Organic Syntheses

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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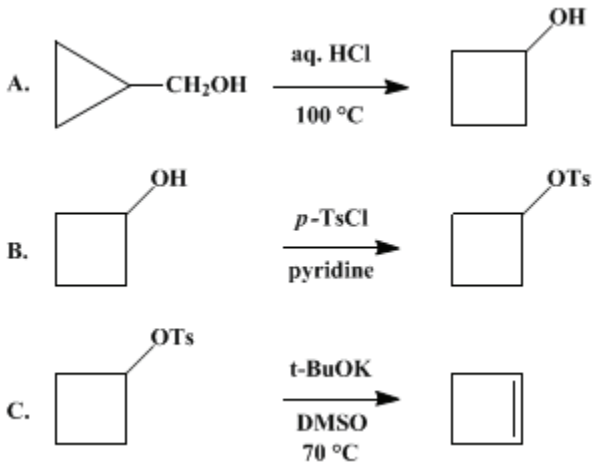
CYCLOBUTENE



Submitted by J. Salaün and A. Fadel[1].
Checked by Lawrence R. McGee and Bruce E. Smart.

1. Procedure

A. *Cyclobutanol*. A 1-L, three-necked, round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar is charged with 600 mL of water, 57.5 mL (ca. 0.68 mol) of concentrated hydrochloric acid, and 57.7 g (0.80 mol) of cyclopropylcarbinol (Note 1). The reaction mixture is stirred and refluxed for 3 hr. Cyclobutanol is only partially soluble in water and soon separates. The reaction mixture is allowed to cool to room temperature, and the flask is then immersed in an ice bath. To the cold, stirred mixture is added 24 g (0.6 mol) of sodium hydroxide pellets, followed by 6.7 g (0.08 mol) of sodium bicarbonate to complete the neutralization. The mixture is saturated with sodium chloride and extracted for 30 hr with diethyl ether using a liquid–liquid continuous extraction apparatus. The ethereal extract is dried over anhydrous sodium sulfate and the drying agent is removed by filtration. The bulk of the solvent is distilled from the filtrate to give 55.0 g of residual liquid containing 88% cyclobutanol and 12% 3-buten-1-ol by gas chromatography (Note 2). The crude product is carefully distilled through spinning band columns to give 32.8 g (57%) of cyclobutanol, bp 122–124°C. Gas chromatographic analysis of the product shows it to be 95% pure (Note 2),(Note 3),(Note 4).

B. *Cyclobutyl tosylate*. A 500-mL, three-necked, round-bottomed flask fitted with a stirrer and a theromometer is charged with 200 mL of pyridine (Note 5) and 32.3 g (0.448 mol) of cyclobutanol. The solution is stirred and chilled to 0°C, and then 89.8 g (0.471 mol) of *p*-toluenesulfonyl chloride (Note 6) is added in portions over a 20-min period. The reaction mixture is allowed to warm to room temperature and is stirred for 16 hr. The mixture is recooled to 0°C, and poured into 260 mL of concentrated hydrochloric acid in 800 mL of ice water. The mixture is extracted with three 300-mL portions of ether and the combined ethereal extracts are dried over anhydrous magnesium sulfate. The drying agent is removed by filtration and the filtrate is concentrated on a rotary evaporator. The residue is held under high vacuum (0.03 mm) at room temperature for 3 hr to give 93.3 g (92%) of cyclobutyl tosylate as a pale-yellow oil (Note 7).

