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.

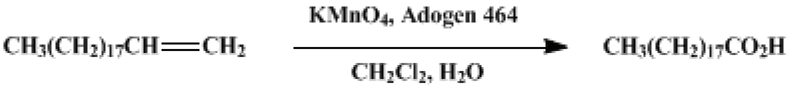
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

DOI:10.15227/orgsyn.060.0011

Organic Syntheses, Coll. Vol. 7, p.397 (1990); Vol. 60, p.11 (1981).

CARBOXYLIC ACIDS FROM THE OXIDATION OF TERMINAL ALKENES BY PERMANGANATE: NONADECANOIC ACID



$$CH_3(CH_2)_{17}CH{=}CH_2 \xrightarrow[CH_2Cl_2,\ H_2O]{KMnO_4,\ \text{Adogen 464}} CH_3(CH_2)_{17}CO_2H$$

Submitted by Donald G. Lee, Shannon E. Lamb, and Victor S. Chang[1].
Checked by Dennis P. Lorah and Andrew S. Kende.

1. Procedure

A 5-L, three-necked, round-bottomed flask fitted with a mechanical stirrer is placed in an ice bath and charged with 1000 mL of distilled water, 120 mL of 9 *M* sulfuric acid, 3.0 g of Adogen 464 (Note 1), 20 mL of glacial acetic acid, 1000 mL of methylene chloride, and 50 g of 1-eicosene (Note 2). The solution is rapidly stirred and 80 g (0.544 mol) of potassium permanganate is added in small portions over a 3-hr period (Note 3). Stirring is continued for an additional 18 hr at room temperature. The mixture is cooled in an ice bath, and 60 g of sodium bisulfite is added in small portions to reduce any precipitated manganese dioxide. The solution is acidified, if basic, with sulfuric acid and separated. The aqueous layer is extracted with two 400-mL portions of methylene chloride. The organic extracts are combined, washed with two 400-mL portions of water, washed once with brine, and concentrated to 400 mL on a rotary evaporator. The resulting mixture is heated to dissolve any precipitated product, a small amount of amorphous solid is removed by filtration, and the filtrate is cooled to 0°C. A first crop of white crystals (33–36 g, mp 67–68°C) is collected by suction filtration and washed with a minimum amount of ice-cold methylene chloride. Concentration of the mother liquor to 150 mL and cooling to 0°C yields a second crop of crystals (7–12 g). The combined products are dissolved, with heating, in 400 mL of methylene chloride and the pale-yellow solution is allowed to cool to room temperature, then *slowly* to −10°C. The white crystals (36–37 g) are collected, washed with a small amount of cold methylene chloride, and dried in vacuum overnight (mp 68–68.5°C, lit[2] 67–68°C). The yield is 75–77% (Note 4).

2. Notes

1. Adogen 464, a methyl trialkylammonium (C_8-C_{10}) chloride, was obtained from Ashland Chemical Co.
2. Technical 1-eicosene was obtained from the Aldrich Chemical Company, Inc. and used without further purification. Analysis by quantitative catalytic hydrogenation over Pd-C and NMR spectroscopy indicated that it contained about 10% unreactive, saturated hydrocarbon material.
3. Potassium permanganate was "Baker Analyzed" reagent. About 7.5 g was added every 15 min.
4. The yield was calculated by assuming that the starting material contained 90% 1-eicosene (see (Note 2)).

3. Discussion

Potassium permanganate is the preferred reagent for the oxidative cleavage of carbon-carbon double bonds.[3] Because of its low solubility in nonpolar solvents, however, the reactions have traditionally been carried out in polar organic solvent systems. For example, the use of aqueous *tert*-butyl alcohol[4] and acetic anhydride[5] for this purpose has been described. An alternative approach involves the use of phase-transfer agents to solubilize permanganate ion in organic solvents and several examples of this approach have been reported.[6] Although benzene has often been used as the solvent,[2] it has been observed that methylene chloride is a superior solvent[7]; better yields are obtained and because of its greater volatility it is more easily removed at the conclusion of the reaction. In addition, methylene chloride is more resistant to oxidation by solubilized permanganate. Adogen 464 was used as the phase-transfer agent because the yields compared well with those obtained when other agents[8] were used and because it is both inexpensive and readily available. The solutions were maintained acidic to neutralize hydroxide ions formed during the reduction of permanganate (MnO_4 + $2H_2O$ ρ MnO_2 + $4OH^-$). In the absence of acetic acid the accumulation of base promotes certain side reactions and increases the stickiness of the manganese(IV) oxides which precipitate as the reaction proceeds.

