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Received November 25, 1997;
in revised form March 17, 1998

The synthesis of menthone by ozonization of menthol

V. N. Odinokov, L. P. Botsman, and G. A. Emel'yanova*

Institute of Petrochemistry and Catalysis, Bashkortostan Republic Academy of Sciences
and Ufa Research Center of the Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750. E-mail: root@ink.ufanet.ru

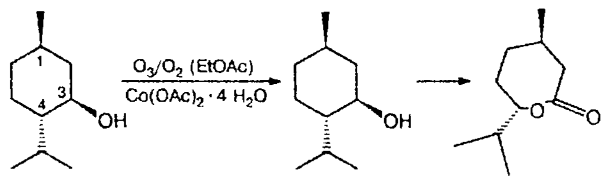
A selective method of oxidation of menthol to menthone by $Co(OAc)_2$-catalyzed ozonization in ethyl acetate or Freon-113 was developed.

Key words: menthol, oxidation, ozonization, catalyst, menthone, 3,7-dimethyl-6-octanolide.

In the synthesis of a series of optically active insect pheromones, oxidative decomposition of natural L-(−)-menthol has been carried out through the corresponding ketone obtained by oxidation of menthol with pyridinium chlorochromate.[1] At the same time, it is known that cyclic ketones can be obtained by aerobic oxidation of the corresponding cyclic alcohols, catalyzed by ruthenium and cobalt salts in the presence of acetaldehyde.[2] It is also known that the ozonolysis of arylsubstituted alicyclic compounds [3] or sulfides [4] in esters as solvents occurs selectively to yield expected stereoisomers of cycloaliphatic acids or, respectively, sulfoxides, while the ozonolysis of low-reactivity (with respect to electrophilic reagents) perfluoroolefins was successful in Freon-113 as a solvent.[5]

We found that the ozonization of racemic menthol (**1**) in EtOAc (5 mol-equiv. of O_3, ~25 °C) in the presence of a catalytic amount of $Co(OAc)_2 \cdot 4H_2O$ yields menthone (**2**) as a sole reaction product (according to GLC data). If the ozone—oxygen mixture is dosed so that a sevenfold molar excess of ozone is attained, not only is compound **2** formed, but also 3,7-dimethyl-6-octanolide (**3**) (*ca.* 10%) is detected in the reaction mixture. The identity of **3** to an authentic sample was determined by GLC.[6] When L-(−)-menthol **1a** was used instead of racemate **1**, (−)-(1*R*,4*S*)-menthone (**2a**) was obtained, which attests that the configuration at the C(1) and C(4) atoms is completely retained upon ozonization.

The ozonization of **1** in a solution of Freon-113 was carried out at a lower temperature because of high volatility of the Freon. When a fivefold excess of O_3 was passed through the reaction mixture at −30 to −40 °C, the conversion of alcohol **1** into ketone **2** reached 95%. The conversion of products **1** and **2** under the action of oxygen alone (without ozone) under the same conditions did not exceed 55%.



1, **1a** (1*R*,3*R*,4*S*) **2**, **2a** (1*R*,4*S*) **3**

Experimental

IR spectra were recorded on a Specord 75-IR spectrometer (thin film). The GLC analysis was performed on a Khrom-5 instrument with SE-30 silicon liquid (5%) as the stationary phase on Chromaton N-AW-DMCS (0.16—0.2 mm) at 50—250 °C (programmed temperature increase, 8 deg min^{-1}).

The ozonolysis of racemic menthol (1) or L-(−)-menthol (1a) in ethyl acetate. *A.* An ozone—oxygen mixture was passed at a rate of 10 L h^{-1} through a solution of **1** or **1a** (0.25 g, 1.6 mmol) and $Co(OAc)_2 \cdot 4\ H_2O$ (0.005 g) in 10 mL of EtOAc at 20 °C for 1 h (the ozonizer capacity was 8 mmol of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2077—2078, October, 1998.

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O_3 per hour). The reaction mixture was poured into 3 mL of a 1 *M* solution of $Na_2S_2O_3$ and extracted with Et_2O (3×10 mL). The extract was successively washed with 10% Na_2CO_3 and a saturated solution of NaCl, dried with $MgSO_4$, and evaporated to give **2** or **2a** (0.24 g, 97.2%), n_D^{20} 1.4504 (for **2a** $[\alpha]_D^{20}$ $-24.6°$ (liquid))[1] as individual compounds (GLC). IR, ν/cm^{-1}: 1700 (C=O).

B. An O_2/O_3 mixture was passed at a rate of 10 L h^{-1} through a solution of compound **1** (0.25 g) and $Co(OAc)_2 \cdot 4\ H_2O$ (0.005 g) in 10 mL of EtOAc at 20 °C for 1.5 h. The reaction mixture was then worked up as described in procedure *A*. The mixture containing product **2** (90%) and **3** (10%) (GLC analysis) was obtained in a total yield of 0.24 g. IR, ν/cm^{-1}: 1700 and 1715 (C=O).

The ozonolysis of menthol (1) in Freon-113. An O_2/O_3 mixture was passed at a rate of 10 L h^{-1} through a solution of compound **1** (0.25 g) and $Co(OAc)_2 \cdot 4\ H_2O$ (0.005 g) in 10 mL of Freon-113 at -30 to -40 °C for 1 h. Freon-113 was periodically added to maintain the initial volume. Then the reaction mixture was worked up as described above in procedure *A*. The mixture containing product **2** (95%) and the starting compound **1** (5%) (GLC analysis) was obtained in a total yield of 0.24 g. IR, ν/cm^{-1}: 1700 (C=O), 3350 br. (OH).

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Received December 11, 1997;
in revised form March 24, 1998

Homolytic cyclization of 1,3-propanedithiol to 1,2-dithiolane in the presence of 2,5-dimethyl-2,4-hexadiene

D. V. Demchuk and G. I. Nikishin*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: demchuk@ioc.ac.ru

2,2-Diethyl-1,3-propanedithiol undergoes cyclization to 4,4-diethyl-1,2-dithiolane upon interaction with 2,5-dimethyl-2,4-hexadiene in benzene in the presence of azodiisobutyronitrile. The reaction proceeds according to the radical chain mechanism.

Key words: 2,2-diethyl-1,3-propanedithiol, cyclization, radical chain mechanism, 4,4-diethyl-1,2-dithiolane.

Conversions of thiols to disulfides are of great importance in synthetic organic chemistry as well as in biochemistry. A great number of works was devoted to studies of these conversions.[1]

Disulfides are generally synthesized by oxidation reactions, which proceed under the action of various oxidizing agents (for example, molecular oxygen,[2] Cu^{II} salts in the presence of oxygen,[3] halogens,[4,5] hypohalides,[6] sodium perborate,[7] potassium ferrate,[8] *etc.*) on thiols. For this purpose, electrochemical oxidation was also successfully used.[9,10]

Under the action of oxidizing agents, 1,3- and 1,4-dithiols were converted to five-membered and six-membered cyclic disulfides (1,2-dithiolanes and 1,2-dithianes), respectively.[11]

As part of continuing studies of free-radical processes with the participation of thiols, in particular, of their addition at multiple carbon—carbon bonds,[12,13] in

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2078—2080, October, 1998.

1066-5285/98/4710-2022 $20.00