



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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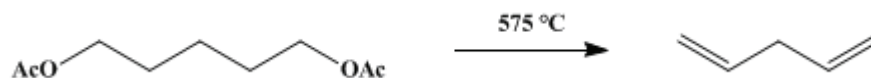
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.746 (1963); Vol. 38, p.78 (1958).

1,4-PENTADIENE

[I. METHOD A]



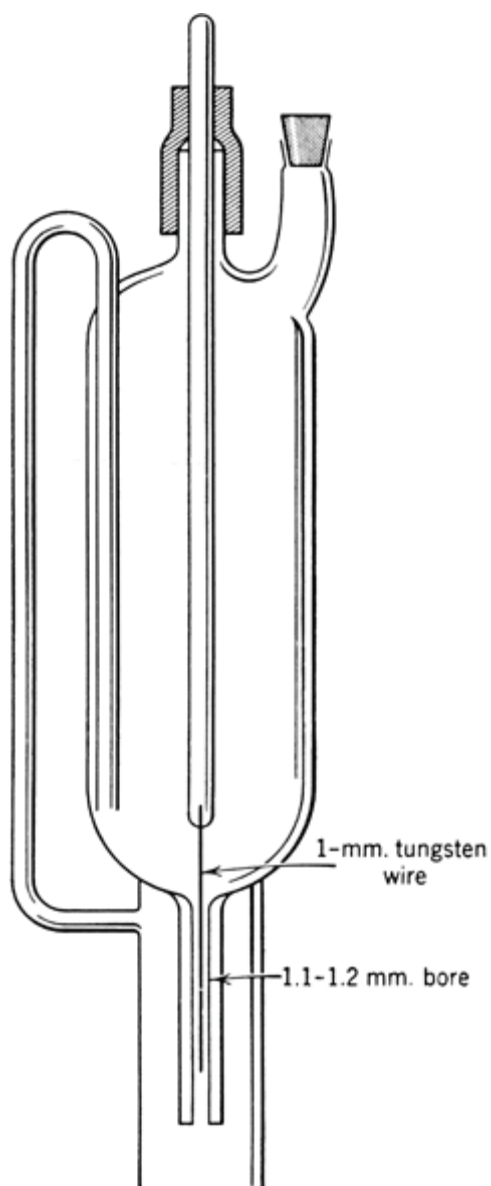
Submitted by R. E. Benson and B. C. McKusick¹.

Checked by N. J. Leonard and A. G. Cook.

1. Procedure

The apparatus (Fig. 14) is similar to that described on p. 795 and in a previous volume.² It consists of a Pyrex glass reaction tube, 90 cm. long by 45 mm. in outside diameter, mounted vertically in an electric furnace about 50 cm. long. Attached to the top of the tube are a graduated dropping funnel (Note 1), an inlet tube for nitrogen, and a thermocouple well extending to the bottom of the heated section and holding a movable thermocouple. The entire heated section, which begins 10 cm. from the top of the tube, is packed with Pyrex glass rings 10 mm. in outside diameter by about 10 mm. in length held in place by a plug of glass wool supported by indentations in the tube. The lower end of the tube is attached to a 1-l. round-bottomed flask immersed in an ice bath and having a side arm from which vapors pass successively through a trap immersed in an ice bath and a trap immersed in a bath of Dry Ice and acetone. Each trap is capable of holding about 200 ml. of liquid. The temperature of the hottest part of the tube, which is located near the middle of the heated section, is raised to $575^{\circ} \pm 10^{\circ}$ while nitrogen (Note 2) is passed successively through a flowmeter and the tube at a rate of 4–6 l./hr. Under these conditions (Note 3), 658 g. (645 ml., 3.5 moles) of 1,5-pentenediol diacetate (Note 4) is added to the tube over a period of 3.5 hours. The contents of the three receivers are combined and distilled at atmospheric pressure through a 15-cm. indented Claisen-type still head; the condenser is cooled with ice water, and the receiver is immersed in an ice bath. The fraction boiling at $25\text{--}55^{\circ}$, wt. 170–190 g., is redistilled through a 60-cm. column packed with glass helices or a column of similar efficiency to give 150–170 g. (63–71%) of 1,4-pentadiene, b.p. $26\text{--}27.5^{\circ}/760\text{ mm.}$, n_D^{25} 1.3861–1.3871 (Note 5).

