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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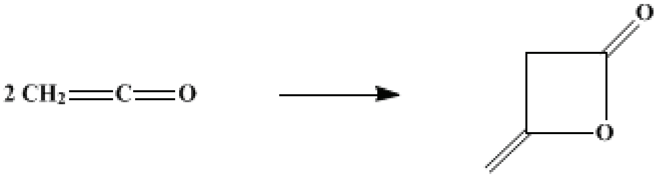
Organic Syntheses, Coll. Vol. 3, p.508 (1955); Vol. 21, p.64 (1941).

KETENE DIMER

[Acetylketene]



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1. Procedure

Three 300-ml. gas-washing cylinders (Note 1) are connected in series, and the second and third cylinders are charged with 150 ml. each of dry acetone. Each of the three cylinders is immersed, in a thermos bottle, in sufficient Dry Ice-acetone cooling mixture to cover half of the cylinder. Ketene gas, prepared by the pyrolysis of acetone (Note 2), is passed through the system (Note 3) until a quantity of 2 moles has been introduced. This process requires 4–4.5 hours. During this time, after the ketene has been passing through the system for 1.5 hours, the Dry Ice-acetone cooling mixture is removed from the thermos bottle around the first cylinder. The cold thermos bottle is then replaced around the cylinder. Two hours after the completion of the ketene passage, the cooling mixture is removed from the second thermos bottle, and 6 hours later the third thermos bottle is emptied, both bottles being immediately restored to position. The entire system should be at room temperature 24 hours after the beginning of the run.

The liquids from all three cylinders are combined and fractionally distilled (Note 4). Most of the acetone is removed at room temperature under a pressure of 20 mm.; the last small portion is removed under atmospheric pressure. When the distillation temperature reaches 120°, the system is evacuated to a pressure of 80–100 mm. (Note 5), and the ketene dimer is collected within the boiling range 67–69°/92 mm. The yield of pure product is 42–46 g. (50–55%) (Note 6) and (Note 7).

2. Notes

1. The gas-washing cylinders are preferably without flanges. Those used by the submitters were prepared from 45-mm. Pyrex tubing, measured 28 cm. in length, and were fitted with 29/42 standard taper ground-glass joints. The inlet tubes extended two-thirds of the way into the cylinders.
2. Ketene may be generated conveniently from acetone by means of a "ketene lamp."[1] This apparatus was used by submitters and checkers. Other apparatus [*Org. Syntheses* Coll. Vol. 1, 331 (1941)] might also be used.
3. The effluent gases from the third cylinder should be conducted to an efficient hood, or passed through a washing bottle containing a 10% aqueous solution of sodium hydroxide.
4. The submitters and checkers used a column of the Whitmore-Lux type.
5. Pressure between these limits is the optimum for this distillation. At higher pressure too much polymerization to dehydroacetic acid occurs, and at a lower pressure special cooling methods are necessary to prevent loss of distillate by evaporation.
6. A viscous dark red residue remains in the distillation flask. This material is mostly dehydroacetic acid.
7. The Ketene dimer may be kept in a tightly stoppered bottle in the dark without appreciable further polymerization for about a week.[2]

3. Discussion

The procedure described is a modification of the method of Chick and Wilsmore,[3] which has been studied by several other workers.[4] [5] [2]

Homologous diketenes have been prepared by the action of tertiary amines on the corresponding acid chlorides.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 10

References and Notes

1. Williams and Hurd, *J. Org. Chem.*, **5**, 122 (1940).
2. Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).
3. Chick and Wilsmore, *J. Chem. Soc.*, **1908**, 946; **1910**, 1978.
4. Hurd, Sweet, and Thomas, *J. Am. Chem. Soc.*, **55**, 335 (1933);
5. Hurd and Williams, *J. Am. Chem. Soc.*, **58**, 962 (1936);
6. Sauer, *J. Am. Chem. Soc.*, **69**, 2444 (1947).

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

Ketene dimer

sodium hydroxide (1310-73-2)

acetone (67-64-1)

Ketene (463-51-4)

Dehydroacetic acid (520-45-6)

Acetylketene