



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.

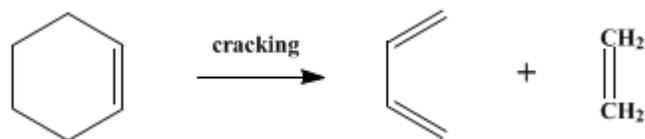
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.102 (1943); Vol. 17, p.25 (1937).

1,3-BUTADIENE



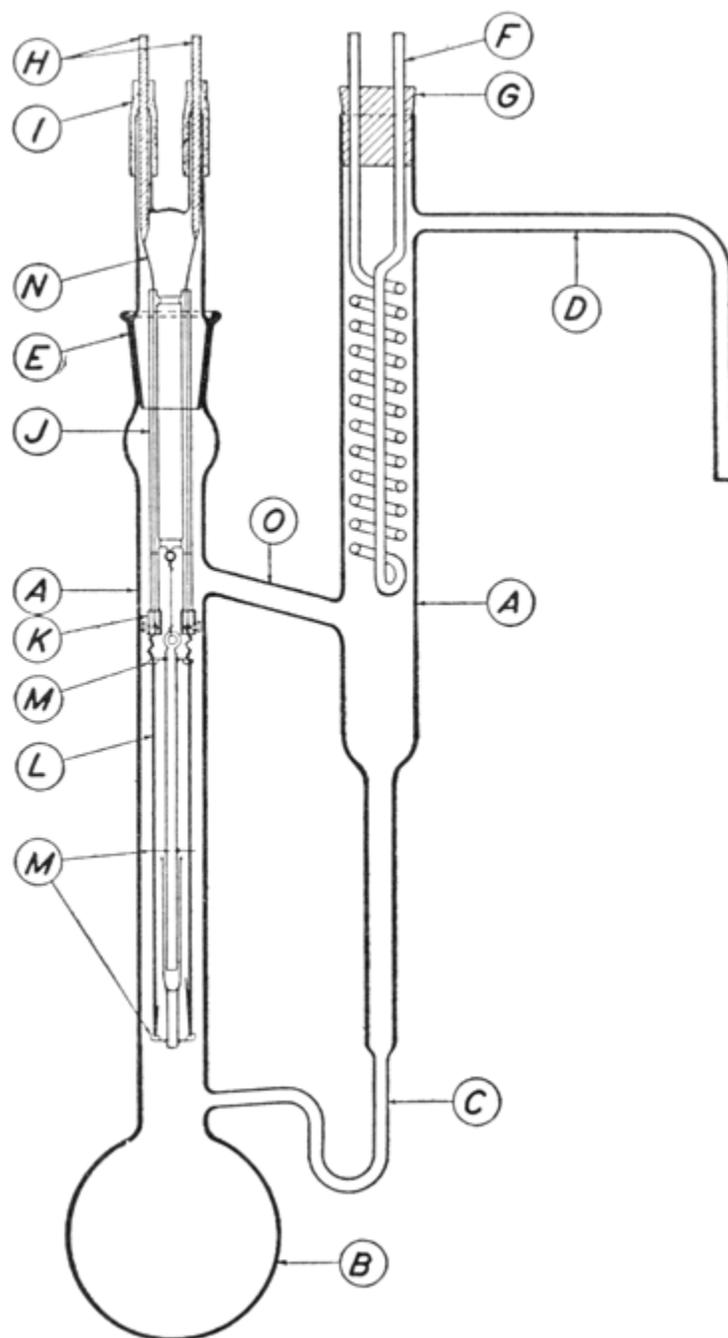
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1. Procedure

Cyclohexene (*Org. Syn. Coll. Vol. I, 1941, 183, and p. 152 below*) is boiled in the flask B, shown in *Fig. 3*, and the vapor is passed over a cracking element consisting of an expansible grid threaded with resistance ribbon L (*Note 1*) and (*Note 2*). The boiling flask B is supported over a 250-watt bowl heater provided with a rheostat, and the current in the cracking element is taken from a 115-volt a-c. or d-c. source and controlled by a second rheostat of 10-ampere capacity (*Note 3*). In order to trap any cyclohexene which passes the coil condenser, the gas-delivery tube D is connected to a tube leading close to the bottom of a 500-cc. distilling flask immersed in an ice bath. The exit tube of the flask is connected with a short section of rubber tubing to a receiver for condensing the butadiene, consisting of a large test tube with the entrance tube leading halfway to the bottom and an exit tube at the top for conducting the ethylene (saturated with butadiene) to a hood or outdoors. The receiver is cooled in a Dewar flask containing solid carbon dioxide and a eutectic mixture of equal parts by weight (or volume) of chloroform and carbon tetrachloride.

Fig. 3



The flask B is two-thirds filled with [cyclohexene](#), and, with the cooling water flowing, this is heated to vigorous boiling. When the vapor has displaced the air from the apparatus *completely* ([Note 4](#)), the current is turned on in the cracking unit. By adjusting both the rate of boiling and the current the ribbon is maintained at a bright red heat over its entire length. Very rapid refluxing is necessary in order to prevent undue carbonization on the filament and tar formation on the glass walls ([Note 5](#)). The generator can be run intermittently or until the charge is exhausted.

