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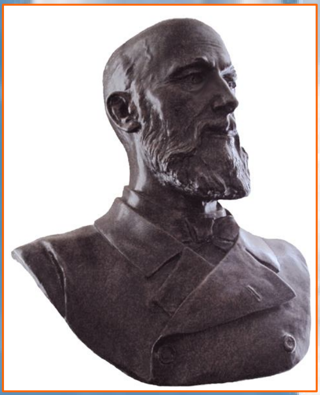

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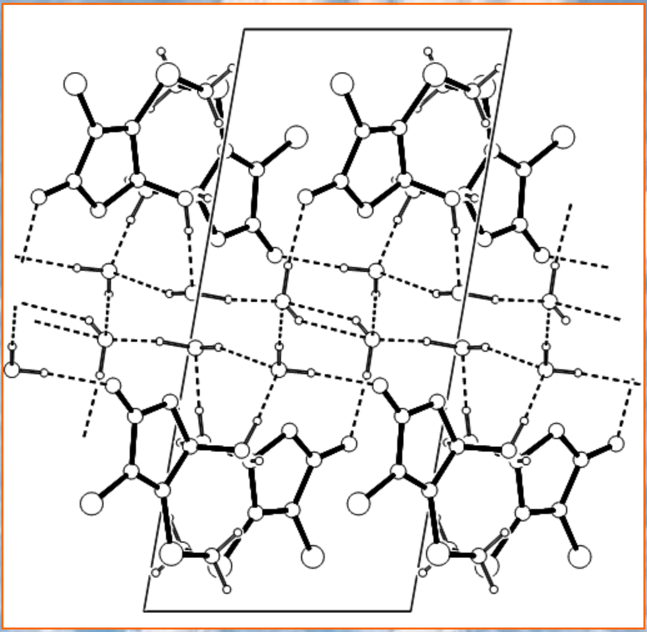

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Editorial address:
Bondarenko St., 33-44. Kazan, 420066. Republic of Tatarstan. Russia.

Contact Information:
Phone: +7 917 891 2622

E-mail: butlerov@mail.ru or journal.bc@gmail.ru
Internet: http://butlerov.com/

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Transformations of peroxide Δ^3-carene and (-)-α-pinene ozonolysis products by the action of hydrazine sulfate in isopropanol

© **Yulia V. Legostaeva**,[+] **Lilia R. Garifullina**, **Ivan S. Nazarov**, and **Gumer Yu. Ishmuratov***
Ufa Institute of Chemistry of RAS. Prospect Oktyabrya, 7. Ufa, 450054. Bashkortostan Republic. Russia.
Phone: +7 (347) 235-60-66. E-mail: insect@anrb.ru

*Supervising author; [+]Corresponding author

Key words: Δ^3-carene, (-)-α-pinene, peroxide ozonolysis products, hydrazine sulphate.

Abstract

The reactivity and chemoselectivity of the hydrazine sulfate as the new reagent in the transformations of peroxide ozonolysis products of cyclic monoterpenes (Δ^3-carene and (-)-α-pinene) in comparison with the known semicarbazide hydrochloride was studied. It is shown that the sulphate hydrazide derivative is less active, and also less selective reagent (with respect to the (-)-α-pinene) in the reaction with peroxidic products of the ozonolysis of Δ^3-carene and (-)-α-pinene in comparison with semicarbazide hydrochloride.

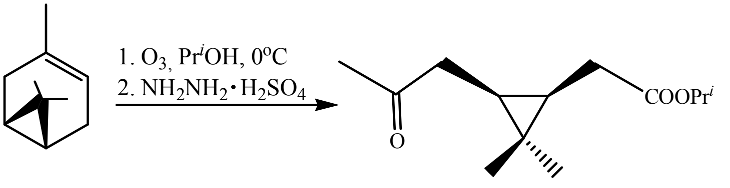
Introduction

Previously, we reported that hydrazine derivatives (2,4-dinitrophenylhydrazine and semicarbaside and thiosemicarbaside, semicarbaside and phenylhydrazine hydrochlorides) are reducing agents of structurally different peroxide olefin ozonolysis products to carbonyl compounds and their derivatives [1].

