



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.

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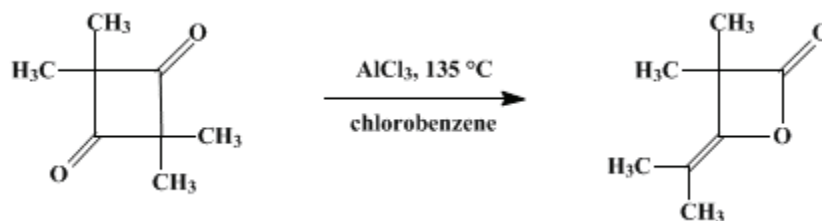
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.456 (1973); Vol. 48, p.72 (1968).

DIMETHYLKETENE β -LACTONE DIMER

[3-Pentenoic acid, 3-hydroxy-2,2,4-trimethyl-, β -lactone]



Submitted by Robert H. Hasek¹, R. Donald Clark¹, and Gerald L. Mayberry².
 Checked by V. Boekelheide, J. Witte, and G. Singer.

1. Procedure

Caution! Dimethylketene β -lactone dimer is a mild but deceptively persistent lachrymator.

In a 500-ml. three-necked flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser are placed 200 g. (1.43 moles) of [tetramethyl-1,3-cyclobutanedione](#) ([Note 1](#)) and 50 g. of [chlorobenzene](#) ([Note 2](#)). The mixture is heated to 135° with stirring while a total of 1.8 g. of reagent grade anhydrous [aluminum chloride](#) is added in 0.3-g. portions over a 3-hour period ([Note 3](#)). After the addition is complete, heating is continued for an additional 5 hours ([Note 4](#)).

The reaction mixture is then cooled to 35–40° and poured into a stirred solution of 230 g. of [sodium chloride](#) and 6.0 g. of [sodium acetate](#) in 600 ml. of water at 40°. The mixture is stirred for 15 minutes and then is transferred to a separatory funnel; the layers are separated, and the lower, aqueous layer is discarded. The crude product is distilled at reduced pressure through a stainless steel spinning-band column ([Note 5](#)). The yield of the β -lactone dimer of dimethylketene is 122–132 g. (61–67%); b.p. 69–71.5° (14 mm.) ([Note 6](#)). The product may be redistilled and the fraction boiling at 119.5–120° (150 mm.), n_D^{20} 1.4380, collected.

2. Notes

- [Tetramethyl-1,3-cyclobutanedione](#) is available from Eastman Organic Chemicals. It melts at 115–116° and is typically 99% pure by vapor-phase chromatography.
- More highly chlorinated aromatic solvents such as [1,2,4-trichlorobenzene](#) can be used with similar results.
- No special drying precautions are required; however, traces of water can be conveniently removed before the catalyst is added by distilling a small portion of the solvent until cloudiness disappears. The checkers found that the distillation of part of the solvent as indicated was necessary in order to obtain satisfactory yields. When the catalyst is added incrementally, no appreciable exotherm is observed.
- The isomerization is usually complete in 5 hours and can easily be followed by vapor-phase chromatography. (Heating periods up to 20 hours are not detrimental. The only failure among numerous preparations occurred when [tetramethyl-1,3-cyclobutanedione](#) contaminated with 4% of [isobutyric acid](#) was used. In case of partial conversion after 5 hours, additional increments (0.5 g.) of [aluminum chloride](#) should be added to complete the reaction.
- The product may be distilled directly from the crude reaction mixture after addition of [sodium acetate](#). The results are similar.
- The distilled product is 99% pure by vapor-phase chromatography.

3. Discussion

The β -lactone dimer of dimethylketene can be prepared by pyrolysis of its polyester, which is formed by the base-catalyzed polymerization of [dimethylketene](#).^{3,4,5} In addition to the rearrangement of the normal dimer described above,⁶ the direct dimerization of [dimethylketene](#) in the presence of [aluminum chloride](#)³ or trialkyl phosphites⁷ leads to the β -lactone dimer.

4. Merits of the Preparation

The β -lactone dimer of dimethylketene reacts with alcohols, phenols, mercaptans, and amines to form derivatives of 2,2,4-trimethyl-3-oxovaleric acid.³ In this respect it is a more powerful acylating reagent than the normal dimer, [tetramethyl-1,3-cyclobutanedione](#). The preparation of [2,2,4-trimethyl-3-oxovaleraniide](#), for example, is accomplished easily with the lactone dimer, but is extremely difficult with the normal dimer.⁸

In the presence of catalytic amounts of [sodium methoxide](#), dimethylketene β -lactone dimer is polymerized at moderate temperature to a polyester.³ At higher temperatures (above 100°), disproportionation to the cyclic trimer, [hexamethyl-1,3,5-cyclohexanetrione](#), takes place.⁹ Addition of a stoichiometric amount of [sodium methoxide](#) to the lactone dimer generates the sodium enolate of methyl 2,2,4-trimethyl-3-oxovalerate. This reaction provides a convenient entry into certain ester anion chemistry that formerly required the use of a strong base like [tritylsodium](#).¹⁰

Although these reactions can be duplicated in most cases with the normal dimer of [dimethylketene](#),¹¹ the more reactive lactone dimer is the preferred reagent. The liquid form of this dimer is convenient to handle. A distinct difference in behavior of the [dimethylketene](#) dimers is noted when they are pyrolyzed. The normal dimer is dissociated at 600° to [dimethylketene](#),¹² but the lactone dimer is decarboxylated almost quantitatively at 450° to [tetramethylallene](#).¹³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 1103](#)

References and Notes

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Appendix

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

Dimethylketene β -lactone dimer

β -lactone dimer of dimethylketene

sodium enolate of methyl 2,2,4-trimethyl-3-oxovalerate

sodium acetate (127-09-3)

sodium chloride (7647-14-5)

sodium methoxide (124-41-4)

chlorobenzene (108-90-7)

aluminum chloride (3495-54-3)

tritylsodium (4303-71-3)

isobutyric acid (79-31-2)

1,2,4-trichlorobenzene (120-82-1)

tetramethyl-1,3-cyclobutanedione (933-52-8)

Dimethylketene (598-26-5)

3-Pentenoic acid, 3-hydroxy-2,2,4-trimethyl-, β -lactone (3173-79-3)

2,2,4-trimethyl-3-oxovaleranimide

hexamethyl-1.3,5-cyclohexanetrione (778-18-7)

tetramethylallene (1000-87-9)