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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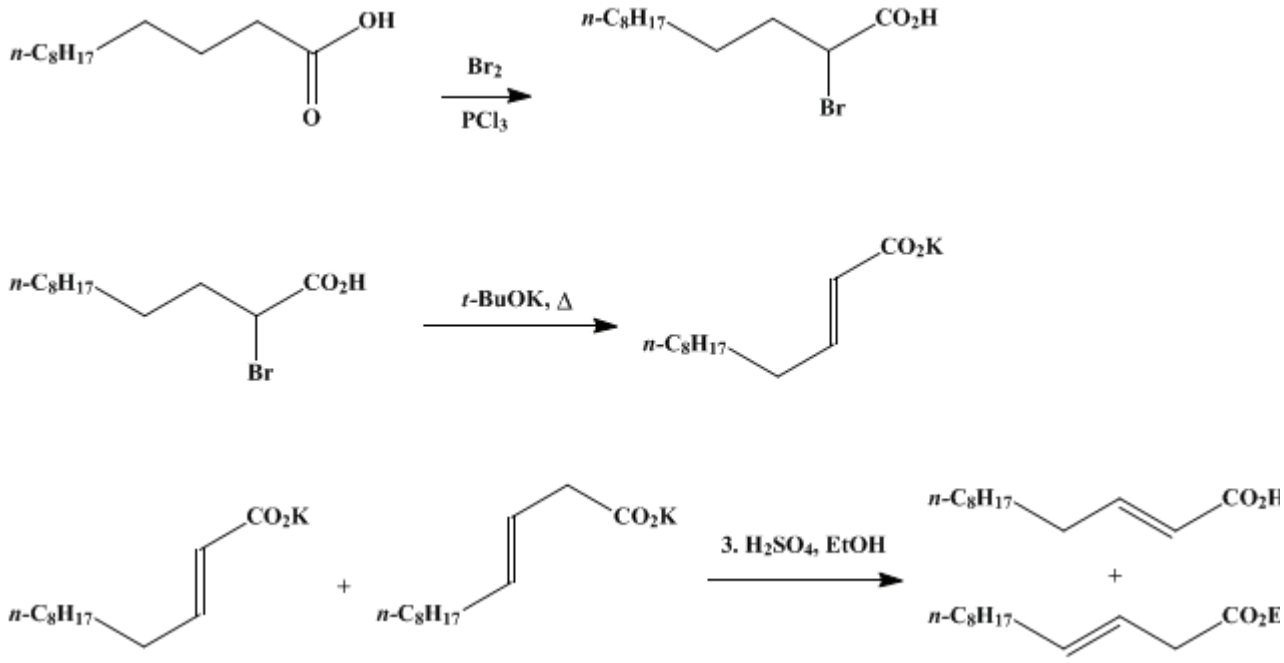
trans-2-DODECENOIC ACID



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1. Procedure

Caution! The bromination step should be carried out in a hood, and appropriate precautions should be employed in handling potassium (Note 1).

A dry 125-ml. three-necked flask fitted (glass joints) with a sealed mechanical stirrer, an addition funnel, and a reflux condenser capped with a calcium chloride drying tube, is charged with 30.0 g. (0.15 mole) of dodecanoic acid (Note 2) and 0.6 ml. (0.007 mole) of phosphorus trichloride. The mixture is heated at 90–95° (bath temperature), and 8.5 ml. (0.165 mole) of dry bromine (Note 3) is added in one portion with stirring. After stirring for 3 hours at 90–95°, an additional 7.7 ml. (0.15 mole) of dry bromine is added, and the heating and stirring are continued for an additional 7 hours. The dark reaction mixture is then cooled, dissolved in about 100 ml. of carbon tetrachloride, and shaken vigorously with two 100-ml. portions of water. The organic solution is filtered through anhydrous sodium sulfate, and the solvent and excess bromine are removed by distillation at steam-bath temperature and reduced pressure (water aspirator). The residue of bromo acid, which is pale orange in color, is slowly and cautiously added at room temperature to a solution of potassium *tert*-butoxide which has been prepared from 14.7 g. (0.375 g. atom) of potassium (Note 1) and 350 ml. of dry *tert*-butyl alcohol (Note 1), and is contained in a 1-l. flask fitted with a reflux condenser that is protected from moisture with a calcium chloride tube. The resultant thick suspension is heated at gentle reflux for 3–4 hours on a steam bath, then cooled, diluted with about 1 l. of water, and acidified to Congo red with 5*N* sulfuric acid. The mixture, containing the precipitated liquid dodecenoic acids, is extracted with two 100-ml. portions of hexane (or a comparable petroleum ether fraction), and the combined hexane solutions are washed with water and dried by filtration through anhydrous sodium sulfate. The hexane is removed by flash distillation, and the residual acid is fractionally distilled through a 2-ft. Podbielniak-type column (Note 4) and (Note 5). After a small fore-run, the main fraction of dodecenoic acids is collected over a 3° range at about 166–169°/3 mm. The yield is 14–15 g. (47–50%), n_D^{25} ca. 1.4610 (Note 6).

