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Ozonides of Mono-, Bi- and Tricyclic Terpenes

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Abstract: Ozonolysis of (+)-limonene (**1**) afforded a monoozonide **2** by attack of ozone at the internal double bond and two diastereomeric diozonides (**3**). Ozonolysis of **1** on polyethylene gave diozonides **3**, and ozonolysis on silica gel gave an epoxy ozonide **5**. Ozonolyses of (-)-β-pinene (**15**), (+)-sabinene (**20**) and (+)-aromadendrene (**23**) gave two diastereomers, each, of the corresponding ozonides **16**, **21** and **24**, respectively. Ozonolysis of camphene (**26**) gave a very labile ozonide **27**, while ozonolysis of (-)-α-pinene (**12**) gave no ozonide. Ozonolysis of (+)-limonene (**1**) in the presence of formaldehyde gave a cross-ozonide (**4**), derived from ozone cleavage of the internal double bond, and ozonolysis of (-)-β-pinene in the presence of acetaldehyde also gave a cross-ozonide (**17**). Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Ozonolyses of terpenes have been studied under a variety of conditions and aspects. Early work was devoted to ozonolysis reactions of terpenes in solution. They were geared at structural elucidations, at the identification of peroxidic ozonolysis products and at the elucidation of the reaction course, particularly in the case of anomalous ozonolysis reactions.[1] In recent years, however, interest in this field has shifted to gas phase reactions in connection with the problems associated with the atmospheric ozone chemistry of such types of terpenes which are emitted from coniferous trees.[2] In particular, gas phase reactions of ozone with camphene[3-6], limonene[3,4,7-16], α-pinene[3,4,10-14,16,17-20], β-pinene[3,4,8,10-15,17,18,20] and sabinene[3-5,13] have been studied extensively. Major organic reaction products were carbonyl compounds, which are derived from ozone cleavage of the double bonds in the respective terpenes, whereas the formation of ozonides has not been reported. This is in line with the results of gas phase ozonolyses of a series of non-terpenoid olefins, for which ozonides have only been reported in a few cases.[21] This could have several reasons: Either ozonides are not formed, as it has been postulated based on modified Criegee-mechanisms proposed for gas phase ozone-olefin reactions[22,23], or ozonides may not be detected by the analytical methods which are commonly used in gas phase reactions such as long-path FTIR spectroscopy[21,24], in which ozonides show no diagnostic bands, or GC[6] and MS analysis[23], which may lead to the premature decomposition of ozonides.

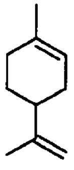
Recently, we became interested in this aspect of gas phase ozonolysis of olefins, and in particular of terpenes, and we would like to answer the question of ozonide formation by more reliable analytical methods. As such, ^{13}C NMR appears to be quite suitable, since ozonides show signals in the range of ca. 100 - 120 ppm for the carbon atoms in the 1,2,4-trioxolane rings. Hence, collected samples of products from ozonolyses of terpenes in the gas phase are to be analyzed by ^{13}C NMR spectroscopy and the presence of ozonides is planned to be verified with the help of authentic samples. To this end, we have now tried to prepare ozonides of the monocyclic terpene limonene (**1**), the bicyclic terpenes α-pinene (**12**), β-pinene (**15**), sabinene (**20**) and camphene (**26**), as well as the tricyclic terpene aromadendrene (**23**).

RESULTS AND DISCUSSION

Treatment of (+)-limonene (**1**) with one molar equivalent of ozone in pentane at -45 °C afforded ozonide **2**, two diastereomers of diozonide **3**, denoted **3a** and **3b**, and ozonide **4**, along with intractable peroxidic products, probably oligomeric ozonides. Treatment of **1** with two molar equivalents of ozone in pentane at -45 °C, as well as ozonolysis of **1** on polyethylene at -45 °C, gave the two diastereomers of **3** as the sole monomeric ozonides, along with oligomeric products. Treatment of **1** on silica gel at -38 °C gave four stereoisomers of epoxy-ozonide **5**, denoted **5a** - **5d**, as well as epoxy-ketone **6** and unidentified products. Individual ozonolyses of cis-**7** and of trans-**7** in pentane at -35 °C, gave in each case two stereoisomeric epoxy-ozonides of structure **5**.

Ozonides **2** and **4**, as well as all diastereomers of ozonides **3** and **5**, have been individually isolated. They are stable at room temperature and their structures have been proven by correct elemental analyses, their ^{1}H and ^{13}C NMR spectra and the formation of the expected products upon their reduction with excess triphenylphosphine (TPP), *viz.* **6** from **5**, **8** from **2** and from **4**, and **9** from **3**. In addition, reduction of diozonide **3** with only one molar equivalent of TPP gave ozonide **10**, which was also isolated, characterized and subsequently reduced with TPP to give **9**. The stereochemical identities of **3a**, **3b**, **5a**, **5b**, **5c** and **5d** have not been elucidated.

The fact that there was no monoozonide in which the exocyclic double bond of **1** was selectively ozonized, indicated that, as it had been reported previously[25,26], the reaction of ozone with the internal double bond of **1** is preferred. Furthermore, the formation of ozonide **4** in the ozonolysis of **1** suggests that, as expected, the direction of cleavage of the internal double bond of **1** is such, that the more highly substituted of the two possible carbonyl oxides, *viz.* **11** is formed, and that the latter undergoes cycloaddition with part of the reactive dipolarophile formaldehyde, which is formed by ozone cleavage of the external double bond of **1**. In line with this postulate, ozonolysis of **1** in CH_2Cl_2 and in the presence of added formaldehyde gave ca. 50% of ozonide **4**, as opposed to only ca. 7% in the absence of added formaldehyde.



