



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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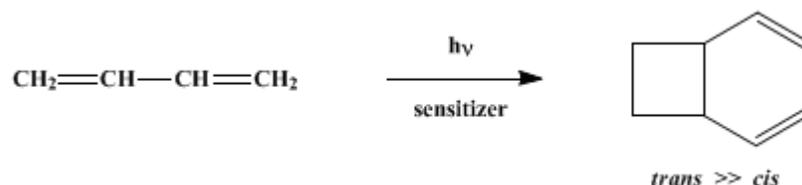
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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***cis*- AND *trans*-1,2-DIVINYLCYCLOBUTANE**



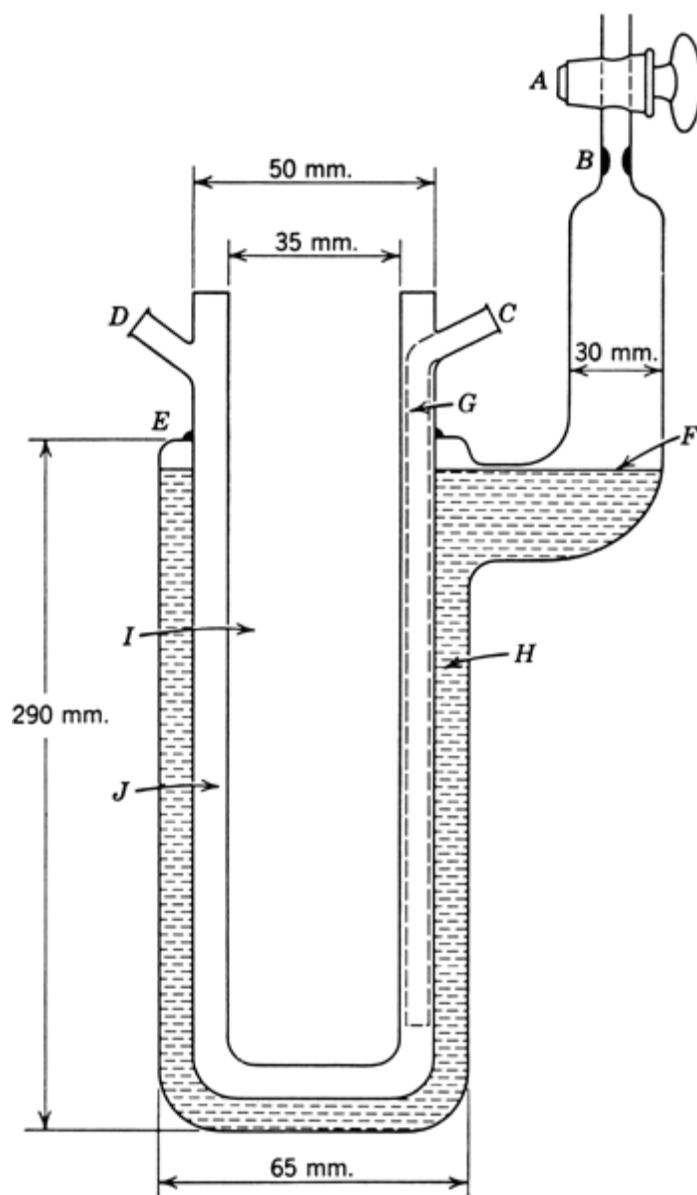
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Checked by William G. Dauben and James H. Smith.

1. Procedure

Caution! This reaction should be carried out in an explosion-proof room behind a safety shield because it involves a glass vessel under pressure.

A reaction vessel as shown in Fig. 1 is made from Pyrex tubing (Note 1). The vessel is evacuated and the stopcock closed. A 500-ml. round-bottomed, two-necked flask equipped with a gas inlet and a cold finger condenser containing dry ice is charged with 1 g. of finely powdered 4,4'-bis(dimethylamino)benzophenone (Michler's ketone) (Note 2), (Note 3). A butadiene tank is connected to the gas inlet, and about 250 ml. (160 g., 3.0 moles) of butadiene is collected in the flask (Note 4). The butadiene is cooled to dry ice temperature. The reaction vessel is immersed to the filling level shown in Fig. 1 in a slurry of dry ice and acetone. A 4-in. length of Tygon tubing is attached between the inlet of the reaction vessel and one neck of the flask containing the butadiene. The other neck of the flask is stoppered, and the flask is tipped to fill the connecting tube and the neck of the stopcock with butadiene. At the same time the stopcock is opened. The flask is shaken to ensure that the suspended Michler's ketone will be swept into the reaction vessel by the butadiene. After the vessel is filled with butadiene the stopcock is closed, the connecting tube removed, and the vessel transferred to a Dewar flask filled with liquid nitrogen. When the butadiene is frozen, the vessel is evacuated with a high-vacuum pump and sealed off below the stopcock with a torch (Note 5). The reaction vessel is fitted with cooling water hoses and a 450-watt Hanovia medium-pressure mercury arc lamp, and then the butadiene is allowed to thaw and come to room temperature (Note 6). The mixture is irradiated for 72 hours, the water jacket dried, and the vessel weighed (Caution! (Note 6)). The reaction vessel is then frozen in a Dewar flask containing a dry ice-acetone mixture, and the seal is cautiously broken. The cooling bath is removed, and the reactor is allowed to come to room temperature. The reaction mixture is removed, the vessel cleaned (Note 7), and weighed again to determine the amount of starting material. The reaction mixture is distilled and the fraction boiling between 109° and 111° (uncor.) is collected (Note 8). The yield is 96–104 g. (60–65%) of 99% pure (by gas chromatography) *trans*-1,2-divinylcyclobutane, n_D^{25} 1.4429–1.4431, the impurities being butadiene and 1,5-cyclooctadiene (Note 9).

