



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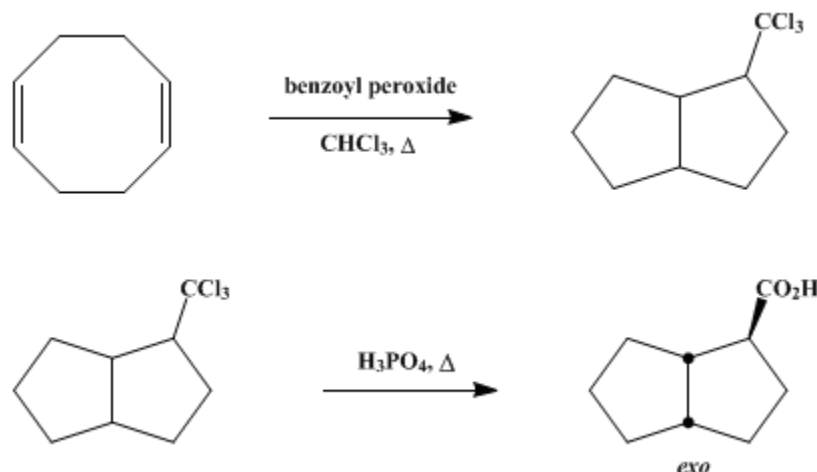
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## ***exo-cis*-BICYCLO[3.3.0]OCTANE-2-CARBOXYLIC ACID**

### **[1-Pentalenecarboxylic acid, octahydro-]**



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### **1. Procedure**

A. *2-(Trichloromethyl)bicyclo[3.3.0]octane*. To a 5-l. three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer are added 325 g. (3.0 moles) of *cis,cis*-1,5-cyclooctadiene (Note 1), 3 l. of chloroform (Note 2), and 14.6 g. (0.06 mole) of benzoyl peroxide. The resulting solution is stirred and refluxed (63–65°) on the steam bath (Note 3) for a total of 5 days. Four 7.3 g.-(0.03 mole-)portions of benzoyl peroxide are added, one on each consecutive day of reaction (Note 4). After a total of 5 days at reflux, the reaction mixture is cooled and washed with three 250-ml. portions of aqueous sodium bicarbonate (Note 5) and with 250 ml. of water, all the washes being discarded. The chloroform solution is dried with 30 g. of magnesium sulfate and filtered. The filtrate is distilled at atmospheric pressure using a short (8-in.) Vigreux column to collect 2760–2790 ml. of chloroform, b.p. 55–64°, which is discarded. The pressure is reduced and distillation continued to obtain two fractions: (1) b.p. 31° (47 mm.) to 65° (0.2 mm.), 300 g.; (2) b.p. 65–153° (0.2 mm.), 169 g. (Note 6). Fraction 2 is refractionated with the same Vigreux column to obtain 106–117 g. (approximately 35% based on unrecovered *cis,cis*-1,5-cyclooctadiene) of 2-(trichloromethyl)bicyclo[3.3.0]octane, b.p. 116–125° (5 mm.),  $n_D^{25}$  1.5110–1.5115 (Note 7). The product is pure (by gas chromatography) (Note 8) and may be used in the next step.

B. *exo-cis*-Bicyclo[3.3.0]octane-2-carboxylic acid. A mixture of 100 g. (0.440 mole) of 2-(trichloromethyl)bicyclo[3.3.0]octane and 500 ml. of 85% phosphoric acid is put into a 1-l. three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. The mixture is stirred and heated at 150° for 16 hours, during which time it evolves hydrogen chloride and darkens. The product is then allowed to cool and is poured into a separatory funnel. One liter of water is added and the resulting mixture is extracted with four 250-ml. portions of ether. The combined ether extract is then extracted with four 250-ml. portions of 2% aqueous sodium hydroxide (Note 9), and the resulting alkaline extract is washed with 100 ml. of ether to remove any neutral material (Note 10). The alkaline extract is acidified (to pH 2–3) with concentrated hydrochloric acid, and the oil which precipitates is extracted with three 250-ml. portions of ether. The resulting ether extract is dried with 15 g. of magnesium sulfate, filtered, and evaporated at 50° (30 mm.). The residue is then distilled at reduced pressure to obtain 29–32 g. (43–47%) of *exo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid, b.p. 91–96° (0.15 mm.),  $n_D^{25}$  1.4839–1.4847 (Note 11).

