When the ethereal extract of the reaction mixture was thoroughly washed with 2*N* aqueous sodium hydroxide before being dried and evaporated, distillation gave directly product II, (7–12.5 g.; 30–50% yield). The 2,4-dinitrophenylhydrazone obtained from II was crystallized from ethanol in reddish orange needles and melted at 180–181°.

Anal. Calcd. for $C_{17}H_{16}O_4N_4$: C, 59.99; H, 4.74; N, 16.46. Found: C, 59.87; H, 4.89; N, 16.45.

A mixture of the 2,4-dinitrophenylhydrazone from I and II had m.p. 180–181°. Semicarbazone and phenylhydrazone could not be obtained under the usual conditions.

With an excess of aluminum chloride (*1.2 moles*). A mixture of benzoyl chloride (11.5 g.) and powdered aluminum chloride (13.1 g.) was prepared and the reaction was run for 11 hr. as described before. The product, worked up as in the foregoing section, gave the compound (II) (2.5 g.; 20% yield) and phenyl vinyl ketone (5.1 g.), characterized as 1,3-diphenylpyrazoline.[1]

Condensation with 2 moles of aluminum chloride. The reaction was effected in just the same way as described above, by the use of 2 moles of aluminum chloride. Working up of the reaction mixture gave a resinous product which could hardly be distilled.

Catalytic hydrogenation of (II). Hydrogenation of the compound II (1.8 g.) in ethyl acetate (20 cc.) was carried out in the presence of 10% palladized charcoal (0.2 g.); one equivalent of hydrogen (182 cc.) was absorbed after shaking for 18 min. The solution was then filtered from the catalyst, evaporated under reduced pressure and distilled to afford 0.8 g. (81%) of phenyl isobutyl ketone, which was characterized by the 2,4-dinitrophenylhydrazone, m.p. 131.5–132°, undepressed on admixture with a synthetic sample.[5]

Ozonolysis. A solution of (II) (1.5 g.) in ethyl acetate (20 cc.) was treated with ozone at −15°. After the reaction was completed, water was added to the solution to extract any soluble substance formed, and the aqueous layer was then distilled. Volatile component was collected in a flask containing alcohol. On treatment of the alcoholic solution with 2,4-dinitrophenylhydrazine, yellow precipitates were obtained. Recrystallization from alcohol gave yellowish orange needles, melting at 128°, which showed no depression in melting point on admixture with 2,4-dinitrophenylhydrazone of acetone. After removal of the volatile fraction, the aqueous solution was extracted with ether. Evaporation of ether left phenylglyoxylic acid, m.p. 66°.

Identification of (*II*) *with seneciophenone.* Seneciophenone was prepared by the condensation of benzene and 3,3-dimethylacryloyl chloride according to Smith and Engelhart.[6] 2,4-Dinitrophenylhydrazone had melting and mixed melting point 180–181°.[7] A solution of (II) in chloroform was cooled in an ice bath and the theoretical amount of bromine was added. Evaporation of the resultant mixture under reduced pressure left a white solid, which was recrystallized from methanol in white needles, m.p. 78–79°.

Anal. Calcd. for $C_{11}H_{12}Br_2O$: C, 41.28; H, 3.78. Found: C, 40.97; H, 3.79.

No depression in melting point was observed on admixture of the dibromide with dibromoseneciophenone.[6]

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Derivatives of Ferrocene. IV. Ferrocene-Containing Unsaturated Ketones[1]

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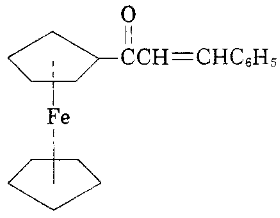
We wish to report the synthesis of a ferrocene analog of chalcone, cinnamoylferrocene (I), and the attempted preparation of both ferrocenyl vinyl ketone and ferrocenyl isopropenyl ketone. These ketones were desired as part of a program designed to study vinyl polymers containing the ferrocene unit, vinylferrocene[2] being the only other ferrocene-containing vinyl monomer thus far described in the literature.



I

Cinnamoylferrocene was prepared in 81.5% yield by the Friedel-Crafts reaction of equimolar quantities of ferrocene, *trans*-cinnamoyl chloride and aluminum chloride in methylene chloride solution. Ketone I was also prepared in 47% yield by the Claisen-Schmidt condensation of acetylferrocene, benzaldehyde, and sodium hydroxide in aqueous ethanolic solution. The Friedel-Crafts procedure is to be preferred in view of the excellent yields obtained, the simplicity of the preparation, and the purity of the product.

