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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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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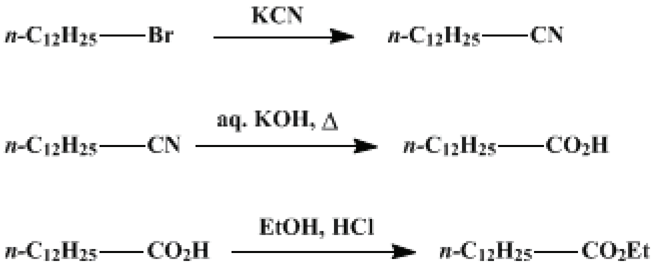
ETHYL *n*-TRIDECYLATE

[*n*-Tridecanoic acid, ethyl ester]



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1. Procedure

In a 12-l. flask fitted with a reflux condenser and an efficient, liquid-sealed mechanical stirrer (Note 1) are placed 2.5 l. of 95 per cent ethyl alcohol, 872 g. (3.5 moles) of pure *n*-dodecyl bromide (Org. Syn. Coll. Vol. I, **1941**, 29, and p. 246 above), and 278 g. (3.85 moles) of powdered 90 per cent potassium cyanide (Note 2). The mixture is refluxed for fifteen hours, with stirring, in a water bath (Note 3). At the end of this time another 278-g. portion of potassium cyanide is added and the mixture refluxed, with stirring, for fifteen hours longer.

The flask is allowed to cool, and a solution of 670 g. of 90 per cent potassium hydroxide in 1 l. of water is added (Note 4). The solution is refluxed and stirred for thirty hours. The flask is fitted with a head for steam distillation (Note 5), and steam is passed in until foaming prevents further distillation. When the flask has cooled somewhat, the steam inlet is replaced by a separatory funnel with a stem reaching to the bottom of the flask, and 1.5 l. of concentrated hydrochloric acid (sp. gr. 1.18) or the equivalent amount of more dilute acid is added. The flask is shaken occasionally to prevent stratification of the hydrochloric acid. The dropping funnel is then replaced by the steam inlet, and steam is passed through for about one-half hour. At the end of this time the water layer is siphoned off and discarded (Note 6).

The crude acid while still warm and fluid is treated with 815 cc. (14 moles) of 95 per cent ethyl alcohol containing 20–30 g. (3–5 per cent by weight) of anhydrous hydrogen chloride, and the solution is filtered from insoluble impurities. The filtrate is placed in a 3-l. flask fitted with a reflux condenser, 160 g. of anhydrous calcium chloride is added, and the mixture is refluxed for twenty-four hours (Note 7). The lower layer is siphoned off and diluted with twice its volume of water to recover any dissolved ester. The recovered ester is combined with the main portion, 408 cc. of alcohol containing 3–5 per cent of anhydrous hydrogen chloride and 80 g. of calcium chloride are added, and the mixture is refluxed for another twenty-four hours. The lower layer is siphoned off and the dissolved ester recovered as before. The upper layer is washed twice with an equal volume of warm water (30–40°) and transferred to a 2-l. separatory funnel; the volume of the oil is approximately 1 l. About 500 cc. of warm water and a few drops of phenolphthalein are also placed in the funnel, and very dilute aqueous ammonia (concentrated aqueous ammonia diluted with twenty volumes of water) is added, with shaking, until the resulting emulsion has a distinctly pink color (50–100 cc. is required). Alcohol is added in portions of about 100 cc. until the emulsion is broken and the layers begin to separate quite rapidly; usually two or three additions of alcohol suffice. The lower layer is drawn off and set aside (Note 8). The oil is washed three times with warm water; if necessary, alcohol is added to break the emulsion. The ester is dried with anhydrous calcium chloride, filtered, and distilled under reduced pressure. The yield of ethyl tridecylate, b.p. 163–165°/5 mm. (178–180°/20 mm.; 197–198°/60 mm.) is 615–660 g. (73–78 per cent of the theoretical amount). By refractionating the fore- and after-runs, an additional 50–70 g. of product is obtained; 15–30 g. of ester and acid are recovered from the ammoniacal washings and from the calcium chloride used to dry the main portion. The total yield is 685–710 g. (81–84 per cent of the theoretical amount) (Note 9) and (Note 10).

2. Notes

1. A mercury-sealed stirrer may be used, but a "vaseline seal" is very satisfactory.
2. Potassium cyanide gives better results than sodium cyanide. It is essential that the material be finely powdered.
3. The entire operation should be carried out in a hood. A small wash tub placed on the bench and heated from the side with a Bunsen burner is a convenient water bath.
4. This corresponds to 3.85 moles of potassium hydroxide plus a quantity sufficient so that, after the hydrolysis is completed, the solution will contain 10 per cent of alkali. When less alkali is used the quantity of unhydrolyzed nitrile is greater.
5. The condenser should lead to a 2-l. suction flask the side arm of which is connected directly to the vent of the hood. The alcohol has the odor of hydrocyanic acid and should be discarded.
6. The crude acid may be used for some purposes, but it contains a small quantity of unhydrolyzed nitrile, some material of very disagreeable odor (possibly isocyanide), and usually a small amount of a blue precipitate (an iron-cyanide complex salt). In the preparation of the ester, the precipitate is removed by filtering the alcohol solution of the acid as its presence will interfere with the removal of the free tridecylic acid after esterification.
7. A few pieces of porous plate should be added to prevent bumping.
8. By addition of acid to the washings a small amount (15–30 g.) of ester and acid may be recovered.
9. For larger runs, the procedure is the same and the percentage yields are somewhat higher. Thus, in runs by the author using twice the above quantities, yields of 88–89 per cent were obtained.
10. Pentadecylic acid and ethyl pentadecylate have been prepared by the same procedure from *n*-tetradecyl bromide (p. 247) with approximately the same yield.

3. Discussion

Tridecylic acid has been prepared by the malonic ester synthesis from undecyl iodide,[1] by the oxidation of α-hydroxymyristic acid in acetone with potassium permanganate,[2] by the action of dodecyl bromide on potassium cyanide and subsequent hydrolysis,[3] and from undecyl iodide and ethyl cyanoacetate.[4] The present method is an adaptation of that of Ruzicka, Stoll, and Schinz.[3]

References and Notes

1. Levene, West, Allen, and van der Scheer, J. Biol. Chem. **23**, 73 (1915).
2. Levene and West, ibid. **18**, 465 (1914).
3. Ruzicka, Stoll, and Schinz, Helv. Chim. Acta **11**, 685 (1928).
4. Robinson, J. Chem. Soc. **125**, 230 (1924).

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

ethyl alcohol,
alcohol (64-17-5)

calcium chloride (10043-52-4)

hydrogen chloride,
hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

potassium permanganate (7722-64-7)

sodium cyanide (143-33-9)

hydrocyanic acid (74-90-8)

Dodecyl bromide,
n-DODECYL BROMIDE (143-15-7)

potassium cyanide (151-50-8)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

Ethyl cyanoacetate (105-56-6)

phenolphthalein (77-09-8)

Ethyl tridecylate,
Ethyl N-tridecylate,
n-Tridecanoic acid, ethyl ester (28267-29-0)

tridecylic acid (638-53-9)

Pentadecylic acid (1002-84-2)

ethyl pentadecylate (41114-00-5)

undecyl iodide (4282-44-4)

α-hydroxymyristic acid (2507-55-3)

n-tetradecyl bromide (112-71-0)