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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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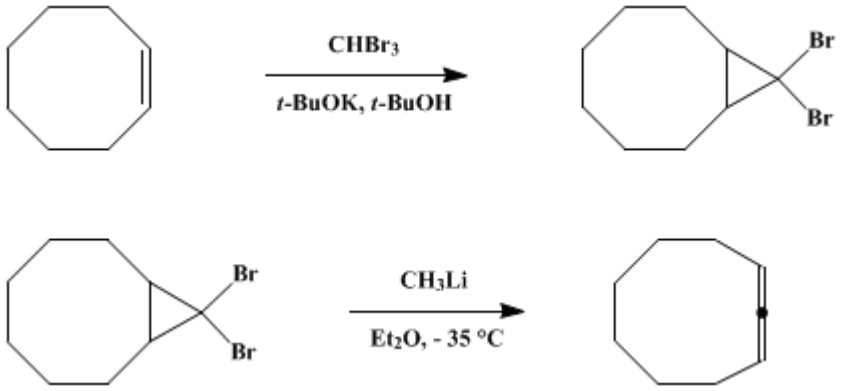
1,2-CYCLONONADIENE



Submitted by L. Skattebøl and S. Solomon[1].
Checked by L. S. Keller and K. B. Wiberg.

1. Procedure

A. *9,9-Dibromobicyclo[6.1.0]nonane*. A dry 3-l. three-necked flask is fitted with a glass stopper, stirrer, and condenser. The flask is kept under a positive nitrogen pressure by means of a gas-trap arrangement connected to the top of the condenser (Note 1). The flask is quickly charged with 2 l. of anhydrous *t*-butyl alcohol (Note 2) and 73 g. (1.87 g. atoms) of potassium metal. *(Caution! See earlier volume[2] for handling of this metal.)* The flow of nitrogen is stopped and the mixture is stirred and boiled under reflux until the potassium has reacted, hydrogen being liberated through the trap. The condenser is arranged for distillation by means of an adapter. The glass stopper is replaced by a pressure-equalized dropping funnel with the nitrogen inlet connected to the top. About 1.5 l. of *t*-butyl alcohol (Note 3) is then distilled into a predried flask under an atmosphere of nitrogen. A water pump is then connected, the nitrogen inlet is closed, and the distillation is continued under reduced pressure while the three-necked flask is gradually heated to 150° in an oil bath. Finally, the water pump is replaced by an oil pump and the white remaining solid is heated at 150° under a pressure of 0.1–1 mm. for 2 hours. The connection to the vacuum system is closed, the oil bath removed, and nitrogen again introduced. The condenser with adapter is replaced by a glass stopper, and the flask is cooled in an ice-salt bath.

Freshly distilled *cis*-cyclooctene, 178 g. (214 ml., 1.62 moles) (Note 4) and 200 ml. of sodium-dried pentane (Note 5) are introduced to the flask, and the dropping funnel is charged with 420 g. (148 ml., 1.66 moles) of bromoform (Note 6). The bromoform is added dropwise to the stirred slurry over a period of 6–7 hours, the color of the reaction mixture changing gradually from light yellow to brown. When the addition is complete, the reaction mixture is allowed to warm to room temperature and left stirring overnight. Water (400 ml.) is added to the reaction mixture followed by enough 10% aqueous hydrochloric acid to neutralize the slightly basic solution. The reaction mixture is transferred to a separatory funnel and the organic layer is separated. The aqueous layer is extracted with three 50-ml. portions of pentane, and the combined pentane solutions are washed with three 50-ml. portions of water. The pentane solution is dried over anhydrous magnesium sulfate, filtered, and stripped of solvent on a rotary evaporator. Distillation of the residue yields 237–299 g. (52–65%) of 9,9-dibromobicyclo[6.1.0]nonane, b.p. 62° (0.04 mm.), n^{23}D 1.5493–1.5507 (Note 7).

