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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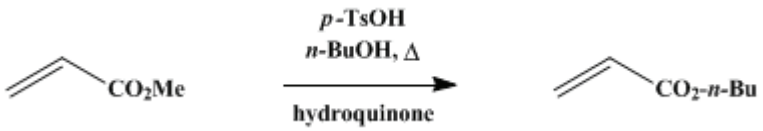
Organic Syntheses, Coll. Vol. 3, p.146 (1955); Vol. 26, p.18 (1946).

n-BUTYL ACRYLATE

[Acrylic acid, *n*-butyl ester]



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1. Procedure

In a 2-l. two-necked round-bottomed flask having a capillary ebullator tube in one neck (Note 1) are placed 371 g. (5 moles) of *n*-butyl alcohol, 861 g. (10 moles) of methyl acrylate, 20 g. of hydroquinone, and 10 g. of *p*-toluenesulfonic acid (Note 2). The flask is attached to an all-glass fractionating column, preferably one without packing such as the Vigreux type (Note 3), and the solution is heated to boiling in an oil bath. The column is operated under total reflux until the temperature of the vapors at the still head falls to 62–63°, which is the boiling point of the methanol-methyl acrylate azeotrope (Note 4). This azeotrope is then distilled as rapidly as it is formed, the temperature at the still head not being allowed to exceed 65°. When the production of methanol has become very slow (6–10 hours), the excess methyl acrylate is distilled, and the butyl acrylate is then distilled, preferably at 10–20 mm. It boils at 39°/10 mm., 84–86°/101–102 mm., and at about 145° at atmospheric pressure. The yield is 500–600 g. (78–94%) (Note 5).

2. Notes

1. The capillary is used to introduce a gas to prevent bumping and superheating during the vacuum distillation of the product. As air has some tendency to catalyze polymerization of the acrylic ester, if it is introduced through the capillary the amount must be as small as possible. The gas introduced should be an inert one, such as carbon dioxide or nitrogen. If polymeriaztion is troublesome, it may be advantageous to pass in a slow stream of carbon dioxide through the capillary during the entire reaction period.
2. Sulfuric acid is also a very satisfactory catalyst; aluminum alkoxides also are useful, especially when the alcohols would be adversely affected by strong acids. Sodium alkoxides produce undesirable side reactions and give lower yields. When alkaline catalysts are employed, an alkaline polymerization inhibitor, such as *p*-phenylenediamine or phenyl-β-naphthylamine, should be used instead of hydroquinone.
3. The fractionating column should be one that can be cleaned readily if a polymer is formed in it. A large number of plates is not required, though the column should be capable of separating the methanol-methyl acrylate azeotrope (b.p. 62–63°) from methyl acrylate (b.p. 80°), and butanol (b.p. 117°) from butyl acrylate (b.p. 145°). The necessity of effecting the latter separation can be practically eliminated by allowing the reaction to go virtually to completion, all the butanol thus being consumed. This can be done by extending the reaction period as long as reaction occurs and by adding a considerable excess of methyl acrylate. Instead of the twofold excess specified, three or four times the theoretical amount may be used with benefit. The larger amount is especially desirable when the acrylate of a relatively unreactive alcohol is being prepared.
4. The methanol-methyl acrylate azeotrope contains about 45% methyl acrylate, which can be recovered by washing out the methanol with a large volume of water or brine; the acrylate is purified by drying and distilling. An inhibitor, such as hydroquinone, should always be added to any acrylic ester before attempting to distil it, and, unless it is stored in a refrigerator, the distilled ester should not be kept more than a few hours without the addition of a small amount (0.1–1.0%) of an inhibitor.
5. Yields of the primary alkyl acrylates vary somewhat, owing to occasional losses through formation of polymer, but are usually in the range of 85–99%. Some secondary alcohols react very slowly, others

readily. The method has been applied to more than fifty alcohols, some of which (with percentage yields) are listed below: ethyl, 99%; isopropyl, 37%; *n*-amyl, 87%; isoamyl, 95%; *n*-hexyl, 99%; 4-methyl-2-pentyl, 95%; 2-ethylhexyl, 95%; capryl, 80%; lauryl, 92%; myristyl, 90%; allyl, 70%; furfuryl, 86%; citronellyl, 91%; cyclohexyl, 93%; benzyl, 81%; β-ethoxyethyl, 99%; β-(β-phenoxyethoxy) ethyl (from diethylene glycol monophenyl ether), 88%.

3. Discussion

n-Butyl acrylate has been prepared by direct esterification,[1] by debromination of *n*-butyl α,β-dibromopropionate with zinc,[2] by treatment of either butyl β-chloropropionate[1] or butyl β-bromopropionate[1] with diethylaniline, and by the pyrolysis of butyl β-acetoxypropionate.[3] Direct esterification and alcoholysis of methyl or ethyl acrylate have been recommended for the preparation of the higher alkyl acrylates.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 350

References and Notes

1. Moureau, Murat, and Tampier, *Ann. chim.*, **15**, 245 (1921) [*C. A.*, **16**, 55 (1922)].
2. Kobeko, Koton, and Florinskii, *J. Applied Chem. U.S.S.R.*, **12**, 313 (1939) [*C. A.*, **33**, 6795 (1939)].
3. Burns, Jones, and Ritchie, *J. Chem. Soc.*, **1935**, 400.
4. Neher, *Ind. Eng. Chem.*, **28**, 267 (1936).

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

phenyl-β-naphthylamine

methyl or ethyl acrylate

ß-ethoxyethyl alcohol

ß-(ß-phenoxyethoxy) ethyl alcohol

ethyl alcohol (64-17-5)

sulfuric acid (7664-93-9)

methanol (67-56-1)

hydroquinone (123-31-9)

Cyclohexanol (108-93-0)

Allyl alcohol (107-18-6)

Lauryl alcohol (112-53-8)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

butanol,
n-butyl alcohol (71-36-3)

zinc (7440-66-6)

isopropyl alcohol (67-63-0)

Benzyl alcohol (100-51-6)

Furfuryl alcohol (98-00-0)

diethylaniline (91-66-7)

n-HEXYL ALCOHOL (111-27-3)

isoamyl alcohol (123-51-3)

n-amyl alcohol (71-41-0)

methyl acrylate (96-33-3)

capryl alcohol (111-87-5)

Myristyl alcohol (112-72-1)

Butyl acrylate,
n-BUTYL ACRYLATE,
Acrylic acid, n-butyl ester (141-32-2)

diethylene glycol monophenyl ether

butyl β-chloropropionate (27387-79-7)

butyl β-bromopropionate

butyl β-acetoxypropionate

p-toluenesulfonic acid (104-15-4)

citronellyl alcohol (106-22-9)

p-phenylenediamine (106-50-3)

n-butyl α,β-dibromopropionate

4-methyl-2-pentanol

2-ethylhexanol