Catalytic hydrogenation of I in the presence of platinum on charcoal produced the saturated ferrocenyl ketone, β-phenylpropionylferrocene. Ketone I also reacted readily with hydroxylamine in ethanolic potassium hydroxide solution to form a derivative, cinnamoylferrocene oxime.

In an attempt to prepare ferrocenyl vinyl ketone by a method similar to that for the preparation of phenyl vinyl ketone,[3] acetylferrocene, paraformaldehyde, and dimethylamine hydrochloride were reacted in absolute ethanol to produce a 68% yield, based on recovered acetylferrocene, of β-dimethylaminopropionyl ferrocene hydrochloride. Pyrolysis of this hydrochloride by steam distillation did not produce any of the desired product, however, and only a brown polymeric residue was isolated, even in the presence of a polymerization inhibitor such as hydroquinone.

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(5) Authentic sample of phenyl isobutyl ketone was prepared according to G. Schroeter, *Ber.*, **40,** 1601 (1907).

(6) L. I. Smith and V. A. Engelhart, *J. Am. Chem. Soc.*, **71,** 2671 (1949).

(7) E. A. Braude and J. A. Coles reported the m.p. 185–186° in ref. 3.

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(1) For paper III of this series, see M. Vogel, M. D. Rausch, and H. Rosenberg, *J. Org. Chem.*, **22,** 1016 (1957).

(2) R. S. Arimoto and A. C. Haven, *J. Am. Chem. Soc.*, **77,** 6295 (1957).

(3) C. Mannich and G. Heilner, *Ber.*, **55,** 356 (1922).

Propionylferrocene[4] was converted to the Mannich base in a similar manner; the latter was not isolated but subjected directly to steam distillation. In contrast to the propiophenone analog,[5] it did not pyrolyze to give the desired isopropenyl ketone.

Cinnamoylferrocene has proved polymerizable, and details will be reported later.

EXPERIMENTAL[6]

Cinnamoylferrocene (I). *Method A.* A solution of 46.7 g. (0.35 mole) of anhydrous aluminum chloride and 58.4 g. (0.35 mole) of *trans*-cinnamoyl chloride in 300 ml. of dried methylene chloride was added with stirring and under a nitrogen atmosphere to a solution of 65.2 g. (0.35 mole) of ferrocene in 300 ml. of methylene chloride. During the addition, vigorous evolution of hydrogen chloride occurred and the formation of a blue-green reaction mixture was noted. After stirring for 22 hr. at room temperature following completion of the addition, the reaction mixture was hydrolyzed with 500 g. of ice. The light blue aqueous phase was extracted twice with 50-ml. portions of carbon tetrachloride, the combined organic layer washed to neutrality with 100 ml. portions of water, and then dried over calcium sulfate. Evaporation of the solvent left a dark red crystalline residue which was dissolved in 400 ml. of hot 95% ethanol and chilled overnight at −20°. After filtering and drying, 90.9 g. (81.5% yield) of violet crystals of I was obtained, m.p. 137.0–137.5°. Several recrystallizations from ethanol produced an analytical sample of I, m.p. 139.5–139.7°.

Anal. Calcd. for $C_{19}H_{16}FeO$: C, 72.17; H, 5.10; Fe, 17.66. Found: C, 72.28, 72.31; H, 5.12, 5.14; Fe, 17.56, 17.40.

Method B. A mixture of 2.18 g. (0.01 mole) of acetylferrocene, 1.06 g. (0.01 mole) of benzaldehyde, 5 ml. of 10% sodium hydroxide solution and 30 ml. of methanol was shaken at room temperature for 40 hr. The solvent was then evaporated and the residue recrystallized from methanol to produce 1.50 g. (47% crude yield) of I in the form of red violet crystals, m.p. 130–131°. Recrystallization from methanol raised the melting point to 139.0–139.5°.

A mixture of samples of I prepared by both methods melted at 138.2–139.0°. Furthermore, the infrared spectra of both samples of I (in chloroform solution) were identical.

An oxime, prepared in the usual manner, was recrystallized from a mixture of methanol and water to produce dark orange crystals of melting point 116–118°.

Anal. Calcd. for $C_{19}H_{17}FeNO$: C, 68.92; H, 5.17; Fe, 16.86; N, 4.23. Found: C, 69.02, 68.80; H, 4.97, 5.09; Fe, 16.80, 16.89; N, 4.19, 4.38.

