



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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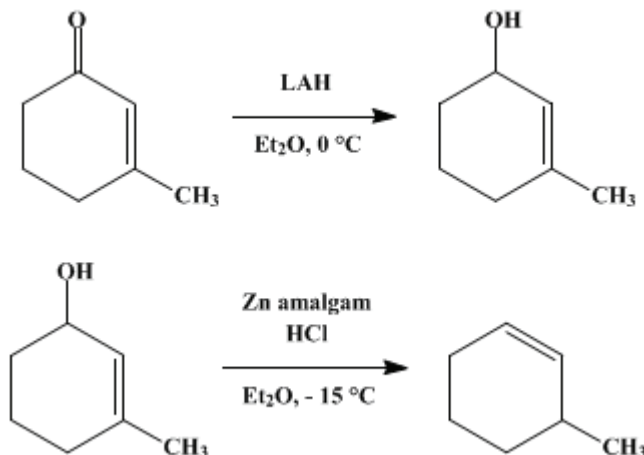
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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REDUCTIVE CLEAVAGE OF ALLYLIC ALCOHOLS, ETHERS, OR ACETATES TO OLEFINS: 3-METHYLCYCLOHEXENE

[Cyclohexene, 3-methyl-]



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Checked by M. L. Lee and G. Büchi.

1. Procedure

A. *3-Methyl-2-cyclohexen-1-ol*. A solution of 33.6 g. (0.305 mole) of *3-methyl-2-cyclohexen-1-one* (Note 1) in 600 ml. of anhydrous diethyl ether is placed in a 2-l., three-necked, round-bottomed flask fitted with a mechanical stirrer, a reflux condenser attached to a source of dry nitrogen, and a pressure-equalizing dropping funnel. The solution is stirred and cooled in an ice bath while 471 ml. (0.0825 mole) of a 0.175 M solution of lithium aluminum hydride in ether (Note 2) is added dropwise. When the addition is complete the reaction mixture is stirred at 0° for another 15 minutes. Cooling and gentle stirring are continued while moist ether is added through the dropping funnel until gas is no longer evolved. The resulting slurry is filtered, and the filtrate is washed with saturated aqueous sodium chloride and dried over magnesium sulfate. Removal of ether on a water bath and distillation of the residue under reduced pressure provide 33.7 g. (98%) of *3-methyl-2-cyclohexen-1-ol*, b.p. 94–95° (31 mm.).

B. *Amalgamated zinc*. Zinc powder (206 g., 3.15 moles) is placed in a 1-l. beaker, covered with 250 ml. of 10% hydrochloric acid, and stirred for 2 minutes. The acid is then decanted and replaced by distilled water, the mixture is stirred, and the supernatant is decanted. Washing is continued in this way until the water is neutral to litmus. A warm solution of 40 g. (0.15 mole) of mercury(II) chloride in 250 ml. of distilled water is then poured onto the zinc, and the mixture is stirred gently for 10 minutes. After filtration, the powder is washed with 250 ml. of distilled water, five 250-ml. portions of 95% ethanol, and five 250-ml. portions of anhydrous ether. Drying under vacuum gives 196 g. of zinc amalgam.

C. *3-Methylcyclohexene*. A 1-l., round-bottomed, three-necked flask equipped with a mechanical stirrer, a reflux condenser connected to a source of dry nitrogen, and a pressure-equalizing addition funnel is charged with 196 g. (3 moles) of dry amalgamated zinc powder (Note 3), 22.4 g. (0.200 mole) of *3-methyl-2-cyclohexen-1-ol*, and 280 ml. of anhydrous ether. The flask is placed in an ethanol–water–dry ice bath maintained at –15° throughout the reaction. The reaction mixture is stirred gently for 5 minutes, then stirred vigorously while 153 ml. (0.40 mole) of 2.6 M hydrogen chloride in anhydrous ether (Note 4) is added dropwise over 1.5 hours. When the addition is complete, stirring is continued for an additional 15 minutes, after which the reaction medium is neutral to moist litmus (Note 5).

