



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.

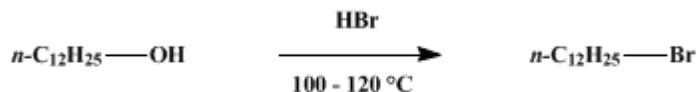
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.246 (1943); Vol. 15, p.24 (1935).

***n*-DODECYL BROMIDE**

[Dodecane, 1-bromo-]



Submitted by E. Emmet Reid, John R. Ruhoff, and Robert E. Burnett.

Checked by W. H. Carothers and W. L. McEwen.

1. Procedure

In a 500-cc. distilling flask, fitted with a thermometer and an inlet tube leading to the bottom (Note 1), is placed 186 g. (1 mole) of *n*-dodecyl alcohol (Note 2). An adapter, one end of which is immersed in about 75 cc. of water contained in a 125-cc. Erlenmeyer flask, is attached to the side arm of the flask. All connections are of rubber. The alcohol is heated to 100°, and dry hydrogen bromide (Note 3) is passed in at 100–120° (Note 4) until no more absorption occurs (Note 5). The crude bromide, together with any of the product that has been carried over into the receiving flask, is transferred to a separatory funnel, separated from the aqueous hydrobromic acid formed during the reaction, and shaken with one-third its volume of concentrated sulfuric acid (Note 6). The lower acid layer is drawn off and discarded (Note 7). The residual bromide is mixed with an equal volume of 50 per cent methyl alcohol (Note 8), and aqueous ammonia is added with intermittent shaking until the solution is alkaline to phenolphthalein. The lower bromide layer is drawn off and washed once with an equal volume of 50 per cent methyl alcohol. It is then dried with calcium chloride, filtered, and distilled. The yield of product boiling at 199.5–201.5°/100 mm. or 134–135°/6 mm. is 220 g. (88 per cent of the theoretical amount) (Note 9).

2. Notes

- In order to obtain more efficient absorption of the hydrogen bromide, a small bulb is blown on the end of the inlet tube, and a number of pin holes are made in it by means of a small, white-hot tungsten wire.
- The dodecyl alcohol used was obtained by the fractionation of "Lorol"; its boiling point was 192.5–193.5°/100 mm. or 151–152°/21 mm. If the alcohol is not of good quality, the yield is somewhat lower. Dodecyl alcohol may also be prepared according to the procedure given on p. 372.
- The hydrogen bromide is conveniently prepared by the direct combination of hydrogen and bromine (p. 338). An excess of hydrogen is to be avoided since it causes loss of product by volatilization.
- The heat of the reaction maintains the alcohol at this temperature until the preparation is nearly completed.
- For each mole of alcohol about 1.5 moles of hydrogen bromide is required, of which 1 mole is used to convert the alcohol to the bromide and approximately 0.5 mole to saturate the water formed in the reaction. The rate of addition should be regulated so as to require not less than an hour and a half. The Erlenmeyer flask that serves as a receiver should be weighed with the water in it before it is put in place. When the reaction is complete, the receiver gains weight rapidly and becomes warm owing to the heat of solution of the hydrogen bromide in the water.
- The crude bromide must be shaken well with the sulfuric acid. The function of the sulfuric acid appears to be to convert any free alcohol to the acid sulfates, which is then soluble in 50 per cent methyl alcohol and ammonia.
- Care must be taken that the separation of the two layers in this and subsequent washings is complete. Failure to observe this precaution is usually the cause of a low yield.
- The use of methyl alcohol prevents, to a large extent, the formation of troublesome emulsions. Less than 0.1 g. of dodecyl bromide dissolves in 100 cc. of 50 per cent methyl alcohol at room temperature.
- The authors have prepared other bromides by this method with the yields indicated below:

Bromide	Yield, %	Solubility of Bromides in Methyl Alcohol
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Cyclohexyl	72–75	Less than 1 g. in 100 cc. of 65% methyl alcohol
<i>n</i> -Heptyl	87–90	Less than 0.5 g. in 100 cc. of 50% methyl alcohol
Tetradecyl	88–89	Less than 0.1 g. in 100 cc. of 50% methyl alcohol
Octadecyl	90–91	Practically insoluble in 90% methyl alcohol

Obviously for the lower bromides it is desirable to use no more methyl alcohol than is necessary to prevent the formation of an emulsion. A convenient method is to place the water, phenolphthalein, and crude bromide in a separatory funnel, and add ammonia until the mixture becomes pink. Methyl alcohol is then added in small portions until the emulsion is broken and two layers separate with a distinct boundary after the mixture has been agitated.

3. Discussion

The above method for preparing *n*-dodecyl (lauryl) bromide is an adaptation of that of Ruzicka¹ and has been published.² It is thought to present some advantages in ease of manipulation and quality of product over the older method involving the action of aqueous hydrobromic acid on the alcohol in the presence of sulfuric acid.³

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 292
- Org. Syn. Coll. Vol. 2, 474
- Org. Syn. Coll. Vol. 3, 363

References and Notes

1. Ruzicka, Stoll, and Schinz, *Helv. Chim. Acta* **11**, 685 (1928).
 2. Ruhoff, Burnett, and Reid, *J. Am. Chem. Soc.* **56**, 2784 (1934).
 3. Kamm and Marvel, *ibid.* **42**, 299 (1920); *Org. Syn. Coll. Vol I*, **1941**, 29.
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Appendix

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

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

methyl alcohol (67-56-1)

hydrogen (1333-74-0)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

bromine (7726-95-6)

Dodecane, 1-bromo-,
Dodecyl bromide,
n-DODECYL BROMIDE (143-15-7)

dodecyl alcohol,
n-dodecyl alcohol (112-53-8)

Cyclohexyl bromide (108-85-0)

phenolphthalein (77-09-8)

n-heptyl bromide (629-04-9)

Tetradecyl bromide (112-71-0)

Octadecyl bromide (112-89-0)