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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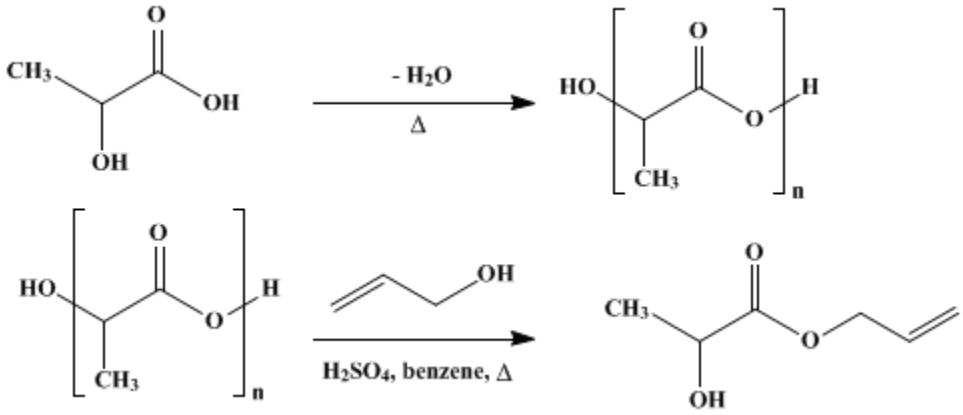
ALLYL LACTATE

[Lactic acid, allyl ester]



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1. Procedure

Six hundred and seventy-five grams (6 moles) of 80% lactic acid (Note 1), 300 ml. of benzene, and 5 ml. of concentrated sulfuric acid are placed in a 3-l. three-necked round-bottomed flask having a capillary ebullition tube in one neck. The flask is attached to a Vigreux column 75 cm. in length, having at its top a trap of the Dean and Stark type, preferably the Barrett modification carrying a stopcock (Note 2), and a reflux condenser. The mixture is refluxed, and the aqueous layer is withdrawn from the trap until liberation of water becomes slow or until noticeable darkening of the material begins (Note 3). Then 1394 g. (1635 ml. or 24 moles) of allyl alcohol is added (Note 4), and refluxing and removal of water are continued until production of water ceases (Note 5). The acid catalyst is then neutralized with anhydrous sodium acetate (18 g.) (Note 6), and the fractionating column is replaced by a short distillation head leading to a 3-l. round-bottomed receiving flask cooled in salt and ice. The liquid is distilled rapidly under diminished pressure, first at the water pump and finally at a pressure of about 5 mm. A viscous residue (about 130 g.) containing inorganic salts is discarded. The distillate is fractionated through the column used in the first steps. The trap at the reflux condenser is replaced with a still head arranged for controlled partial take-off. The first fraction is the benzene-allyl alcohol binary azeotrope, which distils at 76.8° and contains 17.4% of the alcohol. Frequently a small amount of allyl ether is obtained at 94–95°. Allyl alcohol is then distilled at 97° until most of it is removed and the temperature of the residue in the pot reaches about 120°. The pressure is reduced to about 50 mm. while the remainder of the alcohol is removed. Finally the allyl lactate is distilled at 56–60°/8 mm. (Note 7). It amounts to 693–710 g. (89–91%) (Note 8).

2. Notes

1. The lactic acid used was the commercial edible grade and was almost colorless. The checkers used 635.6 g. of 85% lactic acid, U.S.P. The lower grades of commercial acid probably would give somewhat lower yields.
2. A suitable piece of apparatus is listed in Catalog LP-34, p. 43, of the Corning Glass Works.
3. Generally, about 35 ml. of water per mole of 80% lactic acid is obtained at this stage, and 4–6 hours of refluxing is required for its removal. The linear lactic acid polymer thus produced contains approximately 3 lactic acid units.
4. A large excess of alcohol is essential for a high yield of ester. Thus, when the ratio of alcohol to acid is 4:1, the yield is 90%; when it is 3:1, the yield is 85–88%; when it is 2:1, the yield is about 65%; and when it is 5:3, the yield is 58–60%.

5. The checkers found this distillation to require about 16 hours. The distillate is the ternary azeotrope. It consists of 8.6% water,[1] 9.2% allyl alcohol, and 82.2% benzene, and boils at 68.2°. The aqueous layer contains some allyl alcohol, though this loss is insignificant, since only about 15 ml. of the aqueous layer is obtained from each mole of lactic acid used.
6. It is essential to neutralize any strong acid present before distilling lactic ester; otherwise, condensation by ester interchange occurs, with liberation of alcohol and production of "polylactic acid," a linear polyester. Other neutralizing agents, such as alkali or alkaline-earth hydroxides or carbonates, doubtless could be used satisfactorily instead of sodium acetate.
7. Allyl lactate is a clear, colorless, mobile liquid boiling at 60°/8 mm., 79°/25 mm., and 175–176°/740 mm. Other properties are d_4^{20} 1.0452; n_D^{20} 1.4369.
8. This method of preparation is suitable for producing primary alkyl lactates but is unsatisfactory for β-methallyl lactate because the strong mineral acid catalyzes the rearrangement of methallyl alcohol to isobutyraldehyde. Methyl lactate[2] can be made conveniently (80–85% yield) by heating 1 mole of lactic acid condensation polymer with 2.5–5 moles of methanol and a small quantity of sulfuric acid at 100° for 1–4 hours in a heavy-walled bottle, such as is used for catalytic hydrogenation with a platinum catalyst.

3. Discussion

Allyl lactate has been prepared by the repeated treatment of lactic acid or its polymer with allyl alcohol in the presence of mineral acid.[3]

This preparation is referenced from:

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

References and Notes

1. Lange, *Handbook of Chemistry*, 4th ed., p. 1217, Handbook Publishers, Sandusky, Ohio, 1941.
2. Filachione, Fein, Fisher, and Smith, "Continuous Methods for Dehydrating Lactic Acid and Preparing Methyl Lactate and Methyl Acetoxypropionates," presented before the Division of Industrial and Engineering Chemistry at the 105th meeting of the American Chemical Society, Detroit, Michigan, April 12, 1943.
3. Fisher, Rehberg, and Smith, *J. Am. Chem. Soc.*, **65**, 763 (1945).

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

ester

benzene-allyl alcohol binary azeotrope

lactic ester

sulfuric acid (7664-93-9)

Benzene (71-43-2)

methanol (67-56-1)

sodium acetate (127-09-3)

Allyl alcohol (107-18-6)

platinum (7440-06-4)

lactic acid (50-21-5)

isobutyraldehyde (78-84-2)

Allyl lactate,
Lactic acid, allyl ester (5349-55-3)

allyl ether (557-40-4)

β-methallyl lactate

methallyl alcohol (513-42-8)

Methyl lactate (547-64-8)