



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.

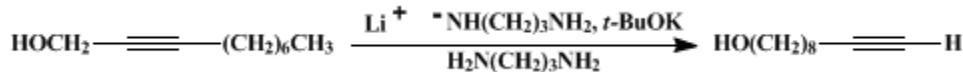
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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TRIPLE-BOND ISOMERIZATIONS: 2- TO 9-DECYN-1-OL



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1. Procedure

Caution! This preparation should be carried out in an efficient hood and the operator should wear gloves to protect against spillage of corrosive 1,3-diaminopropane.

A 1-L, three-necked, round-bottomed flask is equipped with a magnetic stirring bar, a thermometer, a pressure-equalizing dropping funnel to which an argon inlet is attached, and a condenser fitted with a drying tube filled with potassium hydroxide pellets (Note 1). The flask is charged with lithium (4.2 g, 0.6 mol, (Note 2)) and 1,3-diaminopropane (300 mL, (Note 3)). The mixture is stirred at room temperature for 30 min. A slight exothermic reaction takes place as the lithium dissolves.

The mixture is stirred and heated in an oil bath at 70°C until the blue color discharges (ca. 3 hr), affording a white suspension of the lithium amide. The reaction mixture is cooled to room temperature, and potassium *tert*-butoxide (44 g, 0.4 mol, (Note 4)) is added to the flask using a powder funnel. The resultant pale yellow solution is stirred for 20 min at room temperature, and then 2-decyn-1-ol (15.4 g, 0.1 mol, (Note 5)) is added over 10 min by means of the dropping funnel (Note 6). Residual 2-decyn-1-ol is washed into the flask with 1,3-diaminopropane (20 mL). The reddish-brown mixture is stirred for 30 min and then poured into 1 L of ice water and extracted 4 times with 500-mL portions of hexane. The hexane extracts are combined and washed successively with 1 L each of water, 10% hydrochloric acid, and saturated sodium chloride solution. The hexane solution is dried over anhydrous sodium sulfate, filtered, and concentrated with a rotary evaporator. The crude product is distilled under reduced pressure to give 9-decyn-1-ol (12.8–13.5 g, 83–88%) (Note 7) and (Note 8), as a colorless oil, bp 86–88°C/0.5 mm.

2. Notes

1. All glassware should be previously dried in an oven at 110°C for at least 2 hr.
2. Lithium wire (3.2-mm diameter, 0.02% Na, Alfa Products, Morton/Thiokol Inc.) is cut into 1-cm pieces, then washed with hexane and quickly weighed into a tared beaker of hexane. The checkers also used lithium shot (BDH); the lithium did not all dissolve at room temperature, and heating at 70°C for 6 hr was necessary to discharge the blue color.
3. 1,3-Diaminopropane (97%, Aldrich Chemical Company, Inc.) was distilled at atmospheric pressure under nitrogen from barium oxide and stored over molecular sieves (Linde 4A).
4. Potassium *tert*-butoxide (Aldrich Chemical Company, Inc.) was used without further purification, and was added over 1–2 min.
5. 2-Decyn-1-ol (Farchan Labs., Lancaster Synthesis) was used without further purification. On addition of 2-decyn-1-ol to the reaction mixture slight warming is observed. The temperature is maintained at 25–30°C using a water bath.
6. The checkers used a syringe, injecting through a rubber septum.
7. The submitters used a Kugelrohr apparatus with an oven temperature of 80–90°C/0.05 mm.
8. The isomeric purity of the product is greater than 99% as determined by GLC of the trimethylsilyl ether. 9-Decyn-1-ol (n_D^{26} 1.4552) has the following spectroscopic characteristics: ^1H NMR (CDCl_3) δ : 1.1–1.7 (m, 12 H), 1.9 (t, J = 1.5, $\text{C}\equiv\text{CH}$), 2.1 (m, 2 H, $\text{CH}_2\text{C}\equiv\text{C}$), 3.6 (t, 2 H, J = 6, OCH_2); IR (film) ν_{max} cm^{-1} : 3400 (br), 3300 (s), 2100 (w), 1050 (s).

3. Discussion

In 1975 Brown and Yamashita² reported that a triple bond in any position of a straight-chain hydrocarbon or acetylenic alcohol, when treated with a sufficiently strong base, could be isomerized exclusively to the free terminus of the chain. The "zipper reaction" thus provides a general solution to the problem of remote functionalization of a long hydrocarbon chain. Isomerizations along chains of 30 carbon atoms have been achieved. Isomerization is blocked by alkyl or hydroxyl branches; the triple bond then migrates to the free terminus.

The base employed by Brown and Yamashita was the potassium salt of 1,3-diaminopropane, prepared by reaction of potassium hydride with the solvent of the reaction, 1,3-diaminopropane. The reagent is very effective, and yields of isomerically pure products are high, but potassium hydride is hazardous, expensive and difficult to handle.

We and others have developed alternative methods for preparing the isomerization reagent.^{3,4,5,6} Hommes and Brandsma³ first prepared potassium or sodium amide in liquid ammonia and then replaced the solvent with 1,3-diaminopropane. Kimmel and Becker⁴ treated molten potassium or sodium with 1,3-diaminopropane in a flask immersed in an ultrasonic bath at 90°C. We^{5,6} found that sodium hydride reacts with 1,3-diaminopropane, or 1,2-diaminoethane, on warming. All of these methods produce effective isomerization reagents with comparable conversions and yields. The lithium salt alone is a poor isomerization reagent; however, addition of potassium *tert*-butoxide affords a reagent that very effectively isomerizes triple bonds. This procedure, presented here, is our most refined method.⁷ It is straightforward, gives reproducibly high yields, employs inexpensive reagents, and can be safely carried out on a large scale.

It is not satisfactory to employ 1,2-diaminoethane in place of 1,3-diaminopropane. The reagent is not as stable; addition of potassium *tert*-butoxide results in the immediate formation of a deep-purple solution. Isomerizations proceed to completion, but yields are somewhat reduced (by about 10% in the case of the rearrangement of 2- to 9-decyn-1-ol).

References and Notes

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 3. Hommes, H.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 160.
 4. Kimmel, T.; Becker, D. *J. Org. Chem.* **1984**, *49*, 2494–2496.
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

2- to 9-decyn-1-ol

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

barium oxide
nitrogen (7727-37-9)
carbon (7782-42-5)
potassium hydroxide (1310-58-3)
sodium (13966-32-0)
potassium (7440-09-7)
lithium (7439-93-2)
sodium amide (7782-92-5)
lithium amide (7782-89-0)
sodium hydride (7646-69-7)
1,2-diaminoethane (107-15-3)
hexane (110-54-3)
argon (7440-37-1)
acetylenic alcohol (32038-79-2)
trimethylsilyl ether (107-46-0)
potassium hydride (7693-26-7)
9-Decyn-1-ol (17643-36-6)
1,3-diaminopropane (109-76-2)
2-decyn-1-ol (4117-14-0)
potassium salt of 1,3-diaminopropane
potassium tert-butoxide (865-47-4)