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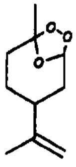

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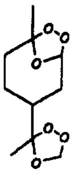

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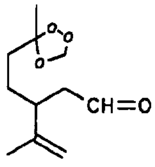

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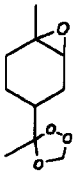

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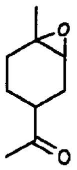

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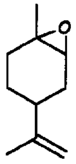

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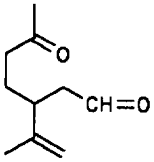

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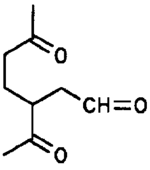

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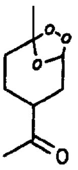

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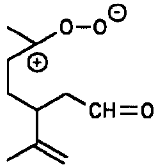

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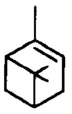
Independent of the technique applied, all ozonolyses of **1** afforded low yields of the corresponding ozonides **2** - **5**. This is in line with the experience gained in the ozonolysis of other 1-substituted cyclohexenes: 1-methylcyclohexene gave 5%[27] and 1-phenylcyclohexene gave none of the corresponding ozonide[28], but rather large proportions of oligomeric ozonides.

Ozonolysis reactions of (-)-α-pinene (**12**) fell in line with the above trend. Ozonolysis of **12** in pentane at -35 °C gave minor amounts of **13**, **14a** and **14b** and major amounts of a peroxidic precipitate, to the exclusion of the monomeric ozonide of **12**. Reduction of the peroxidic precipitate with TPP gave **14a** as the major, and **14b** as the minor product, thus indicating that the precipitate was an oligomeric ozonide. Ozonolysis of **12** on polyethylene at -78 °C gave a non-peroxidic crude product, which contained **13**, **14a** and **14b**, along with unreacted **12**. The lack of formation of an ozonide of **12** is probably due to steric hindrance, caused by the geminal methyl groups.



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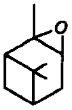

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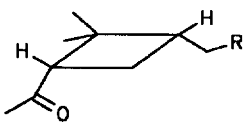

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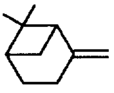
a: R= CH=O
b: R= COOH

Ozonolysis of (-)-β-pinene (**15**) should a priori lead to two diastereomeric ozonides of structure **16**. According to two previous reports, however, only one ozonide was obtained from the ozonolysis of **15** in solution.[28,29] This was confirmed by our results: ozonolysis of **15** in pentane at -40 °C produced only one ozonide in a yield of 83%. By contrast, ozonolysis of **15** on polyethylene at -40 °C gave two isomeric ozonides denoted **16a** and **16b** in a combined yield of 70% and in a ratio of 3.2:1. The major ozonide **16a** was identical with that obtained in pentane and - on the basis of the published ^{1}H NMR data[28,29] - with that obtained previously.

Ozonides **16a** and **16b** were individually isolated and characterized by correct elemental analyses, their ^{1}H, ^{13}C and ^{17}O NMR spectra and by reduction to give **18**. The stereochemical identities of **16a** and of **16b** have not been elucidated. The neat ozonides **16a** and **16b** were stable for months when kept at -30 °C, whereas they decomposed within 24 hours in $CDCl_3$ at room temperature and within ca. 30 hours in C_6D_6 at 40 °C to give a mixture of **18** and formic acid.

The high yield in which ozonide **16a** was formed in pentane suggested that **15** was cleaved to give carbonyl oxide **19**, which was effectively trapped by the complementary fragment formaldehyde, a known potent dipolarophile. However, an attempt to prove this by trapping **19** with acetone failed: ozonolysis of **15** in acetone gave **16a** in a yield of 92%, yet not the anticipated cross-ozonide. By contrast, ozonolysis of **15** in the better dipolarophile acetaldehyde as solvent provided two stereoisomeric cross-ozonides denoted **17a** and **17b** and ozonide **16a** in a molar ratio of 3:1.3:1. While this mixture could not be separated by chromatographic means, selective reduction of the more reactive ozonide **16a** and subsequent chromatographic separation provided a 2.3:1-mixture of ozonides **17a** and **17b**, which were not individually isolated or stereochemically assigned. Reduction of **17a** + **17b** with TPP gave **18** and acetaldehyde as expected.

The exclusive formation of ozonide **16a** in pentane and in acetone is probably due to steric effects, which the $C(CH_3)_2$ bridge in carbonyl oxide **19** exerts upon the mode of cycloaddition of **19** with formaldehyde. It is assumed that formaldehyde approaches **19** from the unhindered side, *i.e.* opposite from the $C(CH_3)_2$ bridge. The fact, that ozonolysis of **15** on polyethylene provided both **16a** and **16b** may be attributed to the restricted mobility of the fragments **19** and formaldehyde and, hence, to the forced partial addition of formaldehyde from the hindered side of **19**.



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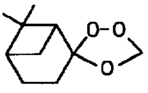

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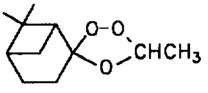

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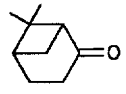

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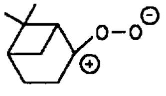

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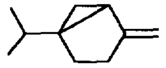
In contrast to (-)-β-pinene, both (+)-sabinene (**20**) and (+)-aromadendrene (**23**) gave two diastereomeric ozonides upon ozonolysis in pentane. The ozonides of sabinene, denoted **21a** and **21b** were obtained in a combined yield of 95% and in a ratio of 1:1. The ozonides of aromadendrene, denoted **24a** and **24b**, were obtained in a combined yield of 99% and in a ratio of 1.5:1. All of the isomers have been individually isolated and structurally assigned based on correct elemental analyses, on their ^{1}H, ^{13}C and ^{17}O NMR spectra and on their reduction to give **22** and **25**, respectively. Their stereochemical identity has not been elucidated.



