Organic Syntheses

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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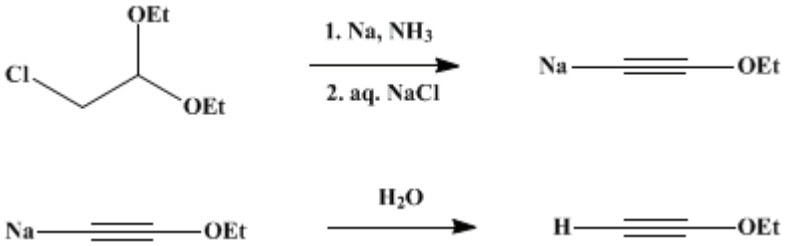
Organic Syntheses, Coll. Vol. 4, p.404 (1963); Vol. 34, p.46 (1954).

ETHOXYACETYLENE

[Ether, ethyl ethynyl]



Submitted by E. R. H. Jones, Geoffrey Eglinton, M. C. Whiting, and B. L. Shaw[1].
Checked by Arthur C. Cope and Ronald M. Pike.

1. Procedure

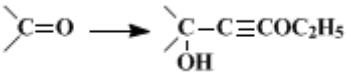
Caution! This preparation should be conducted in a hood to avoid exposure to ammonia, and thorough shielding of the apparatus is recommended.

A solution of sodium amide in liquid ammonia is prepared according to a procedure previously described (Note 1) in a 1-l. three-necked flask (Note 2) equipped with a cold-finger condenser (cooled with Dry Ice) attached through a soda-lime tower to a gas absorption trap[2] and an inlet tube. Anhydrous liquid ammonia (500 ml.) is introduced from a commercial cylinder through the inlet tube, and 0.5 g. of hydrated ferric nitrate is added, followed by 38 g. (1.65 g. atoms) of clean, freshly cut sodium (Note 3). The inlet tube is replaced with a 100-ml. dropping funnel, and the mixture is agitated manually (Note 2) until all the sodium is converted into sodium amide, after which 76.5 g. (0.50 mole) of diethylchloroacetal (Note 4) is added over a period of 15–20 minutes. The mixture is swirled for an additional period of 15 minutes, after which the ammonia is evaporated in a stream of pure nitrogen. The flask is cooled to −70° in a Dry Ice-trichloroethylene bath (Note 5), and 325 ml. of a saturated solution of sodium chloride which has been cooled to −20° is added all at once and as rapidly as possible with vigorous agitation (Note 6). The flask is then fitted with a still head connected to a trap cooled to −70° with Dry Ice, and the contents of the flask are slowly heated to 100° on a steam bath (Note 7). The condensate is allowed to warm to 0°, after which the trap is again cooled to −70° and the mixture is neutralized by the dropwise addition of a saturated aqueous solution of sodium dihydrogen phosphate. The aqueous layer is frozen by cooling with Dry Ice, and the supernatant liquid is decanted and dried over about 4 g. of anhydrous calcium chloride. The drying agent is removed by filtration, and the filtrate is distilled (Note 8) through a column containing a 20-cm. section packed with glass helices at partial reflux, yielding 20–21.2 g. (57–60%) of ethoxyacetylene, b.p. 49–51°/749 mm., n_D^{25} 1.3790 (Note 9), (Note 10), (Note 11), and (Note 12).

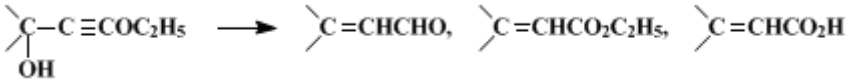
2. Notes

1. One of the procedures for converting sodium to sodium amide described in *Organic Syntheses* is used (p. 763).[3]
2. The flask is clamped to the free end of a long (30-in.) Duraluminium rod which is fixed at the other (top) end to a rigid frame. The rod is clamped in a vertical position, and by moving the free end the contents of the flask can be swirled very conveniently.
The submitters used a 1-l. round-bottomed flask mounted in the same way, without provision for cooling or a condenser cooled with Dry Ice, and were successful in preparing sodium amide and adding diethylchloroacetal before excessive loss of liquid ammonia occurred. Conversion of sodium to sodium amide sometimes requires a considerable period of time, in which case use of the apparatus specified avoids difficulty and the necessity of adding more liquid ammonia.
3. More liquid ammonia should be added through the inlet tube if vaporization reduces the liquid

