaccounted ferrocene was present in the form of tars. If the reaction was carried out at room temperature instead of at reflux, the amount of tar produced was considerably decreased. The yields of the diketones tended to decrease with increasing molecular weight, probably due to steric factors as well as decreased reactivity of the acid chlorides. The properties and analyses of the acylferrocenes and 1,1′-diacylferrocenes are summarized in Table I.

The catalytic hydrogenation of 1,1′-diacetylferrocene to 1,1′-diethylferrocene was successfully carried out by Rosenblum.[7] However, it was not possible to extend this reaction to the higher homologues under similar as well as stronger conditions, although it was possible to duplicate Rosenblum's work. This is in marked contrast to aryl alkyl ketones which in general are readily hydrogenated to hydrocarbons.[8] Consequently, the Clemmensen reduction was used for the reduction of the higher homologs. Recently, Nesmeyanov and Vol'kenau[9] have used this same method for the reduction of

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[1] Presented in part at the 131st Meeting of the American Chemical Society, Miami, Fla., April 7 to 12, 1957; see Abstracts of Papers, pp. 47–0.

[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, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

[5] V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

[6] P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).

[7] M. Rosenblum, Ph.D. Thesis, Harvard University, 1953.

[8] W. H. Hartung and R. Simonoff, *Org. Reactions*, *VII*, 263–326 (1953).

[9] A. N. Nesmeyanov and N. A. Vol'kenau, *Doklady Akad. Nauk SSSR*, **107**, 262 (1956).

TABLE I

ACYLFERROCENES

			Analyses					
			Calcd.			Found		
Ferrocene	M.P., °C.	Yield, %	C	H	Fe	C	H	Fe
1,1′-Diacetyl-[a]	127.0–127.5	74	62.26	5.22	20.67	61.96, 61.98	5.29, 5.16	20.83, 20.91
1,1′-Dicaprylyl-[b]	54.8–56.0	65	71.23	8.74	12.74	71.55, 71.79	8.80, 8.89	13.00, 12.98
1,1′-Dicapryl-[b]	68.6–69.8	41	72.86	9.38	11.29	73.00, 73.17	9.38, 9.27	11.57, 11.46
1,1′-Dilauroyl-[b]	76.6–77.1	44	74.17	9.88	10.14	74.38, 74.37	9.75, 9.75	10.06, 10.05
1,1′-Ditridecanoyl-[b]	80.0–80.4	15	74.71	10.11	9.65	74.87, 74.77	10.19, 10.07	9.88, 9.84
1,1′-Dipalmitoyl-[c]	82.4–83.4	12	76.10	10.65	8.43	76.29, 76.19	10.30, 10.16	8.79, 9.04
Palmitoyl-[d]	59.0–59.8	46	73.57	9.50	13.16	74.07, 74.07	9.53, 9.36	13.20, 13.27

[a] Red crystalline solid. [b] Red-orange crystalline solid. [c] Salmon-colored solid. [d] Yellow crystalline solid.

TABLE II

ALKYLFERROCENES

					Analyses					
					Calcd.			Found		
Ferrocene	M.P., °C.	B.P., °C.	n_D^{25}	Yield, %	C	H	Fe	C	H	Fe
1,1′-Diethyl-[a]	−35.0[b]	87–89/ 0.15 mm.	1.5761	60	69.45	7.49	23.06	69.12, 69.11	7.36, 7.28	23.10, 22.86
1,1′-Dioctyl-[a]	−16.0[c]	190–193/ 0.15 mm.	1.5214	58	76.07	10.32	13.61	76.30, 76.10	10.27, 10.49	13.09, 13.04
1,1′-Didecyl-[a]	11.5[d]	197–205/ 0.04 mm.	1.5142	50	77.23	10.80	11.97	78.01, 77.78	10.89, 10.69	11.47, 11.43
1,1′-Didodecyl-[e,f]	30.6–30.8			—	78.13	11.19	10.68	77.89, 77.93	11.01, 10.98	10.72, 10.93
1,1′-Ditridecyl-[e]	38.0–39.0			32	78.51	11.35	10.14	78.15, 78.17	11.07, 11.01	10.40, 10.41
1,1′-Dihexadecyl-[e]	41.2–42.4			33	79.45	11.75	8.80	79.59, 79.27	11.56, 11.65	8.82, 9.13
Hexadecyl-[e]	55.0–55.6			77	76.08	10.32	13.61	76.00, 76.26	10.32, 10.20	13.43, 13.65

[a] Dark-red liquid. [b] Melting point value obtained from reference 7. [c] d_4^{25} 1.0076; M.R. 124.12. [d] d_4^{25} 0.9863; M.R. 140.91. [e] Yellow crystalline solid. [f] Two unsaturated compounds, melting points 32.4–33.4° and 37.2–38.8° (uncorr.), were the only products isolated from the initial Clemmensen reduction. Both exhibited strong absorption in the *trans* double-bond region of the infrared (10.3 microns) and both could be hydrogenated to the expected compound. In a repeat experiment, 1,1′-didodecylferrocene was obtained directly.

some lower 1,1′-diacylferrocenes. The properties and analyses of the alkylferrocenes and 1,1′-dialkylferrocenes are summarized in Table II.

