



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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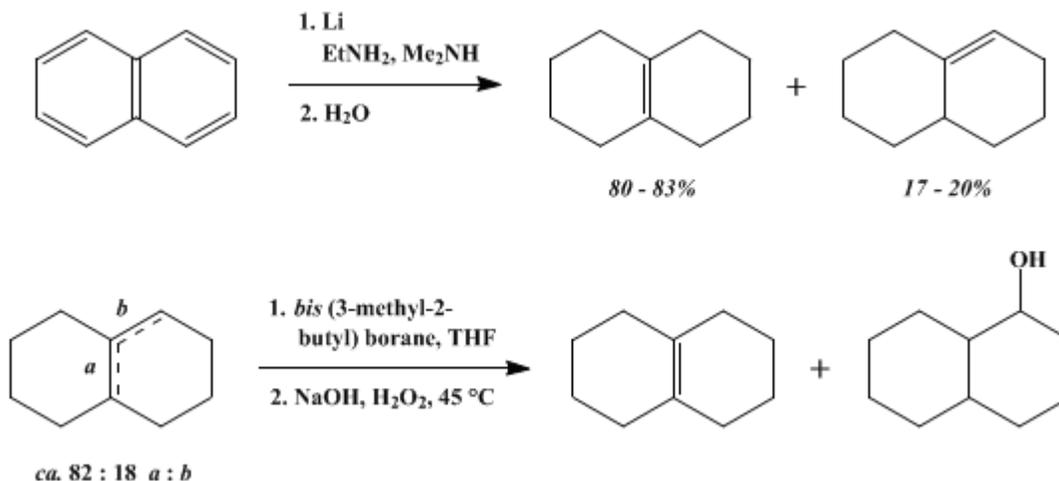
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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$\Delta^{9,10}$ -OCTALIN

[Naphthalene, 1,2,3,4,5,6,7,8-octahydro-]



Submitted by Edwin M. Kaiser¹ and Robert A. Benkeser².

Checked by Frederick J. Sauter and Herbert O. House.

1. Procedure

Caution! This preparation should be performed in a hood to avoid exposure to amine vapors.

A. $\Delta^{9,10}$ -and $\Delta^{1,9}$ -Octalin. Naphthalene (25.6 g. or 0.200 mole, (Note 1)) is dissolved in a mixture of 250 ml. of anhydrous ethylamine and 250 ml. of anhydrous dimethylamine (Note 2) in a 1-l., three-necked flask fitted with a mechanical stirrer (Note 3) and a dry ice condenser and cooled in an ice bath. To this solution is added rapidly (Note 4), piecewise with stirring, 11.55 g. (1.674 g.-atoms) of lithium metal wire cut into 0.5-cm. lengths (Note 5). After the addition is complete, the cooling bath is removed and the blue solution is stirred for 14 hours, additional dry ice being added to the condenser as required. The dry ice condenser is replaced with a water condenser and the mixture is allowed to stand overnight, during which time the volatile amine solvents evaporate (Note 6). The top of the condenser is protected with an anhydrous calcium sulfate drying tube, maintaining anhydrous conditions in the reaction vessel during the evaporation of solvent (Note 7). The reaction flask is placed in an ice bath and the grayish-white residue is hydrolyzed by the cautious, dropwise addition of 500 ml. of water, with occasional stirring. After the resulting suspension has been filtered with suction, the residual solid is washed with four 25-ml. portions of diethyl ether. The ether layer is separated, and the aqueous phase of the filtrate is extracted with four additional 25-ml. portions of ether. The combined ethereal solutions are dried over calcium sulfate and concentrated with a rotary evaporator. The residual liquid is distilled under reduced pressure, separating 19–20 g. (70–74%) of the product, b.p. 72–77° (14 mm.), n_D^{23} 1.4978. Analysis of the product by GC (Note 8) shows the presence of 80–83% of $\Delta^{9,10}$ -octalin and 17–20% of $\Delta^{1,9}$ -octalin. This mixture should be either stored under a nitrogen atmosphere or immediately subjected to the described purification procedure (Note 9).

B. Purification of $\Delta^{9,10}$ -octalin. A 1-l., three-necked flask is equipped with a magnetic stirrer, a pressure-equalizing dropping funnel, and a reflux condenser fitted with a nitrogen inlet tube, to maintain a nitrogen atmosphere in the reaction vessel throughout the portions of this preparation where anhydrous conditions are employed. A solution of 2.35 g. (0.0618 mole) of sodium borohydride and 11.55 g. (0.1650 mole) of 2-methyl-2-butene (Note 10) in 100 ml. of anhydrous tetrahydrofuran is added to the reaction flask. A solution of 11.75 g. (0.08275 mole) of boron trifluoride diethyl etherate in 22 ml. of anhydrous tetrahydrofuran is then added, dropwise and with stirring, over a 45-minute period.

