



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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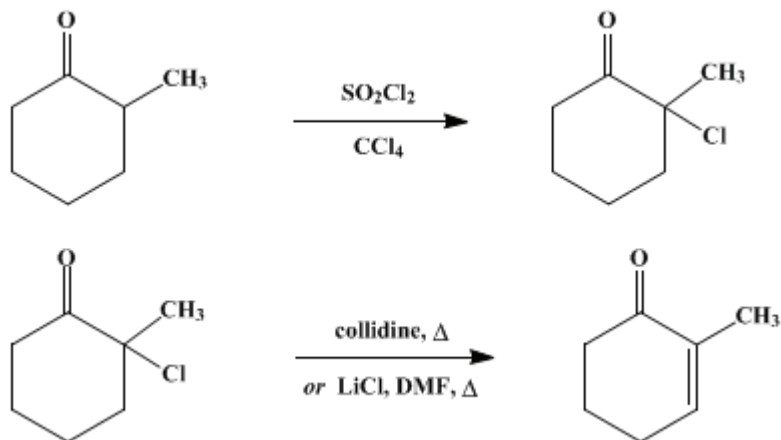
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.162 (1963); Vol. 37, p.8 (1957).

2-CHLORO-2-METHYLCYCLOHEXANONE and 2-METHYL-2-CYCLOHEXENONE

[(Cyclohexanone, 2-chloro-2-methyl-) and (2-Cyclohexen-1-one, 2-methyl-)]



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1. Procedure

A. *2-Chloro-2-methylcyclohexanone.* A 3-l. three-necked flask, fitted with a sealed mechanical stirrer with glass blade, a dropping funnel, and an outlet tube connected to a gas-absorption trap,² is charged with a solution of 224 g. (2.0 moles) of 2-methylcyclohexanone (Note 1) in 1 l. of dry carbon tetrachloride. A solution of 179 ml. (297 g., 2.2 moles) of sulfuryl chloride (Note 2) in 300 ml. of dry carbon tetrachloride is added from the dropping funnel over a 1-hour period with stirring. The slightly exothermic reaction is moderated by cooling the flask with a bath of water at room temperature. After the addition is complete, stirring is continued for 2 hours. The yellow solution is then washed successively with three 300-ml. portions of water, two 200-ml. portions of saturated sodium bicarbonate solution, and one 200-ml. portion of saturated salt solution, and finally dried over anhydrous magnesium sulfate.

The solvent is removed by distillation through a 15-cm. Vigreux column, first at atmospheric pressure and finally at reduced pressure (water aspirator). The residue is satisfactory for the preparation of 2-methyl-2-cyclohexenone described below (part B). Distillation through the column gives, after a small fore-run, 243–248 g. (83–85%) of colorless 2-chloro-2-methylcyclohexanone, b.p. 94–96°/27mm., n_D^{25} 1.4672, d_4^{25} 1.088 (Note 3).

B. *2-Methyl-2-cyclohexenone.* (a) *Collidine method.* The crude (undistilled) 2-chloro-2-methylcyclohexanone prepared as described above (part A) is transferred to a 1-l. three-necked flask fitted with a stout sealed Hershberg wire stirrer and two efficient reflux condensers, one attached to each side neck; and 290 ml. (266 g., 2.2 moles) of 2,4,6-collidine (Note 2) is added rapidly through one of the condensers with stirring. The flask is heated to 145–150° (bath temperature) with an oil bath until there ensues a sudden exothermic reaction which results in vigorous boiling of residual carbon tetrachloride. The reaction is essentially complete within 1 minute, and the mixture becomes very viscous with suspended collidine hydrochloride. The heating is discontinued, and, as the reaction mixture cools and becomes viscous enough to impede stirring, a total of 500 ml. of benzene is added cautiously (with vigorous boiling) through a condenser in order to maintain fluidity. The collidine hydrochloride is collected by suction filtration on a 10-cm. sintered glass suction filter, then transferred to a beaker, triturated with 300 ml. of benzene, and refiltered. After repetition of this treatment, the weight of residual salt is about 303 g. (96%).

The combined dark-brown filtrates are washed (Note 4) with two 300-ml. portions of 10% hydrochloric acid saturated with sodium chloride, with one 300-ml. portion of saturated sodium bicarbonate solution, and with one 300-ml. portion of saturated salt solution, and finally dried over anhydrous magnesium sulfate. The benzene is removed by distillation through a 15-cm. Vigreux column, and then all material boiling at 70–97°/56 mm. is collected (Note 5). Fractionation of this material through a 20-cm. heated column packed with steel saddles gives, after a fore-run of benzene, 100–109 g. (45–49% yield from 2-methylcyclohexanone) of colorless 2-methyl-2-cyclohexenone, b.p. 98–101°/77 mm., n_D^{25} 1.4830–1.4835, d_4^{25} 0.972, $\lambda_{\max}^{\text{alc}}$ 234 m μ (ϵ 9660) (Note 6).