1,1′-Diethylferrocene decomposed to a considerable extent after standing for several months, even in the absence of light and air. This is in accord with observations by other workers[7,9] concerning this and other low molecular weight liquid alkylferrocenes. On the other hand, 1,1′-dioctylferrocene and 1,1′-didecylferrocene, both liquids, appeared completely stable to air and light after several months storage.

A point worth noting is the unusual melting point of hexadecylferrocene (55.0–55.6°) compared to those of 1,1′-dioctylferrocene (−16.0°) and 1,1′-dihexadecylferrocene (41.2–42.4°). Hexadecylferrocene would be expected to have a lower melting point than its symmetrical isomer, 1,1′-dioctylferrocene, but it does not. Also, hexadecylferrocene is higher melting than even 1,1′-dihexadecylferrocene, the corresponding disubstituted derivative, which is very unusual among substituted aromatic compounds.

The question arises whether the diacylferrocenes and dialkylferrocenes are symmetrically or unsymmetrically substituted. Since none of these compounds absorb in the infrared in the region of 9.00 or 9.95 microns (peaks in these regions being indicative of unsymmetrical substitution according to the date of Rosenblum[7] and of Pauson[10]), it was concluded that these compounds were symmetrically substituted. The two monosubstituted compounds, palmitoylferrocene and hexadecylferrocene, did absorb in these regions as expected.

Three methods of direct alkylation of ferrocene were attempted; alcohols and 100% phosphoric acid, as successfully used for alkylating biphenyl,[11] alcohols and aluminum chloride, and alkyl halides and aluminum chloride. All were successful to the extent that little or no unreacted ferrocene could be recovered by steam distillation. However, the product was always a mixture of polyalkylated liquid ferrocenes, boiling over a wide range, or undistillable tars. We were unable to obtain any pure fractions upon distillation, and it appeared that the yield of any one product was small. Nesmeyanov

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(10) P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954).

(11) I. A. Romadan and V. K. Berzinya, *J. Gen. Chem. USSR*, **25**, 265 (1955).

and Kochetkova[12] have recently reported similar work using alkyl halides and aluminum chloride. They were able to isolate by distillation mono-, di-, and penta-alkylated ferrocenes in very small yields.

EXPERIMENTAL[13]

1,1'-Diacylferrocenes (II). All 1,1'-diacylferrocenes were prepared by the reaction of the appropriate acid chloride with aluminum chloride and ferrocene. As a typical example, 1,1'-dicaprylylferrocene was prepared by adding 120 g. (0.90 mole) of anhydrous aluminum chloride to 350 ml. of methylene chloride (dried over calcium hydride) in a 2-liter, 3-necked flask equipped with stirrer, reflux condenser, and addition funnel. A nitrogen atmosphere and stirring were maintained throughout the reaction. Through the addition funnel, 146.5 g. (0.90 mole) of caprylyl chloride (prepared from caprylic acid and thionyl chloride in 80% yield) was slowly added, dissolving the aluminum chloride. A solution of 65.1 g. (0.35 mole) of ferrocene in 350 ml. of methylene chloride was added dropwise over a period of 2 hrs. Reaction was immediate as evidenced by the evolution of hydrogen chloride and the formation of a dark purple complex. After 70 hr. of stirring, hydrogen chloride evolution had ceased and the reaction mixture was hydrolyzed by pouring it onto 500 g. of ice. The two-phase system, which was badly emulsified, was filtered under vacuum and the phases were separated. The organic phase was washed until neutral and dried over anhydrous calcium sulfate. The methylene chloride solution was filtered free of drying agent and the solvent evaporated under an air stream. The crude product was recrystallized twice from methanol yielding 100.0 g. (65% yield) of orange-red crystals, m.p. 50–52° (uncorr.). An analytical sample was obtained after two additional recrystallizations from methanol, m.p. 54.8–56.0°. See Table I for the analysis.

Palmitoylferrocene. The equipment and procedure used were the same as for the preparation of the 1,1'-diacylferrocenes with the exception that the mode of addition was reversed. A solution of 153.4 g. (0.558 mole) of palmitoyl chloride (prepared in 88% yield from palmitic acid and thionyl chloride) and 77.4 g. (0.558 mole) of aluminum chloride in 200 ml. of anhydrous methylene chloride was added dropwise over a 2.5 hr. period to 103.8 g. (0.558 mole) of ferrocene dissolved in 600 ml. of methylene chloride. After stirring overnight the reaction mixture was worked up and the crude product isolated. One recrystallization from methanol produced 116.4 g. (45.8% yield) of yellow crystals, m.p. 57.0–58.7°. An analytical sample was obtained after one recrystallization from methanol, m.p. 59.0–59.8°. See Table I for the analysis.