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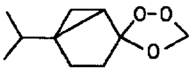

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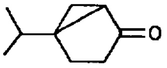

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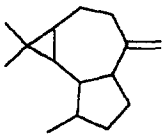

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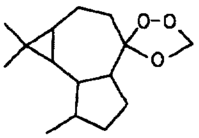

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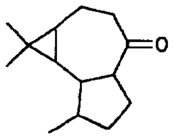

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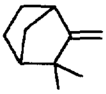
Ozonolysis reactions of camphene (**26**) have thus far failed to afford the corresponding ozonide **27**.[1,29] However, from the anomalous products obtained like **29**[1] and **30**[29], it was inferred that such reactions "undoubtedly involve the highly unstable ozonide **27**[1]". In the present work, ozonolysis of camphene in pentane at -40 °C afforded indeed an ozonide of structure **27**, as evidenced by low temperature ^{1}H and ^{13}C NMR analysis of the crude reaction product. Attempts to isolate **27** failed, however, since it decomposed at temperatures above -20 °C to give **28** and **29** in a ratio of ca. 1:7, along with minor amounts of **30**. Reduction of the crude ozonide **27** with TPP also produced **28** and **29**, but in a different ratio of ca. 1:1.4, again along with minor amounts of **30**. This indicates that the decomposition reaction of **27** to give **29** competes with the reduction of **27** which yields **28**.



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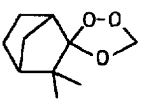

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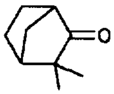

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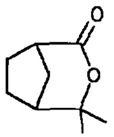

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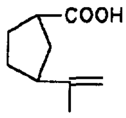

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EXPERIMENTAL

All reagents used were of commercial grade. NMR spectra were recorded on a Bruker AC 250 instrument. Unless mentioned otherwise, ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ with TMS as internal reference, and ^{17}O NMR spectra were recorded by a published procedure[30] in C_6D_6 with H_2O as external reference. Assignments of C atoms in the ^{13}C NMR spectra are based on the results of CW and DEPT spectra. GC analyses were carried out on a Hewlett Packard 5890 instrument using the following conditions: 50 m capillary column HP Ultra 2, 50 - 180 °C at 7 °C/min. GC/MS: Hewlett Packard system 5985 B and the same GC conditions as above. HPLC separations were carried out on a Merck-Hitachi chromatograph 655 A-11 using the following conditions: column 32 x 250 mm, LiChrosorb Si 60 from Knauer.

Ozonolyses of (+)-limonene (1) and of limonene epoxide (7).

Ozonolysis of 1 in pentane with one molar equivalent of ozone: A solution of 545 mg (4.0 mmol) of **1** in 200 mL of pentane was treated with 4.1 mmol of ozone at -45 °C. The mixture was warmed up to room temperature, the peroxidic precipitate (340 mg) was removed by decantation and from the remaining solution the solvent was removed by vacuum distillation at room temperature to leave 340 mg of a peroxidic liquid residue. Its separation by flash chromatography [column 1.4 x 30 cm; pentane/ether, 95:5 (250 mL), 80:20 (100 mL), ether (200 mL)] gave 58 mg (6.2%) of a 1:1 mixture of **3a** and **3b**, 56 mg (6.5%) of **4** and 100 mg of a 3:7 mixture of **1** and **2**. From the latter mixture, 53 mg (7.2%) of **2** was obtained by flash chromatography [column 0.5 x 30 cm; cyclohexane (200 mL), cyclohexane/ether, 80:20 (100 mL].

Ozonolysis of 1 in pentane with two molar equivalents of ozone: A solution of 5.0 g (36.7 mmol) of **1** in 500 mL of pentane was treated with ozone at -45 °C until the solution turned blue. Residual ozone was flushed off with nitrogen and the mixture was worked up as described above to leave 1.55 g (18.2%) of a peroxidic liquid, which consisted of a mixture of **3a** and **3b**. Separation of a sample of this mixture by the HPLC method (column 4 x 124 mm; Supersphere Si 60; pentane/ether, 92:8) afforded the individual isomers **3a** and **3b**.

Ozonolysis of 1 on polyethylene: With the procedure described for the ozonolysis of non-volatile olefins[31], 1.5 g (11.0 mmol) of **1** on 40 g of polyethylene were treated with ozone for 2.5 h at -45 °C. Residual ozone was flushed off with nitrogen, the loaded polyethylene was warmed up to room temperature and extracted with ether. From the extract ether was distilled off at room temperature and reduced pressure to leave 1.84 g of a peroxidic liquid residue, from which 243 mg (9.5%) of a mixture of

3a and **3b** was isolated by flash chromatography [column 2.0 x 75 cm; pentane/ether, 95:5 (800 mL), 80:20 (200 mL), ether (400 mL)].

Ozonolysis of 1 in the presence of formaldehyde: A solution of 2.50 g (18.4 mmol) of **1** and 7.50 g (188 mmol) of formaldehyde in 30 mL of dichloromethane was treated with 17.5 mmol of ozone at -75 °C. The solution was flushed with nitrogen while it was warmed up to room temperature. The solvent was distilled off at reduced pressure and room temperature to leave 4.47 g of a peroxidic liquid residue, from which 1.89 g (48%) of **4** was isolated by flash chromatography (column 3.5 x 45 cm; pentane/ether, 75:25).

