mixture was refluxed overnight, it was distilled to dryness, *in vacuo*, toluene added, salts removed by filtration, and the filtrate distilled. Most of the high-boiling material (14.9 g., b.p. 68–86°/0.07–0.15 mm.) solidified during distillation. Recrystallization from heptane yielded 7.1 g. of crude III, m.p. 83–88°. After two additional crystallizations, the compound, *1,3-(1,1'-ferrocenylene)tetramethyldisiloxane* (III), melted at 87–88°.

Anal. Calcd. for $C_{14}H_{20}FeOSi_2$: C, 53.16; H, 6.38; Fe, 17.66; Si, 17.74; mol. wt. 316. Found: C, 52.88; H, 6.08; Fe, 17.87; Si, 17.47; mol. wt. (camphor), 281.

Extraction of the distillation residue with heptane furnished an additional 1.9 g. of the bridged compound (III), m.p. 87–88°; total yield, 22%.

In a second experiment the cyclopentadiene compound was treated with 1 equivalent of *n*-butyllithium and then followed successively with ferrous chloride, *n*-butyllithium, and again ferrous chloride under conditions similar to those used in the previous experiment. By distillation, crude 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane, m.p. 79–86°, was isolated in 20% yield, and after several recrystallizations from 2-propanol, it melted at 87.5–88°.

Reaction of 1,5-bis(cyclopentadienyl)hexamethyltrisiloxane with n-butyllithium and ferrous chloride. A solution of *n*-butyllithium prepared[17] from 0.274 mole of *n*-butyl bromide was added to 46 g. (0.137 mole) of 1,5-bis(cyclopentadienyl)-hexamethyltrisiloxane in 100 ml. of tetrahydrofuran under nitrogen during a 20-min. period. After the mixture had stirred for 1.5 hr., a slurry of ferrous chloride prepared[16] from 0.092 mole of ferric chloride and 0.046 mole of iron powder was added, followed by 250 ml. of tetrahydrofuran. The mixture was refluxed overnight, solvent removed *in vacuo*, and the residue extracted thoroughly with benzene. The extract was washed with water (emulsion), filtered, and the benzene layer taken to dryness. Lower-boiling components in the resulting residue were removed by distillation up to 105°/0.17 mm., the remainder was extracted with 2-propanol, and the extract was distilled. Solid material in a fraction (8 g.), b.p. 90–110°/0.02–0.1 mm., was recrystallized from 2-propanol, giving 2.9 g. (6%) of 1,5-(1,1'-ferrocenylene)hexamethyltrisiloxane, m.p. 73–75° (see below). A second distillation fraction (11 g.), b.p. 220–240°/0.07 mm., was redistilled, and the fraction (5 g.), b.p. 180–250°/0.02 mm., was analyzed; this material may be a mixture of 1,1' - bis(cyclopentadienylhexamethyltrisiloxanyl)ferrocene, $C_{32}H_{54}FeO_4Si_6$, and a cyclic compound, $C_{32}H_{52}Fe_2O_4Si_6$.

Anal. Calcd. for $C_{32}H_{54}FeO_4Si_6$: C, 52.85; H, 7.49; Fe, 7.68. Calcd. for $C_{32}H_{52}Fe_2O_4Si_6$: C, 49.21; H, 6.71; 14.30. Found: C, 49.53; H, 7.45; Fe, 10.14, 10.33, 10.14.

1,5-Bis(cyclopentadienyl)hexamethyltrisiloxane (20.5 g.) was treated also with 1 equivalent of *n*-butyllithium, followed successively with ferrous chloride, *n*-butyllithium, and again ferrous chloride. By distillation there was isolated 6.5 g. of a mixture of solid and liquid, b.p. 110–137°/0.28 mm., which after refrigeration and washing with 2-propanol yielded 1.3 g. of crystals, m.p. 55–67°. After two recrystallizations from 2-propanol, the solid, *1,5-(1,1'-ferrocenylene)hexamethyltrisiloxane*, melted at 73.5–75°.

Anal. Calcd. for $C_{16}H_{26}FeO_2Si_3$: C, 49.21; H, 6.71; mol. wt., 391. Found: C, 49.43; H, 6.69; mol. wt. (camphor), 397.

