



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.

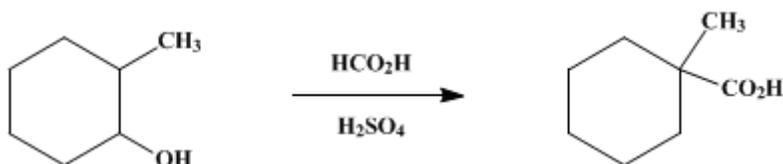
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.739 (1973); Vol. 46, p.72 (1966).*

## 1-METHYLCYCLOHEXANECARBOXYLIC ACID

[Cyclohexanecarboxylic acid, 1-methyl-]



Submitted by W. Haaf<sup>1</sup>

Checked by D. M. Gale and B. C. McKusick.

### 1. Procedure

*Caution! Because carbon monoxide is evolved, the reaction should be carried out in a good hood.*

Two hundred seventy milliliters (497 g., 4.86 moles) of 96% sulfuric acid (Note 1) is poured into a 1-l. three-necked flask equipped with a paddle stirrer driven by a powerful motor, a dropping funnel with a gas by-pass, and a thermometer that dips into the acid. The reaction mixture is stirred vigorously (Note 2) and maintained at 15–20° by means of a cooling bath as 3 ml. of 98–100% formic acid (Note 3) is added dropwise. Under the same conditions, a solution of 28.5 g. (0.25 mole) of 2-methylcyclohexanol (Note 4) in 46 g. (1.00 mole) of 98–100% formic acid is added in the course of 1 hour. The reaction mixture foams during the additions. The mixture, which is a very light cream color, is stirred for 1 hour at 15–20° and then is poured with stirring onto 1 kg. of crushed ice in a 4-l. beaker. The carboxylic acid separates as a white solid.

The acid is taken up in 200 ml. of hexane (Note 5), the hexane layer is separated, and the aqueous layer is extracted with two 150-ml. portions of hexane. The combined hexane solutions are extracted twice with a mixture of 175 ml. of 1.4*N* potassium hydroxide solution and 50 g. of crushed ice. The two alkaline solutions are combined and extracted with 100 ml. of hexane to remove traces of neutral oil, and then acidified to pH 2 with 12*N* hydrochloric acid (about 35 ml.). The liberated carboxylic acid is taken up in 150 ml. of hexane. The aqueous layer is extracted with 100 ml. of hexane, and the combined hexane layers are washed with 75 ml. of water and dried over 3 g. of anhydrous magnesium sulfate. The hexane is evaporated by warming the solution at 30–60° (15–30 mm.) overnight. The residue is 33–36 g. (93–101%) of colorless 1-methylcyclohexanecarboxylic acid, m.p. 34–36°, that is pure enough for most purposes. Distillation from a 100-ml. Claisen flask (Note 6) gives 31.5–33.5 g. (89–94%) of the acid, b.p. 132–140° (19 mm.), 79–81° (0.5 mm.); m.p. 38–39°.

### 2. Notes

- Three moles of 99–100% sulfuric acid may be used in place of the 96% sulfuric acid.
- With slow stirring there is a higher concentration of carbon monoxide and hence less rearrangement. For example, cyclohexanol in a slowly stirred reaction mixture gave 75% cyclohexanecarboxylic acid and 14% 1-methylcyclopentanecarboxylic acid; with rapid stirring the corresponding yields were 8% and 61%.<sup>2</sup>
- Technical grade 85% formic acid can be substituted for 98–100% formic acid if the decrease in sulfuric acid concentration that would result is compensated for by a suitable increase in the amount of sulfuric acid charged.
- The checkers used "*o*-Methylcyclohexanol," available from K & K Laboratories, Jamaica, New York. They redistilled it before use; b.p. 70–80° (20 mm.), *n*<sup>25</sup><sub>D</sub> 1.4617. 3- or 4-Methylcyclohexanol can be used in place of 2-methylcyclohexanol, or mixtures of the three can be used.
- Normal hexane, commercial grade, from the Phillips Petroleum Co., Bartlesville, Oklahoma, was used. Other organic solvents, such as benzene, are satisfactory.