Fig. 1. *A*, 4-mm. stopcock; *B*, thickened for easy sealing; *C*, water inlet; *D*, water outlet; *E*, this seal can be replaced by a ground glass joint for higher-boiling materials than butadiene; *F*, filling level; *G*, the cooling water tube indicated by the dotted lines will permit a higher flow rate if shaped as an oval or rectangle; *H*, reaction well; *I*, lamp well; *J*, cooling water jacket.



2. Notes

1. A reaction vessel, as shown in Fig. 1, is useful for many photochemical reactions because virtually all the light produced can be captured by the reagents. It can be constructed from either Pyrex or quartz tubing, depending on the absorption spectra of the reagents.

2. The choice of a sensitizer for butadiene dimerization depends on three things: the energy of the triplet-singlet transition, the intersystem crossing efficiency, and the absorption spectrum of the sensitizer.³ Michler's ketone has a sufficiently high triplet energy to transfer energy at a diffusion-controlled rate to both *cis* and *trans* forms of butadiene, thus reducing the yield of 4-vinylcyclohexene produced.⁴ Furthermore it has a high intersystem crossing efficiency and a high extinction coefficient at 3660 Å, which is the most intense line from a medium-pressure mercury arc lamp. For photochemical reactions where energy transfer is not diffusion-controlled, the lifetime of the triplet may be an important factor in the choice.

3. The amount of sensitizer is not critical since only enough is needed to absorb all the light. One gram of Michler's ketone will not be totally dissolved in 250 ml. of butadiene, but will be totally dissolved after the reaction is finished. Michler's ketone as obtained from Eastman Organic Chemicals was used without purification.

4. **1,3-Butadiene** obtained from Matheson, Coleman and Bell was used without purification.
5. The **butadiene** should not be degassed by freeze-thaw cycles, because the presence of a small amount of **oxygen** reduces the amount of polymer formed on the walls of the vessel.
6. All experimental manipulations with the reaction vessel while it is sealed and under pressure should be carried out behind a safety shield.
7. The polymer can be conveniently removed by filling the flask two-thirds full with concentrated **nitric acid** and warming gently on a steam bath in a hood behind a safety shield.
8. The **cis-1,2-divinylcyclobutane** in the reaction mixture rearranges rapidly under reflux to the higher-boiling **1,5-cyclooctadiene**.
9. If **cis-1,2-divinylcyclobutane** is desired, it can be isolated in 7–8% yield from the reaction mixture by preparative gas chromatography with the Beckman Megachrom instrument, using columns packed with Apiezon J.

3. Discussion

The *trans* isomer of 1,2-divinylcyclobutane may be isolated in low yield from the mixture formed by thermal dimerization of **butadiene**.⁵ The *cis* isomer has been prepared by a sequence of reactions.⁶

4. Merits of the Preparation

Essentially the same procedure may be used to produce mixtures of cyclodimers from **isoprene**,⁴ **1,3-cyclopentadiene**,⁴ and **1,3-cyclohexadiene**.⁷ Separation of all products is somewhat difficult in most cases but has always been possible by preparative vapor phase chromatography. Despite the problems that may be involved in separation of desired products in some instances, photocyclization frequently is the method of choice for preparation of 1,2-dialkenylcyclobutanes if they can be made major products of photoreactions. Starting materials are readily available, and the preparations are easily carried out on the scale described. There is little doubt that the method is the best for preparation of *trans*-1,2-divinylcyclobutane.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 6*, 962
- *Org. Syn. Coll. Vol. 10*, 718

References and Notes

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2. Department of Chemistry, Columbia University, New York, New York.
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Appendix

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

cis and trans forms of butadiene

trans isomer of 1,2-divinylcyclobutane

1,2-dialkenylcyclobutanes

nitric acid (7697-37-2)

oxygen (7782-44-7)

nitrogen (7727-37-9)

acetone (67-64-1)

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

ISOPRENE (78-79-5)

1,3-cyclopentadiene (542-92-7)

1,3-Cyclohexadiene (592-57-4)

1,5-cyclooctadiene

4-vinylcyclohexene

trans-1,2-divinylcyclobutane (6553-48-6)

cis-1,2-divinylcyclobutane (16177-46-1)

4,4'-bis(dimethylamino)benzophenone