Hydrogenation of 1,1'-diacetylferrocene. In a 500-ml hydrogenation bottle were placed 10.8 g. (0.040 mole) of 1,1'-diacetylferrocene dissolved in 300 ml. of methanol and 1 g. of 5% platinum on charcoal. The mixture was placed in a Parr hydrogenation apparatus at a pressure of 50 p.s.i. After 24 hr. the hydrogen uptake had reached the theoretical value. The solution was filtered free of catalyst and the methanol stripped off. Distillation of the crude product at reduced pressure gave 5.7 g. (60% yield) of a dark-red liquid with a strong camphoraceous odor, b.p. 87–89° at 0.15 mm., n_{D}^{25} 1.5761. Rosenblum reports b.p. 130–131° at 9 mm., n_{D}^{25} 1.5760.[7]

Attempts to hydrogenate the higher 1,1'-diacylferrocenes under similar conditions and also at elevated temperatures gave starting material as the only isolatable product.

Clemmensen reduction of acyl- and 1,1'-diacylferrocenes. The acyl- and 1,1'-diacylferrocenes were reduced to the corresponding alkyl derivatives by refluxing with dilute hydrochloric acid and amalgamated zinc. In a typical experiment, 200 g. of granular zinc was amalgamated by stirring 5 min. with 15 g. of mercuric chloride, 250 ml. of water, and 10 ml. of concentrated hydrochloric acid in a 1-liter, 3-necked flask equipped with a stirrer and reflux condenser. The aqueous phase was pipetted off and 100 ml. of water, 200 ml. of concentrated hydrochloric acid, 43.8 g. (0.10 mole) of 1,1'-dicaprylylferrocene, and 100 ml. of benzene were added quickly in that order. The mixture was brought to reflux and stirred vigorously so that the amalgam was in contact with both phases. At intervals during the reaction, four 50-ml. portions of concentrated hydrochloric acid were added to maintain the acidity of the solution. After 52 hr. the mixture was brought to room temperature and filtered free of amalgam. The amalgam was washed with ether and the combined organic phase extracted with water to neutrality and dried over anhydrous calcium sulfate. After filtration from the drying agent, the solvent was evaporated under an air stream. The crude product was distilled twice under reduced pressure through a heated 9-inch Vigreux column yielding 23.8 g. (58% yield) of a dark red liquid b.p. 190–193° at 0.15 mm. See Table II for the analysis.

The solid alkyl- and 1,1'-dialkylferrocenes were purified by recrystallization from acetone.

Direct alkylation of ferrocene. As a typical example, 35.8 g. (0.192 mole) of ferrocene, 40.0 g. (0.30 mole) of anhydrous aluminum chloride, and 100 ml. of dry methylene chloride were placed in a 250-ml., 3-necked flask equipped with stirrer, reflux condenser, and addition funnel. Stirring and a nitrogen atmosphere were maintained throughout the reaction. A solution of 17.6 g. (0.20 mole) of *t*-amyl alcohol in 50 ml. of dry methylene chloride was added over a period of 1.5 hr. After 18 hr., the mixture was hydrolyzed with ice water and neutralized with sodium hydroxide solution. A steam distillation failed to produce any unreacted ferrocene. The residue from the steam distillation was extracted with benzene, the benzene solution washed with water, and dried over calcium chloride. After filtration from the drying agent, the solvent was evaporated under an air stream. The crude product was distilled twice under reduced pressure through a 24-inch column packed with 0.25-inch glass helices. The main fraction, a dark-red liquid, weighed 5.0 g., b.p. 62–64° at 0.1 mm., n_{D}^{25} 1.5683. The elemental analysis was intermediate between those calculated for the mono- and disubstituted derivatives.

Anal. Calcd. for $C_{15}H_{20}Fe$: C, 70.34; H, 7.87; Fe, 21.79. Calcd. for $C_{20}H_{30}Fe$: C, 73.62; H, 9.27; Fe, 17.11. Found: C, 72.17, 72.28; H, 8.19, 8.13; Fe, 19.57, 19.55.

Similarly, ferrocene was alkylated with *n*-decyl alcohol and with *n*-decyl chloride by refluxing several days with excess aluminum chloride in methylene chloride solution. The reaction of ferrocene with either *t*-amyl alcohol or *n*-amyl alcohol for several hours at 110–115° with 100% phosphoric acid as the solvent also produced alkylated derivatives. The products in every case were mixtures of liquid alkylferrocenes, none of which could be readily separated into pure compounds by distillation or by chromatography on alumina.

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(12) A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk SSSR*, **109**, 543 (1956).

(13) All melting points are corrected unless otherwise noted; boiling points are not corrected. Analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.