A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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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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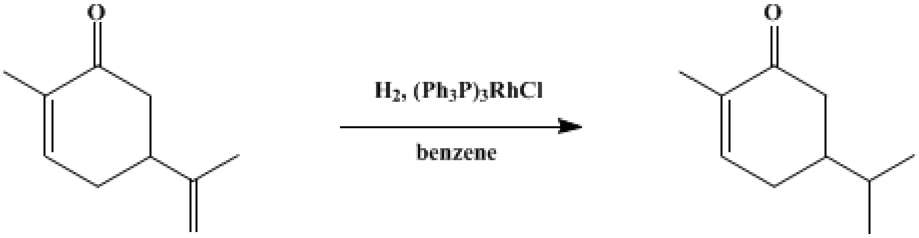
HOMOGENEOUS CATALYTIC HYDROGENATION: DIHYDROCARVONE

[2-Cyclohexen-1-one, 2-methyl-5-(1-methylethyl)-]



Submitted by Robert E. Ireland[1] and P. Bey[2].
Checked by N. Haga and W. Nagata.

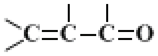
1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A 500-ml., two-necked, creased flask, containing a magnetic stirring bar and connected to an atmospheric pressure hydrogenation apparatus equipped with a graduated burette to measure the uptake of hydrogen, is charged with 0.9 g. (0.9 × 10^{-3} mole) of freshly prepared tris(triphenylphosphine) rhodium chloride (Note 1) and 160 ml. of benzene (Note 2). One neck is stoppered with a serum cap, and the mixture is stirred magnetically (Note 3) until the solution is homogeneous. The system is then evacuated and filled with hydrogen. Using a syringe, 10 g. (0.066 mole) of carvone (Note 4) is introduced into the hydrogenation flask. The syringe is rinsed with two, 10-ml. portions of benzene, and stirring is resumed. Hydrogen uptake starts immediately (Note 5) and stops 3.5 hours later when the theoretical amount of hydrogen has been absorbed. The solution is filtered through a dry column (4 cm. diameter) of 120 g. of Florisil (60–100 mesh). The column is washed with 300 ml. of diethyl ether, and the combined solvent fractions are concentrated under reduced pressure. Vacuum distillation of the yellow residue through an 11-cm. Vigreux column (Note 6) affords 9.1–9.5 g. (90–94%) of dihydrocarvone; b.p. 100–102° (14 mm.), n_D^{24} 1.479 (Note 7) and (Note 8).

2. Notes

1. The tris(triphenylphosphine)rhodium chloride catalyst was prepared according to the procedure of G. Wilkinson and co-workers.[3]
2. The benzene was distilled from calcium hydride.
3. Efficient stirring is necessary to assure good surface contact during hydrogenation.
4. The carvone was distilled before use; b.p. 105–106° (14 mm.). The checkers used *l*-carvone obtained from Shiono Koryo K.K. (Japan).
5. With old catalyst, very erratic results with respect to the initiation time and the rate of hydrogen uptake have been observed.
6. When the hydrogenation is carried out on a smaller scale, purification can be affected by evaporative distillation in a bulb to bulb apparatus.
7. GC analysis shows contamination by less than 3% of carvone. The checkers used a 1 m. by 4 mm. glass column packed with 5% PEG 6000 on Chromosorb W (60/80 mesh). The retention times were 3.7 minutes and 2.75 minutes for carvone and dihydrocarvone, respectively, at 100° with a nitrogen flow rate of 90 ml. per minute.
8. The product shows the following spectral properties: IR (neat) 1678 $cm.^{-1}$



$>C=C-C=O$

; UV (C_2H_5OH) λ_{max} 237 nm (ε = 9150); ^{1}H NMR ($CDCl_3$), δ 0.88 [d, J = 6 Hz., 6H, CH(CH_3)$_2$], 1.71 (d, J = 1.5 Hz., 3H, CH_3C=CH), 6.70 (m, 1H, CH=C).

3. Discussion

[4]

This procedure is an example of the use of a soluble transition metal complex for the catalytic transfer of hydrogen to an olefin. First developed by Wilkinson and co-workers,[3] subsequent extensive investigation in those laboratories and others[5] has shown that the hydrogenation is sensitive to steric congestion; only unhindered double bonds are reduced. As a result, the rhodium complex has been found useful for the selective saturation of unhindered double bonds in polyolefinic substances, such as carvone.[6] Unhindered double bonds may be reduced even in the presence of functions such as keto,[7,6] nitro,[6,8] and sulfide[6] groups. The mechanism[3] and stereochemistry[9] of the catalysis have been investigated, and *cis*-addition of hydrogen is the general rule. The catalyst is effective for deuterium addition to unhindered olefins[10] without the extensive hydrogen–deuterium exchange observed with palladium and platinum heterogeneous catalysis. The rhodium complex causes the decarbonylation of aldehydes and acid halides; the hydrogenation of such unsaturated systems is complicated by the loss of these functional groups.[3], Isomerization of nonreduced olefinic bonds is also an observed side reaction.[11]

References and Notes

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

Benzene (71-43-2)

diethyl ether (60-29-7)

hydrogen (1333-74-0)

nitrogen (7727-37-9)

platinum (7440-06-4)

palladium (7440-05-3)

calcium hydride (7789-78-8)

rhodium (7440-16-6)

deuterium (7782-39-0)

Dihydrocarvone

2-Cyclohexen-1-one, 2-methyl-5-(1-methylethyl)- (43205-82-9)

tris(triphenylphosphine)rhodium chloride

carvone,
l-carvone