

Unsaturated Ozonides from the Ozonolysis of Cyclodienes in the Presence of Carbonyl Compounds

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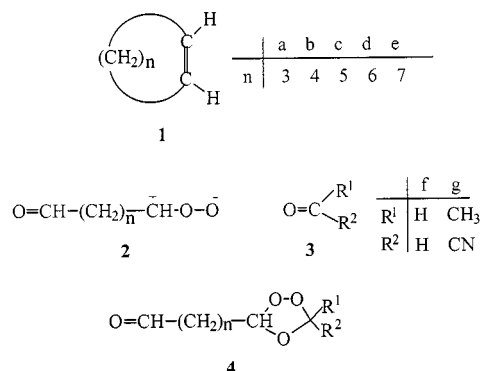
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Treatment of the conjugated C₅- to C₈-cyclodienes (**5a–5b**) with one molar equivalent of ozone in dichloromethane in the presence of added carbonyl compounds (**3**) resulted almost exclusively in monoozonolysis reactions to give the corresponding unsaturated cross-ozonides **8** and/or **10** as the major products. In contrast, ozonolysis of the nonconjugated

olefins 1,5-cyclooctadiene (**6a**) and 1,5-dimethyl-1,5-cyclooctadiene (**6b**) under similar conditions afforded both unsaturated cross-ozonides (**11** and **17**, respectively) derived from monoozonolysis and cross-ozonides (**12** + **16** and **19**, respectively) derived from diozonolysis.

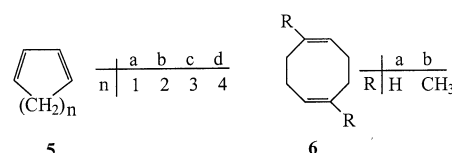
Introduction

Ozonolysis reactions of conjugated cyclic dienes in nonparticipating solvents have not been studied extensively.^[1–4] In previous work, Griesbaum et al. have shown that in methanol ozone attacks the double bonds of conjugated cyclodienes stepwise, in contrast to the reaction with nonconjugated cyclodienes.^[5–8] Ozonolysis of cycloalkenes in anhydrous nonparticipating solvents results in the formation of polymeric ozonides because the intramolecular cycloaddition of carbonyl oxides with aldehydes is much slower than intermolecular reactions. In order to avoid the formation of polymeric ozonides, a good 1,3-dipolarophile is needed to trap the carbonyl oxide intermediates. In previous work we have shown that the carbonyl oxide intermediates **2**, generated from the ozonolysis of cycloalkenes **1**, can be trapped by carbonyl compounds **3** to form the corresponding ozonides **4**.^[9–11]



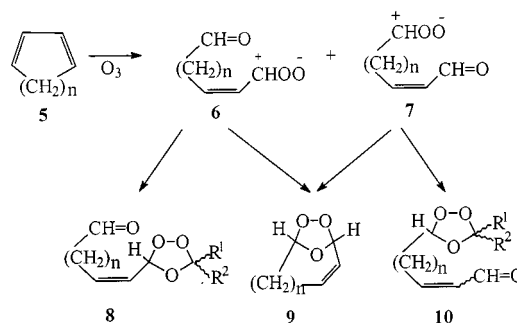
We have now extended this mode of reaction to the ozonolysis of the conjugated cyclodienes **5a–5d** and to the nonconjugated cyclodienes **6a** and **6b** in the presence of carbonyl compounds **3f** and **3g** to obtain the corresponding unsaturated ozonides **8** + **10**, **11** and **17**, respectively.

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Results and Discussion

We treated solutions of compounds **5a–d** in dichloromethane with about one equivalent of ozone in the presence of carbonyl compounds **3f** and **3g**. Ozonolysis of **5a** in the presence of carbonyl compounds **3f** afforded a product mixture in which the ozonides (*Z*)-**8af** (32%), **9a** (14%) and (*E*)-**10af** (11%) were detected by ¹H NMR spectroscopy. Of these, **9a** (11%) and (*E*)-**10af** (7%), although not (*Z*)-**8af**, could be isolated. In a similar manner, ozonolysis of **5a** in the presence of **3g** gave a mixture of (*Z*)-**8ag** (29%), **9a** (14%) and (*E*)-**10ag** (11%), from which **9a** (11%) and (*E*)-**10ag** (7%) could be isolated. The formation of ozonide **9a** is in line with the known fact that five-membered cycloolefins give high yields of ozonides, i.e. the intramolecular reaction of the carbonyl oxide moieties in **6** and **7** can compete favorably with intermolecular reactions with external carbonyl compounds.^[12,13]

