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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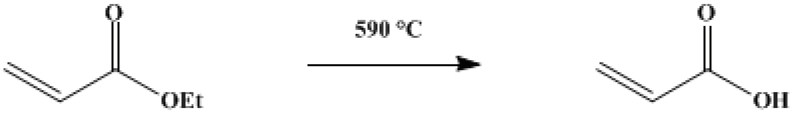
ACRYLIC ACID

[I. PYROLYSIS METHOD]



Submitted by W. P. Ratchford
Checked by Arthur C. Cope, William R. Armstrong, and James J. Ryan.

1. Procedure

A 90-cm. length of 28-mm. (outside diameter) Pyrex tubing packed with pieces of Pyrex tubing (Note 1) is mounted vertically in an electric furnace (Note 2) capable of maintaining a temperature of 585–595°. A 250-ml. long-stemmed separatory funnel is connected to the upper end of the tubing with a stopper (Note 3), and the lower end is connected to a 500-ml. three-necked flask immersed in ice water. The flask, which serves as a receiver, is attached to a 50-cm. water-cooled reflux condenser, which in turn is connected by short lengths of rubber tubing to two traps in series which are immersed in a Dry Icetrichloroethylene mixture. The exit tube of the second trap is vented to a hood. From 0.2 to 0.3 g. of hydroquinone is placed in the receiver, together with a few pieces of Dry Ice which serve to displace air from the entire apparatus. The third neck of the receiver is stoppered.

The furnace is heated to 590° (Note 4), and after the air has been displaced 200 g. (216 ml., 2 moles) of ethyl acrylate (Note 5) is placed in the separatory funnel and admitted to the reaction tube at a rate of about 90 drops a minute (Note 3), so that the addition requires about 2 hours. At the end of the addition the contents of the receiver and the small amount of liquid in the traps are combined. The total weight of crude acrylic acid containing some ethyl acrylate is 126–136 g.

The crude product is placed in a 250-ml. flask containing a capillary inlet tube through which carbon dioxide is admitted. Ten grams of hydroquinone and 15 g. of diphenyl ether are added, and the flask is attached to a suitable fractionating column (Note 6). The product is fractionated carefully (Note 7) at 135 mm. pressure. The pressure is lowered gradually when most of the ethyl acrylate has distilled, and at about 70°/90 mm. the receiver is changed. The first fraction (mostly ethyl acrylate) amounts to 9–10 g. The pressure is lowered further to 50 mm., and the acrylic acid is distilled fairly rapidly, without reflux, at 69–71°/50 mm. The acrylic acid fraction weighs 108–116 g. and is 95–97% pure according to acidimetric titration. The yield is 68–75% based upon 100% acrylic acid content (Note 8) and (Note 9).

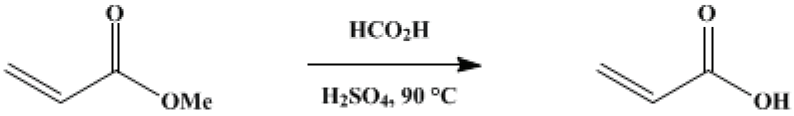
If the acrylic acid is not to be used at once, it is stabilized by the addition of hydroquinone and is stored in a refrigerator.

2. Notes

1. The middle third of the Pyrex tube should be packed with 20-mm. lengths of fire-polished 7-mm. Pyrex tubing. The lower end of the tube is drawn out to a size that permits attachment to the receiver with a rubber stopper.
2. A type FD303 combustion furnace (made and sold by the Hoskins Manufacturing Company, Detroit, Michigan) or any similar furnace is satisfactory.
3. A groove filed in the stopcock of the separatory funnel aids in controlling the rate of addition. If available, a small constant-feed pump may be used to introduce the ester into the pyrolysis tube. The rate of addition of the ester is not critical, but at high rates cracking is incomplete and at low rates the yield is reduced. A stream of nitrogen (100 bubbles per minute) flowing through the tube reduces refluxing and makes the feed rate easier to observe. The nitrogen may be introduced through a tube in the stopper holding the separatory funnel or through a side arm sealed near the upper end of the pyrolysis tube.

