



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.

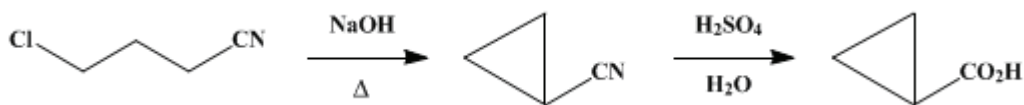
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.221 (1955); Vol. 24, p.36 (1944).*

## CYCLOPROPANECARBOXYLIC ACID



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### 1. Procedure

In a 2-l. three-necked round-bottomed flask surmounted by two large condensers (Note 1) and (Note 2) are placed 150 g. (3.75 moles) of powdered sodium hydroxide (Note 3) and 103.5 g. (1 mole) of  $\gamma$ -chlorobutyronitrile.<sup>1</sup> The contents of the flask are well mixed by shaking, after which the mixture is heated on a steam bath; a rather vigorous reaction sets in (Note 4). The water formed in the reaction hydrolyzes some of the cyclopropyl cyanide, so that after 1 hour's heating very little liquid is apparent. The hydrolysis of the cyanide is completed by the addition of water in small portions over a period of about 2 hours and subsequent heating; 15–20 ml. of water is added at first, and portions of 60–75 ml. later at intervals of 10–15 minutes until 500 ml. in all has been added. The mixture is then heated for an additional 1.5 hours with occasional stirring; at the end of this time the oily layer will have disappeared.

The solution is then cooled in an ice bath and acidified by 200 g. of concentrated sulfuric acid (sp. gr. 1.84) previously mixed with 300 g. of cracked ice. The solution is again cooled in an ice bath. The thick floating layer of cyclopropanecarboxylic acid and various polymers is separated and the cold aqueous solution extracted once with 1 l. of ether, using a stirrer instead of shaking (Note 5). The extract and crude acid are combined and dried over 50 g. of Drierite, and the solvent is removed in a 500-ml. modified Claisen flask on a steam bath. The residue is then distilled under reduced pressure. The yield of acid boiling at 94–95°/26 mm. or 117–118°/75 mm. is 63.5–68 g. (74–79%) (Note 6).

### 2. Notes

1. It is advisable to set up the apparatus in a hood, as small amounts of isocyanide are evolved.
2. The yield is slightly higher if the first vigorous reaction is allowed to take place without external cooling.
3. The commercial flakes are ground in a mortar if powder is not available. The powdered potassium hydroxide on the market can be used equally well.
4. The reaction sets in after about 15 minutes. If potassium hydroxide is used, there is only a 5-minute interval.
5. Since troublesome emulsions tend to form, it is advisable to avoid all vigorous shaking. If the mixture is stirred mechanically for 15 minutes, emulsions are avoided; if formed, they can be broken by treatment with anhydrous sodium sulfate.
6. The submitters have made runs twice this size; the yields were proportional to those given above.

### 3. Discussion

Cyclopropanecarboxylic acid has been prepared by the hydrolysis of cyclopropyl cyanide, although it is unnecessary to isolate the nitrile;<sup>2,3,4</sup> by heating cyclopropanedicarboxylic acid;<sup>5,6</sup> and by the action of alkali on ethyl  $\gamma$ -chlorobutyrate.<sup>7</sup> The last two methods do not appear to be of practical importance. The oxidation of cyclopropyl methyl ketone with sodium hypobromite is reported to be an excellent preparative method for this acid.<sup>8</sup>

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 5*, 126
- *Org. Syn. Coll. Vol. 7*, 117

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## References and Notes

1. *Org. Syntheses Coll. Vol. 1*, 156 (1941).
  2. Henry, *Bull. sci. acad. roy. Belg.*, (3) **36**, 34 (1898) (*Chem. Zentr.*, **1899**, I, 975).
  3. Kishner, *J. Russ. phys. chem. Ges.*, **37**, 304 (*Chem. Zentr.*, **1905**, I, 1703).
  4. Bruylants and Stassen, *Bull. sci. acad. roy. Belg.*, (5) **7**, 702 (1921) [*Chem. Zentr.*, **1922**, I, 1229; *C. A.*, **17**, 2872 (1923)].
  5. Perkin, *J. Chem. Soc.*, **47**, 815 (1885).
  6. Skraup and Binder, *Ber.*, **62**, 1132 (1929).
  7. Rambaud, *Bull. soc. chim. France*, (5) **5**, 1564 (1938).
  8. Jeffery and Vogel, *J. Chem. Soc.*, **1948**, 1804.
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Drierite

sulfuric acid (7664-93-9)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

potassium hydroxide (1310-58-3)

$\gamma$ -Chlorobutyronitrile (628-20-6)

sodium hypobromite

Cyclopropanecarboxylic acid (1759-53-1)

Cyclopropyl cyanide (5500-21-0)

cyclopropanedicarboxylic acid (598-10-7)

ethyl  $\gamma$ -chlorobutyrate (3153-36-4)

cyclopropyl methyl ketone (765-43-5)