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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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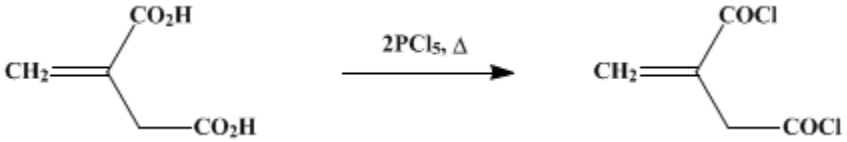
Organic Syntheses, Coll. Vol. 4, p.554 (1963); Vol. 33, p.41 (1953).

ITACONYL CHLORIDE



Submitted by Henry Feuer and Stanley M. Pier[1].
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1. Procedure

In a 500-ml. round-bottomed flask fitted with a reflux condenser and a drying tube leading to a gas-absorption trap[2] are placed 234 g. (1.1 mole) of phosphorus pentachloride (Note 1) and 65 g. (0.5 mole) of itaconic acid (Note 2). The reagents are mixed by shaking the flask; after a few minutes a vigorous reaction commences, resulting in partial liquefaction of the mixture and copious evolution of hydrogen chloride. When the initial reaction subsides, the mixture is gently heated to cause reflux of phosphorus oxychloride until all the solid dissolves; then heating is continued for an additional 15 minutes (Note 3). The reflux condenser is replaced by a 12-in. Vigreux column, and the phosphorus oxychloride is removed by distillation at reduced pressure provided by a water aspirator (Note 4), the major portion coming over at about 45°/85 mm. When all the phosphorus oxychloride has been removed, the pressure is reduced (vacuum pump) and the material boiling at 70–75°/2 mm. is collected. Liquid boiling in this range weighs 50–55 g., representing a yield of 60–66%. This material, n_D^{20} 1.4915, n_D^{25} 1.4900, is pure enough for most purposes, but it may be further refined by distillation through a packed column, yielding 47–53 g. of a water-white liquid, n_D^{20} 1.4919, boiling at 71–72°/2 mm.

2. Notes

1. The slight molar excess of phosphorus pentachloride has been found to increase the yield of product. It is best to use apparatus with ground-glass joints.
2. Chas. Pfizer and Company technical grade itaconic acid was employed without purification.[3]
3. Heating for a longer period results in a rather sudden change in color from pale yellow to deep orange or red, and a decrease in yield.
4. Considerable dissolved hydrogen chloride is liberated at this point and passes into the water aspirator. A mechanical vacuum pump should not be used at this stage because it would be damaged by corrosion.

3. Discussion

Itaconyl chloride has been prepared previously only by the reaction of itaconic anhydride with phosphorus pentachloride.[4]

References and Notes

1. Purdue University, Lafayette, Indiana.
2. *Org. Syntheses Coll. Vol.* **2**, 4 (1943).
3. *Org. Syntheses* Coll. Vol. **2**, 369 (1943).
4. Petri, *Ber.*, **14**, 1635 (1881).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

hydrogen chloride (7647-01-0)

phosphorus pentachloride (10026-13-8)

Phosphorus Oxychloride (21295-50-1)

Itaconic anhydride (2170-03-8)

Itaconic acid (97-65-4)

Itaconyl chloride (1931-60-8)