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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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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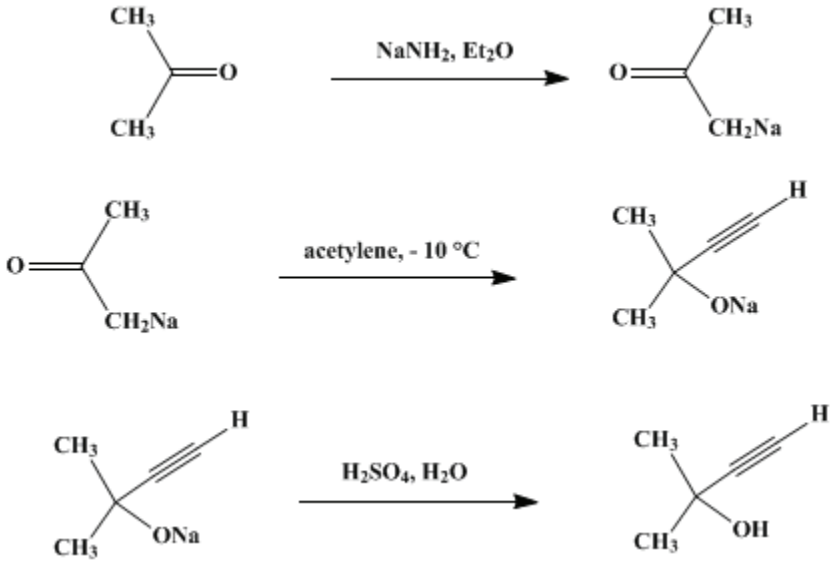
DIMETHYLETHYNYLCARBINOL

[3-Butyn-2-ol, 2-methyl-]



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1. Procedure

In a 2-l. round-bottomed flask fitted with a three-holed stopper bearing a mechanical stirrer, a separatory funnel, and a gas outlet tube leading to a hood (Note 1) are placed 1 l. of anhydrous ether (Note 2) and 156 g. (4 moles) of finely ground sodium amide (p. 778) (Note 3). The flask is surrounded by a well-packed ice-salt bath. To the vigorously stirred mixture 232 g. (4 moles) of dry acetone (Note 4) is added, dropwise, during a period of 3 hours. With the flask cooled to −10° (Note 5), a slow current of acetylene (Note 6) is passed through the reaction mixture for 2 hours to sweep out the ammonia. The three-holed stopper is then replaced by a two-holed stopper having a stopcock and an inlet tube reaching to the bottom of the flask and connected with a cylinder of acetylene. The stopper is wired in. The mixture is placed in an ice-salt mixture (Note 5), the whole being mounted on a shaking machine and agitated vigorously for 10 hours; the mixture is kept under a pressure of 10 lb. of acetylene. Every 30 minutes the pressure is released by means of the stopcock, to sweep out ammonia formed from small amounts of previously unreacted sodium amide.

The reaction mixture is poured cautiously into 800 g. of crushed ice and acidified in the cold by the addition of 400 ml. of 10 *N* sulfuric acid (Note 7). The ether layer is separated and the aqueous layer extracted twice with 100-ml. portions of ether. The combined ethereal solutions are dried over 100 g. of anhydrous potassium carbonate, and the filtered solution is fractionated (Note 8). The portion boiling at 103–107° is collected; any low-boiling fraction is dried and redistilled. The total yield is 135–155 g. (40–46%) of a colorless product that boils at 103–107° (Note 9), (Note 10), and (Note 11).

2. Notes

1. In cold weather, it is convenient to carry out the reaction out-of-doors. This minimizes the attention needed to replace the ice. The outlet tube then opens to the air.
2. A commercial grade of anhydrous ether was dried over sodium.
3. The sodium amide, moistened by the heptane, was rapidly ground and the solvent allowed to evaporate.