C. *Cyclobutene*. A 500-mL, two-necked, round-bottomed flask is fitted with a 100-mL dropping funnel equipped with an argon-inlet tube, a magnetic stirring bar, and a water-cooled condenser. The outlet of the condenser is attached to an all-glass transfer manifold. Two weighed traps fitted with gastight stopcocks and immersed in dry ice–acetone baths are attached to the manifold. A calcium chloride drying tube is attached to the exit of the second trap. While the system is continuously purged with a slow stream of argon, the flask is charged with 33.6 g (0.30 mol) of potassium *tert*-butoxide and 120 mL of anhydrous dimethyl sulfoxide (Note 8), and a solution of 25.6 g (0.113 mol) of cyclobutyl tosylate in 30 mL of anhydrous dimethyl sulfoxide is placed in the dropping funnel. The potassium *tert*-

butoxide suspension is stirred vigorously and heated to 70°C. The cyclobutyl tosylate solution is then added dropwise over a 10-min period (Note 9). After the addition is completed, the reaction mixture is stirred at 70°C for an additional 2 hr. The manifold system is closed off from the reaction vessel and the material collected in the first trap is slowly warmed. The product distills at ca. 2°C into the second dry-ice-cooled trap to give 4.3–5.1 g (70–84%) of cyclobutene [lit.[2] bp 2°C] (Note 10),(Note 11),(Note 12).

2. Notes

1. The checkers obtained cyclopropylcarbinol from the Aldrich Chemical Company, Inc. It can be readily prepared by the reduction of cyclopropanecarboxylic acid with lithium aluminum hydride.[3]
2. A 25-m × 0.3-mm HP Ultra Silicone capillary column at 70°C with 30–psi helium head pressure was used for the chromatographic analysis: retention times of 3-buten-1-ol and cyclobutanol are 1.19 and 1.35 min, respectively. The submitters used a 3-m × 0.3-cm 20 *M* carbowax column at 90°C/8 psi hydrogen and reported retention times of 13 and 20 min for 3-buten-1-ol and cyclobutanol, respectively.
3. The crude product was first distilled on a 50-cm × 0.8-cm spinning band column (reflux ratio 10:1) to give 19.6 g of cyclobutanol, bp 124°C. The forerun fractions, bp 66–123°C (23.0 g), were combined and redistilled on a 30-cm × 0.8-cm spinning band column (reflux ratio 25:1) to give an additional 13.2 g of cyclobutanol, bp 122–123°C. The major by-product, 3-buten-1-ol, boils at 112–114°C. Gas chromatographic analysis of the combined product fractions indicates a mixture of 95% cyclobutanol/3-buten-1-ol (99.7%/0.3%) and 5% unidentified compounds.
4. Cyclobutanol shows the following ^{1}H NMR spectrum ($CDCl_3$): δ: 1.1–2.4 (m, 6 H), 4.16 (quintet, 1 H, J = 7.5), 4.54 (s, 1 H, OH).
5. The pyridine was distilled from calcium hydride and stored over potassium hydroxide.
6. The *p*-toluenesulfonyl chloride was obtained from the Aldrich Chemical Company, Inc., and was recrystallized from hexane prior to use.
7. The product is >99% pure by NMR and shows the following spectrum: ^{1}H NMR ($CDCl_3$) δ: 1.1–2.3 (m, 6 H), 2.47 (s, 3 H), 4.77 (quintet, 1 H, J = 7.5), 7.32 (d, 2 H, J = 9.0), 7.79 (d, 2 H, J = 9.0).
8. Potassium *tert*-butoxide was obtained from the Aldrich Chemical Company, Inc. The dimethyl sulfoxide was distilled from calcium hydride and stored under argon.
9. The reaction mixture turns green, then blue indigo, and finally dark pink during the addition.
10. The submitters report obtaining 5.2 g of 99.2% pure cyclobutene. The product obtained by the checkers was pure by NMR spectroscopy and shows the following ^{1}H NMR spectrum ($CDCl_3$) δ: 2.55 (s, 4 H), 6.00 (s, 2 H).
11. The cyclobutene can be converted to 1,2-dibromocyclobutane by distilling 4.3–7.3 g (0.079–0.135 mol) of cyclobutene into 100 mL of pentane chilled to −40°C, followed by adding a solution of 15.5–32.0 g (0.097–0.200 mol) of bromine in 30 mL of pentane. After the usual workup with aqueous sodium thiosulfate and distillation, 14.3–25.3 g (84–87.5%) of pure 1,2-dibromocyclobutane, bp 60°C (6 mm), is obtained. It shows the following ^{1}H NMR spectrum ($CDCl_3$) δ: 1.90–3.03 (m, 4 H), 4.27–4.70 (m, 2 H). The 1,2-dibromocyclobutane can be conveniently converted back to cyclobutene by debromination with zinc in ethanol.[4]
12. Cyclobutene can be prepared on a larger scale (25–37 g) simply by scaling up the reactants.