Treatment of 1,1-bis(dimethylethoxysilyl)ferrocene (II) *with phenyldimethylchlorosilane in the presence of ferric chloride.* A mixture of 3.90 g. (0.01 mole) of the diethoxy compound (II), 3.41 g. (0.02 mole) of phenyldimethylchlorosilane, and 0.07 g. of ferric chloride was heated in a bath at 200° during a 5-hr. period under nitrogen. A gas (ethyl chloride) which evolved was condensed in a trap at −70°. The mixture was cooled, 50 ml. of petroleum ether was added, and, after 20 hr., the mixture was filtered and the filtrate evaporated *in vacuo*. Distillation of the residue gave a solid fraction (2.33 g.), b.p. 85–92°/0.12 mm., which by recrystallization from 2-propanol yielded 1.54 g. (49%) of 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane (III), m.p. 87–88°; admixture melting with an authentic sample showed no depression. An additional 0.19 g. of the bridged compound, m.p. 86–87°, was recovered from the mother liquor, and 0.10 g., m.p. 85–87°, was precipitated from the distillation residue by addition of a small amount of petroleum ether and cooling to −70°; total yield, 58%.

WYANDOTTE, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Di- and Tetrabenzylations of Mono- and Bisacetylferrocenes with Benzyl Chloride by Potassium Amide. Comparison with Acetophenone

CHARLES R. HAUSER AND T. ARTHUR MASHBURN, JR.

Received September 6, 1960

The methyl group of monoacetylferrocene was alkylated with benzyl chloride by means of potassium amide to form the dibenzylation product. Attempts to isolate the intermediate monobenzylation product were unsuccessful. Evidence was obtained that the second benzyl group was introduced into the molecule more rapidly than the first. Similarly the two methyl groups of bisacetylferrocene were alkylated with benzyl chloride by potassium amide to form the tetrabenzylation product. No intermediates were isolated. These alkylations furnish more convenient methods of syntheses of the corresponding di- and tetrabenzylation products than certain methods that were devised in connection with the proof of their structures. Certain theoretical aspects are considered. The results are compared with the benzylation of acetophenone.

Previous papers have described condensations of mono- and bisacetylferrocene with esters[2-4] and with benzaldehyde.[2,5] The present paper describes benzylations of these methyl ketones and also of acetophenone.

Results with monoacetylferrocene. This methyl ketone (I) was alkylated with benzyl chloride by means of potassium amide to form the dibenzyl

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(1) Union Carbide Corporation Fellow, 1958–1960.

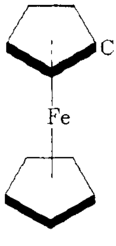
(2) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 482 (1957).

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

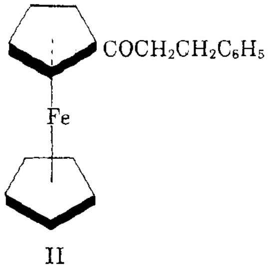
(4) C. E. Cain, T. A. Mashburn, Jr., and C. R. Hauser, *J. Org. Chem.*, **26**, 1030 (1961).

(5) T. A. Mashburn, Jr., C. E. Cain, and C. R. Hauser, *J. Org. Chem.*, **25**, 1982 (1960).

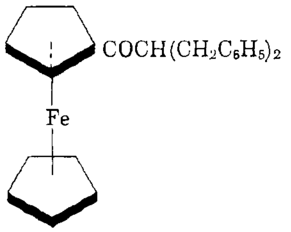
derivative III. The expected monobenzyl derivative II would presumably be an intermediate.



I



II

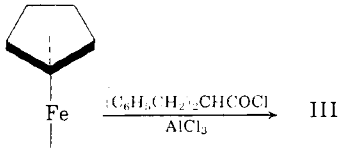


III

The reaction was generally effected in liquid ammonia followed by ether but sometimes it was completed in the former solvent. One experiment was carried out in toluene. Attempts to isolate the intermediate monobenzyl derivative II were unsuccessful even though less than the calculated amounts of the alkali amide and halide for III were employed and/or the reactions stopped before completion.

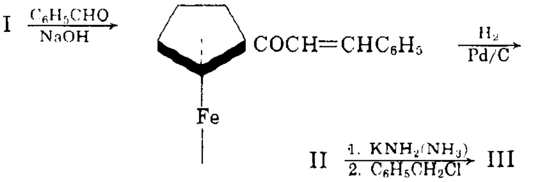
The infrared spectrum of the product showed not only a band at 5.88 μ for the carbonyl group[6] but also bands in the 13–14 μ region attributable to the phenyl group.[7] Incidentally the band for the carbonyl group in I appears at about 6.02 μ, which is slightly higher than the region of 5.88–5.96 μ generally considered to be characteristic of ordinary ketones.[6]

That the product was III and not II was established by analysis and by independent synthesis involving the Friedel-Crafts acylation of ferrocene with the appropriate acid chloride (Equation 1).