## 2. Notes

1. The compound was obtained from Cities Service Research and Development Co., Petrochemical Development Department, Sixty Wall Tower, New York 5, New York. Analysis by gas chromatography showed it to be pure, and it was used without further purification.
2. Either technical or pure grade [chloroform](#) may be used.
3. It may also be refluxed with boiling chips without stirring. A heating mantle may be used in place of a steam bath.
4. The portions of [peroxide](#) may be added as such or, more conveniently and safely, as solutions in 25 ml. of [chloroform](#) over a period of 10–15 minutes.
5. It is important that all [benzoic acid](#) be removed by washing at this point because otherwise it will codistil with the product and will be difficult to separate by distillation.
6. Fraction 1 is discarded. If desired, it may be redistilled at atmospheric pressure to obtain, in addition to [chloroform](#), 182 g. (1.68 moles) of [cis,cis-1,5-cyclooctadiene](#), b.p. 145–157°.
7. The higher-boiling fraction, b.p. 129° (5 mm.) to 138° (0.2 mm.), amounts to 35–50 g. and contains at least four compounds.
8. A 2-ft. column of 20% UCON Polar 50 HB 5100 on Chromosorb W, 130°, retention time 5¼ minutes.
9. Because of the high acidity of the [ether](#) extract it is more convenient to use [sodium hydroxide](#) than [sodium bicarbonate](#).
10. This [ether](#) wash may be combined with the main neutral fraction and distilled to obtain 29–30 g. (33–34%) of [2-\(dichloromethylene\)bicyclo\[3.3.0\]octane](#), b.p. 53–56° (0.1 mm.),  $n_D^{25}$  1.5179–1.5182 (pure by gas chromatography) (column as in [\(Note 8\)](#), 125°, retention time 4 minutes).
11. Analysis by gas chromatography shows the acid to be pure (column as in [\(Note 8\)](#)), retention time 4 ½ minutes at 175°.

## 3. Discussion

[exo-cis-Bicyclo\[3.3.0\]octane-2-carboxylic acid](#) has been prepared from [cis-bicyclo\[3.3.0\]-2-octanone cyanohydrin](#),<sup>2</sup> by Beckmann rearrangement of tetrahydro-*exo*-dicyclopentadiene-9-one oxime,<sup>3</sup> and by the present method.<sup>4</sup>

## 4. Merits of the Preparation

This two-step procedure appears to be by far the most convenient one for preparing [exo-cis-bicyclo\[3.3.0\]octane-2-carboxylic acid](#) from the readily available starting materials. The first step of the procedure is also illustrative of the method of obtaining 2-substituted bicyclo[3.3.0]octanes<sup>4,5</sup> from [cis,cis-1,5-cyclooctadiene](#).

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## References and Notes

1. Pittsburgh Plate Glass Co., Coatings and Resins Division, Springdale, Pa.
  2. A. C. Cope and M. Brown, *J. Am. Chem. Soc.*, **80**, 2859 (1958); R. Granger, P. Nau, and J. Nau, *Trav. Soc. Pharm. Montpellier*, **18**, 142 (1958) [*C. A.*, **53**, 1699 (1959)].
  3. T. H. Webb, Jr., Dissertation, Duke University, 1962.
  4. R. Dowbenko, *J. Am. Chem. Soc.*, **86**, 946 (1964); *Tetrahedron*, **20**, 1843 (1964).
  5. L. Friedman, *J. Am. Chem. Soc.*, **86**, 1885 (1964).
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## Appendix

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

tetrahydro-exo-dicyclopentadiene-9-one oxime

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

ether (60-29-7)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium bicarbonate (144-55-8)

Benzoic acid (65-85-0)

phosphoric acid (7664-38-2)

peroxide (7722-84-1)

benzoyl peroxide (94-36-0)

magnesium sulfate (7487-88-9)

1-Pentalenecarboxylic acid, octahydro-

2-(Trichloromethyl)bicyclo[3.3.0]octane (18127-07-6)

2-(dichloromethylene)bicyclo[3.3.0]octane

exo-cis-Bicyclo[3.3.0]octane-2-carboxylic acid (18209-43-3)

cis,cis-1,5-cyclooctadiene

cis-bicyclo[3.3.0]-2-octanone cyanohydrin