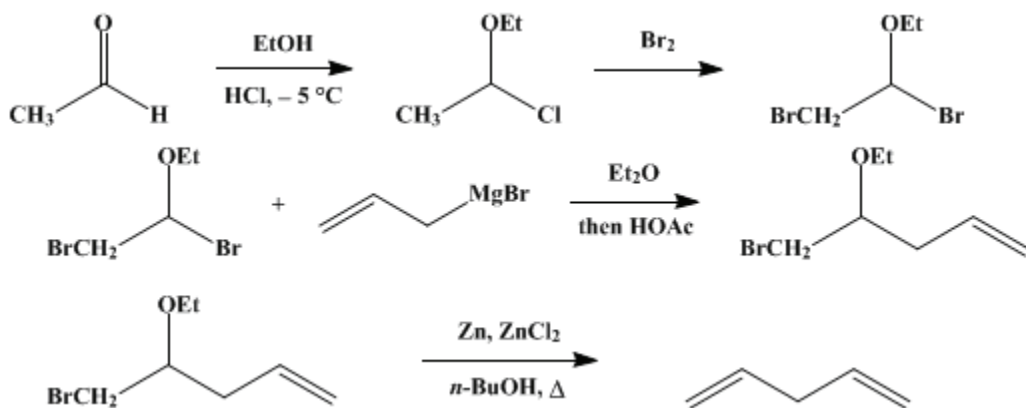
Fig. 14.



2. Notes

1. A Hershberg dropping funnel³ modified by addition of a pressure-equalizing arm (Fig. 14) makes it easy to add the diacetate at a constant rate.
2. A dry, oxygen-free grade of commercial nitrogen is used. Nitrogen can be omitted without diminishing the yield by more than a few per cent.
3. As the addition of the diacetate begins, the temperature of the hottest part of the tube (the location of which generally shifts lower at this time) decreases, necessitating an increase in current in the electric furnace.
4. 1,5-Pentanediol diacetate,^{4,5} b.p. 85–90° /0.9 mm., n_D^{25} 1.4253, is obtained in 92–94% yield by adding a 10% excess of acetic anhydride to 1,5-pentanediol⁶ at 120–140°, heating the mixture under reflux for 2 hours, and distilling it at reduced pressure. The practical grade of 1,5-pentanediol sold by Eastman Kodak Company may be used.
5. The residue from the first distillation is a mixture of acetic acid, 4-penten-1-ol acetate, and 1,5-pentanediol diacetate. Another 15–35 g. (6–15%) of 1,4-pentadiene can be obtained by passing the residue through the pyrolysis tube under the conditions described above.

[II. METHOD B]



Submitted by Oliver Grummitt, E. P. Budewitz, and C. C. Chudd⁷.
 Checked by William S. Johnson, E. Saito, and Donald J. Reif.

1. Procedure

A. *α -Chloroethyl ethyl ether*. A mixture of 200 g. (201 ml.) of redistilled *paraldehyde*, b.p. 121–122.5° (equivalent to 4.54 moles of *acetaldehyde*), and 200 g. (254 ml., 4.34 moles) of absolute *ethanol* is placed in a 1-l. three-necked flask fitted with a mechanical stirrer and a gas inlet tube reaching to the bottom of the flask. The mixture is cooled to -5° in a mixture of Dry Ice and acetone, and dry *hydrogen chloride* (Note 1) is passed into the stirred reaction mixture maintained at about -5° until 200 g. (5.48 moles) has been absorbed. During this operation, which requires about 2 hours, the reaction mixture separates into two layers. The upper layer of crude *α -chloroethyl ethyl ether* is removed, and the dissolved *hydrogen chloride* is swept out by bubbling dry *nitrogen* gas through the mixture. The product is dried overnight with 25–50 g. of anhydrous *calcium sulfate* (Note 2). The yield of crude *α -chloroethyl ethyl ether* (Note 3) is 411–432 g. (87–92% based on *ethanol*). The product is not distilled, since it decomposes readily.

B. *α,β -Dibromoethyl ethyl ether*. Four hundred and twenty-five grams (3.92 moles) of the crude *α -chloroethyl ethyl ether* (part A) is placed in a dry 1-l. three-necked flask, fitted with a dropping funnel, mechanical stirrer, and an outlet tube leading to a gas absorption trap⁸ to dispose of the *hydrogen chloride* evolved. The flask is cooled in an ice bath, and 625 g. (200 ml., 3.92 moles) of *bromine* is added in small portions from the dropping funnel with stirring. The reaction mixture is allowed to become almost colorless after each addition. When all of the *bromine* has been added (5–6 hours), a slow current of dry *nitrogen* is bubbled through the reaction mixture to sweep out the *hydrogen chloride* (Note 4). The product is dried overnight with 25–50 g. of anhydrous *calcium sulfate* and then distilled at reduced pressure (Note 5). The yield of colorless *α,β -dibromoethyl ethyl ether* is 599–663 g. (66–73% based on the *α -chloroethyl ethyl ether*), b.p. 70–75° /27 mm., n_D^{20} 1.5097–1.5102.

