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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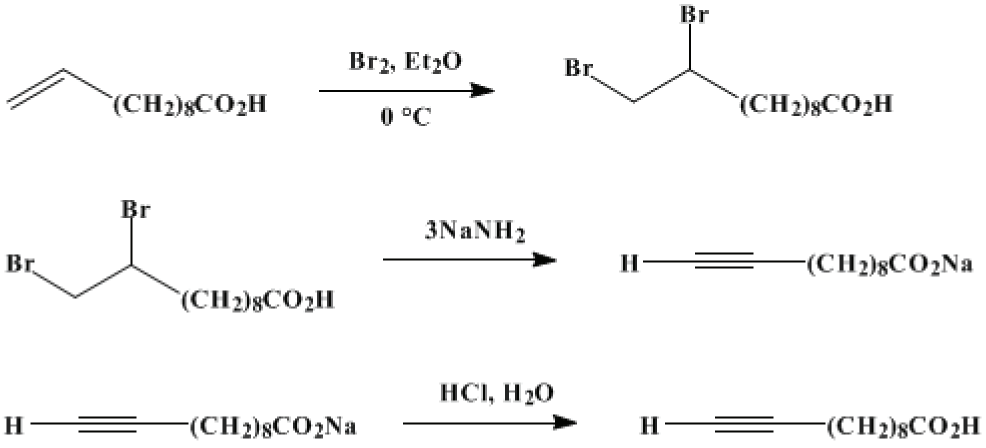
10-UNDECYNOIC ACID



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1. Procedure

Caution! All reactions involving liquid ammonia must be carried out in an effective hood.

Bromine (approximately 15 ml.) is added dropwise to 50 g. (0.271 mole) of 10-undecenoic acid (Note 1) dissolved in 210 ml. of dry ether with constant stirring while the temperature is maintained below 0° until the color of bromine persists. The excess bromine is then removed by the addition of a few drops of 10-undecenoic acid.

The sodamide for dehydrobromination of dibromohendecanoic acid is prepared according to the method of Khan et al.,[2] with some modifications (Note 2). A 3-l. three-necked flask is equipped with a stirrer and a Dry Ice-acetone cold finger reflux condenser attached through a drying tube to a trap and a bubbler filled with a saturated ammonia solution. After the condenser has been cooled with a mixture of Dry Ice and acetone, 1.5 l. of liquid ammonia is introduced into the flask through an inlet tube. Stirring is started, and 1.2–1.5 g. of ferric chloride (C.P., anhydrous, black) is added to the liquid ammonia in one portion as quickly as possible. Within 20 seconds after this addition, 6 g. of metallic sodium is dropped into the brown solution in two portions in order to convert the iron salt into catalytic iron. When the evolution of hydrogen gas ceases, the remainder of the sodium (total amount, 27.7 g., 1.2 g. atoms) is added in pieces and the solution is stirred for an additional 30 minutes (Note 3).

Finally, the solution of 10,11-dibromohendecanoic acid in absolute ether is added slowly from a separatory funnel to the reaction flask. The reaction mixture is then stirred for 6 hours. After an additional hour (Note 4) of stirring, during which time the cold-finger condenser is removed from the system, an excess of solid ammonium chloride (40 g., 0.74 mole) is introduced slowly into the reaction mixture to destroy excess sodamide. The ammonia is allowed to evaporate, 400–500 ml. of water is added, and the mixture is stirred until all the solid is broken up and dissolved (Note 5).

The water solution containing the sodium salt of the product is acidified with 6*N* hydrochloric acid and then extracted with three 200-ml. portions of ether. The ethereal extracts are combined, washed with water (until the aqueous phase shows a pH in the range 5–6), and then dried over anhydrous sodium sulfate. After removal of the solvent, the red-colored residual oil is fractionally distilled through a packed column (Note 6). The middle portion (26–28 g.) distilling at 124–130°/3 mm. is crystallized twice from petroleum ether (b.p. 30–60°) to obtain white crystals of 10-undecynoic acid. The end fractions also yield some white product after 4–5 crystallizations. A total yield of 19–24 g. (38–49%) is obtained; m.p. 42.5–43°.

2. Notes

1. 10-Undecenoic acid (undecylenic acid, commercial grade) may be obtained from the Eastman Kodak Company. The pure grade acid is also used with good results. However, for general purposes, no difficulty is encountered in preparing 10-undecynoic acid from the commercial grade acid if the final fractionation by vacuum distillation is carried out carefully.
2. The experiences with this particular preparation have led to some changes in the procedure of preparing sodamide. However, for large-scale preparation (larger than that reported here), Khan et al.[2] and Greenlee and Henne[3] have given very specific details of the methods that are to be followed. It is to be noted that the use of a Hershberg stirrer (with a rubber stopper and a powerful high-speed motor) is advantageous.
3. The complete transformation of metallic sodium into sodamide may be checked by the method of Greenlee and Henne.[3] When the evolution of hydrogen gas ceases (bubbler), it may be assumed that the above transformation is complete.
4. The checkers observed the yield to be increased somewhat by the less convenient procedure of allowing the ammonia to evaporate slowly for 12–15 hours.
5. More water may be added if needed.
6. The fractionation has also been carried out with better results through a Todd Scientific versatile column.

3. Discussion

Experiments in the submitter's laboratory have shown that the yield obtained on dehydrobromination of dibromohendecanoic acid with ethanolic potassium hydroxide[4,5,6,7] is very poor, usually lower than 30% On the other hand, the dehydrobromination with sodamide in liquid ammonia is smooth and very satisfactory.[8] The directions employed here represent a modification of those of Lauer and Gensler.[9]

References and Notes

1. Ohio State University, Columbus, Ohio.
2. Khan, Deatherage, and Brown, *J. Am. Oil Chemists' Soc.*, **28**, 27 (1951).
3. Greenlee and Henne, *Inorg. Syntheses*, **2**, 128 (1946).
4. Krafft, *Ber.*, **29**, 2232 (1896).
5. Oskerko, *Ber.*, **70**, 55 (1937).
6. Bhattacharyya, Chakravarty, and Kumar, *Chem. & Ind. (London)*, **1959**, 1352.
7. Sparreboom, *Koninkl. Ned. Akad. Wetenschap., Proc., Ser. B*, **59**, 472 (1956) [*C. A.*, **51**, 11992 (1957)].
8. Khan, *J. Am. Oil Chemists' Soc.*, **30**, 355 (1953).
9. Lauer and Gensler, *J. Am. Chem. Soc.*, **67**, 1171 (1945).

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

petroleum ether

Dry Ice

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

hydrogen (1333-74-0)

iron (7439-89-6)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

ferric chloride (7705-08-0)

sodamide (7782-92-5)

undecylenic acid (112-38-9)

10-Undecynoic acid (2777-65-3)

10-undecenoic acid (112-38-9)

dibromohendecanoic acid

10,11-dibromohendecanoic acid