The distilled mixture of dodecenoic acids is dissolved in 150 ml. of commercial absolute ethanol containing 1.3 ml. of concentrated sulfuric acid and allowed to stand in a stoppered flask for 2 hours at

20°. The solution is diluted with 600 ml. of water and extracted with two 150-ml. portions of 60–68° petroleum ether. The extracts are washed with water and percolated through a Kies extraction apparatus (Note 7) consisting of three stages containing, respectively, 9.9 g. of 85% potassium hydroxide (0.15 mole) in 250 ml. of 20% ethanol, 2.5 g. of 85% potassium hydroxide (0.038 mole) in 125 ml. of 20% ethanol, and 125 ml. of water. An additional 250 ml. of petroleum ether is then passed through the extraction apparatus. The three aqueous layers are combined, acidified to Congo red with 5*N* sulfuric acid, and extracted with petroleum ether. The combined organic layers are washed with water and dried over anhydrous sodium sulfate. The solvent is removed by flash distillation and the residue distilled in a modified Claisen flask. The yield of colorless 2-dodecenoic acid, b.p. 155–158°/3 mm., 127–130°/0.15 mm., is 8–10 g. (27–34%), n_D^{25} 1.4629, λ_{max} 210 mμ (ε 13,650) in hexane, m.p. 13–18°.

2. Notes

1. The precautions for handling potassium and the procedure for preparing anhydrous potassium *tert*-butoxide have already been described (p.134).
2. The submitters employed a sample of dodecanoic acid, m.p. 42.5–43°, obtained by fractional distillation of commercial material. The checkers used Eastman Kodak Company yellow label grade dodecanoic acid, m.p. 44.5–45°. If a product free of homologous material is desired, purified dodecanoic acid should be used as starting material.
3. The bromine was dried with phosphorus pentoxide and filtered into the addition funnel through a plug of glass wool.
4. A simplified Podbielniak column[2] was employed. Other columns of comparable efficiency should be suitable.
5. This distillation is of importance; if omitted, the final 2-dodecenoic acid is difficult to purify.
6. The mixture of dodecenoic acids exhibited λ_{max} at 210 mμ (ε 11,980) in hexane. From the extinction coefficient (13,650) for the pure 2-isomer and that (about 1000) for the 3-isomer, it is calculated that this mixture contains about 13% of the latter. A small amount of dodecanoic acid also appears to be present.
7. The Kies extraction apparatus[3] is useful in minimizing emulsion formation. The checkers performed the countercurrent extractions successfully in separatory funnels. The solutions must be mixed by mild rocking of the funnels; otherwise serious emulsions will be produced.

3. Discussion

Higher-molecular-weight normal 2-alkenoic acids have been prepared in poor yields by the Doebner condensation of aldehydes with malonic acid,[4,5,6] and by the Reformatsky reaction of aldehydes with ethyl bromoacetate followed by dehydration.[7] The α-iodo acid, prepared from the bromo acid, has been dehydrohalogenated with potassium hydroxide in ethanol,[8] but large quantities of the α-hydroxy acid are formed as a by-product which is difficult to separate in some instances. It has been reported that 2-dodecenoic acid is formed by the treatment of 3-tridecen-2-one with sodium hypobromite.[9] The present procedure is an adaptation of a published procedure.[4]

References and Notes

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

petroleum ether

ethanol (64-17-5)

sulfuric acid (7664-93-9)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

carbon tetrachloride (56-23-5)

potassium hydroxide (1310-58-3)

phosphorus trichloride (7719-12-2)

potassium (7440-09-7)

Malonic acid (141-82-2)

sodium hypobromite

dodecanoic acid (143-07-7)

Ethyl bromoacetate (105-36-2)

hexane (110-54-3)

tert-butyl alcohol (75-65-0)

2-dodecenoic acid

3-tridecen-2-one

phosphorus pentoxide (1314-56-3)

potassium tert-butoxide (865-47-4)

trans-2-Dodecenoic acid (4412-16-2)