Ozonolysis of 1 on silica gel: A suspension of 40 g of dried silica gel in 120 mL of pentane was admixed with 1.0 g (7.4 mmol) of **1** and stirred for 30 min. Then, the solvent was distilled off in a rotary evaporator at reduced pressure. The loaded silica gel was treated with ozone for 2 h at -38 °C. Residual ozone was flushed off with nitrogen, the loaded silica gel was warmed up to room temperature and extracted with ether. From the extract ether was distilled off at room temperature and reduced pressure to leave 323 mg of a peroxidic liquid residue. Its separation by flash chromatography [column 1.4 x 30 cm; pentane/ether, 95:5 (240 mL), 80:20 (200 mL), 50:50 (200 mL), ether (200 mL)] gave 36 mg (2.5%) of a mixture of **5a** - **5d** and 57 mg (5.0%) of **6**.

Ozonolysis of cis-7 in pentane: A solution of 670 mg (4.4 mmol) of cis-**7**[26] in 200 mL of pentane was treated with ozone at -45 °C for 30 min. Residual ozone was flushed off with nitrogen while the mixture was warmed up to room temperature. The solvent was distilled off at room temperature and reduced pressure to leave 862 mg (98%) of a 3:2 mixture of **5a** and **5b**. From a sample of this mixture **5a** and enriched **5b** (80%) were obtained by HPLC separation (column 32 x 250 mm, LiChrosorb Si 60; pentane/ether, 90:10).

Ozonolysis of trans-7 in pentane: A solution of 800 mg (5.3 mmol) of trans-**7**[26] in 220 mL of pentane was treated with ozone and worked up as described above to give 1040 mg (95%) of 1:1 mixture of **5c** and **5d**. From a sample of this mixture **5c** and **5d** were isolated with the HPLC procedure described above.

***1-Methyl-4-isopropenyl-7,8,9-trioxabicyclo[4.2.1]nonane (2)*:** colorless liquid; ^{1}H NMR δ 1.50 (s, 3H), 1.65 - 1.87 (m), 1.70 (d, *J* = 0.6 Hz, 3H), 1.98 - 2.18 (m), 2.54 (t,d, *J* = 11.3 and 5.3 Hz, 1H), 4.67 (t, *J* = 1.5 Hz, 1H), 4.72 (broad s, 1H), 5.63 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR δ 19.83 (CH_3), 22.15 (CH_3), 28.95 (CH_2), 37.59 (CH_2), 38.97 (CH_2), 42.05 (CH), 103.52 (O-CH-O-O), 109.55 (=CH_2), 109.92 (O-C(CH_3)-O-O), 149.49 (>C=); ^{17}O NMR δ 115 (-O-), 290 (O-O); MS m/z (%) 185 (2) $[M+1]^+$. Anal. calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.19; H, 8.65.

***1-Methyl-4-(3-methyl-1,2,4-trioxolan-3-yl)-7,8,9-trioxabicyclo[4.2.1]nonane (3)*:** Mixture of **3a** and **3b**: colorless liquid. Anal. cald for $C_{10}H_{16}O_6$: C, 51.72; H, 6.94. Found: C, 51.67; H, 6.99. Isomer **3a**:

colorless liquid; ^{1}H NMR δ 1.37 (s, 3H), 1.50 (s, 3H), 1.56 - 2.25 (m), 5.09 (s, 1H), 5.13 (s, 1H), 5.65 (d, J = 3.9 Hz, 1H); ^{13}C NMR δ 18.89 (CH_3), 21.96 (CH_3), 24.43 (CH_2), 33.65 (CH_2), 38.71 (CH_2), 41.61 (CH), 94.02 (O-CH_2-O-O), 103.10 (O-CH-OO), 109.85 (O-C(CH_3)-O-O), 111.24 (O-C(CH_3)-O-O). Isomer **3b**: colorless liquid; ^{1}H NMR δ 1.38, 1.49, 1.58 - 2.32, 5.09, 5.13, 5.67; ^{13}C NMR δ 18.44, 21.95, 24.89, 33.83, 38.68, 41.68, 94.09, 103.16, 109.87, 111.35.

3-Methyl-3-(3-methylethenyl-5-oxopentyl)-1,2,4-trioxolane (4): colorless liquid; ^{1}H NMR δ 1.40 - 1.75 (m), 1.42 (s, 3H), 1.66 (s, 3H), 2.36 - 2.55 (m, 2H), 2.61 - 2.72 (m, 1H), 4.79 (s, broad, 1H), 4.84 (s, broad, 1H), 5.06 (s, 1H), 5.12 (s, 1H), 9.68 (t, J = 2.3 Hz, 1H); ^{13}C NMR δ 18.70, 22.67, 27.01, 34.81, 41.39, 47.56, 94.06, 109.56, 113.01, 145.33, 201.64; ^{17}O NMR δ 99 (-O-), 305 (d, O-O), 598 (C=O). Anal. calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.56; H, 8.47.