(b) *Lithium chloride method.* A 1-l. three-necked flask, fitted with a sealed Hershberg wire stirrer, a thermometer, and a tube leading to a source of nitrogen, is charged with 26 g. of lithium chloride, 250 ml. of dimethylformamide (Note 7) and crude 2-chloro-2-methylcyclohexanone prepared as described above (part A, half-scale) from 112 g. of 2-methylcyclohexanone. The stirrer is started, the air swept out with nitrogen, and the flask immersed in an oil bath maintained at 100°. The temperature of the reaction mixture rises to 100° in about 10 minutes, then to 112° and back to 105° in another 25 minutes. At the end of this time the mixture is cooled, 1-l. each of ether and of 2.5% sulfuric acid is added, and the mixture is stirred for about 4 hours to hydrolyze the dimethylformamide. The aqueous layer is separated, saturated with sodium chloride, and extracted with four 150-ml. portions of ether. These extracts are combined with the original ether layer, washed with saturated sodium chloride solution and saturated sodium bicarbonate solution, and finally dried over anhydrous sodium sulfate. The ether is removed by distillation through a 15-cm. Vigreux column, and then a fraction boiling at 79–107°/28 mm. is collected. Redistillation through a 20-cm. heated column packed with steel saddles gives 47–50 g. (43–45% yield from 2-methylcyclohexanone) of colorless 2-methyl-2-cyclohexenone, b.p. 83–85.5°/35 mm., n_D^{25} 1.4833–1.4840, $\lambda_{\max}^{\text{alc}}$ 234 m μ (ϵ 9680) (Note 6).

2. Notes

1. 2-Methylcyclohexanone is available commercially. In the present work it was prepared as follows. A 3-l. three-necked flask, fitted with a Hershberg wire stirrer, dropping funnel, and a thermometer, is charged with a solution of 228 g. (2.0 moles) of 2-methylcyclohexanol (Eastman Kodak Company practical grade) in 1 l. of benzene. A solution of 238 g. of sodium dichromate dihydrate in 1 l. of water containing 324 ml. of concentrated sulfuric acid and 100 ml. of acetic acid is added from the funnel over a period of 2.5 hours with stirring. The temperature of the reaction mixture is maintained (ice bath) at 10° or slightly below during the addition and also during a 3-hour stirring period after the addition. The aqueous layer is separated, diluted with 250 ml. of water, and extracted with two 300-ml. portions of benzene. These extracts are combined with the original benzene layer, and the whole is washed in sequence with 500 ml. of water, 400 ml. of saturated sodium bicarbonate solution, and 400 ml. of saturated salt solution. After the solution has been dried over anhydrous magnesium sulfate, the benzene is removed by distillation through a 20-cm. Vigreux column. Distillation of the residue through a 20-cm. column packed with steel saddles gives 193–200 g. (85–88% yield) of 2-methylcyclohexanone, b.p. 162.5–163.5°/742 mm., n_D^{25} 1.4459.
2. Eastman Kodak Company practical grade.
3. The homogeneity of this product has been demonstrated.³ It is stable for long periods if stored in a brown bottle over a little magnesium oxide.
4. Excessive washing with aqueous solution is avoided as the product has appreciable solubility in water.
5. The dark oily distillation residue (about 72 g.) distils at 140–200° /1 mm. and consists mainly of the dimer of 2-methylenecyclohexanone which can be isolated in 23% yield.³
6. On standing, the ketone gradually turns yellow, and the refractive index increases. Redistillation of such material gives pure ketone.
7. Supplied by Matheson, Coleman and Bell.

3. Discussion

The only published method for producing pure 2-chloro-2-methylcyclohexanone is by the action of sulfuryl chloride on 2-methylcyclohexanone.³ Direct chlorination gives mixtures of the 2- and 6-chloro compounds.³

2-Methyl-2-cyclohexenone has been prepared by the action of nitrosyl chloride on 1-methylcyclohexene, followed by dehydrohalogenation with sodium methoxide⁴ or sodium acetate,⁵ and hydrolysis of the resulting oxime; in an impure condition by several methods;^{6,7 8,9,10,11,12,13} by dehydration of the ketol produced by the reaction of methylmagnesium iodide with 1,2-cyclohexanedione;^{8,14} by reduction of the enol methyl ether produced by the reaction of diazomethane with 1,2-cyclohexanedione;¹⁵ by bromination of 2-methylcyclohexanone with N-bromosuccinimide, followed by dehydrobromination with pyridine or with 2,4-dinitrophenylhydrazine;¹⁶ by treatment of 5-heptenoic acid chloride with stannic chloride;¹⁷ and by the present method.³ The use of lithium chloride in dimethylformamide for the dehydrohalogenation is an adaptation of the method of Holysz.¹⁸

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 666
- Org. Syn. Coll. Vol. 7, 249

References and Notes

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Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

sodium acetate (127-09-3)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

sodium methoxide (124-41-4)

sulfuryl chloride (7791-25-5)

pyridine (110-86-1)

methylmagnesium iodide (917-64-6)

2,4-Dinitrophenylhydrazine (119-26-6)

nitrosyl chloride (2696-92-6)

stannic chloride (7646-78-8)

magnesium sulfate (7487-88-9)

Diazomethane (334-88-3)

magnesium oxide

sodium dichromate dihydrate (10588-01-9)

dimethylformamide (68-12-2)

N-bromosuccinimide (128-08-5)

2,4,6-collidine (108-75-8)

2-methylcyclohexanone (583-60-8)

2-methylcyclohexanol (583-59-5)

1-methylcyclohexene

2-Methyl-2-cyclohexenone,
2-Cyclohexen-1-one, 2-methyl- (1121-18-2)

2-Chloro-2-methylcyclohexanone,
Cyclohexanone, 2-chloro-2-methyl- (10409-46-8)

collidine hydrochloride

Lithium chloride (7447-41-8)

2-methylenecyclohexanone

1,2-Cyclohexanedione (765-87-7)

5-heptenoic acid chloride