C. *Allylmagnesium bromide* (Note 6). In a dry 5-l. three-necked flask, equipped with a sealed stirrer, a reflux condenser and drying tube, a pressure-equalized dropping funnel, and a nitrogen inlet tube, are placed 195 g. (8.0 g. atoms) of dry *magnesium turnings* and 2.4 l. of anhydrous *ether*. The flask is cooled in an ice bath, a small crystal of *iodine* is added, and a solution of 400 g. (287 ml., 3.31 moles) of *allyl bromide* (redistilled, b.p. 69–71°) in an equal volume of anhydrous ether is added dropwise over a period of 17 hours. During the reaction a slow stream of dry, oxygen-free *nitrogen* is passed through the flask. After the addition is complete, the reaction mixture is stirred for 30 minutes. The Grignard reagent is decanted into a dry, graduated storage bottle; the residue in the flask is washed with 150–200 ml. of dry *ether*; and the wash liquid is added to the storage bottle. Samples of the clear supernatant solution are analyzed by acidimetric titration.⁹ The yield of *allylmagnesium bromide* is 2.62–2.95 moles (79–89%).

D. *α -Allyl- β -bromoethyl ethyl ether*. The same apparatus is used as in the preparation of *allylmagnesium bromide*. The flask is charged with an amount of the Grignard solution (part C) equivalent to 2.78 moles of allylmagnesium bromide (or chloride) and cooled in an ice bath. A solution

of 580 g. (2.5 moles) of α,β -dibromoethyl ethyl ether (part B) in an equal volume of anhydrous ether is added slowly with stirring over a period of 3–4 hours. The mixture is allowed to stand overnight and is then hydrolyzed with 75 ml. of 20% acetic acid followed by 500 ml. of water. The ether layer is separated, washed with four 100-ml. portions of 10% aqueous sodium bicarbonate solution followed by four 100-ml. portions of saturated aqueous sodium chloride solution, dried over 100 g. of anhydrous calcium sulfate, and distilled under reduced pressure. The yield of colorless α -allyl- β -bromoethyl ethyl ether is 370–396 g. (77–82% based on the α,β -dibromoethyl ethyl ether), b.p. 72–75° /21 mm., n_D^{20} 1.4600–1.4606.

E. *1,4-Pentadiene*. A 2-l. three-necked flask is equipped with a sealed stirrer and a 28-cm. reflux condenser, at the top of which is a 2.5 × 35 cm. Vigreux fractionating column attached to an efficient condenser arranged for distillation. Water at 35–40° is pumped through the reflux condenser, ice water is pumped through the downward condenser, and the receiver is ice-cooled and attached to a trap cooled by Dry Ice. The flask is charged with 380 g. (1.97 moles) of α -allyl- β -bromoethyl ethyl ether (part D) in 550 ml. of *n*-butyl alcohol; then 550 g. (8.4 g. atoms) of zinc dust and 2 g. of anhydrous zinc chloride are added. The mixture is stirred vigorously and heated gradually to the point where the pentadiene distils at a rate of about one drop every 2 seconds. The reflux condenser and column return most of the butyl alcohol to the flask. The reaction takes 5–6 hours for completion. The distillate is washed with five 100-ml. portions of ice water to remove most of the butyl alcohol and is then dried overnight with 15 g. of calcium chloride. The crude dry product is distilled through a 2.5 × 35 cm. Vigreux column to give 97–102 g. (72–76%) of colorless 1,4-pentadiene, b.p. 26–27° /740 mm., n_D^{20} 1.3887–1.3890.