1-Methyl-4-(3-methyl-1,2,4-trioxolan-3-yl)-7-oxabicyclo[4.1.0]heptanes (5a - 5d): colorless liquids. Isomer **5a**: ^{1}H NMR δ 1.05 - 1.26 (m, 1H), 1.32 (s, 3H), 1.37 (s, 3H), 1.61 - 1.72 (m, 2H), 1.84 - 1.97 (m, 3H), 2.18 - 2.27 (dm, 1H), 3.06 (t, J = 2.0 Hz, 1H), 5.00 (s, 1H), 5.15 (s, 1H); ^{13}C NMR δ 20.78 (CH_3), 22.22 (CH_2), 24.25 (CH_3), 26.94 (CH_2), 28.67 (CH_2), 36.70 (CH), 57.26 ((CH_3)C-O), 60.30 (CH), 93.98 (O-CH_2-OO), 111.10 (O-C(CH_3)-O-O); MS m/z (%) 201 (100) $[M+1]^+$. Anal. calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.01; H, 8.03. Isomer **5b** (in admixture with 20% of **5a**): ^{1}H NMR δ 1.08 - 1.22 (m), 1.31 (s), 1.36 (s), 1.56 - 1.67 (m), 1.83 - 1.96 (m), 2.22 - 2.30 (dm), 3.06 (t), 5.03 (s), 5.14 (s). Isomer **5c**: ^{1}H NMR δ 1.32 (s, 3H), 1.34 (s, 3H), 1.51 - 1.77 (m, 5H), 2.01 - 2.14 (m, 2H), 2.99 (d, J = 5.4 Hz, 1H), 5.03 (s, 1H), 5.12 (s, 1H); ^{13}C NMR δ 19.37 (CH_3), 20.19 (CH_2), 22.89 (CH_3), 25.71 (CH_2), 30.34 (CH_2), 40.41, (CH), 57.50 ((CH_3)C-O), 58.49 (CH), 93.98 (O-CH_2-OO), 111.04 (O-C(CH_3)-OO); ^{17}O NMR δ 35 (epoxy-O), 97 (-O-), 291 (d, O-O); MS m/z (%) 201 (100) $[M+1]^+$. Anal. calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.82; H, 8.00. Isomer **5d**: ^{1}H NMR δ 1.32 (s, 3H), 1.35 (s, 3H), 1.42 - 1.52 (m, 1H), 1.55 - 1.77 (m, 4H), 1.99 - 2.21 (m, 2H), 3.01 (d, J = 5.4 Hz, 1H), 5.07 (s, 1H), 5.11 (s, 1H); ^{13}C NMR δ 19.25, 20.65, 22.90, 25.70, 30.37, 40.45, 57.50, 58.59, 94.07, 111.13; ^{17}O NMR δ 33, 95, 297 (d); MS m/z (%) 201 (100) $[M+1]^+$. Anal. calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.96; H, 8.06.

Reductions of ozonides 2 - 5.

A solution of ca. 0.25 mmol of an ozonide in ca. 1 mL of $CDCl_3$ was admixed with an excess of triphenylphosphine at room temperature. ^{1}H NMR analyses after several days showed that **2** and **4** were converted into **8**, **5a** and **5b** were converted into cis-**6**, **5c** and **5d** were converted into trans-**6** and **3** was converted into a mixture of **9** and **10** in a ratio of 12:88. From the latter mixture, **10** was isolated in a yield of 83% by flash chromatography [column 0.5 x 30 cm; pentane/ether, 95:5 (160 mL), 80:20 (100 mL), 70:30 (100 mL)]. Reduction of **10** with one molar equivalent of triphenylphosphine gave **9** as the sole product.

cis- and trans-4-Acetyl-1-methyl-7-oxabicyclo[4.1.0]heptane (cis-**6** and trans-**6**) were assigned based on the identity of their ^{1}H and ^{13}C NMR data with those reported.[32]

***3-Isopropenyl-1,6-dioxo-heptane (8)*:** colorless liquid; ^{1}H NMR δ 1.57 - 1.77 (m), 1.64 (d, J = 0.8 Hz), 2.14 (s, 3H), 2.40 - 2.51 (m, 4H), 2.63 - 2.75 (m, 1H), 4.77 (m, 1H), 4.83 (m, 1H), 9.67 (t, J = 2.3 Hz, 1H); ^{13}C NMR δ 18.45, 26.51, 29.88, 40.78, 47.40, 113.08, 145.15, 201.51, 207.99. These data were identical with those of an authentic sample.[33]

***3-Acetyl-1,6-dioxo-heptane (9)*:** colorless liquid; ^{1}H NMR δ 1.64 - 1.81 (m), 1.86 - 2.00 (m), 2.14 (s, 3H), 2.26 (s, 3H), 2.40 - 2.51 (m), 2.89 - 3.12 (m), 9.72 (1H).

***4-Acetyl-1-methyl-7,8,9-trioxabicyclo[4.2.1]nonane (10)*:** colorless liquid; ^{1}H NMR δ 1.50 (s, 3H), 1.69 - 2.28 (m), 2.18 (s, 3H), 2.80 - 2.90 (m, 1H), 5.67 (d, J = 3.9 Hz, 1H); ^{13}C NMR δ 22.27 (CH_3), 25.05 (CH_2), 27.84 (CH_3), 34.14 (CH_2), 37.95 (CH_2), 48.19 (CH), 102.93 (O-CH-OO), 109.90 (O-C(CH_3)-OO), 209.26 (C=O); ^{17}O NMR δ 112 (-O-), 299 (O-O), 563 (C=O). Anal calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.39; H, 7.60.