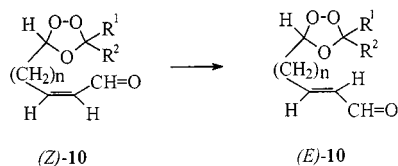


The ozonolysis of **5b** in the presence of carbonyl compounds **3f** and **3g** afforded the corresponding unsaturated ozonides (*Z*)-**8bf**, (*Z*)-**10bf**, (*Z*)-**8bg** and (*Z*)-**10bg**, which

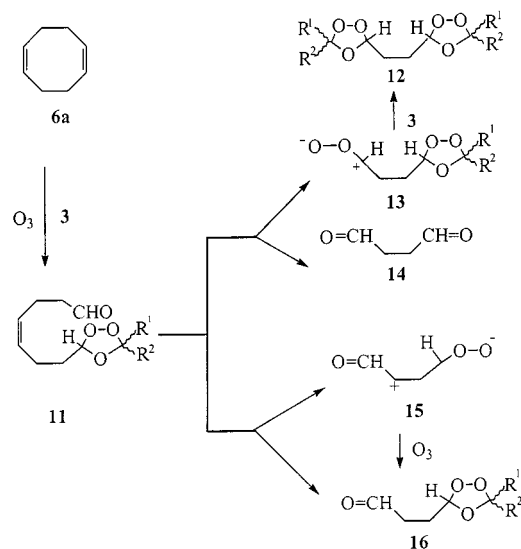
were isolated in yields of 58, 21, 53 and 21%, respectively. These results suggest that the formation of intermediate **6** is favored over that of **7**. In contrast, in the ozonolysis of **5c** in the presence of **3f**, the formation of intermediate **7c** was obviously favored over that of **6c**, as evidenced by the formation of 62% of the ozonide **Z-10cf** and only 10% of **Z-8cf**. Finally, in the ozonolysis of **5c** in the presence of **3g** and of **5d** in the presence of **3f** or of **3g**, only the corresponding ozonides **Z-10cg** (74%), **Z-10df** (74%) and **Z-10dg** (84%) derived from intermediates of type **7** were obtained. This indicates that ozone cleavage of **5c** and of **5d** occurred with high preference in one direction to give the intermediates **7** rather than **6**. This is surprising, since one would have expected the zwitterion in **6** to be resonance stabilized by the double bond more than the zwitterion of **7**.^[10]

In the ozonolysis of **5b**, **5c** and **5d** in the presence of carbonyl compounds **3**, no evidence was found for the formation of the corresponding ozonides **9**. This is in line with the known fact that ozone attacks the double bonds of conjugated cyclodienes stepwise.

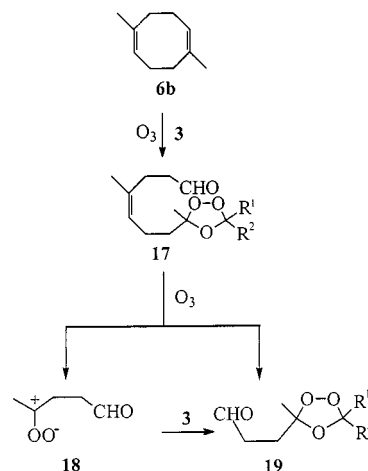
The isomerization of the (*Z*)-ozonides **10bf**, **10cf**, **10df**, **10bg**, **10cg** and **10dg** in dichloromethane at room temperature afforded, in each case, the corresponding (*E*)-ozonides in yields of between 65% and 84%.



Ozonolysis of **6a** in the presence of carbonyl compounds **3f** and **3g** provided the corresponding ozonides (**Z**)-**11f** (30%), **12f** (15%), **16f** (25%), and (**Z**)-**11g** (25%), **12g** (14%), **16g** (27%), respectively, along with 8% of dialdehyde **14**.



Ozonolysis of **6b** in the presence of **3f** and **3g** provided the corresponding ozonides (**Z**)-**17f** (23%) + **19f** (68%) and (**Z**)-**17g** (25%) + **19g** (60%), respectively.