(1)

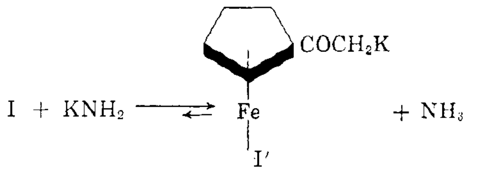
Also III was independently synthesized from I through the aldol type of condensation with benzaldehyde[2,5] (Equation 2), II being an intermediate in this series of reactions as well as in the dibenzylation of I.



(2)

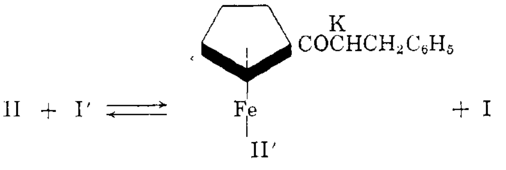
The product obtained from both of these independent syntheses was shown to be identical with that obtained in the benzylation of I by comparison of their infrared spectra and by the mixed melting point method.

The mechanism for the dibenzylation of I employing molecular equivalents of the reactants would presumably involve the four steps represented by equations 3a–d. Since the equilibrium of step 3a is far on the side of the potassio salt I′, step 3c may be considered to be effected by part of I′, the corresponding amount of I being regenerated. The same steps would occur with excess of the alkali amide (and halide), but then 3c as well as 3a should be effected by this relatively strong base.



(3a)

$$I' + C_6H_5CH_2Cl \rightarrow II + KCl \qquad (3b)$$



(3c)

$$II' + C_6H_5CH_2Cl \rightarrow III + KCl \qquad (3d)$$

In agreement with these equations, the yields of III from I were 30–40% with approximately molecular equivalents of the alkali amide and halide, but 60–66% with approximately two equivalents of the amide and halide. Under the former conditions considerable amounts of I were recovered. In the experiments with two equivalents of the amide, the reaction appeared to be accompanied by the self-condensation of some of the benzyl chloride to form stilbene as indicated by the appearance of a transient purple-red color.[8] In a single experiment with about 1.5 equivalents of the amide and two of the halide, this side-reaction was not observed, and a 66% yield of III was isolated.

As none of the intermediate monobenzylation product II was isolated in any of the experiments, the benzylation of this intermediate evidently occurred much faster than that of the original ketone I. In line with this, a 76% yield of III was

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[6] See L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 137.

[7] See ref. 6, page 77.

[8] See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1958).

obtained within three minutes in the benzylation of II prepared as indicated in Equation 2, whereas no appreciable amount of III was isolated on treatment of I with molecular equivalents of potassium amide and benzyl chloride under similar conditions. The slower rate of introduction of the first benzyl group into I may be due partly to a lower solubility of potassio salt I′ than potassio salt II′ in the medium employed.

As a method of synthesis of III, that involving the dibenzylation of I is probably superior to those represented by Equations 1 and 2.

Sodium amide appeared to be less effective than potassium amide, since only a 10% yield of III was obtained with slightly more than an equivalent of the former reagent (and an equivalent of the halide), under which condition potassium amide produced a 35% yield of III. Lithium amide was evidently still less effective, as none of III was isolated with this reagent after thirty minutes or even two hours. No intermediate was isolated in these experiments, and much unchanged I was recovered. The use of an excess of sodium amide or lithium amide was not studied.

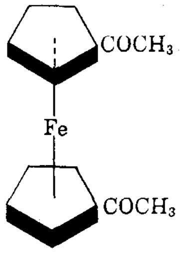
An attempt to benzohydrylate the potassio salt I′ with benzohydryl chloride in liquid ammonia was unsuccessful. Instead of the benzohydrylation product, tetraphenylethylene was obtained in 67% yield, and 88% of I was recovered. This olefin evidently arose through the self-condensation of the halide (Equation 4), since such a reaction is known to occur readily with alkali amides in liquid ammonia.[8]

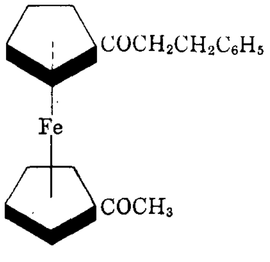
$$\mathrm{I}' + (C_6H_5)_2CHCl \longrightarrow \mathrm{I} + (C_6H_5)_2\overset{-}{C}{-}Cl \quad (4)$$

