



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](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.

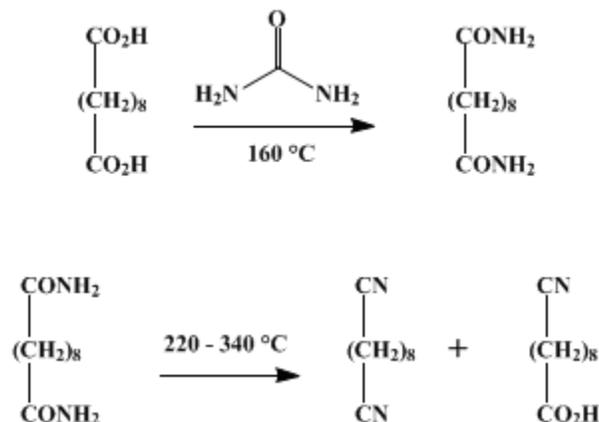
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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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## SEBACONITRILE AND $\omega$ -CYANOPELARGONIC ACID

[Sebaconitrile and pelargonic acid,  $\theta$ -cyano-]



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### 1. Procedure

A. *Sebaconitrile*. A 3-l. three-necked flask (Note 1), equipped with a mechanical stirrer (Note 2) and (Note 3) and a thermometer which dips into the liquid, is heated in an oil bath to 160°. In the flask are placed 505 g. (2.5 moles) of commercial *sebacic acid* (Note 4) and 180 g. (3 moles) of *urea* (Note 5), and the melt is heated with stirring for 4 hours at about 160° (Note 6). The oil bath is removed, the surplus oil is wiped off, the flask is insulated (Note 7), and the temperature is then raised, as rapidly as foaming permits, to 220° by means of a triple burner and wire gauze. It is important to continue the stirring for at least 5 minutes after 220° is attained; otherwise the mass will foam over during the subsequent distillation.

The stirrer is then replaced by a short still head connected to a long (90-cm.) air condenser and receiver (Note 8), and the product is distilled at atmospheric pressure as long as any distillate is obtained. The temperature of the vapor rises gradually to 340°. The distillate, which consists chiefly of water, dinitrile, acid nitrile, and *sebacic acid*, is poured into a large (2-l.) separatory funnel and, after the addition of 500 ml. of *ether* (Note 9), is extracted three times with 650-ml. portions of 5% *ammonium carbonate* (Note 10). The crude dinitrile which remains after the removal of the *ether* is distilled under reduced pressure; after a small fore-run (20–25 ml.) the main product is collected at 185–188°/12 mm. (Note 11). The yield of *sebaconitrile* is 190–200 g. (46–49%) (Note 12).

B.  *$\omega$ -Cyanopelargonic acid*. The combined ammoniacal extracts are heated nearly to boiling in a large enameled pot or 4-l. beaker and neutralized to *phenolphthalein* with concentrated *hydrochloric acid* (about 120 ml.) (Note 13). A hot solution of 400 g. of *barium chloride* is then added slowly with stirring, and the hot solution is filtered from the precipitated *barium sebacate* (Note 14) through a fluted filter paper or "Shark Skin" filter paper (Note 15) on a 20-cm. Büchner funnel. The barium salt of the cyano acid that separates on cooling is filtered on the same sized funnel and dissolved in 1 l. of hot water, and the solution is acidified to litmus with concentrated *hydrochloric acid* (about 30 ml.). The cyano acid separates as a clear oil. The filtrate from which the barium salt was filtered is acidified likewise to litmus with concentrated *hydrochloric acid* (about 50 ml.). The two oils are combined. The cyano acid is washed by decantation with three 200-ml. portions of hot water, separated completely from water, and dried in a vacuum desiccator over *calcium chloride*. The yield of  *$\omega$ -cyanopelargonic acid* melting at 48–49° is 146–155 g. (32–34%) (Note 16).