The [butadiene](#) collected is purified by a bulb-to-bulb distillation, the receiver in the cooling mixture being replaced by a similar container to which it is connected by means of rubber tubing and into which the [butadiene](#) is allowed to distil. The product is quite satisfactory for most uses, as in the Diels-Alder reaction ([Note 6](#)). The cracking element uses about 500 watts at 8.7 amperes and produces 25–30 g. of [butadiene](#) per hour. The yield, based on the [cyclohexene](#) consumed ([Note 7](#)) and on redistilled product, is 65–75 per cent of the theoretical amount. High-boiling residues accumulating in the boiling flask

should be removed after preparing 100–150 g. of [butadiene](#) (Note 8).

2. Notes

1. *Apparatus.*—The unit shown in Fig. 3 is constructed of Pyrex glass, and the following is a summary of satisfactory dimensions for the various tubings (outer diameters) and of other specifications: A, 32-mm. tubing; B, 500-cc. flask; C, 7-mm. tubing; D, 8-mm. tubing; E, No. 35 standard taper joint; F, coil of 3/16-in. copper tubing (see (Note 2)); G, cork stopper; H, 1/8-in. brass rod; I, rubber tubing; J, 3-mm. glass tubing; K, brass electrical connectors; L, Chromel C resistance ribbon No. 37 B. and S. gauge, 1.9–2 ohms per foot, width 1/16 in., length 56 to 60 in. (see below); M, tungsten wire-loop supports sealed into the suspended glass rod; the center supports are of 0.01-in. (dia.) wire, those at the top and bottom of 0.015-in. (dia.) wire; N, copper wire No. 22 B. and S. gauge; O, 12-mm. tubing.

The ribbon L of the cracking element is threaded between the tungsten loops M, of which there are five each at the top and bottom and eight at the center. The unit is suspended with a copper wire from the glass cross-support as shown. The lower end is free to drop down as the resistance wire expands; this prevents short-circuiting of the element.

The composition of the filament is of importance in determining the yield and the performance of the apparatus. With nickel-chromium alloys excessive carbonization occurs and the yield is poor. Much better results are obtained with the nickel-iron-chromium alloys called Chromel C and Nichrome Alloy Wire.

2. To provide for the proper functioning of the coil condenser even in warm weather it is advisable to increase the number of turns to 30–40, although the condenser as shown is satisfactory with tap water at 4–10°.

3. A slide-wire rheostat of 2-ampere capacity wound on a hollow enameled iron tube will carry the required current if a stream of cooling water is passed through the tube.

4. An explosion may occur if the filament is heated while an appreciable amount of air is still present. Furthermore, the heating element will burn out at once if an adequate supply of [cyclohexene](#) vapor is not supplied, since the current passing through the wire is far above the normal rating for air.

5. In case of excessive carbonization the rate of boiling should be increased or the filament temperature slightly lowered. In general the vapor velocity should be as high as possible without exceeding the capacity of the copper condenser.

6. The crude product contains appreciable amounts of C₂, C₃, and C₆ fractions. The actual [butadiene](#) content lies between 82 and 88 per cent. If very pure material is desired the [butadiene](#) is converted into the tetrabromide, which is crystallized and reconverted to the hydrocarbon by means of [zinc](#) and [alcohol](#).¹

7. The [cyclohexene](#) collecting in the ice trap ordinarily is returned to the boiling flask; in determining the percentage conversion this was combined with any material left in the boiler and the pure starting material present recovered by fractionation.

8. The apparatus may be used also for the preparation of ketene from [acetone](#) (Org. Syn. Coll. Vol. I, 1941, 330).

3. Discussion

The methods for the preparation of gaseous products containing more or less [butadiene](#) are too numerous for profitable review here. Especially is this true since the development of commercial processes which are not particularly suitable for laboratory operation. The most satisfactory procedure for preparing [butadiene](#) in the laboratory is the pyrolysis of [cyclohexene](#),² which has been shown to yield a product consisting essentially of [butadiene](#).^{1, 3} For this pyrolysis, the apparatus described above and that described by Williams and Hurd⁴ are available. Other laboratory preparations of [butadiene](#) start from [butyl chloride](#),⁵ 2,3-dibromobutane,⁶ [crotyl chloride](#),⁶ and 1,3-butylene glycol.⁷

This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 28

References and Notes

1. Kistiakowsky, Ruhoff, Smith, and Vaughan, J. Am. Chem. Soc. **58**, 146 (1936).
 2. Badische Anilin- und Soda-Fabrik, Ger. pat. 252,499 (Chem. Zentr. **1912**, II, 1708).
 3. Zelinskii, Mikhailov, and Arbuzov, J. Gen. Chem. (U.S.S.R.) **4**, 856 (1934) [C. A. **29**, 2152 (1935)].
 4. Williams and Hurd, J. Org. Chem. **5**, 122 (1940).
 5. Muskat and Northrup, J. Am. Chem. Soc. **52**, 4043 (1930).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alcohol (64-17-5)

Cyclohexene (110-83-8)

carbon tetrachloride (56-23-5)

carbon dioxide (124-38-9)

acetone (67-64-1)

zinc (7440-66-6)

ethylene (9002-88-4)

Butyl chloride (109-69-3)

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

2,3-dibromobutane (5408-86-6)

crotyl chloride (4894-61-5)

1,3-butylene glycol (107-88-0)