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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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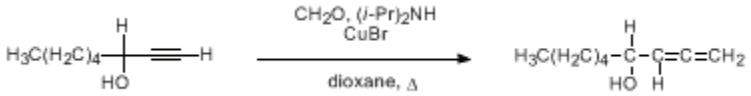
ONE-STEP HOMOLOGATION OF ACETYLENES TO ALLENES: 4-HYDROXYNONA-1,2-DIENE

[1,2-Nonadien-4-ol]



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Checked by Jeffrey S. Stults and Edwin Vedejs.

1. Procedure

In a 500-mL, three-necked flask, equipped with a thermometer, stirrer, and a reflux condenser with drying tube, are placed 12.6 g (0.1 mol) of 1-octyn-3-ol, 154 mL of dioxane, 7.24 g (0.0504 mol) of cuprous bromide, 7.4 g of paraformaldehyde, and 18.54 g (0.183 mol) of diisopropylamine (Note 1). The resulting mixture is gently refluxed and stirred for 2 hr and then cooled to room temperature and filtered through a Celite plug. The dark-brown filtrate is concentrated under vacuum (Rotavapor) to a gummy residue and then diluted with 50 mL of water followed by 100 mL of ether and acidified with 6 *N* hydrochloric acid to pH 2. The ether–water layers are decanted from any residue, the ether layer is separated, and the aqueous solution is extracted with ether (5 × 50 mL). The ether extracts are combined and washed with small portions of water until pH 6.5 is reached. The organic layer is then washed with saturated sodium chloride solution and dried over anhydrous $MgSO_4$. After removal of ether by distillation through a 20-cm Vigreux column (water aspirator vacuum) while heating on a water bath, ≤ 40°C, the residual liquid is fractionated under reduced pressure through a 10-cm Vigreux column. The main fraction is collected at 41–42.5°C(0.15 mm) to give 8.65 g of pure allene (Note 2), with additional fractions of a less pure material.

2. Notes

1. Cuprous bromide and 1-octyn-3-ol were used as supplied by the Aldrich Chemical Company, Inc. Dioxane was dried over sodium–benzophenone and distilled, and diisopropylamine was distilled from barium oxide.
2. The spectral properties of 4-hydroxynona-1,2-diene are as follows: IR (neat) cm^{-1}: 3500 (OH), 1960 (C=C=C), 850 (=CH), 2900–2850 (CH). ^1H NMR ($CDCl_3$) δ: 0.65–1.7 (m); 4.15 (1 H, m); 4.8 (2 H, d of d, J = 2.6 Hz); 5.22, (1 H, q, J = 6 Hz).

3. Discussion

Although allenes were characterized long ago as a distinct class of organic substances, they have only recently received proper attention from chemists, in particular for their potential in organic synthesis.[2] [3] [4] A number of methods are known for the transformation of acetylenes into allenes,[5] but few are known to allow the homologation of an acetylenic group into a propadiene functionality.

A general procedure for the homologation of acetylenic compounds into allenes is described. The reaction conditions are mild and appear to be general, so that they can be applied to plain acetylenic substances as well as to acetylenic alcohols, ethers, and esters. This procedure is essentially a one-step reaction. As such, it is simpler and faster than the previously reported technique that involves the conversion of an acetylenic compound into the Mannich base, the formation of its quaternary ammonium salt and the reduction of this salt with lithium aluminum hydride.[6] Of great advantage over previously available methodology are the mild conditions, as well as the clean and fast procedure, which make this a method of choice for an efficient conversion of acetylenes to allenes.[7] [8] [9]

References and Notes

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

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium chloride (7647-14-5)

barium oxide

Benzophenone (119-61-9)

sodium (13966-32-0)

cuprous bromide (7787-70-4)

$MgSO_4$ (7487-88-9)

dioxane (123-91-1)

propadiene (463-49-0)

lithium aluminum hydride (16853-85-3)

diisopropylamine (108-18-9)

4-Hydroxynona-1,2-diene,
1,2-Nonadien-4-ol (73229-28-4)

1-octyn-3-ol (818-72-4)

paraformaldehyde (30525-89-4)