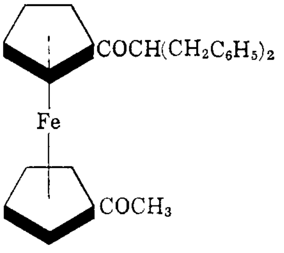
$$\Big\downarrow (C_6H_5)_2CHCl$$

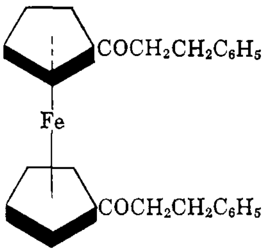
$$(C_6H_5)_2C{=}C(C_6H_5)_2 \xleftarrow[-HCl]{Base} (C_6H_5)_2CH{-}\underset{Cl}{C}(C_6H_5)_2$$

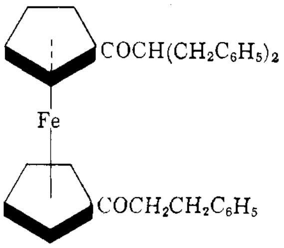
Results with bisacetylferrocene. This diketone (IV) was alkylated with benzyl chloride by means of potassium amide to form the tetrabenzyl derivative IX. Probable intermediates would be V, VI or VII, and VIII.

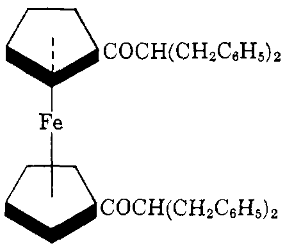

IV


V


VI


VII

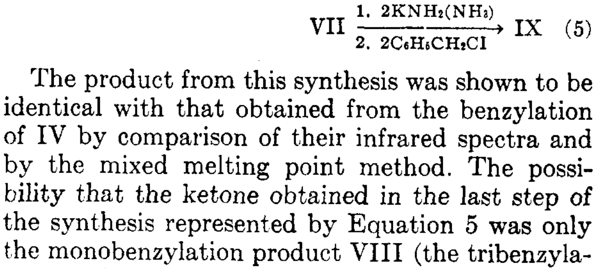

VIII


IX

The reaction was generally effected in liquid ammonia followed by ether, but sometimes it was completed in the former solvent. As the benzylation of I involved the introduction of the second benzyl group into the molecule faster than the first, the dibenzyl intermediate in the benzylation of IV might be expected to be VI rather than VII. Attempts to isolate this or the other possible intermediates, however, were unsuccessful even though less than the calculated amounts of the alkali amide and halide for IX were employed.

The infrared spectrum of the product showed not only a carbonyl group[6] band at 5.92 μ but also bands in the region of 13–14 μ for the phenyl group.[7] Similar to I, IV gave an infrared band at 6.02 μ for the carbonyl group, which is slightly higher than the highest value generally ascribed to the carbonyl group of ordinary ketones.[6]

That the product was the tetrabenzyl derivative IX and not an intermediate was supported by analysis and by independent synthesis from IV through its dibenzal derivative[5] (Equation 5).

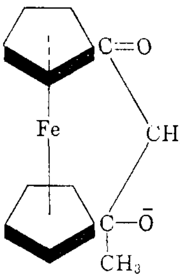


$$\mathrm{VII} \xrightarrow[2.\ 2C_6H_5CH_2Cl]{1.\ 2KNH_2(NH_3)} \mathrm{IX} \quad (5)$$

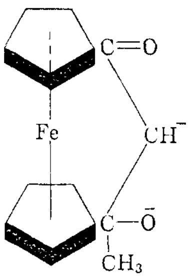
The product from this synthesis was shown to be identical with that obtained from the benzylation of IV by comparison of their infrared spectra and by the mixed melting point method. The possibility that the ketone obtained in the last step of the synthesis represented by Equation 5 was only the monobenzylation product VIII (the tribenzylation product of ketone IV) would not be supported by analysis. Furthermore, benzylation at both of the side-chains of VII might be expected under the conditions employed, as the corresponding benzylation of ketone II was shown to occur rapidly (see above).

The yields of IX in the tetrabenzylation of IV with approximately one, two, and four molecular equivalents each of the alkali amide and halide were 0, 24, and 42–62%, respectively. Under the last condition, the reaction was accompanied by the self-condensation of some of the benzyl chloride to form stilbene.[8] This side-reaction appeared to be avoided by the use of three equivalents of the alkali amide and four of the halide; this experiment, which was performed only once, gave a 53% yield of IX.