From the results of the ozonolysis of **6a** and **6b** it can be concluded that, in contrast to the conjugated cyclodienes **5**, the two double bonds in nonconjugated cyclodienes **6** are attacked almost simultaneously by ozone to give approximately equal amounts of mono- and diozonolysis products. It can be further concluded that ozone cleavage of the double bonds in **6b** occurs predominantly in one direction only, with the formation of higher substituted carbonyl oxides.

All of the peroxidic products were isolated by column chromatography on silica gel. The (*Z*)- and (*E*)-double bond isomers were assigned by NOESY measurements. The ozonides (**Z**)-**8bg**, (**Z**)-**10bg**, (**Z**)-**10cg** and (**Z**)-**10dg** were obtained as mixtures of two diastereoisomers at the ozonide rings.^[14,15]

The structures of all isolated ozonides were established by ¹H and ¹³C NMR spectroscopy, and by their reduction with triphenylphosphane to give the expected diols and carbonyl compounds **3**.

The ozonide moieties of all ozonides could be recognized by the appearance of ¹³C NMR signals for the carbon atoms in the trioxolane rings in the typical range of $\delta = 94.49\text{--}106.28$.^[10,11,16,17] The ozonide moieties of structures (**Z**)-**8**, (**Z**)-**10** and (**Z**)-**11** were additionally confirmed by the appearance of ¹H NMR signals for the CH groups in the ozonide rings in the expected range and multiplicities.^[10,11,15–17]

The successful coozonolysis of the conjugated cyclodienes **5** in the presence of carbonyl compounds opens a convenient short-path synthesis for the hitherto unknown types of ozonides **8**, **10** and **11** which bear double bonds and an aldehyde group in the side chains.

Experimental Section

NMR Spectra: Bruker AC-300. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ with TMS as internal reference. Chromatographic separations: Flash chromatography on silica gel.

Ozonolysis Reactions: All ozonolyses were carried out in 50 mL of dichloromethane at -78°C using one molar equivalent of ozone. Residual ozone was flushed out with nitrogen, the solvent was distilled off at room temperature under reduced pressure and the residue was separated by flash chromatography. All chromatography described below was carried out with dichloromethane/diethyl ether in a ratio of 15:1. The formaldehyde (**3f**) used in the coozonolysis reactions was freshly prepared by pyrolysis of paraformaldehyde in each case.

Reductions of Ozonides: A solution of 20–40 mg of an ozonide and an excess of triphenylphosphane in 0.6 mL of CDCl_3 was kept at room temperature for 24 hours. The products were analyzed by ^1H NMR spectroscopy.

Caution: All ozonolysis reactions, chromatographic separations, and reductions of ozonides were carried out behind protective safety-glass shields in a fumehood. Ozonides were transported, for example to the analytical laboratory, in thick-walled steel containers. Safety glasses and gloves must be worn at all times.

Ozonolysis of 5a in the Presence of 3f: Ozonolysis of **5a** (0.40 g, 6.0 mmol) and 1 mL of **3f** gave a liquid residue, from which **9a** (0.07 g, 0.61 mmol, 11%) and (*E*)-**10af** (0.06 g, 0.42 mmol, 7%) were isolated.

6,7,8-Trioxabicyclo[3,2,1]-2-octene (9a): Colorless liquid. ^1H NMR: δ = 2.31 (dd, J = 6.71 and 2.13 Hz, 1 H), 2.63 (dd, J = 6.76 and 2.31 Hz, 1 H), 5.82 (d, J = 7.83 Hz, 1 H), 5.87 (t, J = 3.06 Hz, 1 H), 5.91–6.02 (m, 2 H). ^{13}C NMR: δ = 34.00, 95.72, 100.30, 126.07, 127.39. $-\text{C}_5\text{H}_6\text{O}_3$ (114.1): calcd. C 52.63, H 5.30; found C 52.37, H 5.16.

Reduction of **9a** with TPP gave pentene-1,5-dial. [^1H NMR: δ = 2.93 (m, 2 H), 6.30 (dd, 1 H), 6.82 (dt, 1 H), 9.57 (d, 1 H), 9.78 (s, 1 H)].

