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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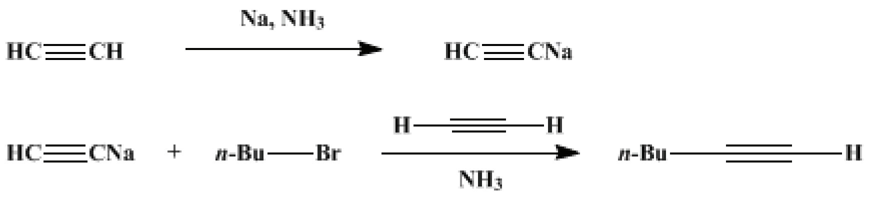
n-BUTYLACETYLENE

[1-Hexyne]



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1. Procedure

Caution! This preparation should be conducted in a hood to avoid exposure to ammonia.

A 5-l. three-necked flask is fitted with an efficient stirrer, mounted through a short glass bushing, and a long gas inlet tube which dips below the surface of the liquid ammonia. The third neck carries a device for holding sodium; this consists of a short piece of 10–12 mm. glass tubing, bent at a 45° angle, through which is passed a 12-in. piece of stout, flexible iron wire (picture wire is satisfactory). The lower end of the wire is attached to a stout iron fish-hook. (Sneck Hook No. 5/0 is satisfactory.)

The flask is charged with about 3 l. of liquid ammonia (Note 1), the stirrer is started, and a rapid stream of acetylene gas (about 5 bubbles per second) is passed in for about 5 minutes to saturate the ammonia. The acetylene from a tank is sufficiently purified by passage through a sulfuric acid wash bottle; a safety trap also should be inserted in the line. Sodium (92 g., 4 g. atoms) is cut in strips (about ½ by ½ by 3 in.) so that they can be inserted through the side neck of the flask. One of these pieces of sodium is attached to the fish-hook and is gradually lowered into the liquid ammonia while a rapid stream of acetylene is passed in. The sodium should be added at such a rate that the entire solution does not turn blue. If it does, the sodium should be raised above the level of the ammonia until the color is discharged (Note 2). The rest of the sodium is added in a similar manner; the addition requires about 45 minutes, depending on the rate of passage of the acetylene.

The acetylene is shut off, and the gas inlet tube and iron wire are removed, but not the bent glass tubing. A potassium hydroxide tower (Note 3) is attached to the end of this tubing, and a dropping funnel (Note 4) is mounted in the other neck of the flask. *n*-Butyl bromide (548 g., 428 ml., 4.0 moles) is added dropwise with stirring over a period of 45–60 minutes (Note 5). The mixture is stirred for an additional 2 hours. Ammonium hydroxide (500 ml.) is then added dropwise, followed by about 1–1.5 l. of distilled water. When the frost on the outside of the flask is loose and can be pulled off easily, the contents of the flask are transferred to a large separatory funnel, and the lower aqueous layer is removed. The organic layer is washed with 100 ml. of distilled water, then with about 100 ml. of 6*N* hydrochloric acid (the aqueous layer should be tested to make sure that it remains acid; if not, another washing with acid should be carried out), and finally with about 100 ml. of 10% sodium carbonate solution. The material is dried over potassium carbonate, a small amount of solid sodium carbonate is added, and the liquid is fractionated through a helix-packed column of about 10–14 plates. The yield of pure *n*-butylacetylene is 230–252 g. (70–77%); b.p. 71–72°, n_D^{20} 1.3984–1.3990 (Note 6) and (Note 7).

2. Notes

1. More liquid ammonia should be added from time to time to maintain approximately the same level. Liquid ammonia can be handled in ordinary apparatus, and it is not necessary to use a Dewar flask or to cool the reaction flask in a Dry Ice bath, as a thick frost forms on the outside and partially insulates the

contents. In making very volatile alkylacetylenes, such as ethylacetylene and propylacetylene, it is advisable to cool the apparatus in a Dry Ice bath, to minimize loss by entrainment, and to use a Dry Ice condenser. With the higher alkylacetylenes the use of a Dry Ice condenser, as recommended by Henne and Greenlee,[2] does not improve the yields enough to justify the extra trouble.

2. In order to see inside the flask a little alcohol may be poured over the outside.
3. This is not absolutely necessary except in damp weather, for the ammonia escaping through the outlet tube prevents the entrance of appreciable amounts of moisture.
4. A calibrated funnel is convenient, as the rate of addition may be judged better.
5. If the addition is carried out more slowly, the yield of product is lowered, unless a Dry Ice condenser is used.
6. The reaction may be carried out on a smaller scale without much loss in yield.
7. Other alkylacetylenes can be made in the same way from primary alkyl bromides. With *n*-propylacetylene the time of addition of *n*-propyl bromide should be about 45–60 minutes, and the yield is lower (40–50%), owing to losses by entrainment unless a Dry Ice condenser is used (b.p. 39–40°; n_{D}^{20} 1.3850). *n*-Amylacetylene (b.p. 98°; n_{D}^{20} 1.4088) and isoamylacetylene (b.p. 91–92°; n_{D}^{20} 1.4060) can be prepared in 70–80% yields by this method; the time of addition of the halide is 1.5–2.0 hours. *n*-Hexylacetylene (b.p. 76–77° /150 mm.; n_{D}^{20} 1.4157) can be obtained in 65% yields if a 1-mole excess of sodium acetylide is used. The halide is added during the course of 1 hour, and the mixture is stirred for an additional 3 hours before hydrolysis.

The method is not satisfactory for methyl- and ethylacetylenes or with secondary and tertiary alkyl halides or with primary alkyl halides above hexyl.

3. Discussion

n-Butylacetylene has been prepared from *n*-butyl bromide and sodium acetylide in liquid ammonia[2,3] or a mixture of tetrahydrofuran and dimethylformamide,[4] from *n*-butyl bromide and a slurry of calcium carbide and potassium hydroxide in dibutyl carbitol,[5] and from *n*-butyl bromide and ethynylmagnesium bromide at 80–90°.[6] It also has been obtained from the reaction of alcoholic potassium hydroxide on dibromohexanes,[7,8] and sodamide in xylene on 2-bromo-1-hexene.[9] *n*-Butylacetylene is formed, along with 2-ethoxy-1-hexene when 1-bromo-2-ethoxyhexane is caused to react with sodium in liquid ammonia.[10] It has been found[11] that a mixture of xylene and dimethylformamide is an excellent medium in which to carry out the alkylation of sodium acetylide with alkyl bromides.

The method described here is a modification of the one published by Vaughn, Vogt, Hennion, and Nieuwland.[3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 532

References and Notes

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

calcium carbide

dibutyl carbitol

dibromohexanes

potassium carbonate (584-08-7)

acetylene (74-86-2)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

sodium carbonate (497-19-8)

n-butyl bromide (109-65-9)

n-PROPYL BROMIDE (106-94-5)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

ammonium hydroxide (1336-21-6)

xylene (106-42-3)

n-Amylacetylene (628-71-7)

sodamide (7782-92-5)

Tetrahydrofuran (109-99-9)

dimethylformamide (68-12-2)

sodium acetylide

1-Hexyne,
n-BUTYLACETYLENE (693-02-7)

ethylacetylene (107-00-6)

propylacetylene,
n-propylacetylene (627-19-0)

isoamylacetylene (2203-80-7)

ethynylmagnesium bromide

2-bromo-1-hexene

2-ethoxy-1-hexene

n-Hexylacetylene (629-05-0)

1-bromo-2-ethoxyhexane