The fact that none of IX was isolated in the experiment with molecular equivalents of the amide and halide suggests that the monocarbanion of IV was converted to cyclic anion IV′, which might not be expected to undergo benzylation under the conditions employed. The carbanion produced with two equivalents of the amide would then be IV″, which should form V on benzylation. These anions were recently proposed[4] as intermediates in acylations of IV.



IV′



IV″

Similar cyclic carbanions are also possible as reactive intermediates in the further benzylations leading to the tetrabenzyl derivative IX.

As a method of synthesis of IX, the tetrabenzylation of IV is probably to be preferred to that represented by Equation 5.

Comparison with acetophenone. The isolations of only the dibenzylation product from monoacetylferrocene and of only the tetrabenzylation product from bisacetylferrocene under various conditions are rather remarkable, since there has generally been no difficulty in obtaining monoalkylation products from methyl · ketones. For example, long ago Claisen and Feyerabend[9] reported that the alkylation of acetophenone with benzyl chloride by means of sodium amide in ether produces the monobenzylation product X in 38% yield. Later, Haller and Bauer[10] showed that the reaction produces not only X but also the dibenzylation product XI, though no yields were given.

$C_6H_5COCH_2CH_2C_6H_5$ X

$C_6H_5COCH(CH_2C_6H_5)_2$ XI

We have observed that the alkylation of acetophenone with molecular equivalents of benzyl chloride and potassium amide produces both X and XI but that the relative yields of these two products are dependent on the conditions employed. Thus, the ratio of X to XI was about 1:2 in liquid ammonia followed by ether at room temperature, whereas it was approximately 2:1 in toluene at 25–80°.

Although the combined yield of the two products was only about 12% in the former experiment, 80% of the starting material was recovered. These two experiments indicate that the ratio of the products is dependent on the solvent and/or temperature.

EXPERIMENTAL[11]

Dibenzylation of monoacetylferrocene (I)[12] *to form* III. This reaction has been carried out numerous times; typical experiments are described below.

A. With approximately molecular equivalents of reactants. To a stirred solution of approximately 0.024 mole of potassium amide[13] in about 150 ml. of commercial anhydrous liquid ammonia was added 5.0 g. (0.022 mole) of solid monoacetylferrocene (I). The resulting red suspension was stirred for 0.5 hr., and a solution of 2.78 g. (0.022 mole) of benzyl chloride in 50 ml. of dry ether was added. Within 3–4 min., the suspension became yellow. After stirring for 1 hr., the liquid ammonia was evaporated on the steam bath as an equal volume of ether was added. The resulting ethereal suspension was stirred with water and the mixture filtered. The ether was allowed to evaporate from the aqueous-ethereal filtrate and the resulting solid collected. The combined solids on the funnel were washed well with water and recrystallized from absolute ethanol to give 3.5 g. (39%) of α,α-dibenzylacetylferrocene (III) as yellow needles, m.p. 154–155°.

Anal. Calcd. for $C_{26}H_{24}FeO$: C, 76.70; H, 5.93; Fe, 13.75. Found: C, 76.71, 76.30; H, 5.80, 5.83; Fe, 14.43, 14.27.

Infrared bands: 5.88, 7.15, 8.95, 10.05, 13.25, 13.56, and 14.22 μ.

I was sometimes recovered on evaporation of the ethanolic filtrate from the recrystallizations or recovered by stirring the crude III with hot hexane.

In a similar experiment the reaction mixture was neutralized in liquid ammonia after 0.5 hr. by the addition of solid ammonium chloride to give 3.1 g. (35%) of ketone III. When this experiment was repeated and excess ammonium chloride added after only 3 min., no appreciable amount of III was isolated and 90% of I was recovered.

When the reaction was carried out in liquid ammonia employing sodium amide rather than potassium amide and excess ammonium chloride added after 0.5 hr., a 10% yield of II was obtained and 80% of I was recovered. When lithium amide was employed similarly and the reaction mixture neutralized after 30 or 120 min., none of III was isolated and 90% of ketone I was recovered.

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(9) L. Claisen and R. Feyerabend, *Ber.*, 38, 697 (1905).

(10) A. Haller and E. Bauer, *Ann. Chem.*, [8] 28, 373 (1913).