(E)-4-(1,2,4-Trioxolan-3-yl)-2-butenal (10af): Colorless liquid. ^1H NMR: δ = 2.79 (m, 2 H), 5.15 (s, 2 H), 5.16 (s, 1 H), 5.37 (t, J = 4.52 Hz, 1 H), 6.25 (dd, J = 15.81 and 7.08 Hz, 1 H), 6.79 (dt, J = 15.81 and 6.11 Hz, 1 H), 9.55 (d, J = 7.82 Hz, 1 H). ^{13}C NMR: δ = 18.29, 35.67, 94.67, 101.57, 136.45, 149.17, 193.67. $-\text{C}_6\text{H}_8\text{O}_4$ (144.1): calcd. C 50.01, H 5.60; found C 50.38, H 5.34.

Reduction of (*E*)-**10af** with TPP gave pentene-1,5-dial.

Ozonolysis of 5a in the Presence of 3g: Ozonolysis of **5a** (0.40 g, 6.0 mmol) and **3g** (0.82 g, 12.0 mmol) gave a liquid residue, from which **9a** (0.08 g, 0.67 mmol, 11%) and (*E*)-**10ag** (0.08 g, 0.42 mmol, 7%) were isolated.

(E)-3-Methyl-5-[4-oxobut-2-enyl]-1,2,4-trioxolane-3-carbonitrile (10ag): Colorless liquid. ^1H NMR: δ = 1.87 (s, 3 H), 2.94 (m, 2 H), 5.41 (t, J = 4.26 Hz, 1 H), 6.27 (dd, J = 15.81 and 7.06 Hz, 1 H), 6.78 (dt, J = 15.81 and 6.02 Hz, 1 H), 9.53 (d, J = 7.82 Hz, 1 H). ^{13}C NMR: δ = 21.14, 33.18, 98.24, 104.26, 137.20, 146.56, 193.31. $-\text{C}_8\text{H}_9\text{NO}_4$ (183.2): calcd. C 52.45, H 4.95; found C 52.14, H 4.77.

Reduction of (*E*)-**10ag** with TPP gave pentene-1,5-dial and acetyl cyanide.

Ozonolysis of 5b in the Presence of 3f: Ozonolysis of **5b** (0.24 g, 3.0 mmol) and 1 mL of **3f** gave a liquid residue, from which (*Z*)-**8bf** (0.27 g, 1.74 mmol, 58%) and (*E*)-**10bf** (0.11 g, 0.69 mmol, 23%) were isolated.

(Z)-5-(1,2,4-Trioxolan-3-yl)-4-pentenal (8bf): Colorless liquid. ^1H NMR: δ = 2.52 (m, 2 H), 2.58 (m, 4 H), 5.11 (t, 2 H), 5.27 (s, 1

H), 5.46 (dd, J = 11.23 and 8.04 Hz, 1 H), 5.85 (d, J = 6.24 Hz, 1 H), 5.91 (dd, J = 11.16 and 8.21 Hz, 1 H), 9.79 (s, 1 H). ^{13}C NMR: δ = 21.04, 43.60, 94.85, 98.73, 123.26, 138.93, 200.93. $-\text{C}_7\text{H}_{10}\text{O}_4$ (158.2): calcd. C 53.14, H 6.37; found C 53.47, H 6.15.

Reduction of (*Z*)-**8bf** with TPP gave 2-hexene-1,6-dial. [^1H NMR: δ = 2.41 (m, 2 H), 2.81 (m, 2 H), 6.18 (dd, 1 H), 6.85 (dt, 1 H), 9.50 (d, 1 H), 9.79 (s, 1 H)].

(Z)-5-(1,2,4-Trioxolan-3-yl)-2-pentenal (10bf): Colorless liquid. ^1H NMR: δ = 1.95 (m, 2 H), 2.77 (m, 2 H), 5.07 (s, 1 H), 5.17 (s, 1 H), 5.24 (t, J = 4.56 Hz, 3 H), 5.99 (dd, J = 11.16 and 5.82 Hz, 1 H), 6.57 (dt, J = 11.16 and 8.21 Hz, 1 H), 10.07 (d, J = 7.34 Hz, 1 H). ^{13}C NMR: δ = 22.71, 31.22, 94.54, 102.82, 150.61, 191.35. $-\text{C}_7\text{H}_{10}\text{O}_4$ (158.2): calcd. C 53.14, H 6.37; found C 53.56, H 6.22.