β-Phenylpropionylferrocene. Catalytic hydrogenation of I in 1-butanol solution using 5% platinum on charcoal catalyst produced a 57% yield of β-phenylpropionylferrocene in the form of orange crystals, m.p. 81.5–82.5°. An additional recrystallization from ethanol produced an analytical sample, m.p. 84.5–84.8°.

Anal. Calcd. for $C_{19}H_{18}FeO$: C, 71.72; H, 5.70; Fe, 17.55. Found: C, 71.89, 71.91; H, 5.74, 5.60; Fe, 17.71, 17.57.

Propionylferrocene. In a procedure similar to that described above for the preparation of I (Method A), a methylene chloride solution of 27.8 g. (0.30 mole) of propionyl chloride and 40.0 g. (0.30 mole) of anhydrous aluminum chloride was added to 57.7 g. (0.31 mole) of ferrocene dissolved in the same solvent. After hydrolysis and product workup, a dark oily residue was obtained. The residue was purified by chromatography on an alumina column using chloroform as the eluent. Evaporation of the chloroform and recrystallization of the solid residue from petroleum ether (b.r. 39–51°) produced 34.8 g. (48% yield) of yellow orange needles of propionylferrocene, m.p. 38.0–38.2°.

An oxime, prepared in the usual manner, was recrystallized from a mixture of ethanol and water to yield golden yellow leaflets of melting point 135.4–136.0°.

Anal. Calcd. for $C_{13}H_{15}FeNO$: C, 60.73; H, 5.88; Fe, 21.72; N, 5.45. Found: C, 60.91, 60.98; H, 5.95, 6.09; Fe, 22.09, 21.92; N, 5.35, 5.32.

β-Dimethylaminopropionylferrocene hydrochloride. A mixture of 11.4 g. (0.05 mole) of acetylferrocene, 4.08 g. (0.05 mole) of dimethylamine hydrochloride, 2.25 g. (0.075 mole) of paraformaldehyde, 0.15 ml. of concentrated hydrochloric acid and 50 ml. of absolute ethanol was warmed to reflux. After 1 hr. an additional 1.50 g. of paraformaldehyde was added and refluxing was continued for an additional 2 hr. The mixture was cooled to room temperature, the solvent was evaporated, and the residue extracted repeatedly with ether. From the ether extracts 7.1 g. of acetylferrocene, m.p. 83.5–84.0°, was recovered. The oily ether-insoluble residue was recrystallized from a mixture of ethanol and methyl ethyl ketone to produce 4.1 g. of fine yellow brown crystals of β-dimethylaminopropionylferrocene hydrochloride, m.p. 171–172°, with decomposition. The yield, based on the recovered acetylferrocene, was 68%.

Anal. Calcd. for $C_{15}H_{20}ClFeNO$: C, 56.01; H, 6.27; Cl, 11.02; Fe, 17.36; N, 4.36. Found: C, 56.03, 55.93; H, 6.33, 6.11; Cl, 11.17, 11.32; Fe, 17.13, 17.41; N, 4.65, 4.58.

Steam distillation apparently pyrolyzed this hydrochloride, although no ferrocenyl vinyl ketone could be isolated. A small amount of brown solid was obtained from the distillate, however, and a much larger amount from the distillation flask. After thoroughly washing with water, benzene, and acetone and then drying, the latter solid analyzed as follows:

C, 56.75; H, 4.83; Fe, 25.10; N, 0.63.

Both products appeared to be polymeric in nature and were insoluble in water, benzene, and ether. Addition of a polymerization inhibitor, hydroquinone, during the pyrolysis did not change the result.

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[4] Propionylferrocene has recently been reported by Dr. K. L. Rinehart, Jr., as an intermediate for the preparation of β-ferrocenylpropionic acid; see Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April 7 to 12, 1957, pp. 47–0.

[5] J. H. Burckhalter and R. C. Fuson, *J. Am. Chem. Soc.*, 70, 4184 (1948).

[6] All melting points are corrected; analyses were made by Schwarzkopf Microanalytic Laboratory, Woodside 77, New York, N. Y.

Esterification with Trapping Phase

HENRY KLOSTERGAARD

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Synthesis of an ester from alcohol and acid presents special problems in cases where the ester has a higher boiling point than the alcohol or acid. The method described below is a simple solution to the problems in many cases. It is based on phase separation.

Alcohol and acid are heated with a catalyst and an ester solvent, nonmiscible with water, is added. On the subsequent addition of large amounts of dehydrants phase separation occurs, and it can be