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

(12) We are indebted to Dr. R. L. Pruett, Union Carbide Chemicals Company, South Charleston, W. Va. for a generous sample of this compound.

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

B. With excess alkyl halide and potassium amide. To a stirred solution of approximately 0.12 mole of potassium amide[13] in 250 ml. of liquid ammonia was added 11.4 g. (0.05 mole) of monoacetylferrocene followed, after 30 min., by 12.6 g. (0.1 mole) of benzyl chloride in 100 ml. of dry ether. The liquid ammonia was replaced by ether and the resulting ethereal suspension decomposed with water and worked up as in A to give 13.6 g. (66%) of III, m.p. 154–155° (recrystallized from absolute ethanol). This product was shown to be identical with that obtained in A by comparison of the infrared spectra and by the mixed melting point method.

C. Benzylation of I *in toluene.* A solution of 0.025 mole of potassium amide was prepared in liquid ammonia[13] and the ammonia replaced by 100 ml. of dry toluene. To the resulting suspension was added, with stirring, 5.0 g. (0.022 mole) of monoacetylferrocene (I) followed, after 25 min., by 2.78 (0.022 mole) of benzyl chloride in 50 ml. of dry toluene. The reaction mixture was stirred for 35–40 min. and heated on the steam bath for 1.5 hr. The reaction mixture was cooled, decomposed with water and worked up to give 2.0 g. (23%) of III (recrystallized from absolute ethanol), and 60% of the recovered ketone I.

Independent syntheses of III, *A. From ferrocene.* To a stirred suspension of 12.5 g. (0.093 mole) of aluminum chloride in 50 ml. of dry methylene chloride was slowly added 24.1 g. (0.093 mole) of *φ*-benzylhydrocinnamoyl chloride in 50 ml. of dry methylene chloride. To this mixture was added 16.0 g. (0.085 mole) of ferrocene in 150 ml. of dry methylene chloride. After stirring at room temperature for 9 hr., the brown-red mixture was poured into ice and the two layers were separated. The aqueous layer was extracted twice with methylene chloride and the combined organic solution was dried over Drierite. The solvent was removed, leaving an oil which slowly crystallized. The crystals were collected on a funnel and recrystallized three times from ethanol to give 15.0 g. (42%) of *α,α*-dibenzylacetylferrocene (III), m.p. 154–155°. Infrared spectra and mixed melting points showed that this material was identical with that prepared by the direct benzylation of monoacetylferrocene (I).

B. From monoacetylferrocene (I). Monoacetylferrocene (9.8 g., 0.043 mole) was condensed with benzaldehyde by means of dilute, ethanolic-aqueous alkali and the resulting benzal derivative was hydrogenated over 5% palladium on charcoal to form *α*-benzylacetylferrocene (II) as described previously.[5]

To a stirred solution of 0.0125 mole of potassium amide[13] in 100 ml. of liquid ammonia was added 4.0 g. (0.0125 mole) of *α*-benzylacetylferrocene (II) to produce a deep green suspension. After 5 min., 1.59 g. (0.0125 mole) of benzyl chloride in 50 ml. of dry ether was added and within 3 min. the deep green suspension had turned a bright yellow. The ammonia was replaced with ether on the steam bath and the resulting ethereal suspension was stirred for 15 min., and then neutralized with water and dilute hydrochloric acid. The precipitate was collected on a funnel and recrystallized from ethanol-water to give 3.7 g. (78%) of *α,α*-dibenzylacetylferrocene (III), m.p. 154–155°. This material was shown by infrared spectra and mixed melting points to be identical with that prepared by the direct benzylation of monoacetylferrocene (I). Essentially the same yield (77%) of this material was obtained in a similar experiment on neutralization of the reaction mixture in liquid ammonia with excess ammonium chloride 3 min. after the addition of the benzyl chloride.

Attempted benzhydrylation of monoacetylferrocene (I). To a stirred solution of 0.048 mole of potassium amide[13] in 100 ml. of liquid ammonia was added 10.0 g. (0.044 mole) of monoacetylferrocene (I) to produce a red-brown color. After 0.5 hr., 8.9 g. (0.044 mole) of benzhydryl chloride in 100 ml. of dry ether was slowly added. The ammonia was replaced with dry ether after 0.5 hr. and the ethereal suspension stirred at room temperature for 2 hr. The suspension was neutralized with water and filtered to give, after recrystallization from ethanol-benzene, 4.9 g. (67%) of tetraphenylethylene, m.p. 227–228°. Admixture with an authentic sample gave no depression of the melting point. Most (88%) of the starting ketone was recovered.

