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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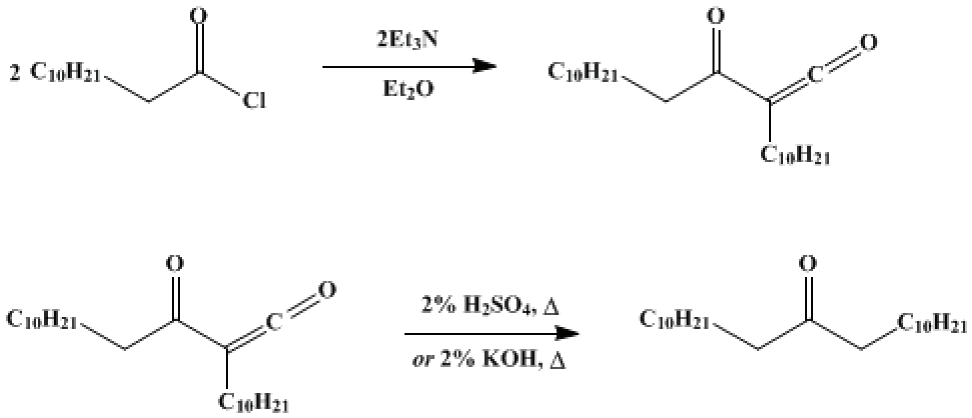
LAURONE

[12-Tricosanone]



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Checked by William S. Johnson and H. C. Dehm.

1. Procedure

Into a 3-l. three-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser provided with a calcium chloride drying tube is placed 1260 ml. (approximately 900 g.) of anhydrous ether. Stirring is commenced, and 153.0 g. (0.7 mole) of lauroyl chloride (Note 1) is added rapidly through one of the flask openings. The solution is cooled in ice water, and 70.7 g. (0.7 mole) of triethylamine (Note 2) is added over a period of 10 minutes through the dropping funnel in a fine stream. Stirring is discontinued after 1 hour, and the mixture is allowed to come to room temperature. After 12 to 24 hours, the mixture of decylketene dimer (Note 3) and triethylamine hydrochloride is extracted once with 125 ml. of an aqueous 2% sulfuric acid solution to remove the amine salt.

Procedure A. The wet ether layer is transferred to a 3-l. distillation flask and distilled to remove most of the solvent. The warm oily residue is transferred to a 1-l. beaker and mixed with 500 ml. of 2% potassium hydroxide solution. The mixture is heated on a steam bath for 1 hour with occasional stirring and is then chilled in ice water. The waxy cake which settles out on top of the aqueous suspension is skimmed from the surface and dissolved in a mixture of 400 ml. each of acetone and methanol. The hot solution is filtered through a steam-jacketed funnel and cooled in ice water, and the precipitate is collected on a Büchner funnel with suction. The product is washed on the funnel with cold methanol; after air drying overnight it amounts to 55–65 g. (46–55%), m.p. 62–64°.

Procedure B. The following alternative isolation procedure yields a somewhat purer product. The wet ether layer which has been washed with dilute sulfuric acid to remove amine salt is transferred to a 3-l. distillation flask, 150 ml. of 2% sulfuric acid is added, and the mixture is distilled until nearly all the ether is removed. The hot, oily layer is separated in a separatory funnel and distilled (Note 4). The yield of the fraction distilling at 215–230°/3 mm. is 64–75 g. (54–63%). After recrystallization from 750 ml. of acetone, the laurone weighs 55–65 g. (46–55%), m.p. 68–69° (Note 5).

