A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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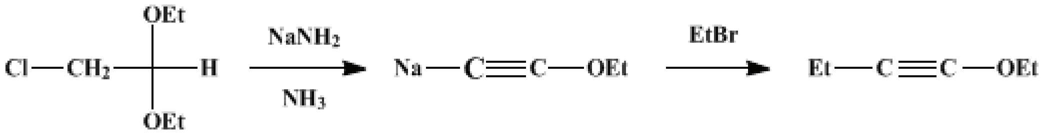
1-ETHOXY-1-BUTYNE

[1-Butyne, 1-ethoxy-]



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1. Procedure

A 1-l., three-necked, round-bottomed flask equipped with an efficient dry-ice condenser (Note 1), a mechanical stirrer, and a gas-inlet tube is immersed in an acetone–dry ice bath, and 600 ml. of anhydrous ammonia is introduced. After replacing the inlet tube with a stopper, the cooling bath is lowered but kept beneath the flask. To the slowly stirred ammonia is added 0.5 g. of hydrated iron(III) nitrate. Air, dried by passing through calcium chloride, is bubbled through the solution for about 10 seconds (Note 2) after a small piece of freshly cut sodium is added (Note 3). Once hydrogen evolution has ceased, the blue color is discharged, leaving a finely divided, black precipitate. Small pieces of freshly cut sodium are then added over a 20 minute period until 36.0 g. (1.56 g.-atom) has been added. After the formation of sodium amide is complete (Note 4), the stopper is replaced with a pressure-equalizing dropping funnel containing 76.1 g. (0.499 mole) of chloroacetaldehyde diethyl acetal (Note 5), and the addition is made over a period of 20 minutes (Note 6). After 30–60 minutes the mixture becomes light gray, and 120 g. (1.10 mole) of freshly distilled ethyl bromide is added rapidly through the addition funnel (Note 7). The mixture is stirred vigorously for 2.5 hours, after which 30 ml. of cooled, saturated ammonium chloride solution is *cautiously* added through the addition funnel, followed by 120 ml. of pentane and an additional 370 ml. of the cooled, saturated ammonium chloride solution. The contents of the flask are transferred to a 2-l. separatory funnel (in the hood); the lower aqueous layer is removed and extracted with two 75-ml. portions of pentane (Note 8). The combined organic layers are filtered through glass wool to dissipate any emulsions, dried over magnesium sulfate, and filtered through a coarse-fritted funnel with gentle suction into a 500-ml., round-bottomed flask. A magnetic stirring bar is added, and the pentane is removed by distillation at atmospheric pressure through a 20 × 2 cm. column packed with glass beads (Note 9) and fitted with a well-cooled fractionating head. With an acetone–dry ice trap between the receiver and the vacuum source, the yellow residue is distilled under reduced pressure (Note 10), with rapid magnetic stirring, into dry-ice-cooled receivers, giving 1-ethoxy-1-butyne as a clear, colorless liquid at 43–45° (50 mm.). A lower-boiling fraction collection at 20–42° (50 mm.) is combined with any material removed from the dry-ice trap and redistilled, yielding additional product, for a total of 30.2–32.3 g. (62–66%) (Note 11).

2. Notes

1. A gas bubbling device is attached to the dry-ice condenser. A simple apparatus consists of two, 500-ml. filtering flasks equipped with one-hole neoprene stoppers and glass tubing extending to the bottom of the flasks. The two flasks are connected through the glass tubing by a short piece of Tygon tubing. About 150 ml. of mineral oil is then placed in the flask distant from the condenser.
2. The checkers found that air was not necessary to initiate the formation of sodium amide. See Ref.[3]
3. The sodium is cut under dry pentane just before introducing each sample into the flask.
4. Complete conversion into sodium amide is indicated by cessation of gas evolution and disappearance of the blue color of the solution. This generally requires 20–30 minutes and results in a gray suspension of sodium amide in a dark-gray reaction medium.
5. Chloroacetaldehyde diethyl acetal was used as obtained from Aldrich Chemical Company, Inc.
6. During any of the additions in this preparation excessive foaming may occur. This may be effectively diminished by interrupting the addition of the reagent or by brief immersion of the reaction flask in the

acetone–dry-ice bath. If foaming has reached the condenser, be certain that the condenser is not plugged before proceeding.
7. The addition of ethyl bromide is accompanied by vigorous reflux of the ammonia and should be carefully monitored.
8. Since 1-ethoxy-1-butyne is very volatile, extreme care should be taken during the work-up to minimize loss of product due to evaporation. Extractions should be accompanied by careful and frequent venting of the separatory funnel to prevent excessive pressure.
9. The checkers used a 20-cm. Widmer column for the distillation.
10. The pot temperature should be kept below 80°. Distillation must be conducted at temperatures below 90° to preclude dimerization.[4]
11. IR (CCl_4) cm.$^{-1}$, strong peaks: 1245, 1230, 1015, 855. ^{1}H NMR (CCl_4), δ (multiplicity, number of protons, assignment): 1.23 (overlapped t, 6H, $2CH_3$), 2.13 (q, 2H, $C{=}CCH_2$), 3.99 (q, 2H, OCH_2).

3. Discussion

The synthesis of 1-ethoxy-1-butyne has been reported previously, but the preparations have required multistep sequences. Two of the procedures use 1,2-dibromo-1-ethoxy butane which is dehydrohalogenated in two successive steps, first by an amine base and then by either powdered potassium hydroxide[5] or sodium amide;[6] no yields are given. The other procedure starts with 1,2-dibromoethyl ethyl ether which, upon treatment with *N,N*-diethylaniline, yields 2-bromovinyl ethyl ether. When 2-bromovinyl ethyl ether is allowed to react with lithium amide in ammonia, followed by alkylation with diethyl sulfate, 1-ethoxy-1-butyne is isolated in about 55% yield.[7]

Some studies seeking preferred conditions for this reaction have been reported.[8] Optimum yields of 1-ethoxy-1-propyne and 1-ethoxy-1-butyne are found when the product is worked up before allowing the ammonia solvent to evaporate, as the product evidently volatilizes with the ammonia. An experiment with 1-ethoxy-1-propyne showed a marked increase in yield when ammonia predried over calcium hydride was used instead of ammonia directly obtained from a cylinder. A twofold excess of ethyl bromide is required to obtain a good yield of 1-ethoxy-1-butyne, since elimination apparently competes with alkylation in this case.

References and Notes

1. Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. This research was conducted at The Ohio State University and supported in part by National Science Foundation Grant No. 12445.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

calcium chloride (10043-52-4)

ammonia (7664-41-7)

ammonium chloride (12125-02-9)

hydrogen (1333-74-0)

Ethyl bromide (74-96-4)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

N,N-diethylaniline (91-66-7)

Pentane (109-66-0)

diethyl sulfate (64-67-5)

magnesium sulfate (7487-88-9)

sodium amide (7782-92-5)

iron(III) nitrate

1,2-dibromoethyl ethyl ether (2983-26-8)

lithium amide (7782-89-0)

chloroacetaldehyde diethyl acetal (621-62-5)

2-bromovinyl ethyl ether

calcium hydride (7789-78-8)

1-Ethoxy-1-butyne,
1-Butyne, 1-ethoxy- (14272-91-4)

1,2-dibromo-1-ethoxy butane

1-ethoxy-1-propyne