Ozonolyses of (-)-α-pinene (12)

Ozonolysis of 12 in pentane: A solution of 1.00 g (7.34 mmol) of **12** in 600 ml of pentane was treated with 7.35 mmol of ozone at -35 °C. The mixture was warmed up to room temperature, the peroxidic precipitate (1.1 g) was removed by decantation. From the separated solution, the solvent was removed by vacuum distillation room temperature to leave 330 mg of a non-peroxidic liquid residue. GC analysis showed the presence of **13** (t_R = 14.7 min), **14a** (t_R = 18.7 min) and **14b** (t_R = 22.9 min) in molar proportions of ca. 1:1:1, as evidenced by coinjection with authentic samples. The peroxidic precipitate was dissolved in trichloro methane, admixed with 1.9 g of TPP at 0 °C and kept at room temperature for 24 h. The solvent was distilled off at reduced pressure and room temperature and the residue was separated by flash chromatography (column 2 x 75 cm; pentane/ether, 60:40) to give 330 mg of a mixture of **14a** and **14b**. Renewed separation (column 1.4 x 30 cm; pentane/ether, 97:3) gave 224 mg (18%) of **14a** and 14 mg (1%) of **14b**. They were assigned based on the identity of their ^{1}H NMR data with those published for **14a**[34] and **14b**.[35]

Ozonolysis of 12 on polyethylene: With the procedure described for the ozonolysis of volatile olefins,[31] 2.7 g (19.8 mmol) of **12** on 70 g of polyethylene were treated with 59 mmol of ozone at -78 °C. Residual ozone was flushed off with nitrogen, the loaded polyethylene was warmed up to room temperature and extracted with ether. From the extract ether was distilled off at room temperature and reduced pressure to leave 2.62 g of a non-peroxidic liquid residue. GC analysis showed the presence of **12** (t_R = 10.8 min), **13**, **14a** and **14b** in a molar ratio of 21:1:2:2.

Ozonolyses of (-)-β-pinene (15)

Ozonolysis of 15 in pentane: A solution of 1.2 g (8.8 mmol) of **15** in 500 mL of pentane was treated with 8.8 mmol of ozone at -40 °C. The solution was warmed up to room temperature and the solvent was distilled off at reduced pressure to leave 1.55 g of a colorless liquid from which 1.35 g (83%) of **16a** was isolated by flash chromatography (column 1.8 x 75 cm; pentane/ether, 3:1).

Ozonolysis of 15 on polyethylene: With the procedure described for the ozonolysis of non-volatile olefins,[31] 2.1 g (15.4 mmol) of **15** on 70 g of polyethylene were treated with 41 mmol of ozone at -45 °C. Residual ozone was flushed off with nitrogen, the loaded polyethylene was warmed up to room temperature and extracted with ether. From the extract, ether was distilled off at room temperature to leave 2.34 g of a liquid residue. Flash chromatography (column 3.5 x 45 cm; pentane/ether, 98:2) afforded 1.98 g (70%) of a 3.2:1 mixture of **16a** and **16b**. HPLC separation (pentane/ether, 96:4) gave 1324 mg (47%) of **16a** and 352 mg (12%) of **16b**.

β-Pinene ozonides (16)

***Isomer 16a*:** colorless liquid; ^{1}H NMR and [Lit. data] δ 0.93 [0.93[28a,b], 0.91[29]] (s, 3H), 1.23 [1.23[28a,b,29]] (s, 3H), 1.42 [1.42[28a], 1.58[28b]] (d, J = 10.5 Hz, 1H), 1.83 - 2.40 [1.64 - 2.38[28a], 1.85 - 2.35[28b]] (m, 7H), 5.00 [4.99,[28a,b] 4.91[29]] (s, 1H), 5.07 [5.07[28a,b,29]] (s, 1H); ^{13}C NMR and [Lit. data] δ 22.48 [22.40[28a,b]] (CH_2), 22.80 [22.77[28a], 22.8[28b]] (CH_3), 26.25 [26.16[28a], 26.2[28b]] (CH_2), 26.48 [26.40[28a], 26.4[28b]] (CH_2), 27.79 [27.73[28a], 27.7[28b]] (CH_2), 38.21 ($C(CH_3)_2$), 40.17 [40.02[28a], 40.0[28b]] (CH), 49.25 [49.10[28a], 49.1[28b]] (CH), 92.90 [92.86[28a], 92.9[28b]] (CH_2-OO), 113.84 (C-OO); ^{17}O NMR δ 108 (-O-), 271 and 318 (-O-O-). Anal. calcd for $C_{10}H_{16}O_3$: C, 65.18; H, 8.76. Found: C, 64.98; H, 8.62.

***Isomer 16b*:** colorless liquid; ^{1}H NMR δ 0.94 (s, 3H), 1.06 (s, 3H), 1.43 (d, J = 9.5 Hz, 1H), 1.52 - 1.73 (m, 3H), 1.99 - 2.29 (m, 4H), 4.63 (s, 1H), 4.71 (s, 1H); ^{13}C NMR δ 22.73 (CH_2), 22.97 (CH_3), 26.53 (CH_2), 26.58 (CH_3), 28.11 (CH_2), 38.33 ($C(CH_3)_2$), 40.49 (CH), 49.70 (CH), 92.99 (CH_2-OO), 113.75 (C-OO); ^{17}O NMR δ 114 (-O-), 280 and 312 (-O-O-). Anal. calcd for $C_{10}H_{16}O_3$; C, 65.18; H, 8.76. Found: C, 64.19; H, 8.71.

Reductions of ozonides 16a and 16b: Solutions of ca. 82 mg (0.44 mmol) of **16a** or **16b** in 2 mL of $CDCl_3$ were admixed with 145 mg (0.55 mmol) of triphenylphosphine at room temperature. ^{1}H NMR and GC analysis with the help of an authentic sample showed that **16a** and **16b** were converted into **18** [δ 0.85 (s, 3H), 1.31 (s, 3H), 1.56 (d, J = 9.8 Hz, 1H), 1.89 - 2.64 (m, 7H); t_R = 15.5 min].

