



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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

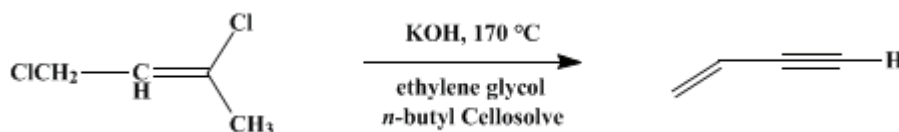
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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MONOVINYLACETYLENE

[1-Buten-3-yne]



Submitted by G. F. Hennion, Charles C. Price, and Thomas F. McKeon, Jr.¹
 Checked by Max Tishler and John E. Allegretti.

1. Procedure

A 2-l. three-necked flask, heated by a Carbowax bath, is equipped with a motor-driven Trubore stirrer, Teflon paddle, Trubore bearing (Note 1), a Friedrichs condenser, and a 250-ml. dropping funnel. The dropping funnel is connected to the flask by a 24/40 ground-glass joint with a side arm made of 7-mm. tubing. The side arm is connected through a calcium chloride drying tower and a bubbler to a nitrogen tank.

The top of the condenser is connected to a horizontal tube (ca. 2 × 25 cm.) partially filled with granular anhydrous calcium chloride. The horizontal tube is then connected to a 100-ml. graduated cylinder immersed in an acetone-Dry Ice mixture for collection of the product. The cylinder is also equipped with an escape tube protected by a calcium chloride drying tube.

Four hundred grams of powdered technical potassium hydroxide flakes (Note 2) is placed in the flask, and 500 ml. of ethylene glycol is added. This mixture is stirred vigorously while adding 100 ml. of *n*-butyl Cellosolve (Note 3). The system is swept with a rapid stream of nitrogen for 15–20 minutes while the temperature of the oil bath is raised to 165–170°. The flow of nitrogen is then reduced to a rate just sufficient to maintain an atmosphere of nitrogen in the system.

One hundred and twenty-five grams of 1,3-dichloro-2-butene (1.0 mole) (Note 4) is added at a rate of about 3 drops per second. Addition should be complete in 0.75–1 hour (Note 5). During the addition the temperature of the oil bath is maintained at 165–170° (Note 6), and the reaction mixture is stirred vigorously. Heating is continued for 1 hour after the addition of dichlorobutene is complete.

The yield of crude product obtained is 31.2 g. (39 ml., 60%) (Note 7) and (Note 8). The crude product may be purified by distillation through a low-temperature column (Note 9) to yield 22.4–24.8 g. (28–31 ml., 43–48%) of monovinylacetylene, b.p. 0–6° (Note 10) The storage of monovinylacetylene in the presence of oxygen has been reported to lead to explosive compounds. It is therefore suggested that the product be stored under an inert atmosphere.

2. Notes

1. An oil-sealed stirrer was found unsuitable because the pressure drop through the system was greater than the pressure drop across the oil-sealed stirrer. The Trubore stirrer and bearing were purchased from Ace Glass Inc., Vineland, New Jersey.
2. The potassium hydroxide was weighed as flakes, then ground rapidly with a mortar and pestle to roughly the consistency of granulated sugar, and added as soon as possible to the reaction flask to minimize moisture uptake. The flakes may be used directly without grinding, the only difference being that the mixture of potassium hydroxide, glycol, and Cellosolve should be heated for a slightly longer time before any dichlorobutene is added in order to allow as complete a dispersion as possible.
3. The butyl Cellosolve is added to control the foaming during the reaction.
4. The dichlorobutene used was Eastman Kodak Company technical grade. Distillation before use was not observed to increase the yields.
5. The rate of addition is very important. If the time of addition of 1 mole of dichlorobutene goes much

beyond 1 hour, the yield will decrease noticeably.

6. This is apparently an optimum temperature. Lower temperatures lead to lower yields, while higher temperatures do not change the yield appreciably.

7. The calculations of yields are based on $d^{80} = 0.8$ extrapolated from data at higher temperature.²

8. The preparation also has been run on a 2-mole scale, using double the quantities specified in a 3-l. flask. The yields obtained were comparable to those obtained on the 1-mole scale.

9. The low-temperature column shown in Fig. 12 was 75 cm. long, made of 7-mm. glass tubing. The entire column was surrounded by an evacuated, silvered jacket. The column, for the lower 60 cm., was a tightly coiled spiral (3.8 cm. diameter). The remaining length was straight and was surrounded by a coolant cup in which liquid of any temperature could be placed to control the refluxing temperature. For the purpose, a calcium chloride-water-Dry Ice mixture was used to keep the temperature of the cup at approximately -5 to 0° . The vapor from the column was condensed and collected in a graduated cylinder immersed in an acetone-Dry Ice bath (Note 10). The major features of infrared spectra of the vapor from redistilled product are summarized in Table I (Note 11).

10. Warming the still pot with 60° water was necessary to distil all the volatile gases toward the end of the distillation.

11. The spectrum of the fractionated monovinylacetylene was comparable, in band peaks and intensities, with previously reported spectra. A previously reported band at 5.8μ , however, was not found in any of the samples, suggesting that an impurity was present in the sample previously reported.

Fig. 12. Low-temperature distillation column.