In continuation of the research, this paper presents the data on transformations of peroxide ozonolysis products of accessible natural monoterpenes (Δ^3-carene (**1**) and (-)-α-pinene (**2**)) in isopropanol under the action of hydrazine sulfate as a new reducing agent.

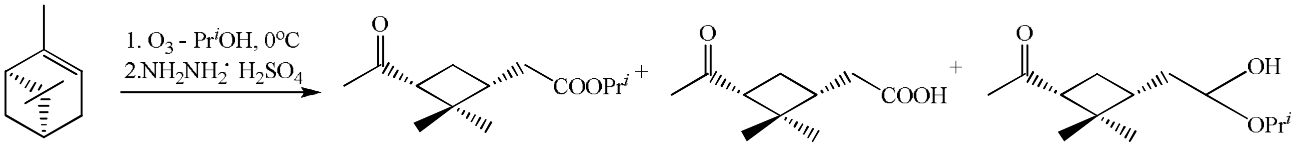
Results and discussion

It is revealed that intermediate peroxides with a high (83%) yield formed from cyclic olefin **1** become the only product, i.e. keto-isopropyl ether **3**, as in the case of semicarbaside hydrochloride we have previously used [2]. Note also the lower reactivity of hydrazine sulfate as compared to the latter compound: peroxides disappeared in the reaction mixture after 120 hours, not 48 hours.



1 **3**, 83%

Identical keto-isopropyl ether **4** was obtained as a major product (with a yield of 56%) after treating peroxide ozonolysis products of another cyclic alkene **2** within 144 hours. However, the reaction mixture was also observed to contain smaller amounts of other two compounds. These are keto acid **5** and keto semiacetal **6**. The former is obviously the product of acid hydrolysis of ether **4**. The latter is likely to be its precursor and transforms into it under the action of reduction products of the agent itself ($NH_2NH_2\cdot H_2SO_4$) with peroxide products of (-)-α-pinene ozonolysis (**2**).



2 **4**, 56% **5**, 20% **6**, 13%

Experimental part

Measurements were made using the equipment of the Chemistry Centre for Shared Use. The thin layer IR spectra were recorded using the *IR Prestige-21* (*Fourier Transform Spectrophotometer – Shimadzu*). The NMR spectra were recorded using the *Bruker AM-300* spectrometer [operating frequency 300 MHz and 500 MHz for ^{1}H and 75.47 MHz for ^{13}C] in $CDCl_3$ solution with the inner standard of TMS. The ^{13}C NMR spectra were detected in the JMOD regime. The GLC analyses were performed using the *Chrom-5* chromatograph [column length 1.2 m, silicon SE-30 (5%) as a stationary phase with the Chromaton N-AW-DMCS (0.16-0.20 mm), operating temperature 50-300 ºC] and *Chrom-41* chromatograph [column length 2.4 m, PEG-6000 as a stationary phase, operating temperature 50-200 ºC], with helium taken as a carrier gas. The TLC analysis was made with *Sorbfil* plates (Russia). For column chromatography we applied SiO_2 (70-230) from *Lancaster* (UK). The data on elemental analysis for all the compounds were consistent with those calculated earlier. The productivity of the ozonizer was 35 mmol O_3 per hour.

Treatment of peroxide terpene (**1**,**2**) **ozonolysis products with hydrazine sulfate**. The ozone-oxygen mixture was bubbled through a solution of 3.7 mmol olefin **1** or **2** in 25 ml *i*-PrOH at 0 ºC on the basis of 1 mol O_3 per 1 mol double bond. The reaction mixture was blown through argon. Under stirring at the same temperature, 1.70 g (13.1 mmol) of $NH_2NH_2 \cdot H_2SO_4$ was added, kept stirring at room temperature until peroxides disappeared (iodine test for starch), distilled from *i*-PrOH and the residue was dissolved with $CHCl_3$ (150 ml), washed with water (4x15 ml), dried with Na_2SO_4 and evaporated.

Ozonolysis of Δ^3-carene (1). The residue (1.0 g) was chromatographed (SiO_2, hexane/*tert*-butylmethyl ether, 10:1→1:1) and 0.69 g (83%) of keto isopropyl ether **3** was obtained.