3. Discussion

Cyclobutene has been prepared (1) by pyrolysis of cyclobutyldimethylamine oxide[4,5,6] and cyclobutyltrimethylammonium hydroxide[4,6,7] (50–73% yield), which were prepared in eight steps from malonate esters (2.0–2.1% overall yield of cyclobutene contaminated with 1,3-butadiene), (2) by pyrolysis of the products of cycloaddition of dimethyl acetylenedicarboxylate with cyclooctatriene[8,9,10] (30–32% overall yield) or with cyclooctatetraene[11,12,13] (34–39% overall yield), (3) by photolysis of butadiene leading to cyclobutene (30% yield) and bicyclo[1.1.0]butane (5% yield),[14,15] (4) by oxidation of cyclobutylcarboxylic acid[16] with lead tetraacetate[17] (67% yield) (11.8% overall yield), (5) by fragmentation of 1,2-cyclobutyl thiocarbonate with trialkyl phosphite[18] (68% yield based on *cis*-1,2-dihydroxycyclobutane), (6) by ring expansion of cyclopropylcarbene[19] (7) from cyclobutylidene[20 21] and (8) by base-induced ring expansion of cyclopropylmethyl tosylate with potassium *tert*-butoxide in dimethyl sulfoxide leading to a 1 : 1 mixture of cyclobutene and methylenecyclopropane.[22] None of these methods appears to be practical.

The present procedure offers in good yields a simple and ready preparation of pure cyclobutene from the easily available cyclopropylcarbinol. The product is free of the impurities (e.g., 1,3-butadiene, bicyclobutane, methylenecyclopropane) usually obtained with the various methods so far reported. The procedure described for the synthesis of cyclobutanol is patterned after the acid-catalyzed rearrangement of cyclopropylcarbinol reported by Roberts[23] and Rocek.[24]

References and Notes

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

1,2-cyclobutyl thiocarbonate

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ether,
diethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

sodium thiosulfate (7772-98-7)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

zinc (7440-66-6)

Pentane (109-66-0)

magnesium sulfate (7487-88-9)

1,3-Butadiene,
butadiene (106-99-0)

lithium aluminum hydride (16853-85-3)

cyclobutylcarboxylic acid (3721-95-7)

Cyclopropanecarboxylic acid (1759-53-1)

hexane (110-54-3)

dimethyl sulfoxide (67-68-5)

argon (7440-37-1)

Dimethyl acetylenedicarboxylate (762-42-5)

calcium hydride (7789-78-8)

cyclobutene (822-35-5)

cyclopropylcarbinol (2516-33-8)

3-buten-1-ol (627-27-0)

Cyclobutanol (2919-23-5)

Bicyclo[1.1.0]butane (157-33-5)

bicyclobutane

p-Toluenesulfonyl chloride (98-59-9)

Methylenecyclopropane (6142-73-0)

Cyclobutyl tosylate (10437-85-1)

1,2-dibromocyclobutane (89033-70-5)

cyclobutyldimethylamine oxide

cyclobutyltrimethylammonium hydroxide

cyclooctatriene (1871-52-9)

cyclooctatetraene

cyclopropylcarbene (19527-12-9)

cyclobutylidene

cyclopropylmethyl tosylate

potassium tert-butoxide (865-47-4)

cis-1,2-dihydroxycyclobutane (35358-33-9)

lead tetraacetate (546-67-8)