



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.

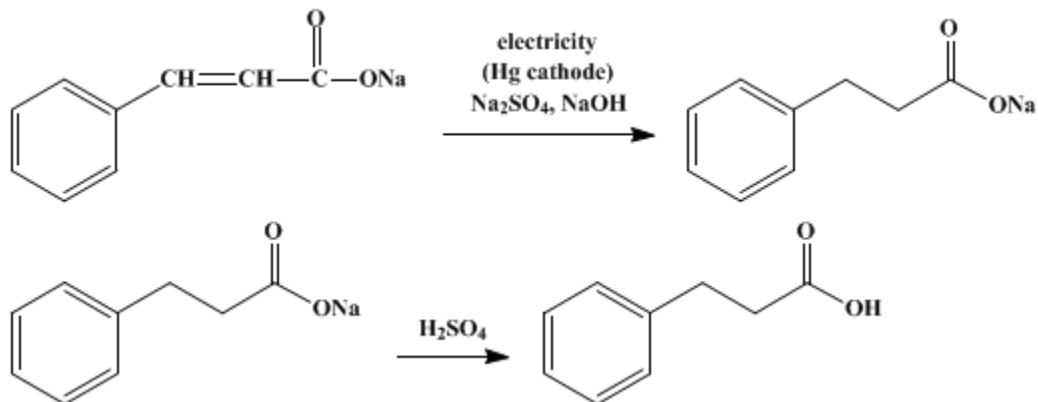
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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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HYDROCINNAMIC ACID



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1. Procedure

(A) *Apparatus*.—The reduction is carried out in an 18 by 25 cm. battery jar (Note 1) which is surrounded by a vessel of cold water. The bottom of the battery jar is just covered with mercury which serves as the cathode of the cell. The anode is a coil of heavy sheet lead separated from the catholyte by suspending it in a porous cup. The latter is supported in the battery jar so that it just clears the surface of the mercury (Note 2). The cathode is connected with the circuit by means of a copper wire well insulated with rubber except for one-eighth inch at the end which is immersed in the mercury. Efficient mechanical stirring is provided for the catholyte. The current used for these experiments was drawn from a storage battery delivering 30 volts, through a rheostat and ammeter each capable of carrying 15 amperes. Current may be taken from any source which will supply 80 to 85 ampere-hours at the rate of 5 to 10 amperes. Several reduction cells of the size described may be run at one time by connecting them in series. The diagram given on p. 486 shows the arrangement of the apparatus.

(B) *Reduction of Cinnamic Acid*.—After the apparatus is assembled, 2 l. of 7–8 per cent sodium sulfate solution (Note 3) is placed in the battery jar and the porous cup is filled to the same level with more of this solution. The stirrer is started, and 200 g. (1.35 moles) of a good grade of cinnamic acid (Note 4) is suspended in the catholyte. A solution of 35 g. (0.88 mole) of sodium hydroxide in 150 cc. of water is then added at such a rate as to avoid forming lumps of sodium cinnamate (Note 5). The current is turned on and the rheostat adjusted until a steady current of 5 to 10 amperes is flowing (Note 6). From this point only occasional attention is required. The suspended sodium cinnamate and cinnamic acid gradually dissolve as the reduction proceeds. Portions adhering to the walls of the cell should be worked down with a stirring rod and finally with a little water from a wash bottle. The liquor inside the porous cup should be kept alkaline by adding very concentrated sodium hydroxide solution at about one-half hour intervals (Note 5). About 110 g. (2.7 moles) will be required. The reduction will require 76 to 80 ampere-hours (Note 7); considerable hydrogen is evolved near the end. The temperature need not be controlled (Note 8).

When reduction is complete (Note 7) the cathode liquor is decanted or siphoned from the mercury, filtered from traces of solid matter, and acidified with an excess of sulfuric acid (sp. gr. 1.1). The hydrocinnamic acid separates as an oil and solidifies on thorough cooling. The yield of crude product, which contains water and other impurities, is 180–200 g. It is purified by distillation under reduced pressure. The product boiling at 194–197°/75 mm. (145–147°/18 mm.) is colorless and melts at 47.5–48°. The yield of distilled acid is 160–180 g. (80–90 per cent of the theoretical amount) depending upon the quality of the cinnamic acid used (Note 4).