Isopropyl[(1*R*,3*S*)-2,2-dimethyl-3-(2-oxopropyl)cyclopropyl]acetate (3). R_f 0.58 (hexane/*tert*-butylmethyl ether, 3:2), IR and ^{13}C NMR spectra were identical to those reported earlier [2].

Ozonolysis of (-)-α-pinene (2). The residue (1.1 g) was chromatographed (SiO_2, hexane/*tert*-butyl methyl ether, 10:1→1:1) and 0.46 g (56%) of keto isopropyl ether **4**, 0.13 g (20%) of keto acid **5** and 0.11 g (13%) of semiacetal **6** were obtained.

Isopropyl [(1*S*,3*S*)-3-acetyl-2,2-dimethylcyclobutyl]acetate (4). R_f 0.62 (hexane/*tert*-butylmethyl ether, 2:1), IR and ^{13}C NMR spectra were identical to those reported earlier [2].

(3-Acetyl-2,2-dimethylcyclobutyl acid (5). R_f 0.22 (hexane/*tert*-butyl methyl ether, 2:1), IR and ^{13}C NMR spectra were identical to those reported earlier [3].

1-[3-(2-Hydroxi-2-isopropoxiethyl)-2,2-dimethylcyclobutyl]ethanone (6). R_f 0.37 (hexane/*tert*-butylmethyl ether, 2:1).

The IR spectrum (KBr), ν, cm^{-1}: 1110 (C-O-C), 3392 (OH). The ^{1}H NMR spectrum, δ, ppm: 0.82 s ($C^{cis}H_3$), 1.23 d (6H, 2 CH_3), 1.32 s ($C^{trans}H_3$), 1.83-2.05 m (1H, C^4H_2), 2.08 s (3H, $CH_3C(O)$), 2.15 m (2H, $C\underline{H}_2CH$), 2.25-2,35 m (1H, C^1H), 2.90 m (1H, C^3H), 4.02 m (1H, $CH(CH_3)_2$), 4.9 m ($C\underline{H}OH$), 5.7 bs (OH).

The ^{13}C NMR spectrum, δ, ppm: 22.12 q (CH_3), 23.23 q (CH_3), 24.77 q ($2CH_3$), 29.98 t (C^4H_2), 30.16 q ($\underline{C}H_3C(O)$), 38.09 t (CH_2), 38.37 d (C^3H), 43.16 s (C^2), 53.79 d (C^1H), 67.54 d ($\underline{C}H(CH_3)_2$), 103.45 d ($\underline{C}H(OH)OCH(CH_3)_2$), 208.03 s (C=O).

Conclusions

Hydrazine sulfate is less active and in relation to (-)-α-pinene less selective agent regarding peroxide products of Δ^3-carene and (-)-α-pinene ozonolysis as compared to semicarbaside sulfate.

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Превращения пероксидных продуктов озонолиза Δ^3-карена и (-)-α-пинена при действии сернокислого гидразина в изопропаноле

© **Легостаева**[+] **Юлия Викторовна**, **Гарифуллина Лилия Рашидовна**,
Назаров Иван Сергеевич и **Ишмуратов*** **Гумер Юсупович**
Уфимский институт химии РАН. пр-т Октября, 71. г. Уфа, 450054. Республика Башкортостан. Россия. Тел.: +7 (8347) 235-58-01. E-mail: insect@anrb.ru

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*Ведущий направление; [+] Поддерживающий переписку

Ключевые слова: Δ^3-карен, (-)-α-пинен, пероксидные продукты озонолиза, сернокислый гидразин.

Аннотация

Исследована реакционная способность и хемоселективность сернокислого гидразина как нового реагента в превращениях пероксидных продуктов озонолиза циклических монотерпенов (Δ^3-карена и (-)-α-пинена) в сравнении с известным гидрохлоридом семикарбазида. Показано, что сернокислое производное гидразина является менее активным, а в отношении к (-)-α-пинену в меньшей степени селективным реагентом в реакции с пероксидными продуктами озонолиза Δ^3-карена и (-)-α-пинена по сравнению с гидрохлоридом семикарбазида.