Tetrabenzylation of bisacetylferrocene (IV)[12] *to form* IX. This reaction was carried out numerous times; some typical experiments are described below.

A. With approximately two equivalents of amide and alkyl halide. To a stirred solution of approximately 0.11 mole of potassium amide[13] in 300 ml. of liquid ammonia was added 13.5 g. (0.05 mole) of solid bisacetylferrocene (IV). The resulting red suspension was stirred for 0.5 hr. and 12.6 g. (0.1 mole) of benzyl chloride in 50 ml. of dry ether was added to produce a yellow suspension. After stirring for 1 hr., the liquid ammonia was evaporated on the steam bath as an equal volume of ether was added. The resulting ethereal suspension was stirred with water and the mixture filtered. The crude solid on the funnel was washed well with water and recrystallized from chloroform-hexane to give 3.1 g. (24%) of bis(*α,α*-dibenzylacetyl)ferrocene (IX) as yellow needles, m.p. 185–186°.

Anal. Calcd. for $C_{42}H_{38}FeO_2$: C, 79.99; H, 6.07; Fe, 8.86. Found: C, 79.92; H, 5.88; Fe, 8.78.

Infrared bands: 5.92, 7.16, 13.26, 13.49, and 14.2 μ.

B. With four equivalents of amide and alkyl halide. To a solution of approximately 0.16 mole of potassium amide[13] in 300 ml. of liquid ammonia was added 10.0 g. (0.037 mole) of bisacetylferrocene (IV) followed, after 30 min., by 16.7 g. (0.148 mole) of benzyl chloride in 100 ml. of ether (transient purple color). The reaction mixture was worked up as in A to give 9.4–10.4 g. (42–62%) of IX. This material was shown to be identical with that formed in A by a mixed melting point.

Independent synthesis of IX *from bisacetylferrocene* (IV). Bisacetylferrocene (IV) (5.4 g., 0.02 mole) was condensed with benzaldehyde by means of dilute ethanolic-aqueous alkali and the resulting dibenzal derivative was hydrogenated over 5% palladium on charcoal to yield bis(*α*-benzylacetyl)ferrocene as described previously.[5]

To a stirred solution of approximately 0.008 mole of potassium amide[13] in 100 ml. of liquid ammonia was added 1.9 g. (0.004 mole) of bis(*α*-benzylacetyl)ferrocene to produce a green suspension. After 10 min., 1.1 g. (0.008 mole) of benzyl chloride in 25 ml. of dry ether was slowly added to give a yellow-red suspension. The ammonia was replaced by ether and the resulting ethereal suspension was treated with water. The aqueous ethereal mixture was filtered and the solid on the funnel was recrystallized from chloroform-hexane to give 1.25 g. (48%) of ketone IX. Infrared spectra and mixed melting points showed that this material was identical with that obtained by the direct benzylation of bisacetylferrocene (IV).

Benzylation of acetophenone. A. In liquid ammonia. To a stirred solution of 0.415 mole of potassium amide[13] in 500 ml. of liquid ammonia was added 50.0 g. (0.415 mole) of acetophenone in 100 ml. of dry ether followed, after 30 min., by 52.0 g. (0.415 mole) of benzyl chloride in 100 ml. of dry ether. After stirring for 1 hr., the ammonia was replaced by ether, and the resulting ethereal suspension stirred for 0.5 hr. Water was added and the mixture was worked up to give 76.7 g. of a mixture of benzyl chloride and acetophenone, b. p. 59–79° at 9.3 mm., 3.5 g. (4%) of *α*-benzylacetophenone (X), b.p. 100–125° at 0.1 mm. (reported[9,10] b.p. 175–190° at 11 mm.), and 9.3 g. (7.5%) of *α,α*-dibenzylacetophenone (XI), b.p. 160–190° at 0.1 mm. (reported[10] b.p. 245–260° at 11 mm.). Derivative X crystallized on standing to give needles, m.p. 72–73° (reported[9,10] m.p. 72–73°). A mixed melting point of X with an authentic sample gave no depression. Derivative XI crystallized to give needles, m.p. 77–78° (reported[10] m.p. 78°).

