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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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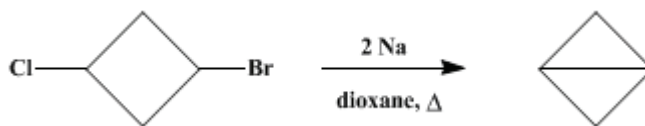
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.133 (1988); Vol. 51, p.55 (1971).

BICYCLO[1.1.0]BUTANE

[Bicyclo[1.1.0]butane]



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Checked by R. A. Fenoglio and K. B. Wiberg.

1. Procedure

A 300-ml., three-necked, round-bottomed flask is equipped with a mechanical stirrer, a reflux condenser, and a pressure-equalizing addition funnel. The condenser is connected in series with two traps, immersed in liquid nitrogen, with the exit leading to a drying tube (Note 1). A line for dry nitrogen that has a T-tube joined to a U-tube containing mercury is connected to the top of the addition funnel (Note 2). To the flask are added 150 ml. of purified dioxane (Note 3) and 13.6 g. (0.591 g.-atom) of freshly cut sodium (Note 4). The mixture is heated to reflux, and the molten sodium is broken up with the stirrer. A solution of 20.0 g. (0.118 mole) of 1-bromo-3-chlorocyclobutane (Note 5) in 20 ml. of dioxane (Note 3) is added to the refluxing dioxane over a 1-hour period; refluxing is maintained for an additional 2 hours (Note 6) and (Note 7). The product in the traps is separated from any dioxane with the vacuum manifold system shown in Figure 1 (Note 8). The two traps containing the product are cooled in liquid nitrogen and connected to one of the stopcocks on the manifold. A gas storage bulb (Figure 2) is attached to the other stopcock. All the stopcocks are opened, and the system is evacuated. The stopcock to the pump is then closed, and the liquid nitrogen bath is removed from the traps and used to cool the gas storage bulb. The traps are warmed slightly, and the bicyclobutane condenses in the storage bulb, leaving the dioxane behind, yielding 5–6 g. (78–94%) (Note 9) of bicyclobutane.

Figure 1. Vacuum manifold.

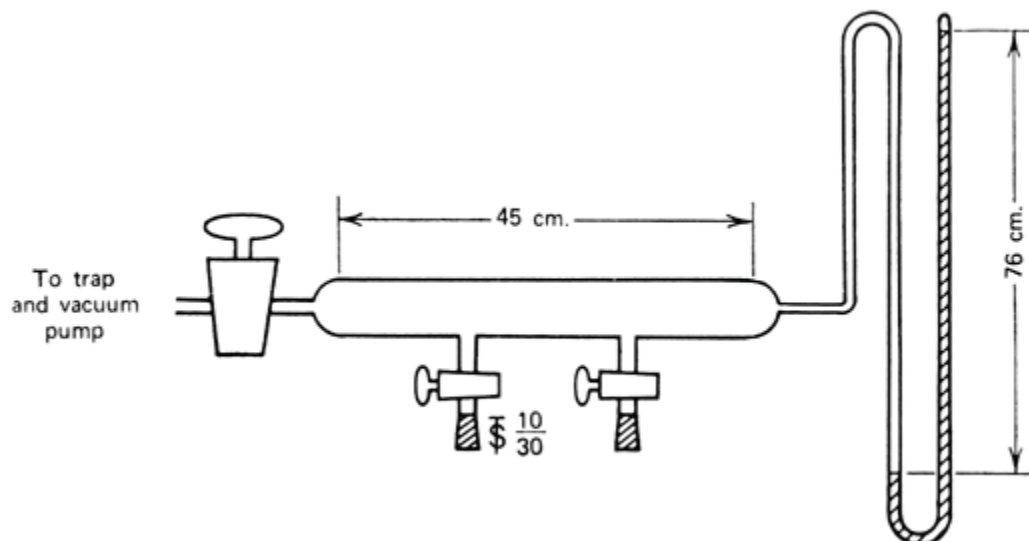
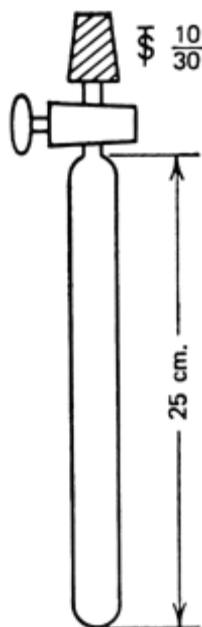


Figure 2. Gas storage bulb.



