Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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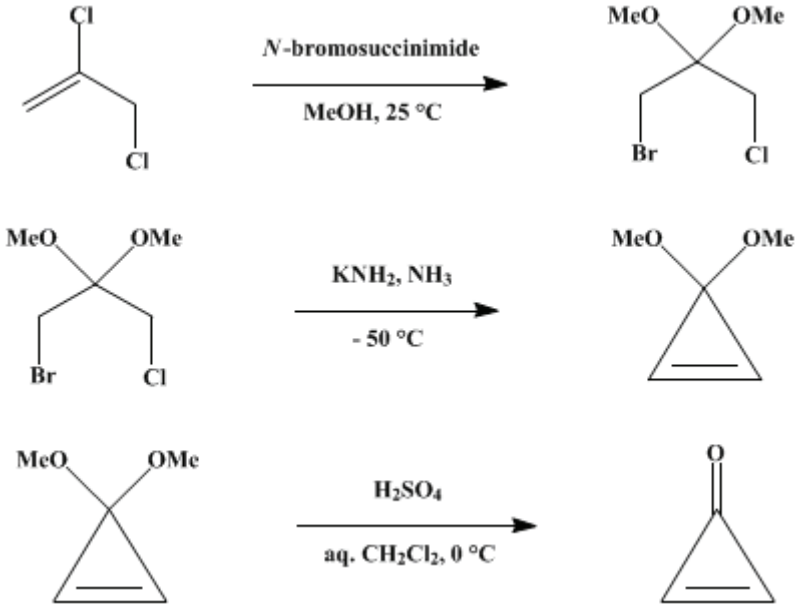
CYCLOPROPENONE



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1. Procedure

Caution! Because liquid ammonia is used in Part B, this part of the procedure should be conducted in a well-ventilated hood.

A. 1-*Bromo*-3-*chloro*-2,2-*dimethoxypropane*. In a good hood, a 1-l., three-necked, round-bottomed flask equipped with magnetic stirrer and reflux condenser is charged with 300 ml. of anhydrous methanol, 111 g. (1.00 mole) of 2,3-dichloro-1-propene (Note 1), and a few drops of concentrated sulfuric acid. With stirring, 178 g. (1.00 mole) of *N*-bromosuccinimide is added in small portions through the condenser. After the final addition, the reaction mixture is stirred for another hour at room temperature before 5 g. of anhydrous sodium carbonate is added to neutralize the catalyst. The solution is stirred for an additional 15 minutes and poured into a large separatory funnel containing 300 ml. of water. The lower, organic layer is removed, and the aqueous layer is extracted with two 500-ml. portions of pentane. The combined organic extracts are washed twice with an equal volume of water, dried over anhydrous magnesium sulfate, filtered, and evaporated, giving a white semicrystalline mass, which is dissolved in refluxing pentane (250 ml.). The solution is cooled in an acetone–dry-ice bath for 30 minutes, yielding 89–99 g. (41–45%) of the white crystalline ketal, m.p. 69.5–70.5° (Note 2).

B. 3,3-*Dimethoxycyclopropene*. A 500-ml., three-necked, round-bottomed flask is equipped with a magnetic stirrer, a gas-inlet tube, a thermometer, and an acetone–dry-ice condenser topped with a drying tube containing sodium hydroxide pellets. An acetone–dry-ice bath is placed under the flask, and ammonia is condensed into the flask from a commercial cylinder. When 350–400 ml. of ammonia has condensed, the inlet tube is replaced by a stopper, and a small piece (0.5 g.) of potassium metal is added to the ammonia. The cooling bath is removed, and *ca.* 0.05 g. of anhydrous iron(III) chloride is added. When the ammonia reaches reflux temperature, the blue color of the dissolved potassium turns to gray, and the remainder of the potassium (11.7 g., 0.300-g.-atom total) is added in 0.5-g. pieces at such a rate that a gentle relux is maintained. The stopper is then replaced by an addition funnel containing a solution of 1-bromo-3-chloro-2,2-dimethoxypropane (21.7 g., 0.100 mole) in 50 ml. of anhydrous diethyl ether, which is added to the gray potassium amide–ammonia suspension over a period of 15

minutes, during which time the mixture is maintained at −50° to −60° with the cooling bath (Note 3). After 3 hours at this temperature, solid ammonium chloride (10.8 g., 0.20 mole) is added with stirring. Ammonia is allowed to evaporate by removing the cooling bath, and during the course of the evaporation it is replaced with 350 ml. of anhydrous ether. When the reaction temperature reaches *ca.* 0°, the resulting brown solution is filtered from inorganic salts and placed in a 500-ml., round-bottomed flask (Note 4). The ethereal solution is then subjected to a vacuum (50–80 mm.) applied through a carbon tetrachloride–dry-ice condenser (*ca.* −25°), while the flask is immersed in an ice bath. After 4–5 hours, when the quantity of residue seems to remain constant, the dry-ice condenser is replaced with a distilling head. The pressure is decreased to 1–2 mm., the receiver is maintained at −78° with a cooling bath, and distillation yields 4.0–6.5 g. (40–65%) of 3,3-dimethoxycyclopropene as a clear liquid (Note 5). This material has been purified further,[2] but it can be used directly in the next step. If it is stored, it should be kept below 0°.