4. An Eastman grade of acetone was used, after standing over anhydrous potassium carbonate.
5. It was found convenient to add Dry Ice to the freezing mixture, thus decreasing the frequency of packing. The temperature never rose above −10° and was usually considerably less.
6. Commercial acetylene used for welding was dried by passing over anhydrous calcium chloride.
7. This is prepared by adding 110 ml. of concentrated sulfuric acid to 290 ml. of water.
8. The checkers used a modified Widmer column.
9. There is a considerable quantity of high-boiling material; the quantity and boiling-point range are greater when the shaking is insufficient.
10. The reaction may be interrupted at several points. After the ammonia has been swept out by acetylene, it is usually convenient to place the mixture in a refrigerator overnight and start the shaking the next day. The shaking period need not be continuous; in this event the chilled mixture is placed in the icebox.
11. By the same procedure the submitter obtained methylethylethynylcarbinol, b.p. 119–123° (33% yield), using methyl ethyl ketone,[1,2] and 1-ethynylcyclohexanol-1, b.p. 53–55°/2 mm. (50% yield), using cyclohexanone and double the amount of ether.

3. Discussion

Dimethylethynylcarbinol has usually been prepared by the addition of acetylene to the sodium derivative of acetone,[3,4,5,6,7,8] but potassium metal[9] and sodium ethoxide[10] have also been used. The above method is based upon that described by Sung Wouseng.[3] Other methods use potassium hydroxide with calcium carbide,[11] or with acetylene and an immiscible alcohol such as butanol[12] or amyl alcohol.[13] Dimethylethynylcarbinol has also been prepared by the action of sodium acetylide on the bisulfite addition compound of acetone.[14]

A modified procedure, involving the addition of acetone to sodium acetylide in liquid ammonia, has been reported to give a 67% yield.[15]

The general procedure of Campbell, Campbell, and Eby[16] gives excellent yields of ethynylcarbinols.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 416

References and Notes

1. Ger. pat. 289,800 [*Frdl.*, **12**, 57 (1914–1916)].
2. Ger. pat. 285,770 [*Frdl.*, **12**, 55 (1914–1916)].
3. Sung Wouseng, *Ann. chim.*, (10) **1**, 359 (1924).
4. Scheibler and Fischer, *Ber.*, **55**, 2903 (1922).
5. Ger. pat. 280,226 [*Frdl.*, **12**, 51 (1914–1916)].
6. U. S. pat. 2,106,180 [*C. A.*, **32**, 2547 (1938)].
7. Ger. pat. 286,920 [*Frdl.*, **12**, 54 (1914–1916)].
8. Froning and Hennion, *J. Am. Chem. Soc.*, **62**, 654 (1940).
9. Ger. pat. 284,764 [*Frdl.*, **12**, 53 (1914–1916)].
10. Ger. pat. 291,185 [*Frdl.*, **12**, 56 (1914–1916)].
11. Kazarian, *J. Gen. Chem. U.S.S.R.*, **4**, 1347 (1934) [*C. A.*, **29**, 3978 (1935)].
12. Brit. pat. 627,474 [*C. A.*, **44**, 3514 (1950)].
13. U. S. pat. 2,488,082 [*C. A.*, **44**, 2544 (1950)].
14. Cymerman and Wilks, *Nature*, **165**, 236 (1950); *J. Chem. Soc.*, **1950**, 1208.
15. Newman, Fones, and Booth, *J. Am. Chem. Soc.*, **67**, 1053 (1945).
16. Campbell, Campbell, and Eby, *J. Am. Chem. Soc.*, **60**, 2882 (1938).

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

calcium carbide

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetylene (74-86-2)

ammonia (7664-41-7)

ether (60-29-7)

Cyclohexanone (108-94-1)

butanol (71-36-3)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

potassium (7440-09-7)

amyl alcohol (71-41-0)

bisulfite (7782-99-2)

methyl ethyl ketone (78-93-3)

sodium amide (7782-92-5)

heptane (142-82-5)

1-ethynylcyclohexanol-1 (78-27-3)

Dimethylethynylcarbinol,
3-Butyn-2-ol, 2-methyl- (115-19-5)

methylethylethynylcarbinol (77-75-8)

sodium acetylide