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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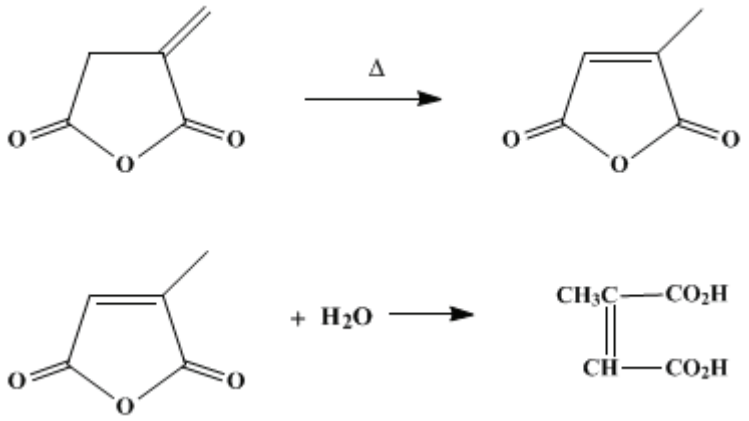
Organic Syntheses, Coll. Vol. 2, p.140 (1943); Vol. 11, p.28 (1931).

CITRACONIC ANHYDRIDE AND CITRACONIC ACID



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1. Procedure

(*A*) *Citraconic Anhydride*.—Two hundred and fifty grams of itaconic anhydride (Note 1) is distilled rapidly at atmospheric pressure in a 500-cc. modified Claisen flask with a 15-cm. (6-in.) fractionating column (Note 2). The receivers for the distillate must be changed without interrupting the distillation. The distillate passing over below 200° consists of water and other decomposition products. The fraction which distils at 200–215° consists of citraconic anhydride and is collected separately. The yield is 170–180 g. (68–72 per cent of the theoretical amount) of a product melting at 5.5–6°. On redistillation under reduced pressure there is obtained 155–165 g. (62–66 per cent of the theoretical amount) of a product which boils at 105–110°/22 mm. and melts at 7–8° (Note 3).

(*B*) *Citraconic Acid*.—To 22.4 g. (0.2 mole) of pure citraconic anhydride in a 100-cc. beaker is added from a pipet exactly 4 cc. (0.22 mole) of distilled water. The mixture is stirred on a hot plate until a homogeneous solution is formed, then covered with a watch glass and allowed to stand for forty-eight hours. At the end of this time the mixture has solidified completely. The yield is 26 g. of a product melting at 87–89°. For further purification it is finely ground in a mortar, washed with 50 cc. of cold benzene, dried in the air, and then dried for twenty-four hours in a vacuum desiccator over phosphorus pentoxide. This furnishes 24.4 g. (94 per cent of the theoretical amount) of citraconic acid which melts at 92–93°.

2. Notes

1. The crude itaconic anhydride obtained as described on p. 368 was used. Itaconic acid may be substituted for the anhydride.
2. The success of the preparation depends upon a rapid distillation and changing the receivers without interrupting the distillation. The best yields are obtained when the heating period is of short duration.
3. The crude citraconic anhydride contains a small amount of water, acetone, and citraconic acid. Vacuum distillation allows the removal of these impurities without materially decreasing the yield.

3. Discussion

Citraconic anhydride has been prepared by the distillation of citraconic acid and of citric acid.[1]

Citraconic acid has been obtained by distillation of citric acid,[2] of lactic acid,[3] and of hydroxypyrotartaric acid;[4] and by treating citric acid with hydriodic acid.[5] A mixture of citraconic and itaconic acids is obtained by flowing a concentrated aqueous solution of citric acid into a heated

evacuated vessel, distilling under reduced pressure the mixture of anhydrides formed, and allowing the mixture to react with water.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 368
- Org. Syn. Coll. Vol. 2, 382

References and Notes

1. Anschütz, Ber. **14**, 2788 (1881).
2. Crasso, Ann. **34**, 68 (1840); Kekulé, "Lehrbuch der organischen Chemie," **2**, 317 (1866); Wilm, Ann. **141**, 28 (1867).
3. Engelhardt, ibid. **70**, 243, 246 (1849).
4. Demarçay, Ber. **9**, 963 (1876).
5. Kämmerer, Ann. **139**, 269 (1866).
6. Boehringer Sohn A.-G., Brit. pat. 452,460 [C. A. **31**, 1045 (1937)].

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

citraconic and itaconic acids

Benzene (71-43-2)

citric acid (77-92-9)

acetone (67-64-1)

hydriodic acid (10034-85-2)

Citraconic anhydride (616-02-4)

Citraconic acid (498-23-7)

Itaconic anhydride (2170-03-8)

Itaconic acid (97-65-4)

lactic acid (50-21-5)

hydroxypyrotartaric acid

phosphorus pentoxide (1314-56-3)