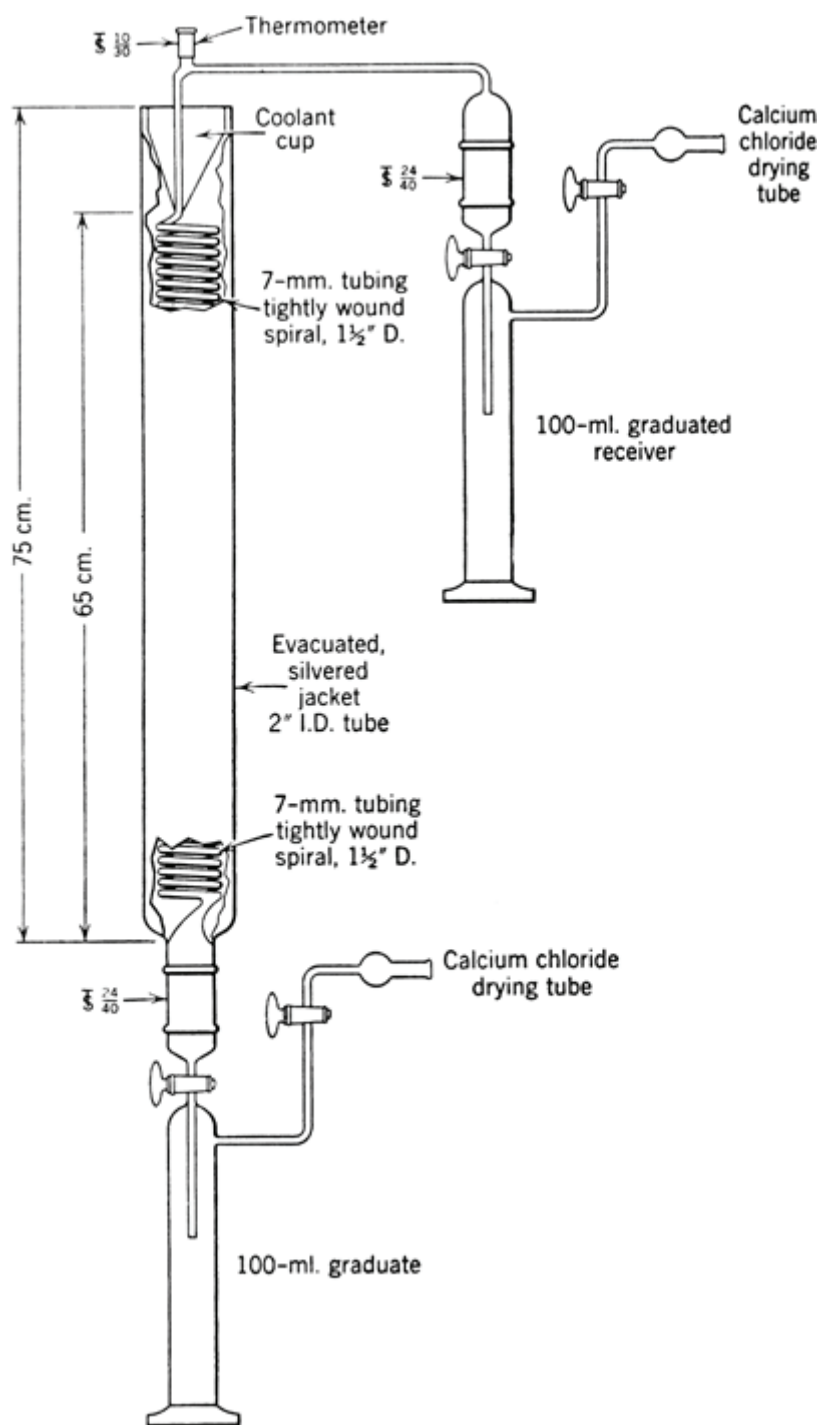


TABLE I THE MAJOR BANDS FOR THE INFRARED SPECTRUM OF MONOVINYLAETHYLENE GAS

(350 mm. pressure, 5-cm. cell)

Wavelength, μ	Absorption, %	Wavelength, μ	Absorption, %
3.02	93	6.20	87
3.22	62	7.0-7.15	33
3.30	67	7.9-8.1	98
4.73	9	9.17	49

5.13	19	9.37	18
5.41	59	10.2–11.2	99
5.46	52	13.67	27
5.80	—		

3. Discussion

Monovinylacetylene has been prepared by the decomposition of a diquatery ammonium base,³ by the dimerization of acetylene,⁴ by the dehydrohalogenation of dihalobutenes in liquid ammonia,⁵ and by heating dimethylvinylethynylcarbinol with potassium hydroxide.⁶ The procedure described has been published.⁷

References and Notes

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Appendix

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

calcium chloride (10043-52-4)

acetylene (74-86-2)

ammonia (7664-41-7)

oxygen (7782-44-7)

nitrogen (7727-37-9)

potassium hydroxide (1310-58-3)

ethylene glycol,
cellosolve (107-21-1)

Monovinylacetylene,
1-Buten-3-yne (689-97-4)

1,3-dichloro-2-butene

dichlorobutene

butyl Cellosolve,
n-butyl Cellosolve (111-76-2)

dimethylvinylethynylcarbinol (690-94-8)