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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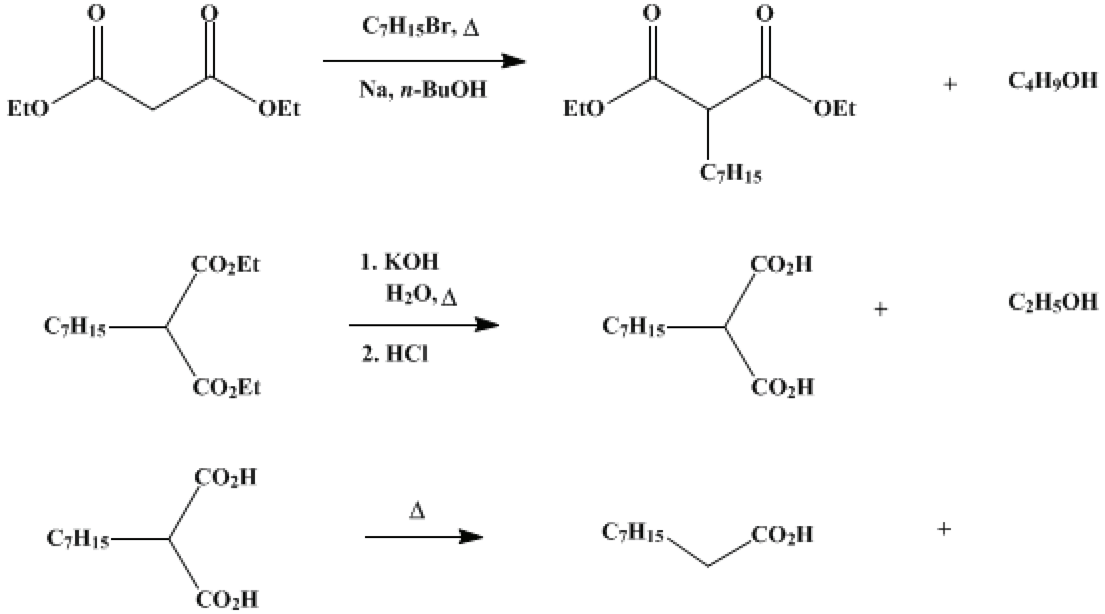
Organic Syntheses, Coll. Vol. 2, p.474 (1943); Vol. 16, p.60 (1936).

PELARGONIC ACID



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1. Procedure

A 5-l. three-necked flask is fitted with a liquid-sealed mechanical stirrer, reflux condenser, dropping funnel, and thermometer. In the flask is placed 2.5 l. of anhydrous butyl alcohol (Note 1), and 115 g. (5 gram atoms) of clean, bright sodium cut in small pieces is added at one time. Solution of the sodium may be facilitated by stirring, but heating is unnecessary. After the sodium has dissolved completely, the solution is allowed to cool to 70–80°, and then 800 g. (5 moles) of redistilled ethyl malonate (b.p. 135–136°/100 mm.) is added rapidly with stirring. After heating the reaction solution to 80–90°, 913 g. (5.1 moles) of pure heptyl bromide (p. 247, b.p. 179–180°) is added. The bromide should be added rather slowly at first, until precipitation of sodium bromide begins; it may then be added at such a rate that the butyl alcohol refluxes gently. Usually about one hour is required for the introduction of the heptyl bromide. The mixture is refluxed gently until it is neutral to litmus (about one hour).

The entire mixture, including the precipitated sodium bromide, is transferred to a 12-l. flask together with a small amount of water used to rinse the reaction flask. A solution of 775 g. (12.5 moles) of 90 per cent potassium hydroxide in an equal weight of water is added slowly with shaking. The mixture is heated cautiously, with occasional shaking, until refluxing starts (Note 2), and refluxing is continued until saponification is complete (about four or five hours). The flask is fitted at once for steam distillation (Org. Syn. Coll. Vol. I, **1941**, 479), and the mixture is distilled until no more butyl alcohol passes over (Note 3). To the residue 1350 cc. (15.5 moles) of concentrated hydrochloric acid (sp. gr. 1.18) is added carefully, with shaking, and the mixture is refluxed for about one hour (Note 4). After cooling, the water layer is siphoned off and discarded (Note 5).

The oil obtained in the preceding step is transferred to a 3-l. round-bottomed flask and heated under an air-cooled reflux condenser in an oil bath at about 180°. When the evolution of carbon dioxide has ceased (about two hours), the oil is decanted from a small amount of solid material. The solid residue on treatment with 200–300 cc. of concentrated hydrochloric acid gives an additional small quantity of oil which is added to the main portion.

The crude pelargonic acid is distilled in a modified Claisen flask having a fractionating side arm, and the material boiling at 140–142°/12 mm. (188–190°/100 mm.) is collected. The yield is 525–590 g. (66–75 per cent of the theoretical amount). The melting point of the pure acid is 12–12.5° (Note 6).

2. Notes

1. Commercial butyl alcohol was dried over solid potassium carbonate and distilled through a 90-cm. indented column. The portion boiling at 117–118° was used.
2. Two layers are formed at first, but the solution becomes homogeneous as saponification occurs. Boiling chips should be placed in the flask, and heating should be done carefully at first, with occasional shaking, or the reaction may get beyond control.
3. The flask should not be allowed to cool between saponification and distillation. It is advisable to heat the flask to prevent the volume of distillate from becoming too large. Usually about 7 l. of distillate is collected, from which the butyl alcohol can be recovered.
4. When the oily layer ceases to increase, decomposition of the potassium heptylmalonate is complete. A layer of salt sometimes accumulates at the bottom of the flask. Care must be taken in heating to prevent cracking the flask.
5. It is unnecessary to extract the aqueous layer with an organic solvent.
6. *n*-Caproic acid may be prepared by this method from *n*-butyl bromide in similar yields (see also p. 417). In this preparation a partial decomposition of the substituted malonic acid is brought about by refluxing the aqueous solution in the 12-l. flask after the addition of the hydrochloric acid. Butylmalonic acid is appreciably soluble in water, and separation of the oily layer does not occur until the malonic acid has been largely decomposed to caproic acid. The time required is about eight to ten hours. It is advisable to heat the acid layer under air reflux as in the preparation of pelargonic acid.

3. Discussion

Pelargonic acid has been prepared by the oxidation of oleic acid[1] and by hydrolysis of octyl cyanide[2] or heptylacetoacetic ester.[3]

References and Notes

1. Redtenbacher, Ann. **59**, 52 (1846); Harries and Thieme, ibid. **343**, 355 (1905); Harries and Türk, Ber. **39**, 3737 (1906); Molinari and Soncini, ibid. **39**, 2739 (1906); Molinari and Barozi, ibid. **41**, 2795 (1908); Jegorow, J. prakt. Chem. (2) **86**, 531 (1912).
2. Zincke and Franchimont, Ann. **164**, 333 (1872).
3. Jourdan, ibid. **200**, 107 (1880).

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

heptylacetoacetic ester

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

n-butyl bromide (109-65-9)

sodium bromide (7647-15-6)

carbon dioxide (124-38-9)

butyl alcohol (71-36-3)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

Caproic acid,
n-caproic acid (142-62-1)

ethyl malonate (1071-46-1)

Malonic acid (141-82-2)

oleic acid (112-80-1)

Heptyl bromide (629-04-9)

Pelargonic acid (112-05-0)

potassium heptylmalonate

Butylmalonic acid (534-59-8)

octyl cyanide (2243-27-8)