6. The checkers used a 30-cm. spinning-band column for the distillation.

### 3. Discussion

1-Methylcyclohexanecarboxylic acid can be prepared by carbonation of the Grignard reagent from 1-chloro-1-methylcyclohexane<sup>3</sup> or by Friedel-Crafts condensation of 1-chloro-1-methylcyclohexane with methyl 2-furancarboxylate followed by saponification and oxidation.<sup>4</sup> It can also be prepared by successive hydrogenation and saponification of the Diels-Alder adduct from butadiene and methyl methacrylate,<sup>5</sup> by oxidation of 1-methyl-1-acetylcyclohexane with nitric acid<sup>6</sup> or sodium hypobromite,<sup>7</sup> and by the present method of synthesis.<sup>8</sup>

### 4. Merits of the Preparation

Carboxylation by formic acid is a rapid and simple method of preparing many tertiary carboxylic acids.<sup>8</sup> It can be applied to primary, secondary, and tertiary alcohols as well as to olefins and other compounds equivalent to the alcohols under the reaction conditions. The reaction often proceeds with rearrangement of the carbon skeleton. The scope of the reaction is indicated by Table I, which lists 13 alcohols to which the reaction has been applied.

TABLE I CARBONYLATION OF ALCOHOLS TO ACIDS

Alcohol		Acids Formed <sup>a</sup>	Yield of RCO <sub>2</sub> H, % <sub>b</sub>
1- or 2-Butanol	100	2-Methylbutyric acid	36 or 43
<i>t</i> -Butyl alcohol	95	Trimethylacetic acid	75
1- or 2-Pentanol	80	2,2-Dimethylbutyric acid	76 or 81
	20	C <sub>11</sub> acids	
2-Methyl-2-butanol	10	Trimethylacetic acid	73
	42	2,2-Dimethylbutyric acid	
	12	C <sub>7</sub> acids	
	36	C <sub>11</sub> acids	
2,3,3-Trimethyl-2-butanol	100	2,2,3,3-Tetramethylbutyric acid	88
2,2-Dimethyl-1-propanol	100	2,2-Dimethylbutyric acid	83
Cyclopentanol	63	Cyclopentanecarboxylic acid	26
	37	<i>cis</i> -9-Decalincarboxylic acid	
Cyclohexanol	80	1-Methylcyclopentanecarboxylic acid	78
	9	Cyclohexanecarboxylic acid	
	11	C <sub>13</sub> acids	
Cycloheptanol	100	1-Methylcyclohexanecarboxylic acid	91
2-Decalol	80	<i>cis</i> -9-Decalincarboxylic acid	95
	20	<i>trans</i> -9-Decalincarboxylic acid	
1-Hydroxyadamantane	100	1-Adamantanecarboxylic acid <sup>11,9</sup>	95

<sup>a</sup> The number before each acid is its volume percent in the mixture of carboxylic acids formed.

<sup>b</sup> Total yield of all carboxylic acids formed.

In a related reaction, saturated hydrocarbons with a tertiary hydrogen are carboxylated by a mixture of formic acid, *t*-butyl alcohol, and sulfuric acid.<sup>10,11</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 20

## References and Notes

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

3- or 4-Methylcyclohexanol

1- or 2-Butanol

1- or 2-Pentanol

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

carbon monoxide (630-08-0)

nitric acid (7697-37-2)

Cyclohexanol (108-93-0)

formic acid (64-18-6)

potassium hydroxide (1310-58-3)

2-Methylbutyric acid (600-07-7)

Cyclohexanecarboxylic acid (98-89-5)

Trimethylacetic acid (75-98-9)

sodium hypobromite

magnesium sulfate (7487-88-9)

butadiene (106-99-0)  
cyclopentanol (96-41-3)  
2-Methyl-2-butanol (75-85-4)  
hexane (110-54-3)  
2-methylcyclohexanol (583-59-5)  
t-butyl alcohol (75-65-0)  
cyclopentanecarboxylic acid (3400-45-1)  
1-Adamantanecarboxylic acid (828-51-3)  
1-Hydroxyadamantane (768-95-6)  
2,2-Dimethylbutyric acid (595-37-9)  
1-Methylcyclohexanecarboxylic acid,  
Cyclohexanecarboxylic acid, 1-methyl- (1123-25-7)  
1-methylcyclopentanecarboxylic acid (5217-05-0)  
1-chloro-1-methylcyclohexane (931-78-2)  
methyl 2-furancarboxylate (611-13-2)  
methyl methacrylate (80-62-6)  
1-methyl-1-acetylcyclohexane  
2,2,3,3-Tetramethylbutyric acid  
2,2-Dimethyl-1-propanol (75-84-3)  
Cycloheptanol (502-41-0)  
2-Decalol (825-51-4)  
cis-9-Decalincarboxylic acid  
trans-9-Decalincarboxylic acid  
2,3,3-Trimethyl-2-butanol