TABLE I

PHASE-TRANSFER-ASSISTED PERMANGANATE OXIDATIONS OF TERMINAL ALKENES

Alkene[a]	Product (Yield)[b]	Purification Method	mp or bp (°C)
1-Docosene	Heneicosanoic acid (84%)	Recrystallization (acetone)	72–74° (75°, 82°)[c]
1-Eicosene	Nonadecanoic acid(80%)	Recrystallization (methylene chloride)	68–68.5° (67–68°)[d]
1-Octadecene	Heptadecanoic acid (81%)	Recrystallization (pet. ether)	60–62° (60–61°)[e]
1-Hexadecene	Pentadecanoic acid (84%)	Recrystallization (ethanol-water)	52–53° (53°)[e]
1-Tetradecene	Tridecanoic acid (83%)	Recrystallization (acetone-water)	43–44° (44.5–45.5°)[e]
1-Decene	Nonanoic acid (92%)	Vacuum distillation	109–111°/2.4 mm (121°/4 mm)[e]
1-Octene	Heptanoic acid (70%)	Vacuum distillation	107–108°/7 mm (115–116°/11 mm)[e]
Styrene	Benzoic acid (96%)	Recrystallization (water)	121–122° (122°)[e]

[a] The alkenes were obtained from the Aldrich Chemical Company, Inc. Purity ranged from 99 to 87%.

[b] The purity of the starting material was taken into consideration in yield calculations.

[c] "Handbook of Chemistry and Physics," The Chemical Rubber Co., 52nd ed.

[d] 2.

[e] "Dictionary of Organic Compounds," Eyre and Spottiswoode, 4th ed.

The results obtained with a number of other representative terminal alkenes have been summarized in Table I.

References and Notes

1. Department of Chemistry, University of Regina, Regina, Canada S4S OA2.
2. Krapcho, A. P.; Larson, J. R.; Eldridge, J. M. *J. Org. Chem*. **1977**, *42*, 3749–3753.
3. Lee, D. G. In "Techniques and Applications in Organic Syntheses," Augustine, R. L., Ed.; Dekker: New York, 1969; Vol. 1, pp. 6–28.
4. ApSimon, J. W.; Chau, A. S. Y.; Craig, W. G.; Krehm, H. *Can. J. Chem*. **1967**, *45*, 1439–1445. In these reactions sodium metaperiodate was used as a cooxidant.
5. Sharpless, K. B.; Lauer, R. F.; Repic, O.; Teranishi, A. Y.; Williams, D. R. *J. Am. Chem. Soc*. **1971**, *93*, 3303–3304; Jensen, H. P.; Sharpless, K. B. *J. Org. Chem*. **1974**, *39*, 2314. These two

references describe oxidation of olefins to α-diketones.
6. Starks, C. M. *J. Am. Chem. Soc*. **1971**, *93*, 195–199; Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc*. **1972**, *94*, 4024–4025; Herriott, A. W.; Picker, D. *Tetrahedron Lett*. **1974**, 1511–1514.
7. Foglia, T. A.; Barr, P. A.; Malloy, A. J. *J. Am. Oil Chem. Soc*. **1977**, *54*, 858A; *Chem. Abstr*. **1978**, *88*, 37210m.
8. Lee, D. G.; Chang, V. S. *J. Org. Chem*. **1978**, *43*, 1532–1536.

Appendix

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

brine

Adogen 464

manganese(IV) oxides

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

acetic anhydride (108-24-7)

potassium permanganate (7722-64-7)

Benzoic acid (65-85-0)

sodium bisulfite (7631-90-5)

acetone (67-64-1)

manganese dioxide (1313-13-9)

methylene chloride (75-09-2)

styrene (100-42-5)

Tridecanoic acid (638-53-9)

Pentadecanoic acid (1002-84-2)

Heptanoic acid (111-14-8)

1-hexadecene (629-73-2)

Nonanoic acid (112-05-0)

tert-butyl alcohol (75-65-0)

1-octene (111-66-0)

1-octadecene (112-88-9)

1-decene (872-05-9)

Nonadecanoic acid (646-30-0)

1-eicosene (3452-07-1)

1-Docosene (1599-67-3)

1-Tetradecene (1120-36-1)

Heneicosanoic acid (2363-71-5)

Heptadecanoic acid (506-12-7)