2. Notes

1. Although the entire gaseous product is caught in the first trap, this trap tends to plug during the reaction. Therefore, the second trap is used as a safety measure to collect the bicyclobutane as the first trap is thawed to open the system.
2. It is essential that a U-tube containing mercury is connected by a T-connector to the nitrogen inlet. The U-tube monitors the pressure on the system and acts as a safety valve in the event of a plugged trap. A slight positive pressure is maintained.
3. Reagent grade dioxane (2 l.) was heated to reflux with the sodium ketyl of benzophenone, prepared from 10 g. of benzophenone and 1 g. of sodium, until a deep blue solution results. If the color is not developed, another portion of benzophenone and sodium is added and heating continued until the color persists. The peroxide-free dioxane was distilled from the flask and used immediately.
4. The excess sodium allows the reaction to proceed at a greater rate and decomposes any peroxides remaining in the dioxane.
5. 1-Bromo-3-chlorocyclobutane was prepared as described in *Org. Synth., Coll. Vol. 6*, 179 (1988).
6. The reflux rate and flow of nitrogen gas must be kept at a minimum to assure that the amount of dioxane carried over to the traps in liquid nitrogen is kept as small as possible.
7. This reflux time is a minimum since decreased yields were observed when the reflux time was shortened. There was no increase in yield when the refluxing time was increased to 4 hours.
8. The basic apparatus consists of a large diameter (about 25 mm.) glass tube to which are attached at least two stopcocks, a closed-end manometer, and a large stopcock, used to isolate the manifold from the vacuum pump.
9. The product, which is about 90% bicyclobutane and 10% cyclobutene, is sufficiently pure for most purposes. The purity of the product can be determined by GC analysis at room temperature, using a 275-cm.-long column containing 20% β,β' -oxydipropionitrile on Chromosorb W (45/60). The retention times are 2.7 and 3.8 minutes for cyclobutene and bicyclobutane, respectively. Bicyclobutane (b.p. 8°) can be stored temporarily in the gas storage bulb as a liquid in an acetone-dry ice bath or for longer periods of time in an ampoule, sealed under vacuum, and stored in a freezer.

3. Discussion

Bicyclobutane has been prepared by intramolecular addition of divalent carbon to an olefinic double bond,² irradiation of butadiene,³ decomposition of cyclopropanecarboxaldehyde tosylhydrazide,⁴ and deamination of cyclobutylamine and cyclopropylcarbinylamine.⁵ The present procedure, based upon a published method,⁶ gives the highest yield of the known methods and provides a process for making

moderate quantities of material.

The procedure provides a good example of a high-yield intramolecular Wurtz reaction. Intermolecular Wurtz reactions normally do not give high yields of coupled products and are accompanied by formation of alkenes and alkanes corresponding to the alkyl halide.⁷ In contrast, intramolecular reactions of 1,3-dihalides with metals such as sodium are important synthetic methods for making cyclopropane derivatives. Examples are the reactions of sodium with pentaerythrityl tetrabromide, giving spiropentane⁸ and of sodium-potassium alloy with 1,3-dibromohexamethylcyclobutane, giving hexamethylbicyclo[1.1.0]butane.⁹ If 1,3-dihalides are not used, the yields of cyclic compounds may be considerably reduced. Thus, 1,4-dibromobutane¹⁰ and 3-(bromomethyl)cyclobutyl bromide¹¹ give very little cyclobutane and bicyclo[1.1.1]pentane, respectively.

Metals other than sodium may be considered for the reduction in intramolecular Wurtz reactions.¹¹ One of the most common of these is zinc under various reaction conditions. Examples of use of this reagent that have resulted in high yields of cyclopropane and derivatives of cyclopropane include cyclopropane from 1,3-dichloropropane,¹² spiropentane from pentaerythrityl tetrabromide in the presence of a chelating agent,¹³ spiro[2.5]octane from 1,1-bis-(bromomethyl)cyclohexane,¹⁴ and 1,1-dialkylcyclopropanes from 1,3-dibromo-2,2-dialkylpropanes.¹⁴ However, 1-bromo-3-chlorocyclobutane yields no bicyclobutane on reaction with zinc,⁶ even in the presence of a chelating agent.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 179

References and Notes

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Appendix

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

sodium ketyl of benzophenone

nitrogen (7727-37-9)

mercury (7439-97-6)

Benzophenone (119-61-9)

zinc (7440-66-6)

sodium (13966-32-0)

cyclopropane (75-19-4)

1,3-dichloropropane (142-28-9)

dioxane (123-91-1)

butadiene (106-99-0)

Pentaerythrityl tetrabromide (3229-00-3)

sodium-potassium

1,4-dibromobutane (110-52-1)

cyclobutane (287-23-0)

cyclobutene (822-35-5)

1-Bromo-3-chlorocyclobutane (4935-03-9)

Cyclobutylamine (2516-34-9)

cyclopropylcarbinylamine (2516-47-4)

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

bicyclobutane

cyclopropanecarboxaldehyde tosylhydrazone

spiropentane (157-40-4)

1,3-dibromohexamethylcyclobutane

hexamethylbicyclo[1.1.0]butane

3-(bromomethyl)cyclobutyl bromide

bicyclo[1.1.1]pentane

spiro[2.5]octane (185-65-9)

1,1-bis-(bromomethyl)cyclohexane

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