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# Isolation of Ozonides from Gas-Phase Ozonolyses of Terpenes

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Ozonolyses of (–)- $\beta$ -pinene (**1**) and of (+)-sabinene (**6**) in the gas phase afforded the corresponding ozonides 6,6-dimethylbicyclo[3.1.1<sup>1.5</sup>]heptane[2-spiro-3]-1,2,4-trioxolane (**2**) and 5-isopropylbicyclo[3.1.0<sup>1.5</sup>]hexane[2-spiro-3]-1,2,4-trioxolane (**7**), which were isolated as mixtures of two diastereomers each. Major products were the corresponding ketones 6,6-dimethyl-2-oxobicyclo[3.1.1<sup>1.5</sup>]heptane (**3**) and 5-isopropyl-2-oxobicyclo[3.1.0<sup>1.5</sup>]hexane (**8**). Additional products were the lactones 7,7-dimethyl-2-oxa-3-oxobicyclo[4.1.1<sup>1.6</sup>]octane (**4**) and 7,7-dimethyl-3-oxa-2-oxobicyclo[4.1.1<sup>1.6</sup>]octane (**5**) derived from  $\beta$ -pinene (**1**) as well as 6-isopropyl-2-oxa-3-oxobicyclo[4.1.0<sup>1.6</sup>]heptane (**9**) and 6-isopropyl-3-oxa-2-oxobicyclo[4.1.0<sup>1.6</sup>]heptane (**10**) derived from sabinene (**6**).

## Introduction

Gas-phase ozonolyses of olefins is an area of active research, particularly with respect to atmospheric ozone chemistry (*1*). Compared with the great number of publications in this field, there are only very few reports about the formation of ozonides, and they have been only detected in ozonolysis reactions of small olefins or in co-ozonolyses of small olefins and added small carbonyl compounds (*2–5*). Identifications of these ozonides were based either on long-path FTIR analysis by computational subtraction of contributions of other components to the spectrum (*2–4*) or by GC/MS analysis (*5*), yet not by isolation and the usual methods of characterization.

Among the olefins examined in gas-phase ozonolyses, terpenes are the most prominent class of compounds, since they are emitted from coniferous trees (*6*) at an estimated global rate of  $10^8$  t/a (*7*). In particular, gas-phase ozonolyses of  $\beta$ -pinene (**1**) (*8–18*) and of sabinene (**6**) (*8, 9, 13, 19*) have been studied by a number of groups, but none of them reported the detection of ozonides. Recently, we have ozonized **1** and **6** in the liquid phase, and we have isolated two diastereomers each of the corresponding stable ozonides **2** and **7** (*20*). With the help of these authentic samples, which exhibit characteristic <sup>1</sup>H NMR signals for the CH<sub>2</sub> groups, we have now tried to find out whether such ozonides are present in the crude products from gas-phase ozonolyses of **1** and **6**.

## Experimental Section

All reagents and solvents were of commercial grade. <sup>1</sup>H NMR spectra were obtained in CDCl<sub>3</sub> with TMS as internal reference on a Bruker AC 250 instrument. GC analyses were carried out on a Hewlett-Packard 5890 instrument using the following conditions: 50 m capillary column SE 54, 50–200 °C at 10 °C/min.

**Ozonolysis Procedure.** A 6-L two-neck round-bottom flask, equipped with a septum and a connection to a vacuum line was evacuated to 10<sup>–2</sup> Torr at room temperature. The vacuum line was closed, the liquid substrate was injected with a syringe, and after ca. 30 min a O<sub>3</sub>/O<sub>2</sub> mixture containing 1 mmol of O<sub>3</sub>/L was slowly injected within 1 min with a gas syringe. After a reaction time of ca. 10 min, the flask was cooled in an ice–water bath, filled with nitrogen, opened, and rinsed with ether. From the combined ether solutions of several runs, ether was distilled off at room temperature and reduced pressure, and the remaining residue was separated by flash chromatography on silica gel.