volume to less than 300 ml.
4. Diethylchloroacetal (chloroacetaldehyde diethylacetal) supplied by Eastman Kodak Company is satisfactory.
5. *Important! This sodium derivative is extremely pyrophoric, and at this point and during the addition of the saturated sodium chloride solution it is essential that the contents of the flask be kept out of contact with air.* When the flask is immersed in the Dry Ice bath the nitrogen stream is increased to counteract the diminution in pressure due to rapid cooling.
6. The checkers found that a dropping funnel equipped with a pressure-equalizing tube provided the most satisfactory mode of addition.
7. It is advisable to allow the mixture to warm to room temperature gradually before applying heat.
8. The distillation should be conducted in a hood since the product has lachrymatory properties.
9. Others have reported b.p. 28°/300 mm., n_D^{20} 1.3812,[4] and b.p. 48–50°/760 mm.[5]
10. The submitters have used a similar procedure for the preparation of methoxyacetylene, b.p. 22.5–23.5°, n_D^{16} 1.3693, from commercial dimethylchloroacetal in 60% yield. *Caution! Minor explosions have been reported to occur during the addition of saturated sodium chloride solution to the sodium derivative of methoxyacetylene. They may have resulted from ignition of the methoxyacetylene by particles of sodium which adhered to the walls of the flask. It is recommended that all apparatus be shielded during the preparation of methoxyacetylene.*
11. Ethoxyacetylene has proved to be a useful reagent for the conversion of ketones to acetylenic carbinols:



which can be converted to α,β-unsaturated aldehydes, esters, and acids:[6]



It has been used in the synthesis of vitamin A aldehyde[7] and in the preparation of an intermediate in one of the total syntheses of cortisone.[8]
12. It has been reported[9] that the following modified procedure eliminates the dangers associated with the preparation of ethoxyacetylene.
The initial operations were the same as described above except that 46 g. (2 g. atoms) of sodium was employed (per 76.5 g. of chloroacetal), and the reaction mixture was stirred mechanically for 2 hours after the addition of the diethylchloroacetal. The dropping funnel and stirrer were removed and the flask was closed with a stopper provided with a wide plastic tube that came within 1 mm. of the bottom. The other end was placed near the bottom of an open 2-l. flask which contained 1 kg. of finely crushed ice.
When the stopper was fitted, the contents of the reaction flask were transferred to the ice by the ammonia pressure. The walls of the flask were rinsed with a little liquid ammonia and the washings also were forced onto the ice. The cold hydrolysis mixture was shaken repeatedly with 50-ml. portions of high-boiling petroleum (b.p. > 160°). The combined extracts were washed with ice water and dried over anhydrous sodium sulfate. Distillation afforded 21–23 g. (60–66%) of material which boiled at 49–55°/760 mm., n_D^{20} 1.3820.

3. Discussion

Ethoxyacetylene has been prepared from β-bromovinyl ethyl ether[4] or β-chlorovinyl ethyl ether[10] and potassium hydroxide; from α,β-dibromoethyl ethyl ether and potassium hydroxide;[5] and from diethyl chloroacetal, diethyl bromoacetal, α,β-dichloroethyl ethyl ether, or α,β-dibromoethyl ethyl ether and sodium amide.[11]

References and Notes

1. University of Manchester, Manchester, England.

2. *Org. Syntheses Coll. Vol.* **2**, 4 (1943).
3. *Org. Syntheses Coll. Vol.* **3**, 219 (1955).
4. Jacobs, Cramer, and Hanson, *J. Am. Chem. Soc.*, **64**, 223 (1942).
5. Favorskii and Shostakovskii, *J. Gen. Chem. U.S.S.R.*, **13**, 1 (1943) [*C. A.*, **38**, 330 (1944)].
6. Heilbron, Jones, Julia, and Weedon, *J. Chem. Soc.*, **1949**, 1823.
7. van Dorp and Arens, *Nature*, **160**, 189 (1947).
8. Sarett, Arth, Lukes, Beyler, Poos, Johns, and Constantin, *J. Am. Chem. Soc.*, **74**, 4974 (1952).
9. Arens and Brandsma, Private communication.
10. Arens, *Rec. trav. chim.*, **74**, 271 (1955); van Dorp, Arens, and Stephenson, *Rec. trav. chim.*, **70**, 289 (1951).
11. Eglinton, Jones, Shaw, and Whiting, *J. Chem. Soc.*, **1954**, 1860.

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

diethyl bromoacetal

diethylchloroacetal

dimethylchloroacetal

sodium derivative of methoxyacetylene

petroleum

diethyl chloroacetal

calcium chloride (10043-52-4)

ammonia (7664-41-7)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

sodium amide (7782-92-5)

ferric nitrate

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

Ethoxyacetylene,
Ether, ethyl ethynyl (927-80-0)

sodium dihydrogen phosphate (7558-80-7)

chloroacetaldehyde diethylacetal (621-62-5)

methoxyacetylene (6443-91-0)

cortisone

β-bromovinyl ethyl ether

β-chlorovinyl ethyl ether

α,β-dichloroethyl ethyl ether (623-46-1)