

cyclopentanone by means of the Wittig reaction. Descriptions of procedures generally indicate that any methyltriphenylphosphonium halide may be used to prepare the desired triphenylphosphine-methylene. The halide is usually the bromide,³ although the chloride has also been used.⁴ We have experienced considerable difficulty in the use of the iodide. Four attempts were made, following the procedure of Sondheimer and Mechonlan,⁵ but using triphenylmethylphosphonium iodide (prepared from triphenylphosphine and methyl iodide, m.p. 179–180°) instead of the bromide. When attempts were made to filter or centrifuge the precipitate, presumed to be triphenylphosphine oxide, after the completion of the reaction of the reagent with cyclopentanone, a dark green semi-solid formed on contact with air or moisture. This interfered with the separation. As a final product, only a rather viscous, dark colored liquid, which showed no olefinic or methylenic bands in an infrared spectrum, could be isolated from the tetrahydrofuran solution.

It is felt that this difficulty is due to the presence of some iodine containing byproduct, as substitution of methyltriphenylphosphonium bromide in the reaction sequence allows the preparation of the desired methylenecyclopentane.

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(3) See the references listed in the following reviews: (a) U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959); (b) J. Levisalles, *Bull. Soc. chim. (France)*, 1021 (1958); (c) G. Wittig, *Experientia*, **12**, 41 (1956).

(4) G. Wittig and U. Haag, *Chem. Ber.*, **88**, 1654 (1955).

(5) F. Sondheimer and R. Mechonlan, *J. Am. Chem. Soc.*, **79**, 5029 (1957).

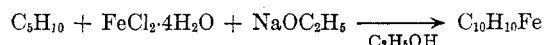
Preparation of Ferrocene from Anhydrous and Hydrated Ferrous Chloride in Alcohol

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Two convenient laboratory preparations of ferrocene in high yields have been reported.¹ In the original report of the preparation of ferrocene from anhydrous ferrous chloride and cyclopentadiene in anhydrous aliphatic amine solvents,² it was mentioned that low yields of ferrocene could be obtained with ferrous chloride, cyclopentadiene, and sodium methoxide. Lindstrom and Barusch³ reported that ferrocene can be conveniently prepared in 43% yield from cyclopentadiene, anhy-

drous ferrous chloride, and sodium ethoxide in ethanol. We wish to submit an experimental procedure for this preparation leading to 90% yield of ferrocene. Since the starting materials are identical in our preparation and that of Lindstrom and Barusch, the principal differences in the two procedures lie in the order of addition of reactants, our use of a 10% excess of base, and a longer reaction time in our preparation. Excess base was found crucial in the observation that commercial hydrated ferrous chloride can also be used in the preparation with a sacrifice in yield:



When iron(II) chloride-4-hydrate is used, the addition of slightly more than six moles of sodium ethoxide per mole of ferrous chloride is necessary, and yields up to 30% can be realized. Attempts to remove the hydration water by azeotropic distillation (added benzene) of part of the alcohol from the solution of ferrous chloride prior to the addition of base did not improve the results. Use of potassium hydroxide as the base in place of sodium ethoxide failed to yield any ferrocene.

Commercial anhydrous ferrous sulfate gave no ferrocene by this method, presumably due to the insolubility of ferrous sulfate in alcohol.

EXPERIMENTAL

Use of anhydrous ferrous chloride. To a suspension of 1 mole of ferrous chloride in 400 ml. of dry tetrahydrofuran, prepared in the usual manner¹ from 108 g. of anhydrous ferric chloride and 30 g. of iron powder, was added under nitrogen a solution of sodium ethoxide, prepared by dissolving 50.5 g. (2.2 moles) of sodium in 800 ml. of absolute ethanol. A blue-green precipitate was formed, and to the thick slurry was added with stirring 132 g. (2.0 moles) of freshly distilled cyclopentadiene in one portion. After about 10 min. the slurry had taken on an orange hue and the temperature had risen to 45°. The mixture was stirred for 3 hr. without heat. At the end of this time crystals of ferrocene had precipitated, and 200 ml. of water was added slowly, followed by the addition of 0.5 g. of sodium hydrosulfite and sufficient dilute hydrochloric acid to reduce the small amount of the blue ferrocenium ion formed. Addition of 2 l. of water completed the precipitation of the ferrocene, which was collected by filtration. The crude product was recrystallized from a mixture of 1 l. of petroleum ether (b.p. 90–100°) and about 200 ml. of methylene chloride to yield 138 g. of ferrocene, m.p. 174.5–175.5°, and an additional 29.5 g. melting at 172–174° from evaporation of the mother liquor. The total yield of ferrocene from this procedure was 90%.

Use of hydrated ferrous chloride. A solution of 19.9 g. (0.1 mole) of iron(II) chloride-4-hydrate in 300 ml. of absolute ethanol was prepared and de-oxygenated with nitrogen introduced under the surface of the solution through a fritted disk. A small amount of iron powder was added to reduce any ferric ions present. The mixture was allowed to reflux for an hour and was cooled to room temperature. At the end of the reflux period the solution had turned from

(3) (a) M. E. Barusch and E. G. Lindstrom, U. S. Patent **2,834,796**, May 13 (1958); *Chem. Abstr.*, **52**, 16366 (1958); (b) E. G. Lindstrom and M. E. Barusch, Abstracts of the 131st Meeting of the American Chemical Society, Miami, Fla., April 7–12, 1957.

(1) G. Wilkinson, *Org. Syntheses*, **36**, 31 (1956).