**Ozonolysis of (–)- $\beta$ -Pinene (**1**).** Treatment of 20 mg (0.15 mmol) of **1** with 120 mL of a O<sub>3</sub>/O<sub>2</sub> mixture (containing 0.12 mmol of O<sub>3</sub>) and workup as described above was repeated 10 times. From the residue, a mixture of **2a** and **2b** as well as **3–5** have been isolated (solvent: pentane/ether, 4:1) in amounts sufficient to get NMR spectra. GC analysis of the residue showed the presence of **2–5** in the ratios reported.

**6,6-Dimethylbicyclo[3.1.1<sup>1.5</sup>]heptane[2-spiro-3]-1,2,4-trioxolanes (**2a** and **2b**).** <sup>1</sup>H NMR: **2a**  $\delta$  0.93 (s, CH<sub>3</sub>), 1.23 (s, CH<sub>3</sub>), 5.00 (s, OCH<sub>2</sub>OO), 5.07 (s, OCH<sub>2</sub>OO); **2b** (*2f*)  $\delta$  0.99 (s, CH<sub>3</sub>), 1.25 (s, CH<sub>3</sub>), 5.03 (s, OCH<sub>2</sub>OO), 5.17 (s, OCH<sub>2</sub>OO); the intensity ratio of the signals for **2a** and **2b** was 10:1. GC *t<sub>R</sub>* = 22.4 min for **2a** + **2b**. Treatment of the above mixture with an excess of TPP in CDCl<sub>3</sub> gave **3**, as shown by <sup>1</sup>H NMR spectroscopy.

**6,6-Dimethyl-2-oxobicyclo[3.1.1<sup>1.5</sup>]heptane (**3**).** <sup>1</sup>H NMR:  $\delta$  0.85 (s, 3H), 1.30 (s, 3H), 1.54 (d, 1H), 1.85–2.63 (m, 7H); GC *t<sub>R</sub>* = 22.1 min.

**7,7-Dimethyl-2-oxa-3-oxobicyclo[4.1.1<sup>1.6</sup>]octane (**4**).** <sup>1</sup>H NMR:  $\delta$  0.89 (s, 3H), 1.30 (s, 3H), 1.83–2.02 (m, 2H), 2.11 (d, *J* = 14.09 Hz, 1H), 2.25–2.31 (m, 1H), 2.60–2.70 (m, 1H), 2.86–2.94 (m, 2H), 4.33 (dd, *J* = 5.77 and 4.86 Hz, 1H); <sup>13</sup>C NMR:  $\delta$  18.41, 22.19, 26.49, 27.35, 34.02, 41.23, 43.18, 84.08, 174.86; GC *t<sub>R</sub>* = 28.4 min.

**7,7-Dimethyl-3-oxa-2-oxobicyclo[4.1.1<sup>1.6</sup>]octane (**5**).** <sup>1</sup>H NMR:  $\delta$  1.04 (s, 3H), 1.39 (s, 3H), 1.82–1.94 (m, 1H), 2.22–2.35 (m, 2H), 2.40–2.53 (m, 2H), 2.91–2.97 (m, 1H), 4.27–4.35 (m, 1H), 4.70 (dt, *J* = 13.09 and 3.58 Hz, 1H); <sup>13</sup>C NMR:  $\delta$  19.79, 20.68, 27.57, 28.48, 40.42, 41.00, 53.34, 66.19, 174.32; GC *t<sub>R</sub>* = 28.8 min.

**Ozonolysis of (+)-Sabinene (**6**).** Treatment of 42 mg (0.31 mmol) of **6** with 250 mL of a O<sub>3</sub>/O<sub>2</sub> mixture (containing 0.25 mmol of O<sub>3</sub>) and workup as described above was repeated 12 times. From the residue, a mixture of **7a** and **7b** as well as **8–10** have been isolated (solvent: petroleum/ether, 95:5) in amounts sufficient to get NMR spectra. GC analysis of the residue showed the presence of **7–10** in the ratios reported.

