EXPERIMENTAL

1,2-Diphenyl-3,3-dichloroethylenimine Hexachloroacetone (97%, technical grade, Baker and Adams) (26 g., 0.1 mole), was added with stirring under dry nitrogen, over 1 hr. to a mixture of commercial sodium methoxide (5.4 g., 0.1 mole) (Matheson, Coleman, and Bell) and benzalaniline[6] (9 g., 0.05 mole) in dry petroleum ether (b.p. 37-39°) (200 ml., treated to remove any unsaturation present), cooled in an ice bath. Stirring was continued for 5-6 hr. under nitrogen, with the reaction mixture cooled in ice and water. The flask was then stoppered and kept overnight. It was then filtered and the residue separately treated with water, to remove inorganic materials; the desired product remained, 5 g., m.p. 95-98°. From the petroleum ether solution was obtained another 3 g. of product, m.p. 95-98° (total yield, 61%). Careful crystallization of a sample from petroleum ether gave creamy white crystals, m.p. 98-99° (reported,[4] m.p. 98-99°), identical with the product obtained by using ethyltrichloroacetate[3] in place of hexachloroacetone.

The compound has a characteristic unpleasant odor and precipitates silver chloride from an alcoholic solution of silver nitrate. It undergoes rearrangement in water; the reaction is very slow at room temperature but is complete in 30 min. at 100°, to give α-chloro-α-phenylacetanilide in quantitative yields. The amide was crystallized from acetone–petroleum ether mixture to give colorless crystals, m.p. 148-149° (reported,[4] m.p. 146-148°).

7,7-Dichlorobicyclo[4.1.0]heptane (dichloronorcarane). The reaction was carried out in essentially the same manner as before. It was then poured into cold water, extracted with ether, the ether extracts dried over anhydrous sodium sulphate, and concentrated. The residue was distilled through a short fractionating column and the dichloronorcarane collected at 78-79.5°/15 mm. (reported[7] b.p. 78-79°/15 mm.).

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.9; H, 6.1; Cl, 43.0. Found: C, 50.80; H, 5.95; Cl, 43.23.

The oily residue left behind in the distillation flask, on cooling solidified to give hexachloroisopropyl alcohol which crystallized from hexane to give colorless, stout crystals, m.p. 86-87° (reported[5] m.p. 87-87.5°).

Anal. Calcd. for $C_3H_2OCl_6$: C, 13.50; H, 0.76; Cl, 79.75. Found: C, 13.98; H, 0.93; Cl, 79.65.

Four experiments with variation in reactant concentrations gave yields of dichloronorcarane ranging from 34 to 43%. Yields of hexachloroisopropyl alcohol varied from 3% to 10%; the higher values were obtained with short reaction times and with equimolar amounts of hexachloroacetone and sodium methoxide.

1,1-Dichloro-2,2,3-trimethylcyclopropane. Hexachloroacetone (53.0 g., 0.2 mole) was added with stirring over 1.5 hr. under dry nitrogen, to a cold mixture of sodium methoxide (10.8 g., 0.2 mole) and 2-methyl-2-butene (150 ml., excess). The mixture was stirred for 3.5 hr. and worked up in the same manner as above. Fractional distillation yielded the product (b.p. 144°)[7] mixed with small amounts of methyltrichloroacetate (b.p. 154°). The ester was destroyed by refluxing with a 15% aqueous solution of potassium hydroxide (50 ml.) for 15 min., and 1,1-dichloro-2,2,3-trimethylcyclopropane distilled at 69.5°/55 mm., yield 7 g. (23%), (reported[7] b.p. 69-70°/55 mm.).

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 46.93; H, 6.66; Cl, 46.60.

From the residue was obtained hexachloroisopropyl alcohol, 4.0 g., m.p. 86-87°, identical in properties with that obtained in the reaction using cyclohexene.

Reaction media. After the above data were obtained, Dr. Francis T. Smyth found that more consistent yields could be obtained if 5 ml. of methanol were added to the petroleum ether solvent.

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Hexachloroacetone as a Source of Dichlorocarbene

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Since the original observation of Doering and Hoffman[1] that cyclopropane derivatives are formed by the reaction of chloroform, olefins, and potassium *t*-butoxide, a number of attempts have been made to increase the efficiency of this conversion by varying the base[2,3] and the chlorinated species.[3] Recently, Parham and Schweizer[3] have developed an elegant procedure based on ethyl trichloroacetate as the progenitor of the dichlorocarbene intermediate in this reaction. Yields of cyclohexene adduct of up to 79%, based on trichloroacetate, were obtained using sodium methoxide as the base.

The reaction of sodium methoxide with hexachloroacetone presents a mechanistically similar situation where the latter reagent has the advantage of offering two equivalents of dichlorocarbene per molecule. Preliminary experiments

$$Cl_3CCOCCl_3 \xrightarrow{OR^-} :CCl_2 + Cl^- + Cl_3CCOOR$$

$$Cl_3CCOOR \xrightarrow{OR^-} :CCl_2 + Cl^- + CO(OR)_2$$

carried out with cyclohexene as the carbene acceptor have resulted in a 59% yield of 2,2-dichlorobicyclo[4.1.0]heptane based on the indicated stoichiometry.

EXPERIMENTAL[4]

2,2-Dichlorobicyclo[4.1.0]heptane. Sodium (5.75 g., 0.25 g.-atoms) was added in portions to 30 ml. of anhydrous methanol. Excess methanol was removed by heating and flushing with dry nitrogen. Hexachloroacetone[5] (26.5 g., 0.10 mole) was added dropwise with stirring to a mixture of the sodium methoxide and 82.0 g. (1.0 mole) of cyclohexene at 0-5°. Stirring was continued for 5 hr. at this temperature

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[1] W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[2] H. E. Winberg, *J. Org. Chem.*, **24**, 264 (1959).

[3] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

[4] Boiling points are uncorrected.

[5] We wish to thank the General Chemical Division of Allied Chemical Corporation for a sample of this material.

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, (2.67*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 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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