(2) L. Birmingham, D. Seyferth, and G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 4179 (1954).

green to colorless. To this solution was added with stirring a solution formed by adding 14.9 g. of sodium (0.65 mole) to 500 ml. of absolute ethanol. A greyish white precipitate was formed immediately, and to the slurry was added at once 13.2 g. (0.2 mole) of cyclopentadiene. The mixture was stirred at room temperature for 3 hr. and was then brought to reflux for 3 hr. The volume of the solution, filtered through asbestos, was reduced to 300 ml., and 1700 ml. of water was added. The ferrocene precipitated and after drying weighed 5.6 g. for 30% yield melting at 169–172°.

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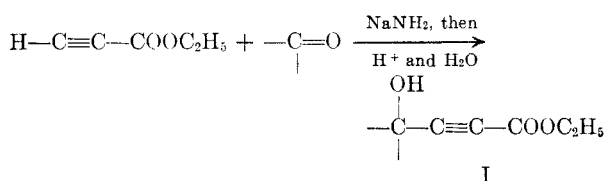
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Potassium Hydroxide as a Catalyst for the Condensation of Propiolic Acid or Propiolic Esters with Ketones

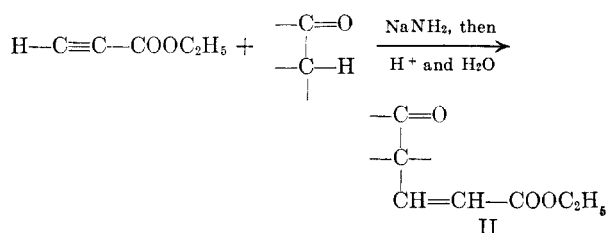
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In previous communications^{2,3} we have reported that sodamide in liquid ammonia will bring about the condensation of ethyl propiolate with various cyclic ketones to yield either acetylenic carbinols (I) or esters of substituted acrylic acids (II), depending upon the ketone used.



or



The ability of potassium hydroxide to bring about analogous condensations of acetylene with ketones is well known.⁴ This fact prompted us to try potassium hydroxide as a condensing agent for

(1) Taken in part from the master's degree thesis of Louis P. Remsberg, Jr., June, 1956.

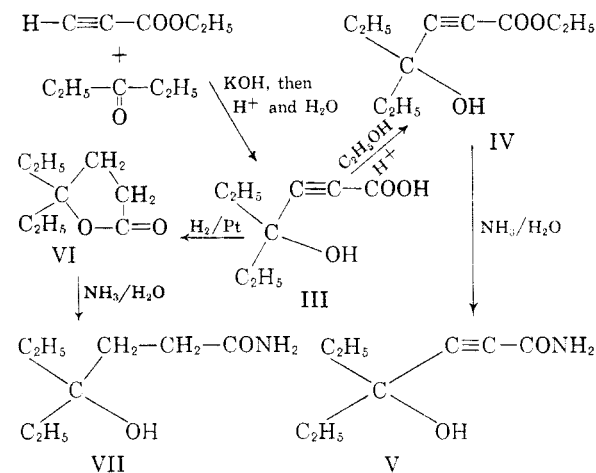
(2) W. E. Bachmann and E. K. Raunio, *J. Am. Chem. Soc.*, **72**, 2530 (1950).

(3) W. E. Bachmann, G. I. Fujimoto, and E. K. Raunio, *J. Am. Chem. Soc.*, **72**, 2533 (1950).

(4) Louis F. Fieser and Mary Fieser, *Organic Chemistry*, third edition, D. C. Heath and Co., Boston, 1956, p. 91.

the condensation of both propiolic acid and of ethyl propiolate with certain ketones. It was found that propiolic acid will add to cyclohexanone in the presence of a solution of potassium hydroxide in aqueous alcohol to yield the acetylenic carbinol.

Furthermore, a suspension of powdered potassium hydroxide in ether brought about the condensation of ethyl propiolate with cyclohexanone in as high yields as were obtained using sodamide in liquid ammonia as the condensing agent.² Likewise, a suspension of powdered potassium hydroxide in ether brought about the condensation of the acyclic ketone, diethyl ketone, with ethyl propiolate. In this case the product was isolated as the crystalline 4-ethyl-4-hydroxy-2-hexynoic acid (III).



This acid was further characterized through its crystalline amide (V) which was prepared through the ester (IV). The structure of the acid was established by conversion through the lactone (VI) to the amide (VII) of the known 4-hydroxy-4-ethylhexanoic acid. An authentic sample of this amide was obtained from the lactone which was prepared by the procedure of Hepworth.⁵

In the case of the diethyl ketone and ethyl propiolate, powdered potassium hydroxide in ether gave as good a yield of III, as did sodium hydride in ether. No identifiable condensation product was obtained when the condensation was attempted with sodamide in liquid ammonia as the condensing agent.

EXPERIMENTAL

Condensation of propiolic acid with cyclohexanone. A solution containing 25 g. (0.36 mole) of propiolic acid, 38 g. (0.39 mole) of cyclohexanone, 35 g. (0.52 mole, based on 85% purity) of potassium hydroxide, 5 ml. of water, and 100 ml. of ethanol was allowed to stand at room temperature for 2 days. The solution was refluxed for 10 min., cooled, diluted with 250 ml. of water, and was washed with three portions of ether (washings discarded). The aqueous layer was acidified with sulfuric acid and was extracted with three 35-ml. portions of ether. Removal of the ether under reduced pressure left 50 g. of acidic material from which 18 g. of β (1-hydroxycyclohexane)propiolic acid crystallized

(5) H. Hepworth, *J. Chem. Soc.*, 115, 1207 (1919).