Although the initial rate of addition must be slow to control the exothermic reaction, the rate can be increased during the latter part of the reaction. To the resulting tetrahydrofuran solution of bis(3-methyl-2-butyl)borane is added, dropwise and with stirring over 10 minutes, the mixture of $\Delta^{9,10}$ - and $\Delta^{1,9}$ -octalins (19–20 g. containing *ca.* 0.03 mole of $\Delta^{1,9}$ -octalin) obtained in Part A. The reaction mixture is stirred at room temperature for 3.5 hours and treated with 50 ml. of water. After 35 ml. of 3 M aqueous sodium hydroxide has been added, dropwise and with stirring over 10 minutes, 35 ml. of 30% aqueous hydrogen peroxide is added dropwise over a 45-minute period, with continuous stirring. The resulting mixture is heated to 45° (Note 11) with stirring for 5 hours, then allowed to cool to room temperature. The organic layer is separated, washed with four 30-ml. portions of water, and dried over calcium sulfate. After the organic solution has been tested with moist starch-iodide paper to ensure the absence of peroxides, the volatile solvents are removed with a rotary evaporator, and the residual liquid is distilled under reduced pressure in an apparatus fitted with a capillary tube to admit nitrogen as an ebullator (Note 12). After 1–2 g. of forerun has been separated, 9–13 g. (33–48% based on the starting naphthalene) of $\Delta^{9,10}$ -octalin is collected at 75–77° (14 mm.), n_D^{20} 1.4990. The product is at least 99% $\Delta^{9,10}$ -octalin, by GC analysis (Note 8), and is stored under a nitrogen atmosphere (Note 9).

2. Notes

1. Naphthalene purchased from Eastman Organic Chemicals was used without purification.
2. Ethylamine (b.p. 16.6°) and dimethylamine (b.p. 7.4°) may be distilled into the reaction flask from cylinders. The checkers employed amines, sealed in ampules, purchased from Eastman Organic Chemicals. After the ampules had been cooled to 0° in an ice bath, they were opened and the contents were added to flasks cooled in ice baths. Small portions (0.5–1.0 g.) of sodium metal were added to each of the cold amines. The cooling baths were then removed, and the amines were allowed to distill from the sodium into the reaction flask.
3. Stirrers with Teflon paddles should not be used. Although the reaction proceeds satisfactorily, the Teflon parts are blackened (and presumably partially degraded) by the reaction solution.
4. The reaction is very exothermic during the initial addition of lithium metal. The use of an external ice bath reduces the number of times additional dry ice must be added to the acetone–dry ice condenser.
5. The lithium wire is coated with a hydrocarbon grease. As 0.5-cm. pieces are cut with scissors, they should be dropped into a beaker of anhydrous hexane to dissolve the grease. The pieces of bare lithium wire are then removed with forceps, drained briefly by touching them to a dry towel, and weighed in a second beaker of anhydrous hexane. The pieces of metal are then removed from the second beaker with forceps and added to the reaction mixture.
6. If evaporation of the solvent is not complete, the remainder can be removed by immersing the reaction flask in a bath of warm water.
7. If anhydrous conditions are not maintained, the product becomes contaminated with a tarry material.
8. A GC column packed with Apiezon L suspended on Chromosorb P was employed for this analysis. In a typical analysis at 140° the retention times were: $\Delta^{1,9}$ -octalin, 46.2 minutes; $\Delta^{9,10}$ -octalin, 49.2 minutes. The ^1H NMR spectrum (CCl_4 at 60 MHz.) of this mixture exhibits a multiplet at δ 0.8–2.6 (aliphatic CH) with a weak, partially resolved multiplet at δ 5.25 (vinyl CH of $\Delta^{1,9}$ -octalin).
9. The octalins usually react rapidly with oxygen, forming unidentified, oxygenated products. The checkers found that, if the crude product is not protected from air oxidation, the yield of $\Delta^{9,10}$ -octalin isolated from the purification procedure is lowered substantially.
10. 2-Methyl-2-butene, purchased either from Phillips Petroleum Company or Aldrich Chemical Co., was used without purification.
11. The checkers found a large oil bath to be a convenient method for heating the reaction mixture to 45°.
12. The mixture tends to foam badly during this distillation.