B. *1,2-Cyclononadiene*. A dry 2-l. three-necked flask is equipped with mechanical stirrer, pressure-equalized dropping funnel, and a nitrogen inlet tube connected to a gas-trap arrangement (Note 1). To the flask are added 187 g. (116 ml., 0.66 mole) of 9,9-dibromobicyclo[6.1.0]nonane and 100 ml. of anhydrous ether. The dropping funnel is charged with 450 ml. of 1.9*M* ether solution of methyllithium (0.85 mole) (Note 8). The flask is cooled by means of an acetone-dry ice bath maintained at −30° to −40°, and the methyllithium is added dropwise with stirring during 1 hour (Note 9). After the addition is complete, the reaction mixture is stirred for 30 minutes, and excess lithium reagent is decomposed by

dropwise addition of 100 ml. of water. An additional 400 ml. of water is then added, and the ether layer is separated. The aqueous layer is extracted with three 30-ml. portions of ether. The combined ether solutions are washed with 30-ml. portions of water until neutral and dried over magnesium sulfate. The latter is filtered and the ether is distilled through a 40-cm Vigreux column. Distillation of the residue (Note 10) yields 66–73 g. (81–91%) of 1,2-cyclononadiene, b.p. 62–63° (16 mm.), n^{20}D 1.5060 (Note 11).

2. Notes

1. A suitable gas-trap has been described.[3] Mercury can conveniently be replaced by paraffin oil.
2. Reagent grade *t*-butyl alcohol distilled from calcium hydride was used.
3. The *t*-butyl alcohol thus recovered can be used for a second preparation without further purification.
4. *cis*-Cyclooctene was obtained from Columbia Organic Chemicals or Aldrich Chemical Co. It was distilled from sodium and a fraction, b.p. 81–82° (95 mm.), n^{25}D 1.4682, was used. Gas chromatography showed 98% purity, the impurity being mainly cyclooctane.
5. Pentane is added as a diluent in order to obtain an easily stirred slurry. Amounts varying from 100 to 250 ml. per mole of olefin have been used with no appreciable change in yield of product.
6. Reagent grade bromoform was used without further purification.
7. The submitters have also used commercially available dry potassium *t*-butoxide with varying success in this reaction; with a sample purchased from M.S.A. Research Corporation a 65% yield of product was obtained. The submitters reported a 65–76% yield range for this step.
8. An ethereal solution of methyllithium was either prepared from lithium metal and methyl bromide or purchased from Alfa Inorganics, Inc. Concentrations of 0.5–2*M* were used with no change in result.
9. Solid methyllithium and lithium halide occasionally separate out on the tip of the dropping funnel, probably owing to the low temperature, and this may cause plugging. It can be avoided by using a faster rate of addition.
10. The submitters used a 40-cm. spinning band column. Owing to polymerization of the product, the checkers obtained consistently low yields when this column was used. Distillation through a 40-cm. Vigreux column gave the indicated yield without a significant decrease in product purity.
11. The product is more than 99% pure as shown by gas chromatography.

3. Discussion

Cyclic allenes have previously been obtained only admixed with the isomeric acetylenes.[4] The present two-step synthesis is a practical method for the preparation of cyclic allenes, and at the same time it describes a general method for the preparation of allenes.[5,6] It is based on the original work of Doering and co-workers.[7] Examples of the reaction sequence above are known in which allenes are not produced,[8] or they represent only a part of the reaction products.[9] A one-step synthesis of 1,2-cyclononadiene has been reported.[10]

R-(+)-1,2-Cyclononadiene and S-(−)-1,2-cyclononadiene have been prepared from R-(−)- and S-(+)-*trans*-cyclooctene, respectively.[11] Optically active 1,2-cyclononadiene has also been obtained when the reaction of the dibromo bicyclo intermediate with methyllithium is carried out in the presence of an optically active amine.[12] Reduction of 1,2-cyclononadiene with sodium in liquid ammonia gives *cis*-cyclononadiene in almost quantitative yield.[13]

References and Notes

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

sodium-dried pentane

S-(−)-1,2-cyclononadiene

R-(−)- and S-(+)-trans-cyclooctene

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

hydrogen (1333-74-0)

nitrogen (7727-37-9)

mercury (7439-97-6)

sodium (13966-32-0)

methyl bromide (74-83-9)

potassium (7440-09-7)

Pentane (109-66-0)

bromoform (75-25-2)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

Methyllithium (917-54-4)

t-butyl alcohol (75-65-0)

calcium hydride (7789-78-8)

1,2-Cyclononadiene,
R-(+)-1,2-Cyclononadiene (1123-11-1)

9,9-Dibromobicyclo[6.1.0]nonane (1196-95-8)

cyclooctane (292-64-8)

potassium t-butoxide (865-47-4)

cis-cyclooctene (931-87-3)

cis-cyclononadiene