C. *Cyclopropenone*. A stirred solution of 3.0 g. (0.030 mole) of 3,3-dimethoxycyclopropene in 30 ml. of dichloromethane, cooled to 0°, is treated dropwise with 5 ml. of cold water containing 3 drops of concentrated sulfuric acid. The reaction mixture is stirred at 0° for an additional 3 hours before 30 g. of anhydrous sodium sulfate is added in portions, with stirring, to the 0° solution. The drying agent is removed by filtration, and the solvent is evaporated at 50–80 mm. with a water bath maintained at 0–10°. The brown, viscous residue is then distilled at 1–2 mm, at a water bath temperature of 10°. The distillate, a mixture of methanol and dichloromethane, is collected in a receiver cooled to −78°. A new receiver is attached, and the bath temperature is gradually raised to 35° (Note 6), yielding 1.42–1.53 g. (88–94%) of cyclopropenone as a white solid, b.p. 26° (0.46 mm.), m.p. −29 to −28° (Note 7).

Cyclopropenone prepared in this way is quite pure and suitable for most chemical purposes. It can be repurified by crystallization from 3 volumes of ethyl ether at −60° using a cooled filtering apparatus. The residual ethyl ether is then removed by evaporation at 1–2 mm. and 0°; very pure cyclopropenone is obtained in 60–70% recovery from the distilled material.

2. Notes

1. Commercial material was used without further purification. The reflux condenser is used to decrease evaporative losses of this material.
2. ^{1}H NMR (CCl_4), δ (multiplicity, number of protons): 3.27 (s, 6H), 3.48 (s, 2H), 3.63 (s, 2H); the IR and mass spectra are also as reported.[2]
3. Any crystals which may form at the tip of the addition funnel are scraped off and allowed to drop into the reaction flask.
4. The checkers found it inconvenient to complete Part B in one day and stored this ethereal solution overnight in the freezer compartment of a refrigerator.
5. The product usually contains small amounts of ether, as judged by its ^{1}H NMR spectrum. The yields given are based on pure cyclopropenone ketal. ^{1}H NMR ($CDCl_3$), δ (multiplicity, number of protons): 3.33 (s, 6H), 7.88 (s, 2H).
6. The bath temperature should be raised slowly to prevent decomposition of cyclopropenone.
7. IR ($CHCl_3$) cm.$^{-1}$: 1870, 1840, 1493; ^{1}H NMR ($CDCl_3$), δ: 9.11 (s).

3. Discussion

Cyclopropenone was first synthesized[3,4,5] by the hydrolysis of an equilibrating mixture of 3,3-dichlorocyclopropene and 1,3-dichlorocyclopropene (prepared by reduction of tetrachlorocyclopropene with tributyltin hydride), a procedure that has been adapted[5,4] for the preparation of labeled and deuterated cyclopropenones for use in physical studies. The current procedure is somewhat more convenient. It is closely based on the work of Baucom and Butler,[2] who have described this synthesis of dimethoxycyclopropene and shown that it can be hydrolyzed to cyclopropenone. The isolation of pure cyclopropenone by ketal hydrolysis parallels the method of Breslow and Oda,[5] which involves the hydrolysis of dichlorocyclopropenes.

Cyclopropenone is a molecule of considerable theoretical interest, since it combines remarkable stability with extreme strain. Various physical studies[6] suggest that much of its stability is derived from

the special conjugative stabilization of the two-pi electron system, which is related to the cyclopropenyl cation. In addition, cyclopropenone has a number of interesting chemical properties[7,8] which suggest that it could be a useful synthetic intermediate. It has been used in the synthesis of cyclopropanone derivatives[7] and tropones,[7] the latter by rearrangement of products derived from Diels–Alder reactions. In addition, it undergoes a very interesting cyclization–rearrangement reaction with diazo compounds which leads to the overall insertion of a three-carbon unit between the diazo group and its original attachment point.[7] Perhaps the most remarkable reaction of cyclopropenone so far reported is its conversion with Grignard reagents into 2-substituted resorcinols.[8] This reaction seems to be of some generality, and it represents a simple way to elaborate a resorcinol ring (all six carbons of the resorcinol system are derived from two molecules of cyclopropenone) onto a variety of alkyl groups. The ready availability of this compound should lead to other synthetic applications.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 173

References and Notes

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

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

methanol (67-56-1)

ether,
ethyl ether,
diethyl ether (60-29-7)

ammonium chloride (12125-02-9)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

iron(III) chloride (7705-08-0)

potassium (7440-09-7)

2,3-dichloro-1-propene (78-88-6)

Pentane (109-66-0)

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

N-bromosuccinimide (128-08-5)

potassium amide

1-Bromo-3-chloro-2,2-dimethoxypropane (22089-54-9)

3,3-Dimethoxycyclopropene (23529-83-1)

cyclopropenone ketal

3,3-dichlorocyclopropene

1,3-dichlorocyclopropene

tetrachlorocyclopropene

tributyltin hydride (688-73-3)

dimethoxycyclopropene

cyclopropenyl cation

cyclopropenone (2961-80-0)