2. Notes

1. Commercial hydrogen chloride from a cylinder is dried by passage through a train consisting of a wash bottle of concentrated sulfuric acid, a 25-cm. calcium chloride tube, and finally an empty safety trap.
2. This ether is a lachrymator, hydrolyzes rapidly in the presence of moisture, and resinifies readily at temperatures above 0°. It is advisable to store it in a Dry Ice chest during drying and until the next step is to be run. Hydrolysis at low temperatures appears to be negligible.
3. Analysis of the crude material for chlorine gave 31.74% (calcd. 32.69%).
4. It is necessary to remove the hydrogen chloride because it promotes decomposition of the dibromoether.
5. Distillation is required to remove aldehyde, alcohol, and water which would react with the Grignard reagent in the next step. α,β -Dibromoethyl ethyl ether is also a lachrymator.
6. Either allylmagnesium bromide or allylmagnesium chloride may be used. The former is more conveniently prepared in higher yield and in a more concentrated solution, but allyl chloride is considerably less expensive than allyl bromide. The submitters state that the chloride is prepared just as the bromide with the following exceptions: the temperature is maintained between –10 and –15° with a Dry Ice-acetone cooling bath; 76.5 g. (82 ml., 1 mole) of allyl chloride (b.p. 45–47°) dissolved in an equal volume of dry ether is used (the amounts of all other reagents are unaltered); the addition is carried out over a 12-hour period, then the cooling bath is removed, and the mixture (containing considerable solid) is stirred until it reaches room temperature, during which time most of the solid material dissolves. The yield of allylmagnesium chloride as determined by acidimetric titration⁹ is 0.67–0.69 mole (67–69%).

3. Discussion

1,4-Pentadiene has been prepared by the interaction of allyl bromide and vinyl bromide in the presence of magnesium;¹⁰ by the pyrolysis of 1,5-pentanediol diacetate^{4,5} or 4-penten-1-ol acetate;^{5,11} by the reaction of α -allyl- β -bromoethyl ethyl ether with zinc;^{12,13} by the thermal decomposition of dimethyl (4-pentenyl)amine oxide;¹⁴ and by the reaction of vinylmagnesium bromide with allyl bromide.¹⁵

Method I is based on the work of Schniepp and Geller⁴ and of Paul and Tchelitcheff,⁵ while Method II is essentially that of Shoemaker and Boord¹² with some modifications.¹³

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 235
- Org. Syn. Coll. Vol. 5, 679
- Org. Syn. Coll. Vol. 5, 949
- Org. Syn. Coll. Vol. 6, 606
- Org. Syn. Coll. Vol. 9, 28

References and Notes

1. Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
2. *Org. Syntheses Coll. Vol. 3*, 30 (1955).
3. *Org. Syntheses Coll. Vol. 2*, 129 (1943).
4. Schniepp and Geller, *J. Am. Chem. Soc.*, **67**, 54 (1945).
5. Paul and Tchelitcheff, *Bull. soc. chim. France*, [5] **15**, 108 (1948).
6. *Org. Syntheses Coll. Vol. 3*, 693 (1955).
7. Western Reserve University, Cleveland, Ohio.
8. *Org. Syntheses Coll. Vol. 2*, 4 (1943).
9. Gilman, Zoellner, and Dickey, *J. Am. Chem. Soc.*, **51**, 1577 (1929).
10. Kogerman, *J. Am. Chem. Soc.*, **52**, 5060 (1930).
11. Paul and Normant, *Bull. soc. chim. France*, [5] **11**, 367 (1944).
12. Shoemaker and Boord, *J. Am. Chem. Soc.*, **53**, 1505 (1931).
13. Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936); Elsner and Wallsgrove, *J. Inst. Petrol.*, **35**, 259 (1949).
14. Cope and Bumgardner, *J. Am. Chem. Soc.*, **79**, 960 (1957).
15. Normant, *Compt. rend.*, **239**, 1811 (1954).

Appendix

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

allylmagnesium bromide (or chloride)

ethanol (64-17-5)

calcium chloride (10043-52-4)

acetaldehyde (75-07-0)

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

acetic anhydride (108-24-7)

sodium bicarbonate (144-55-8)

magnesium,
magnesium turnings (7439-95-4)

sodium chloride (7647-14-5)

 bromine (7726-95-6)

Allyl bromide (106-95-6)

 nitrogen (7727-37-9)

allyl chloride (107-05-1)

calcium sulfate (7778-18-9)

 butyl alcohol,
n-butyl alcohol (71-36-3)

 iodine (7553-56-2)

 chlorine (7782-50-5)

 zinc (7440-66-6)

zinc chloride (7646-85-7)

vinyl bromide (593-60-2)

vinylmagnesium bromide (1826-67-1)

1,5-Pentanediol (111-29-5)

α,β -Dibromoethyl ethyl ether (2983-26-8)

 pentadiene (504-60-9)

Allylmagnesium chloride (2622-05-1)

Allylmagnesium bromide (1730-25-2)

 1,4-Pentadiene (591-93-5)

1,5-pentanediol diacetate (6963-44-6)

α -chloroethyl ethyl ether (51202-81-4)

α -Allyl- β -bromoethyl ethyl ether (22089-55-0)

 4-penten-1-ol acetate (1576-85-8)

 dimethyl(4-pentenyl)amine oxide

 paraldehyde (123-53-7)