Decanting the reaction mixture separates residual zinc, which is washed thoroughly with two 200-

ml. portions of ether. The ethereal solutions are combined, washed sequentially with two 50-ml. portions of water, 50 ml. of 10% aqueous sodium hydrogen carbonate, and two 50-ml. portions of saturated aqueous sodium chloride (Note 6), and dried over magnesium sulfate. After filtration, ether is removed by careful distillation through a Dufton column at atmospheric pressure (Note 7). When the residual solution is approximately 100 ml. in volume, it is transferred to a smaller apparatus and distilled slowly at atmospheric pressure. After a forerun of ether, 13.2–14.4 g. (68–75%) of 3-methylcyclohexene distils at 103–104° (Note 8).

2. Notes

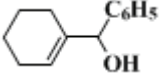
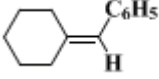
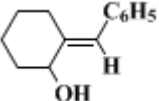
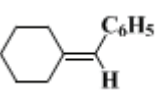
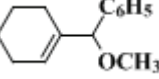
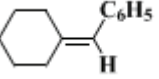
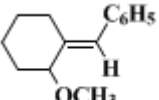
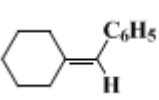

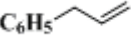
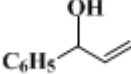
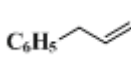
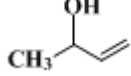
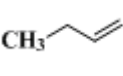
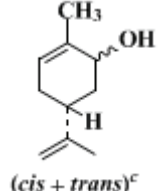
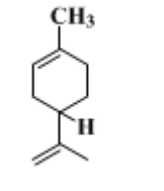
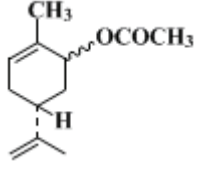
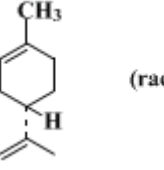
1. The unsaturated ketone² can be purchased from Ega Chemie K.G. or from Frinton Laboratories, P.O. Box 301, South Vineland, New Jersey.
2. The concentration of this solution was established by decomposing the lithium aluminum hydride with excess iodine according to the following equation: $\text{LiAlH}_4 + 2\text{I}_2 \rightarrow 2\text{H}_2 + \text{LiI} + \text{AlI}_3$
The amount of unreacted iodine was determined by titration with sodium thiosulfate; the amount of iodine initially present was determined by a separate blank titration.³
Working solutions were prepared by dissolving 40 g. of iodine in 1 l. of anhydrous benzene and by dissolving 248 g. of sodium thiosulfate pentahydrate in 1 l. of water (ca. 1 M); an accurately prepared 0.100 N aqueous sodium thiosulfate solution is also required. For titration, a 25.0-ml. portion of the iodine solution was stirred vigorously in a 500-ml. Erlenmeyer flask, and 1.00 ml. of the lithium aluminum hydride solution was added rapidly, followed by 20 ml. of water, 2 drops of acetic acid, and 5.00 ml. of the 1 M sodium thiosulfate solution. With continued stirring, the solution was titrated to the colorless end point by adding V_a ml. of the 0.100 N sodium thiosulfate solution.
Separately, another 25.0-ml. portion of the iodine solution was stirred in a 500-ml. Erlenmeyer flask and treated with 5.00 ml. of the 1 M aqueous sodium thiosulfate, 20 ml. of water, and 2 drops of acetic acid. Titration was continued to the end point by adding, with continuous stirring, V_b ml. of 0.100 N aqueous sodium thiosulfate. The molarity of the lithium aluminum hydride solution was then calculated from the following equation: $M = 0.025(V_b - V_a)$
3. A large excess of zinc is used to make the reaction faster and to reduce the formation of polymeric by-products.
4. The solution of dry hydrogen chloride in ether was prepared as follows. Commercial hydrogen chloride gas was dried by passing it through an empty safety trap, a wash bottle of concentrated sulfuric acid, a calcium chloride tube, and another empty safety trap. Anhydrous ether was cooled in an ice bath, and the hydrogen chloride was bubbled through rapidly. Gas uptake was followed by weighing the ethereal solution occasionally, and the concentration of the final solution was determined by alcalimetric titration. The optimum concentration of hydrogen chloride is 2.5–3 M. Use of excess acid led to overreduction in the case of 2-phenyl-2-cyclohexen-1-ol, the desired 1-phenylcyclohexene being contaminated by phenylcyclohexane.
5. If the total reaction time is less than approximately 1.75 hours, starting material remains. Therefore, if the ethereal hydrogen chloride is added in less than 1.5 hours, the subsequent stirring must be lengthened accordingly.
6. If zinc chloride is not removed by washing, it causes polymerization of the olefin during distillation.
7. Slow distillation of the ether is essential in order to prevent the low-boiling olefin from codistilling with the solvent. For higher-boiling olefins the ether can be removed on a water bath prior to distillation of the olefin under reduced pressure.
8. GC analysis, using an HMDS-treated Chromosorb W column with 7% Craig polyester as the stationary phase, indicated the product to have a purity of 97%. The 3% impurity is most probably the isomeric 1-methylcyclohexene.

