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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Chromic Acid Oxidation of Cyclohexanols to Cyclohexanones

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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, (2.67M in chromium trioxide, 4.3M 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 μ.

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; $[\alpha]_D^{27}$ $-28.9°$ (α_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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A Difficulty Encountered in the Use of Methyltriphenylphosphonium Iodide in the Wittig Reaction

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

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