2. Notes

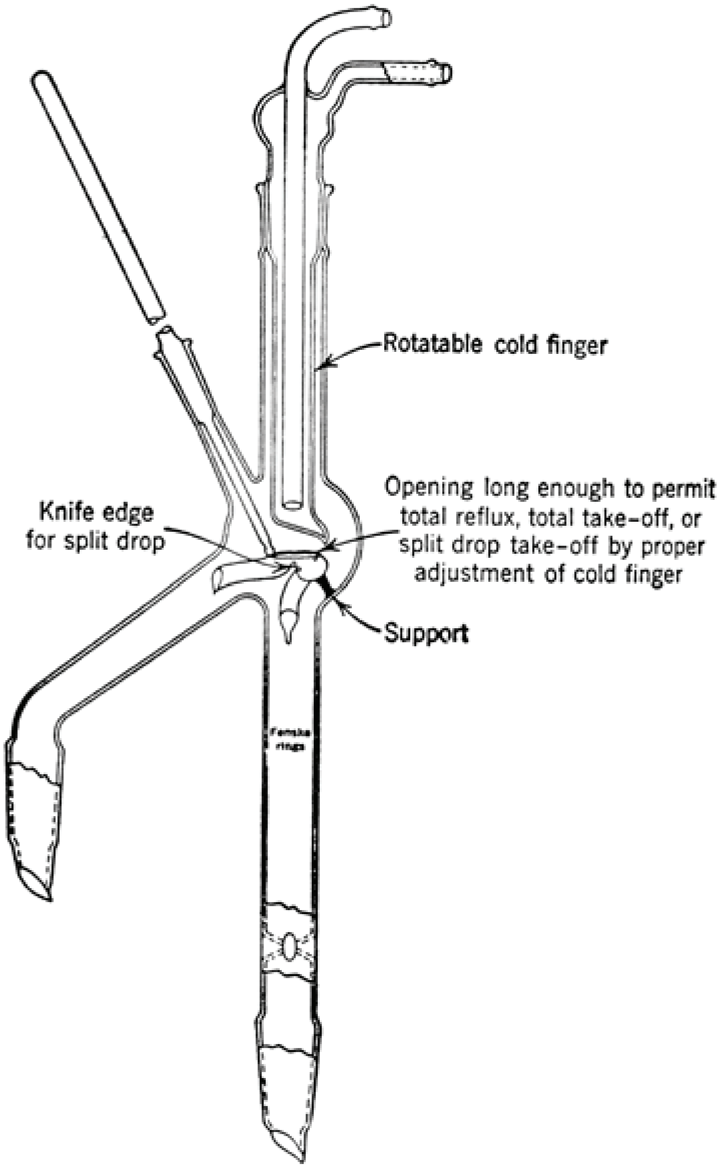
1. A commercial lauric acid, such as that available from Armour and Company, was converted into the acid chloride by reaction with thionyl chloride. The checkers employed 1 kg. of thionyl chloride for 1201 g. of acid. The product was distilled through a 12-in. Vigreux column, giving 1145 g. (87%) of colorless acid chloride, f.p. −15° to −18°.

2. Triethylamine was purified by the following procedure: fractional distillation, addition of about 2% phenyl isocyanate to the distillate, and redistillation.

3. If desired, decylketene dimer can be isolated at this point by filtering the reaction mixture and concentrating the filtrate. The mixture should be handled at all times under anhydrous conditions. The filtration should be carried out by the inverted filtration method.[2] Difficulties are usually encountered in the filtration step since the amine salt frequently separates as a gel. Seeding the ether solution of lauroyl chloride with triethylamine hydrochloride usually aids in preventing this gel formation. It is necessary to rinse the amine salt several times with ether to extract the dimer, which is usually contaminated with traces of triethylamine hydrochloride.

4. The electrically heated fractionating column used by the submitter for distilling laurone is pictured in part in Fig.11. This still, with a column length of 8 in., was designed by Dr. H. J. Sampson of the Rayon Department of E. I. du Pont de Nemours and Company, Inc., Waynesboro, Virginia.

Fig. 11.



5. Other acid chlorides of the type RCH_2COCl can be similarly dehydrochlorinated. For example, caproyl chloride (1.2 moles) was converted to di-*n*-amyl ketone, b.p. 98–102°/15 mm., in 60–71.5% yield. In this case, it was found preferable to remove the amine salt from the reaction mixture by washing with 2% sulfuric acid. The butylketene dimer was then extracted from the reaction mixture by washing with 5% sodium hydroxide solution; the alkaline solution was acidified with sulfuric acid and

steam-distilled. The oily layer in the distillate was separated and fractionated.

3. Discussion

Laurone has been prepared by hydrating and decarboxylating decylketene dimer.[3] It has also been prepared by distilling calcium laurate;[4] by heating lauric acid with phosphorus pentoxide;[5] by heating barium laurate under reduced pressure;[6] by the ester condensation of ethyl laurate with sodium ethoxide[7] or of methyl laurate with sodium hydride[8] or diisopropylamino-magnesium bromide[9] followed by ketonic hydrolysis; by catalytic ketonization of lauric acid over a chromate catalyst;[10] or by passing lauric acid over thorium dioxide at 400°.[11]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 514

References and Notes

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

sulfuric acid (7664-93-9)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

thionyl chloride (7719-09-7)

thorium dioxide

acetone (67-64-1)

potassium hydroxide (1310-58-3)

sodium ethoxide (141-52-6)

Triethylamine hydrochloride (554-68-7)

phenyl isocyanate (103-71-9)

ethyl laurate (106-33-2)

lauric acid (143-07-7)

sodium hydride (7646-69-7)

lauroyl chloride (112-16-3)

chromate

triethylamine (121-44-8)

Laurone,
12-Tricosanone (540-09-0)

decylketene

caproyl chloride (142-61-0)

butylketene

calcium laurate (4696-56-4)

barium laurate (4696-57-5)

methyl laurate (111-82-0)

diisopropylamino-magnesium bromide

phosphorus pentoxide (1314-56-3)

di-n-amyl ketone (927-49-1)