3. Discussion

Among the preparative routes to the octalin mixtures, the acid-catalyzed dehydration of 2-decalol³ and the metal-amine reduction of naphthalene⁴ appear most satisfactory. Apart from the purification method described in this preparation, pure $\Delta^{9,10}$ -octalin has also been obtained by reaction of the octalin mixture with nitrosyl chloride. After separation of the adducts by fractional crystallization, the pure $\Delta^{9,10}$ -octalin has been regenerated from its nitrosyl chloride adduct.^{3,5}

Lithium dissolved in amines of low molecular weight constitutes a useful and convenient reagent for reducing aromatic hydrocarbons to monoolefins.⁶ Although mixtures of isomeric olefins are usually obtained with primary amine solvents, the use of secondary amines as co-solvents dramatically increases the selectivity of these reductions so that the more thermodynamically stable olefin usually becomes the predominant product. Thus, in the reduction of naphthalene, the yield of $\Delta^{9,10}$ -octalin increases from 52% in pure ethylamine to 80–82% in an ethylamine–dimethylamine mixture. As another example, the reduction of *tert*-butylbenzene with lithium in pure ethylenediamine yields a product mixture 70% in 1-*tert*-butylcyclohexene.⁷ When a mixture of ethylenediamine and morpholine is used as the reaction solvent, the product mixture is 84% 1-*tert*-butylcyclohexene.⁸

Aromatic hydrocarbons may also be reduced to monoolefins by calcium in low molecular weight amines.⁹ For example, this metal in methylamine–ethylenediamine converts naphthalene to $\Delta^{9,10}$ - and $\Delta^{1,9}$ -octalin in yields identical to those obtained from the lithium–amine system used in this preparation. Calcium may even be employed to effect such reductions in ether provided small amounts of hexamethylphosphoric triamide (HMPA) are present; for a warning concerning the use of HMPA, see J. A. Zapp, Jr., *Science*, **190**, 422 (1975).

The separation procedure⁴ described in this preparation illustrates the *in situ* generation of a tetrahydrofuran solution of bis(3-methyl-2-butyl)borane and use of this sterically hindered borane to react with a trisubstituted olefin ($\Delta^{1,9}$ -octalin) in preference to a more hindered tetrasubstituted olefin ($\Delta^{9,10}$ -octalin).¹⁰ The alkylborane adduct produced from $\Delta^{1,9}$ -octalin is oxidized with alkaline hydrogen peroxide to 1-decalol, which is easily separated from the olefinic product.

References and Notes

1. Department of Chemistry, University of Missouri, Columbia, Missouri 65211.
 2. Department of Chemistry, Purdue University, W. Lafayette, Indiana 47907.
 3. W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958).
 4. R. A. Benkeser and E. M. Kaiser, *J. Org. Chem.*, **29**, 955 (1964).
 5. A. S. Hussey, J. F. Sauvage, and R. H. Baker, *J. Org. Chem.*, **26**, 256 (1961).
 6. R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1954).
 7. R. A. Benkeser, R. K. Agnihotri, and M. L. Burrous, *Tetrahedron Lett.*, 1 (1960); R. A. Benkeser, R. K. Agnihotri, M. L. Burrous, E. M. Kaiser, J. M. Mallan, and P. W. Ryan, *J. Org. Chem.*, **29**, 1313 (1964).
 8. T. J. Hoogeboom, M. S. thesis, Purdue University, 1965.
 9. R. A. Benkeser and J. Kang, *J. Org. Chem.*, **44**, 3737 (1979).
 10. H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).
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Appendix

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

$\Delta^{9,10}$ -Octalin

$\Delta^{9,10}$ -and $\Delta^{1,9}$ -Octalin

$\Delta^{9,10}$ - and $\Delta^{1,9}$ -octalin

($\Delta^{1,9}$ -octalin)

($\Delta^{9,10}$ -octalin)

$\Delta^{1,9}$ -octalin

ether,
diethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

oxygen (7782-44-7)

nitrogen (7727-37-9)

calcium sulfate (7778-18-9)

calcium (7440-70-2)

sodium (13966-32-0)

Naphthalene (91-20-3)

hydrogen peroxide (7722-84-1)

dimethylamine (124-40-3)

methylamine (74-89-5)

nitrosyl chloride (2696-92-6)

lithium,
Lithium wire,
lithium metal wire (7439-93-2)

2-methyl-2-butene (513-35-9)

Tetrahydrofuran (109-99-9)

ethylenediamine (107-15-3)

morpholine (110-91-8)

hexane (110-54-3)

1-Decalol (529-32-8)

boron trifluoride diethyl etherate (109-63-7)

ethylamine (75-04-7)

sodium borohydride (16940-66-2)

hexamethylphosphoric triamide (680-31-9)

2-Decalol (825-51-4)

Naphthalene, 1,2,3,4,5,6,7,8-octahydro- (493-03-8)

Bis(3-methyl-2-butyl)borane (1069-54-1)

tert-butylbenzene (98-06-6)

1-tert-butylcyclohexene