2. Notes

1. This is a commercial size. Any sturdy glass vessel of similar dimensions may be used.
2. The lead anode should have about the same surface area as the cathode. The porous cup used was 8 by 21 cm., but similar sizes will do. A three-legged desiccator plate makes a convenient support for the cup.
3. Any dilute solution of sodium sulfate may be used. If several runs are to be made, the solution recovered from the filtration of the hydrocinnamic acid should be neutralized with sodium hydroxide, diluted if necessary, and used again. Traces of hydrocinnamic acid contained in this solution are thus saved. Chemically pure reagents are not necessary.
4. The quality of the cinnamic acid used is important. The yield from a commercial c.p. acid melting at 132.5–133° was 86–90 per cent. From a lot melting at 131.5–133° obtained by recrystallizing a crude acid with the use of animal charcoal the yield was 81–83 per cent. With a technical grade of material the yield fell, in some runs, below 60 per cent, the reduction mixture foamed considerably, and much high-boiling residue was left on distillation.
5. The addition of too much sodium hydroxide at this point produces a thick sludge which does not stir well. It should be noted that during the reduction two molecular equivalents of sodium hydroxide are produced at the cathode and an equivalent amount of sulfuric acid at the anode.
6. The current may vary somewhat, especially if the anode liquor becomes too dilute or highly acid. The sodium hydroxide solution added to the anolyte should be concentrated so that the diffusion which always occurs will not dilute the catholyte excessively. High amperage shortens the time required but promotes heating. Seven amperes is a convenient rate.
7. The theoretical quantity of current is 72 ampere-hours. It is necessary to pass an excess of 4 to 8 ampere-hours to insure complete reduction. The end of the reduction is reached when a sample of the catholyte on acidification with excess sulfuric acid precipitates an oil and no solid.
8. The reaction is favored by moderately high temperatures. Excessive heating may be avoided by reducing the amperage or by placing cold water in the cooling bath.
9. It may be noted that this process is essentially a sodium amalgam reduction. By the same procedure β -furylacrylic acid was reduced to β -furylpropionic in yields of 60–70 per cent. With suitable modifications it may be applied to the reduction of other substances reducible with sodium amalgam.

3. Discussion

Hydrocinnamic acid can be prepared by the reduction of cinnamic acid with sodium amalgam,¹ with hydriodic acid at 100°,² with phosphorus and hydriodic acid,³ with amalgamated zinc and hydrochloric acid,⁴ electrolytically in alkaline solution on cathodes of lead⁵ and mercury,⁶ catalytically with palladium black⁷ and by the action of potassium cyanide on β -phenylethyl chloride followed by hydrolysis.⁸

References and Notes

1. Erlenmeyer and Alexejeff, *Ann.* **121**, 375 (1862).
 2. Glaser, *Z. Chem.* 111 (1865).
 3. Gabriel and Zimmerman, *Ber.* **13**, 1680 (1880).
 4. Mitchell and Reid, *J. Am. Chem. Soc.* **53**, 325 (1931); Clemmensen, *Ber.* **46**, 1837 (1913); **47**, 51, 681 (1914).
 5. Norris and Cummings, *Ind. Eng. Chem.* **17**, 305 (1925).
 6. Marie, *Compt. rend.* **136**, 1331 (1903).
 7. Akabori and Suzuki, *Proc. Imp. Acad., Tokyo* **5**, 255 (1929) [*Chem. Zentr.* II, 2033 (1929)].
 8. Fittig and Kiesow, *Ann.* **156**, 249 (1870).
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Appendix

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

β -furylpropionic

amalgamated zinc

palladium black

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

PHOSPHORUS (7723-14-0)

sodium sulfate (7757-82-6)

potassium cyanide (151-50-8)

mercury (7439-97-6)

sodium (13966-32-0)

hydriodic acid (10034-85-2)

cinnamic acid (621-82-9)

Hydrocinnamic acid (501-52-0)

sodium cinnamate

β -furylacrylic acid (539-47-9)

β -phenylethyl chloride (622-24-2)