### 2. Notes

1. Ground-glass equipment is preferable, since the final temperature is high enough to decompose rubber or cork stoppers.
2. The stirrer is a bent glass rod that will break up the foam produced.
3. Attention is called to the powerful but compact compressed-air stirrer, catalog No. 9224, of the A. H. Thomas Company. When a compressed-air line is available, such a stirrer is preferable to an electric motor.
4. Commercial grades of [sebacic acid](#) (m.p. 127–130°) and [urea](#) (m.p. 132–134°) were used; pure [sebacic acid](#) (m.p. 132–133°) gives only a slightly (13%) higher yield. Since the acid is light and bulky, it is convenient to melt it in an enameled pot ([p. 614, Note 2](#)) and pour the liquid into the preheated flask.
5. It is important to use the amount of [urea](#) which is specified. When 2 moles of [urea](#) per mole of [sebacic acid](#) was employed, the yield of [sebaconitrile](#) was only 27%.
6. At the end of this time the product consists almost entirely of [sebacamide](#), which may be isolated if desired.
7. This insulation is easily accomplished by wrapping with asbestos rope, starting at the neck and winding as far down the bulge of the flask as possible. After the flask is clamped in place on the wire gauze, asbestos paper is bent around to enclose the bottom. Magnesia can also be used.
8. If the condenser is short, it is advisable to have a second receiver with a reflux condenser attached, because some dinitrile may be carried through by uncondensed steam. A water-cooled condenser should not be placed ahead of the first receiver, however, since the distillate contains some solid products ([sebacic acid](#) and products from [urea](#)).
9. Although not absolutely essential, the [ether](#) facilitates the operation. [Benzene](#) is not satisfactory.
10. [Ammonium hydroxide](#) (about 3%) is equally satisfactory. The aqueous extracts are saved.
11. Another boiling point is 201–203°/16 mm.
12. The submitters obtained 410–450 g. (50–55%) in runs twice this size.
13. The checkers used a pH meter and neutralized to pH 7.8.
14. This amounts to 43–45 g.
15. S & S "Shark Skin" filter paper has "high wet-strength" and a high resistance to acids and alkalis.
16. If the cyano acid obtained from the precipitated barium salt is worked up separately, it melts at 51–52°.

### 3. Discussion

[Sebaconitrile](#) has been obtained by heating [sebacic acid](#) in a stream of [ammonia](#),<sup>1</sup> and from [sebacamide](#) by pyrolysis<sup>2,3</sup> or by dehydration with [phosphorus pentachloride](#)<sup>4</sup> or [phosphorus oxychloride](#).<sup>5</sup> [Sebacamide](#) has been prepared from [ethyl sebacate](#),<sup>6,7</sup> [sebacoyl chloride](#),<sup>7</sup> or polysebacic anhydride<sup>8</sup> and [ammonia](#); by heating [sebacic acid](#) with [urea](#)<sup>2,3,9</sup> or [ammonium thiocyanate](#);<sup>10</sup> and by the electrolysis of [adipic acid monoamide](#).<sup>11</sup>

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### References and Notes

1. Greenewalt and Rigby, U. S. pat. 2,132,849 [*C. A.*, **33**, 178 (1939)].
  2. Biggs and Bishop, *J. Am. Chem. Soc.*, **63**, 944 (1941).
  3. Biggs, U. S. pat. 2,322,914 [*C. A.*, **38**, 118 (1944)].
  4. Phookan and Krafft, *Ber.*, **25**, 2252 (1892).
  5. Wilcke, U. S. pat. 1,828,267 [*C. A.*, **26**, 735 (1932)].
  6. Rowney, *Ann.*, **82**, 123 (1852).
  7. Aschan, *Ber.*, **31**, 2350 (1898).
  8. Coffman, Cox, Martin, Mochel, and Van Natta, *J. Polymer Sci.*, **3**, 85 (1948).
  9. U. S. pat. 2,109,941 [*C. A.*, **32**, 3419 (1938)].
  10. Ssolonina, *J. Russ. Phys. Chem. Soc.*, **28**, 558 (1896).
  11. Offe, *Z. Naturforsch.*, **2B**, 185 (1947) [*C. A.*, **42**, 4548 (1948)].
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

pelargonic acid,  $\theta$ -cyano-

polysebacic anhydride

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ammonium carbonate (506-87-6)

ammonia (7664-41-7)

Benzene (71-43-2)

ether (60-29-7)

ammonium thiocyanate (1762-95-4)

phosphorus pentachloride (10026-13-8)

barium chloride (10361-37-2)

Phosphorus Oxychloride (21295-50-1)

urea (57-13-6)

ammonium hydroxide (1336-21-6)

phenolphthalein (77-09-8)

Ethyl sebacate (693-55-0)

sebacamide (1740-54-1)

sebacic acid (111-20-6)

Sebaconitrile (1871-96-1)

$\omega$ -CYANOPELARGONIC ACID (5810-19-5)

barium sebacate

adipic acid monoamide

sebacoyl chloride (111-19-3)