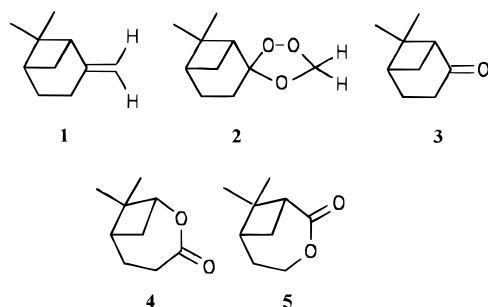
**5-Isopropylbicyclo[3.1.0<sup>1.5</sup>]hexane[2-spiro-3]-1,2,4-trioxolanes (**7a** and **7b**).** <sup>1</sup>H NMR: **7a**  $\delta$  5.07 (s), 5.24 (s); **7b**  $\delta$  5.07 (s), 5.15 (s); from the intensities of the signals at  $\delta$  5.24 and  $\delta$  5.07, a ratio of 2:3 has been calculated. GC *t<sub>R</sub>* = 23.1 min. Treatment of the above mixture with TPP in CDCl<sub>3</sub> gave **8**, as shown by <sup>1</sup>H NMR spectroscopy.

**5-Isopropyl-2-oxobicyclo[3.1.0<sup>1.5</sup>]hexane (**8**).** <sup>1</sup>H NMR:  $\delta$  0.93 (d, *J* = 6.72 Hz, 3H), 0.99 (d, *J* = 6.80 Hz, 3H), 1.05–1.10

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## CHART 1



(m, 1H), 1.16–1.20 (m, 1H), 1.51–1.68 (m, 2H), 1.94–2.21 (m, 4H); GC  $t_R$  = 22.7 min.

**6-Isopropyl-2-oxa-3-oxobicyclo[4.1.0]heptane (9).**  $^1\text{H}$  NMR:  $\delta$  0.78 (t,  $J$  = 6.80 Hz, 1H), 0.92 (d,  $J$  = 6.42 Hz, 3H), 1.01 (d,  $J$  = 6.05 Hz, 3H), 0.85–1.20 (m), 1.69–1.80 (m, 1H), 2.07–2.48 (m, 3H), 3.82 (dd,  $J$  = 6.70 and 2.83 Hz, 1H);  $^{13}\text{C}$  NMR:  $\delta$  17.87, 18.81, 18.82, 21.81, 23.99, 28.68, 34.15, 61.10, 171.10; GC  $t_R$  = 27.7 min.

**6-Isopropyl-3-oxa-2-oxobicyclo[4.1.0]heptane (10).**  $^1\text{H}$  NMR:  $\delta$  1.01 (m, 6H), 0.83–1.31 (m, 2H), 1.60 (t,  $J$  = 4.25 Hz, 1H), 1.69 (dd,  $J$  = 12.50 and 3.68 Hz, 1H), 4.28 (ddd,  $J$  = 12.03, 6.17 and 1.50 Hz, 1H);  $^{13}\text{C}$  NMR:  $\delta$  14.77, 18.84, 18.93, 20.76, 22.96, 30.88, 35.08, 64.40, 171.56; GC  $t_R$  = 29.9 min.

## Results

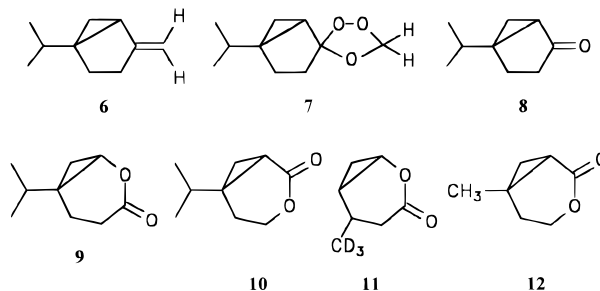
Ozonolysis of **1** was carried out in the gas phase at room temperature at a total pressure of 15.7 Torr and at a partial pressure of 0.42 Torr for **1** and of 0.35 Torr for ozone. From the reaction product, we have isolated a 10:1 mixture of the two diastereomers of ozonide **2**, designated **2a** and **2b**, as well as ketone **3** and the lactones **4** and **5**. GC analysis of the crude reaction mixture revealed the following product distribution (22): 1% of **2**, 55% of **3**, 24% of **4**, and 20% of **5**. In addition,  $^1\text{H}$  NMR analysis showed the presence of small amounts each of formaldehyde ( $\delta$  = 9.67), formic acid ( $\delta$  = 8.05), and unreacted **1** ( $\delta$  = 4.62 and 4.63, =CH<sub>2</sub>).