B. In toluene. A solution of 0.415 mole of potassium amide was prepared in liquid ammonia and the ammonia was replaced with 400 ml. of dry toluene. To the resulting suspension was added, with stirring, 50 g. (0.415 mole) of acetophenone followed, after 30 min., by 52 g. (0.415 mole) of benzyl chloride in 75 ml. of dry toluene. The mixture became warm reaching approximately 80°. The suspension was stirred until it had cooled to room temperature (about 2 hr.) and worked up as in A to give 15.7 g. (31%) of acetophenone, b.p. 75–77° at 10.3 mm. (reported[14] b.p. 83–85° at 12 mm.), 38.5 g. (46%) of X, and 32.8 g. (23%) of XI. Both of these derivatives crystallized, and were shown to be identical with those prepared in A by mixed melting points.

Durham, N. C.

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[14] I. Heilbron, *Dictionary of Organic Compounds*, Oxford, New York, 1953, Vol. 1, p. 16.

[Contribution from Duke University and Union Carbide Corp.]

Mannich Reaction of Acetylferrocene with Formaldehyde and Secondary Amines[1,2]

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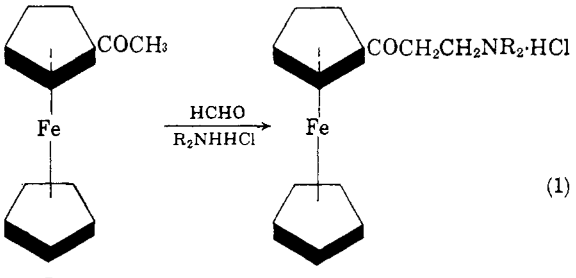
Acetylferrocene was condensed with formaldehyde and dimethylamine hydrochloride or diethylamine hydrochloride to form Mannich type salts, which were converted to the free amines and to acryloylferrocene. One of the salts was cyclized with phenylhydrazine to form a pyrazoline. One of the free amines was hydrogenated to give the hydroxyamine.

Rausch and Coleman[4] have recently reported the Mannich reaction of acetylferrocene (I) with formaldehyde and dimethylamine hydrochloride to form salt II (Equation 1); this salt was pyrolyzed by steam distillation to give a polymeric material.

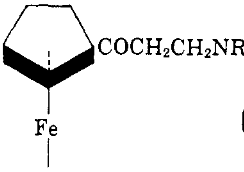


(1)

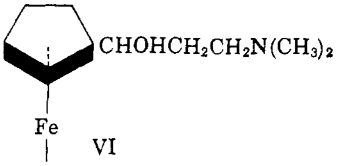
I

II. R = CH$_3$
III. R = C$_2$H$_5$

In the present investigation, which was initiated some time ago,[2] I was found to undergo the Mannich reaction with certain secondary amines, and the products were shown to exhibit reactions that are typical of ordinary Mannich salts.[5] Thus, salts II and III were prepared in good yields as indicated in Equation 1, and aqueous solutions of them were treated with sodium bicarbonate to liberate the free bases IV (80%) and V, respectively. The use of sodium hydroxide instead of bicarbonate brought about decomposition. Free base IV was then hydrogenated over Raney nickel to give the hydroxyamine VI in 80% yield.

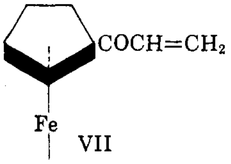


IV. R = CH$_3$
V. R = C$_2$H$_5$



VI

Another reaction of salts II and III involved heating aqueous solutions of them on the steam bath for one hour, under which condition the elements of the secondary amine were eliminate to form the α,β-unsaturated ketone VII. Good yields of VII were isolated, however, only under carefully controlled conditions since this product tends to undergo polymerization. The product was shown to have structure VII not only by analysis but also by its infrared spectrum, which exhibited strong bands at 6.04 and 6.22 μ for the carbonyl group[6] and conjugated carbon-carbon double bond,[7] respectively.



VII

Still another reaction of salt III involved its cyclization with phenylhydrazine to form the pyrazoline VIII in 49% yield. Two or more courses of reaction appear possible in the formation of such a compound.[8] The structure of the product was supported by analysis and by its infrared spectrum,

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[2] A portion of this work was completed in 1955 by R.L.P. at Linde Air Products Company, Tonawanda, N. Y.

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[4] M. D. Rausch and L. E. Coleman, Jr., *J. Org. Chem.*, 23, 107 (1958).

[5] F. F. Blicke, *Org. Reactions*, 1, 303 (1942).

[6] See L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley and Sons, New York, 1958, p. 136.

[7] See Ref. 6 p. 24.

[8] See Ref. 5, p. 320.