and for 10 hr. at 25°. Water was added and the organic layer separated, dried, and distilled. A 19.5-g. (59%) yield of product, b.p. 85–87°/22 mm., was obtained and characterized by comparison of the infrared spectrum with that of an authentic sample.[1]

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HAMILTON COLLEGE
CLINTON, N. Y.

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## Chromic Acid Oxidation of Cyclohexanols to Cyclohexanones

ALLEN S. HUSSEY AND ROBERT H. BAKER

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Having invested several hours in the preparation of 4-ethylcyclohexanol,[1] we were reluctant to carry out the time-honored oxidation with Beckmann's chromic acid[2] by the usual procedure.[3] This procedure involves the addition of the alcohol in portions,[3] or all at once,[4] to the chromic acid solution and the yields are realatively low (50–70%[1,4]).

By reducing the considerable excess of sodium dichromate commonly used[3] to 20% more than the stoichiometric amount, using the stoichiometric quantity of sulfuric acid, *and adding these reagents in aqueous solution to a warm slurry of 4-ethylcyclohexanol in water*, the yield of 4-ethylcyclohexanone was increased from 70–75%[1] to 90%. A similar procedure increased the yield of 2-methylcyclohexanone from 50–60%[5] to 80% and of menthone, from 85%[3] to 94%.

Infrared spectra indicate the once-distilled products to be somewhat less contaminated by unoxidized alcohol than they are when prepared by the usual procedure,[4,5] and the method has the distinct advantage that it can be used safely to oxidize secondary alcohols in several mole batches. Considerable saving of oxidizing agent is also realized.

It seems quite reasonable to ascribe the improved yield of product to the excess of alcohol over oxidizing agent during the reaction as carried out by this procedure. The carboxylic acid oxidation products, which result from secondary oxidation of the ketone, seldom amount to more than 4–5% of the product.

This procedure is a modification of that developed by Jones and co-workers[6] wherein acetone solutions of unsaturated secondary alcohols maintained below 30° are titrated with standard chromic acid solution, (2.67*M* in chromium trioxide, 4.3*M* in sulfuric acid). The latter procedure is the preferred one for alcohols with other easily oxidized functions or for small scale preparations.

### EXPERIMENTAL

*4-Ethylcyclohexanone.* A solution of 120 g. (0.400 mole, 20% excess) of sodium dichromate dihydrate and 135 g. (1.33 mole) of 96% sulfuric acid in 500 ml. of water was added over 40 min. to a well stirred slurry of 128.0 g. (1.00 mole) of 4-ethylcyclohexanol[1] and 200 ml. of water in a 2-l. 3-neck flask fitted with a dropping funnel, condenser, and mechanical stirrer. The mixture became greenish-black within the first 2 min. and the temperature rose from 30° to 68° during the addition of the first half of the oxidizing agent. Immediately after the addition of the reagent was complete, the temperature began to fall and in 25 min. was at 55°. The mixture was cooled, extracted twice with 400 ml. of 3:1 ether-pentane and the extracts were washed several times with water. The dried extracts furnished 113.6 g. (90%) of 4-ethylcyclohexanone which distilled at 109–112°, 50 mm. ($n_D^{25}$ 1.4533) and 4.9 g. of alkali-soluble residue. An infrared spectrum of the product (12% chloroform) showed no hydroxyl absorption at 2.7–3.0 $\mu$.

*2-Methylcyclohexanone.* By a similar treatment, 114.0 g. (1.00 mole) of 2-methylcyclohexanol and 200 ml. of water gave 89.3 g. (80%) of 2-methylcyclohexanone (b.p. 104–107° at 116 mm.; $n_D^{23}$ 1.4473) when 120.0 g. of sodium dichromate dihydrate and 135 g. of sulfuric acid (96%) in 500 ml. of water were added over 45 min. The temperature rose to 60° and stirring was continued for 20 min. after the addition was complete. A highly purified sample prepared earlier by the alternate procedure[3] had $n_D^{23}$ 1.4472.

*l-Menthone. l*-Menthol (101.7 g., 0.652 mole) and 200 ml. of water were similarly treated, but at an initial temperature of 60°, with 77.7 g. (0.261 mole) of sodium dichromate dihydrate and 88.9 g. (0.870 mole) of 96% sulfuric acid in 400 ml. of water to give 94.0 g. (94%) of *l*-menthone, b.p. 116–119° at 41 mm.; $n_D^{23}$ 1.4490; $[\alpha]_D^{27}$ $-28.9°$ ($\alpha_D^{27}$ $-25.6°$, neat). The addition of oxidizing agent required 40 min. during which time the temperature was maintained at 65 to 72° by external heat. The mixture was stirred for 40 min. additional time and then was cooled and worked up in the usual way. By the alternate procedure the yield is 82–85%.[3]

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NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

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## A Difficulty Encountered in the Use of Methyltriphenylphosphonium Iodide in the Wittig Reaction

CAROL H. COLLINS[1] AND GEORGE S. HAMMOND[2]

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In connection with another study, we have attempted to prepare methylenecyclopentane from

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[1] Present address: University of Wisconsin, Madison, Wisconsin.

[2] Present address: California Institute of Technology, Pasadena, California.

cyclopentanone by means of the Wittig reaction. Descriptions of procedures generally indicate that any methyltriphenylphosphonium halide may be used to prepare the desired triphenylphosphinemethylene. 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 semisolid 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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IOWA STATE UNIVERSITY
AMES, IOWA

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# Preparation of Ferrocene from Anhydrous and Hydrated Ferrous Chloride in Alcohol

WILLIAM F. LITTLE, ROBERT C. KOESTLER,
AND ROBERT EISENTHAL

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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 Barusch[3] reported that ferrocene can be conveniently prepared in 43% yield from cyclopentadiene, anhydrous 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:

$$C_5H_{10} + FeCl_2{\cdot}4H_2O + NaOC_2H_5 \xrightarrow[C_2H_5OH]{} C_{10}H_{10}Fe$$

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 manner[1] 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 ferrocinium 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

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