Ozonides **2a** and **2b** have been assigned based on the identity of the  $^1\text{H}$  NMR signals of the CH<sub>3</sub> groups and of the CH<sub>2</sub> groups at the ozonide rings (23) with those of the authentic samples (20) and by reduction of the mixture of **2a** and **2b** with triphenyl phosphine (TPP) to give the expected ketone **3**. Compound **3** was assigned based on the identity of its  $^1\text{H}$  NMR data with those of an authentic sample (20), while **4** (24) and **5** (25) have been assigned based on the identities of their  $^1\text{H}$  NMR data with those published and additionally based on their  $^{13}\text{C}$  NMR spectra (Chart 1).

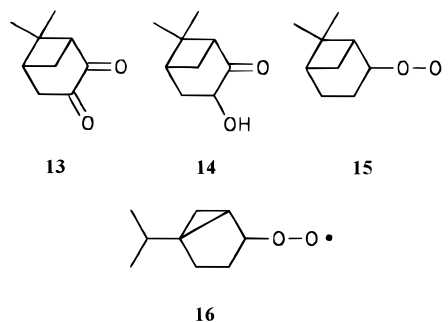
Ozonolysis of **6** was carried out in the gas phase at room temperature at a total pressure of 32.6 Torr and at partial pressures of 0.88 Torr for **6** and of 0.71 Torr for ozone. From the reaction product, we have isolated a 2:3 mixture of the two diastereomers of **7**, designated **7a** and **7b**, as well as ketone **8** and lactones **9** and **10**. The product distribution (22) in the crude reaction mixture was 1% of **7**, 58% of **8**, 13% of **9**, and 28% of **10** according to GC analysis. The  $^1\text{H}$  NMR data for the CH<sub>2</sub> groups in the ozonides **7a** and **7b** were identical with those of the authentic samples (20), and reduction of the mixture of **7a** and **7b** gave ketone **8**. The  $^1\text{H}$  NMR data of **8** were identical with those published (20). Lactone **9** was assigned based on the similarity of its  $^1\text{H}$  and  $^{13}\text{C}$  NMR data with those of respective structural units of the known lactone **11** (25). Similarly, lactone **10** was assigned by analogy of respective  $^1\text{H}$  and  $^{13}\text{C}$  NMR data with those of lactone **12** (26) (Chart 2).

The results obtained in this study differ both from those obtained in ozonolyses of **1** and **6** in solution (20)—which gave predominantly the corresponding ozonides **2** and **7**—and

## CHART 2



## CHART 3



in the gas phase. The latter reactions have been reported to give formaldehyde and the corresponding ketones **3** (8, 27–29) and **8** (8) as the predominant organic products. In the gas-phase ozonolysis of **1**, additional organic products have been assigned structures **13** and **14** by some authors (30, 31), whereas others described them as “unidentified carbonyl products” (29) or “neutral” products (27).

The products that we obtained in addition to **3** or **8**, viz., the ozonides **2** and **7**, and the lactones **4**, **5**, **9**, and **10** can be explained by cleavage of the substrates **1** and **6** to give the carbonyl oxide intermediates **15** and **16**, respectively. In the ozonolysis of **1** in solution, this direction of cleavage had indeed been verified by the formation of a cross-ozonide in the presence of acetaldehyde (20). Reactions of **15** or **16** with formaldehyde afford ozonides **2** and **7**, respectively, while intramolecular Baeyer–Villiger type reactions of **15** and **16** give the corresponding lactones **4** + **5** and **9** + **10**, respectively (Chart 3).

To our knowledge, the present paper describes the first isolation and subsequent unequivocal structural assignment of ozonides derived from gas-phase ozonolyses of olefins. Furthermore, it is the first time that ozonides have been shown to be formed in the gas-phase ozonolysis of terpenes.

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