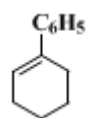
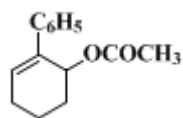
3. Discussion

The model procedure described above is applicable to allylic alcohols, ethers, and acetates. The submitters' results for the conversion of several such compounds to the corresponding olefins, performed on a smaller scale, are summarized in Table I. Reductive cleavage of allylic alcohols, ethers, and acetates has often been reported in the literature. Typical reagents used are sodium in liquid ammonia,^{4,5} zinc and acetic acid,⁶ chloroaluminum hydride,⁷ and propylmagnesium bromide in the

presence of dichlorobis(triphenylphosphine)nickel.⁸ In all of these procedures, however, when two or more isomeric olefins can be formed, the thermodynamically more stable olefin generally predominates. The advantage of the present procedure⁹ is that it leads, depending on the structure of the starting material, either exclusively or predominantly to the less stable isomer (see Table I). These results have been interpreted⁹ by assuming that reduction takes place through an intermediate that behaves like an allylic metal halide. Studies of allylic metal halides such as crotyl zinc halides¹⁰ and the crotyl Grignard reagent¹¹ suggest that such an intermediate would be protonated predominantly at the more substituted end of the allylic system. The method has been applied recently to the synthesis of some natural products.¹²

TABLE I
OLEFINS FROM ALLYLIC ALCOHOLS, ETHERS, AND ACETATES⁹

Starting Material	Total yield of Olefins (%) ^a	Major Olefin (relative %) ^b
	85–90	 70 70
	85–90	 70 70
	85–90	 70 70
	85–90	 70 70
	70	 80 80
	80	 80 80
	not determined	 80 80
 (<i>cis + trans</i>) ^c	70	 (r a c e m i c) (racemic)
	70	 (racemic) (racemic)
	80	



*a*Distilled product.

*b*Determined by GC.

*c*From lithium aluminum hydride reduction of (-)carvone.

References and Notes

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

amalgamated zinc

amalgamated zinc powder

ethanol (64-17-5)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

sodium hydrogen carbonate (144-55-8)

sodium chloride (7647-14-5)
sodium thiosulfate (7772-98-7)
nitrogen (7727-37-9)
iodine (7553-56-2)
zinc,
zinc powder (7440-66-6)
sodium (13966-32-0)
zinc chloride (7646-85-7)
mercury(II) chloride (7487-94-7)
magnesium sulfate (7487-88-9)
phenylcyclohexane (827-52-1)
1-phenylcyclohexene (771-98-2)
lithium aluminum hydride (16853-85-3)
1-methylcyclohexene
3-methyl-2-cyclohexen-1-one
3-Methylcyclohexene,
Cyclohexene, 3-methyl- (591-48-0)
sodium thiosulfate pentahydrate
3-Methyl-2-cyclohexen-1-ol (21378-21-2)
2-phenyl-2-cyclohexen-1-ol
chloroaluminum hydride
propylmagnesium bromide
dichlorobis(triphenylphosphine)nickel (14264-16-5)