4. The temperature is measured by a movable Chromel-Alumel thermocouple located in the furnace by the side of the tube and connected to a potentiometer or millivoltmeter. The thermocouple junction is adjusted so that during the run it is at the hottest point in the furnace. For the Hoskins Company furnace this point is about 9 in. from the top of the furnace. The temperature is controlled manually to 590 ± 5° by means of an autotransformer (Variac) rated at 5 amperes, 110 volts.
5. Commercial ethyl acrylate, containing hydroquinone inhibitor, may be used directly if it is of good quality.
6. The submitter used an insulated column with a 38 by 1.1 cm. section packed with 1/8-in. copper helices made of No. 26 B & S gauge copper wire. He states that a column packed with glass helices is unsatisfactory. The checkers used a 100 by 1.7 cm. Vigreux column. Either type of column should be equipped with a total-condensation partial take-off head.
7. Ethyl acrylate and acrylic acid polymerize easily, and overheating must be avoided in the distillation. The flask is heated in an oil bath which is not permitted to rise above 115°. The diphenyl ether that is added serves to expel the acrylic acid at the end of the distillation.
8. The submitter states that the product may be purified by freezing and decanting the supernatant liquid several times. The acrylic acid may be obtained in 97% purity by this method, but it has a faint yellow color. The yield is 50–60%.
9. The submitter states that methacrylic acid may be prepared in a similar manner by pyrolyzing ethyl methacrylate. Under the same conditions of temperature and feed rate, the conversion is slightly higher and the yield is about the same.

[II. ACIDOLYSIS METHOD]



Submitted by C. E. Rehberg
Checked by Arthur C. Cope and Elbert C. Herrick.

1. Procedure

One hundred and eighty-four grams (151 ml., 4 moles) of formic acid (Note 1), 1032 g. (1060 ml., 12 moles) of methyl acrylate (Note 2), 30 g. of hydroquinone, and 2 ml. of sulfuric acid are mixed in a 2-l. two-necked round-bottomed flask fitted with a capillary inlet tube. The flask is attached to a 100 by 1.7 cm. Vigreux column (Note 3) and is heated in an oil bath at 85–95°. The mixture is heated under total reflux until the temperature of the vapor at the still head falls to 32° (after 1–3 hours). Methyl formate then is distilled slowly at 32–35° as long as it is formed (8–10 hours). A reflux ratio of about 5 to 1 is maintained during the first part of the distillation, which is decreased to total take-off at the end. When no more methyl formate is produced, the excess methyl acrylate is distilled at 32–35°/140 mm. with the bath temperature at 60–65°. During the distillation, a slow stream of carbon dioxide is admitted through the capillary inlet. When all the methyl acrylate has been removed, the acrylic acid is distilled at 53–56°/25 mm. Upon redistillation through the same column (Note 4) acrylic acid of 97% purity (by acidimetric titration) is obtained in a yield of 220–230 g. (74–78% based upon 100% acrylic acid content), b.p. 54–56°/25 mm.

2. Notes

1. Acetic acid may be used, but it reacts much less rapidly and less completely, and fractionation of the reaction mixture is more difficult. Pure formic acid (98–100%) is preferred.
2. Commercial methyl acrylate may be used without purification if it is of good quality.
3. Either a Vigreux column or a column containing an open spiral of copper or Nichrome wire is satisfactory. The column should be jacketed and fitted with a total-condensation variable take-off head.
4. Hydroquinone or another polymerization inhibitor should be added before distillation of acrylic acid or its esters.

3. Discussion

Acrylic acid free of water has been prepared by treating lead acrylate with hydrogen sulfide;[1,2] by heating α,β-dibromopropionic acid with copper;[3] by dry distillation of a mixture of equivalent amounts of sodium acrylate and β-chloropropionic acid;[4] by pyrolysis of the polymer of β-propiolactone;[5] by heating β-chloropropionic acid with potassium fluoride;[6] by heating β-acetoxypropionic acid in the presence of hydroquinone;[7] by heating lactic acid with metal chlorosulfonates;[8] and by the two methods described here.[9] It also has been prepared by dehydration of hydracrylic acid in the presence of copper and concentrated acids,[10] by acid exchange of acrylates in the presence of polymerization inhibitors,[11] and by the reaction of β-hydroxypropionitrile with 100% sulfuric acid, followed by addition of water and distillation.[12]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 746

References and Notes

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

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

hydroquinone (123-31-9)

hydrogen sulfide (7783-06-4)

formic acid (64-18-6)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

copper (7440-50-8)

β-hydroxypropionitrile (109-78-4)

Acrylic acid (9003-01-4)

hydracrylic acid (503-66-2)

β-Chloropropionic acid (107-94-8)

ethyl acrylate (140-88-5)

methyl formate (107-31-3)

methyl acrylate (96-33-3)

lactic acid (50-21-5)

diphenyl ether (101-84-8)

methacrylic acid (79-41-4)

ethyl methacrylate (97-63-2)

α,β-dibromopropionic acid (600-05-5)

sodium acrylate (7446-81-3)

β-propiolactone (57-57-8)

potassium fluoride (7789-23-3)

β-acetoxypropionic acid

lead acrylate