Thermal decomposition of 16a and 16b: Solutions of 27 mg (0.14 mmol) of **16a** or **16b** and 26 mg (0.15 mmol) of 1,1,2,2-tetrachloroethane (as internal standard) in 1 mL of C_6D_6 were heated to 40 °C. ^{1}H NMR analysis showed that after 17 h ca. 80% and after 43 h 100% of the ozonides were decomposed to give an equimolar mixture of **18** [δ 0.57 (s, 3H), 0.93 (s, 3H), 1.04 (d, J = 10.0 Hz, 1H), 1.41 - 1.48 (m), 1.67 - 1.71 (m), 1.96 - 2.27 (m)] and of formic acid [δ 7.50 (s)].

Ozonolysis of 15 in acetone: A solution of 680 mg (5 mmol) of **15** in 100 mL of acetone was treated with 5 mmol of ozone at -40 °C. The solution was warmed up to room temperature and the solvent was distilled off at reduced pressure to leave 902 mg (92%) of a colorless liquid, which was identified as **16a** on the basis of its ^{1}H and ^{13}C NMR data.

Ozonolysis of 15 in acetaldehyde: A solution of 1.36 g (10 mmol) of **15** in 200 mL of freshly distilled acetaldehyde was treated with 10 mmol of ozone at -40°C and the product was worked up as described above to leave 3.13 g of a liquid residue. From this residue, 982 mg of a mixture of **17a**, **17b** and **16a** (molar ratio 3:1.3:1) was isolated by flash chromatography (column 3.6 x 75 cm; pentane/ether, 98:2). A solution of 700 mg of this mixture in ether was admixed with 207 mg (0.79 mmol) of triphenylphosphine and kept at room temperature for 24 h. The solvent was distilled off and from the residue 450 mg (23%) of a 2.3:1 mixture of **17a** and **17b** was isolated by flash chromatography (column 1.5 x 30 cm, pentane/ether, 98:2).

6,6-Dimethylbicyclo[3.1.1^{1,5}]heptane-<2-spiro-3> -5-methyl-1,2,4-trioxolanes (17)

Isomer 17a (in admixture with 30% of **17b**): ^{1}H NMR δ 0.92 (s, 3H), 1.22 (s, 3H), 1.35 (d, J = 4.9 Hz, 3H), 5.28 (q, J = 4.9 Hz, 1H); ^{13}C NMR δ 16.99, 22.60, 22.70, 26.36, 26.58, 26.77, 38.18, 40.15, 50.10, 100.28, 114.57.

Isomer 17b (in admixture with 70% of **17a**): ^{1}H NMR δ 0.91 (s, 3H), 1.24 (s, 3H), 1.39 (d, J = 4.9 Hz, 3H), 5.18 (q, J = 4.9 Hz, 1H); ^{13}C NMR δ 16.89, 22.44, 23.07, 26.15, 26.51, 30.12, 38.34, 40.26, 49.53, 99.65, 114.49.

Reduction of 17a and 17b: A solution of 15 mg (0.08 mmol) of **17a** + **17b** in 0.5 mL of C_6D_6 was admixed with 23 mg (0.088 mmol) of triphenylphosphine. ^{1}H NMR analysis after several days showed the presence of equimolar amounts of **18** [δ 0.61 (s), 0.97 (s), 1.15 (d), 1.45 - 2.51 (m)] and of acetaldehyde [δ 1.43 (d), 9.18 (q)].

Ozonolysis of (+)-sabinene (20): A solution of 900 mg (6.6 mmol) of **20** in 100 mL of pentane was treated with 7.3 mmol of ozone at -45 °C and the product was worked up as described above to give 1.16 g (95%) of a 1:1 mixture of **21a** and **21b**. HPLC separation of this mixture (pentane/ether, 97:3) afforded 415 mg (34%) of **21a** and 455 mg (37%) of **21b**.

Sabinene ozonides (21)

***Isomer 21a*:** colorless liquid; ^{1}H NMR δ 0.56 - 0.61 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 1.25 - 1.30 (m, 1H), 1.47 (sept., *J* = 6.8 Hz, 1H), 1.59 - 1.90 (m, 5H), 5.07 (s, 1H), 5.24 (s, 1H); ^{13}C NMR δ 12.84 (CH_2), 19.41 (CH_3), 19.57 (CH_3), 24.87 (CH_2), 26.79 (CH), 30.48 (CH_2), 32.17 (CH), 34.37 (C), 93.93 (CH_2-OO), 118.25 (C-OO); ^{17}O NMR δ 104 (-O-), 285 and 305 (-O-O-). Anal. calcd for $C_{10}H_{16}O_3$: C, 65.18; H, 8.76. Found: C, 65.13; H, 8.31.

***Isomer 21b*:** colorless liquid; ^{1}H NMR δ 0.61 - 0.71 (m, 1H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.19 - 1.24 (m, 1H), 1.43 (sept., *J* = 6.8 Hz, 1H), 1.56 - 1.87 (m, 5H), 5.07 (s, 1H), 5.15 (s, 1H); ^{13}C NMR δ 12.77 (CH_2), 19.40 (CH_3), 19.48 (CH_3), 24.64 (CH_2), 25.01 (CH), 30.93 (CH_2), 31.98 (CH), 33.43 (C), 94.08 (CH_2-OO), 118.39 (C-OO); ^{17}O NMR δ 93 (-O-), 282 and 312 (-O-O-). Anal. calcd for $C_{10}H_{16}O_3$: C, 65.18; H, 8.76. Found: C, 65.15; H, 8.55.

Reduction of 21a and 21b: A solution of ca. 20 mg (0.10 mmol) of **21a** or **21b** in 0.6 mL of $CDCl_3$ was admixed with 30 mg (0.11 mmol) of triphenylphosphine. ^{1}H NMR analysis showed the presence of polymeric formaldehyde (δ 4.89 and 4.92) and of **22** [δ 0.94 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 1.04 - 1.09 (m, 1H), 1.16 - 1.21 (m, 1H), 1.50 - 1.67 (m, 2H), 1.94 - 2.21 (m, 4H)]. The identity of **22** was proven with the help of an authentic sample.

Ozonolysis of (+)-aromadendrene (23): A solution of 1.50 g (7.34 mmol) of **23** in 500 mL of pentane was treated with 7.4 mmol of ozone at -45 °C and the product was worked up as described above to give 1.84 (99%) of a 3:1 mixture of **24a** and **24b**. HPLC separation of this mixture (pentane/ether, 98:2) afforded 1.19 g (64%) of **24a** and 375 mg (20%) of **24b**.

Aromadendrene ozonides (24)

***Isomer 24a*:** colorless solid, mp 43 °C; ^{1}H NMR δ 0.50 - 0.68 (m, 2H), 0.91 (d, *J* = 7.1 Hz, 3H), 1.02 (s, 6H), 1.16 - 1.31 (m, 2H), 1.46 - 1.86 (m, 6H), 1.97 - 2.12 (m, 3H), 5.01 (s, 1H), 5.22 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR δ 15.59, 16.37, 18.54, 19.54, 25.20, 26.94, 27.62, 28.71, 34.39, 35.56, 37.64, 40.08, 51.31, 94.84, 112.40; ^{17}O NMR δ 87 (-O-), 264 and 319 (-O-O-). Anal. calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.74; H, 9.62.

***Isomer 24b*:** colorless solid, mp 30 °C; ^{1}H NMR δ 0.48 - 0.66 (m, 2H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.99 (s, 3H), 1.01 (s, 3H), 1.13 - 1.25 (m, 2H), 1.48 - 1.79 (m, 6H), 1.99 - 2.09 (m, 2H), 2.25 - 2.36 (m, 1H), 5.01 (s, 1H), 5.25 (s, 1H); ^{13}C NMR δ 15.55, 16.03, 18.92, 19.50, 25.16, 26.50, 27.95, 28.69, 34.30, 35.96, 37.52, 39.33, 52.76, 94.26, 112.16; ^{17}O NMR δ 110 (-O-), 270 (-O-O-). Anal. calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.57; H, 9.53.

Reduction of 24a and 24b: A solution of 45 mg (0.18 mmol) of **24a** or **24b** in 0.7 mL of $CDCl_3$ was admixed with 52 mg (0.20 mmol) of triphenylphosphine. ^1H NMR analysis showed the presence of polymeric formaldehyde (δ 4.89 and 4.92) and of **25**. Separation of this mixture by flash chromatography (column 0.5 x 30 cm; pentane/ether, 90:10) gave 35 mg (95%) of **25**.

***Apoaromadendrone (25)*:** colorless solid, mp 83 °C. Lit.[36] mp 82.5 - 83.5 °C; ^1H NMR δ 0.71 - 1.15 (m, 3H), 0.95 (d, J = 7.1 Hz, 3H), 0.97 (s, 3H), 1.08 (s, 3H), 1.29 - 1.48 (m, 2H), 1.56 - 1.65 (m, 1H), 1.74 - 1.83 (m, 1H), 1.99 - 2.14 (m, 3H), 2.40 - 2.51 (m, 2H), 2.74 - 2.84 (m, 1H); ^{13}C NMR δ 15.35, 15.91, 15.84, 20.20, 23.61, 26.58, 27.34, 28.67, 34.44, 36.38, 42.54, 44.28, 58.81, 212.48.

Ozonolysis of camphene (26) in pentane: A solution of 100 mg (0.73 mmol) of **26** in 35 mL of pentane was treated with 0.75 mmol of ozone at -40 °C. The solvent was distilled off at reduced pressure at -40 °C, the solid residue was dissolved in 2 mL of cold $CDCl_3$ and analyzed by NMR spectroscopy at -20 °C.

Camphene ozonide (27) (in admixture with ca. 10% of an unknown impurity): ^1H NMR δ 0.81 - 1.81 (m), 0.96 (s), 1.03 (s), 1.83 - 1.92 (m), 2.21 - 2.26 (m), 5.09 (s), 5.10 (s); ^{13}C NMR δ 20.77 (CH_3), 21.32 (CH_2), 23.60 (CH_2), 25.62 (CH_3), 34.52 (CH_2), 43.65 ($C(CH_3)_2$), 45.50 (CH), 47.91 (CH), 93.61 (OCH_2OO), 116.09 (O-C-O-O).

Reduction of 27: A sample of 0.7 mL of the above solution was admixed with 71 mg of triphenylphosphine. GC and GC/MS analyses showed the presence of 35% of **28** (t_R = 14.2 min; m/z 138 (31%) M^+), 49% of **29** (t_R = 20.4 min; m/z 154 (2%) M^+) and 9% of **30** (t_R = 14.7 min; m/z 154 (16%)M^+). These assignments were confirmed by coinjections with authentic samples.

Decomposition of 27: A second sample of 0.7 mL of the solution of **27** in $CDCl_3$ was kept at room temperature for 24 h. GC analysis showed the presence of 5% of **28**, 34% of **29** and 1% of **30**, along with nine additional products of unknown identity.

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