Reduction of (*Z*)-**10bf** with TPP gave 2-hexene-1,6-dial.

Ozonolysis of 5b in the Presence of 3g: Ozonolysis of **5b** (0.24 g, 3.0 mmol) and **3g** (0.41 g, 6.0 mmol) gave a liquid residue, from which (*Z*)-**8bg** (0.31 g, 1.59 mmol, 53%) and (*Z*)-**10bg** (0.12 g, 0.63 mmol, 21%) were isolated.

(Z)-3-Methyl-5-[5-oxopent-1-enyl]-1,2,4-trioxolane-3-carbonitrile (8bg): Colorless liquid (a mixture of two diastereoisomers at the ozonide ring). ^1H NMR: δ = 1.88 (s, 3 H), 2.50 (m, 2 H), 2.62 (m, 2 H), [5.53 (t, J = 6.23 Hz), 5.56 (t, J = 6.23 Hz)] (1 H), 6.01 (d, J = 6.41 Hz, 1 H), 6.08 (dd, J = 11.12 and 8.21 Hz, 1 H), 6.37 (dt, J = 11.12 and 8.36 Hz, 1 H), 9.78 (s, 1 H). ^{13}C NMR: δ = 20.67, 21.21, 98.99, 100.93, 101.44, 117.00, 120.31, 124.90, 137.51, 142.17, 200.66. $-\text{C}_9\text{H}_{11}\text{NO}_4$ (197.2): calcd. C 54.81, H 5.62; found C 55.11, H 5.73.

Reduction of (*Z*)-**8bg** with TPP gave 2-hexene-1,6-dial and acetyl cyanide.

3-Methyl-5-[(Z)-5-oxopent-3-enyl]-1,2,4-trioxolane-3-carbonitrile (10bg): Colorless liquid (a mixture of two diastereoisomers at the ozonide ring). ^1H NMR: δ = 1.87 (s, 3 H), 2.10 (m, 2 H), 2.85 (m, 2 H), [5.30 (t, J = 4.72 Hz), 5.70 (t, J = 4.72 Hz)] (1 H), 6.03 (dd, J = 11.17 and 7.54 Hz, 1 H), 6.55 (dt, J = 11.17 and 7.76 Hz, 1 H), 10.06 (d, J = 7.52 Hz, 1 H). ^{13}C NMR: δ = 21.24, 22.28, 22.68, 29.42, 33.52, 98.45, 98.91, 105.65, 116.87, 131.29, 149.55, 190.64. $-\text{C}_9\text{H}_{11}\text{NO}_4$ (197.2): calcd. C 56.87, H 6.20; found C 56.11, H 6.29.

Reduction of (*Z*)-**10bg** with TPP gave 2-hexene-1,6-dial and acetyl cyanide.

Ozonolysis of 5c in the Presence of 3f: Ozonolysis of **5c** (0.28 g, 3.0 mmol) and 1 mL of **3f** gave a liquid residue, from which (*Z*)-**8cf** (0.05 g, 0.31 mmol, 10.1%) and (*Z*)-**10cf** (0.32 g, 1.86 mmol, 62%) were isolated.

(Z)-6-(1,2,4-Trioxolan-3-yl)-5-hexenal (8cf): Colorless liquid. ^1H NMR: δ = 1.76 (m, 2 H), 2.24 (m, 2 H), 2.45 (t, J = 6.26 Hz, 2 H), 5.10 (s, 1 H), 5.26 (s, 1 H), 5.46 (dd, J = 11.13 and 8.21 Hz, 1 H), 5.56 (d, J = 4.52 Hz, 1 H), 5.86 (dt, J = 11.12 and 6.23 Hz, 1 H), 9.78 (s, 1 H). ^{13}C NMR: δ = 21.84, 27.55, 43.22, 94.85, 98.79, 122.85, 140.29, 201.78. $-\text{C}_8\text{H}_{12}\text{O}_4$ (172.2): calcd. C 55.80, H 7.02; found C 55.78, H 7.17.

Reduction of (*Z*)-**8cf** with TPP gave 2-heptene-1,7-dial. [^1H NMR: δ = 1.85 (m, 2 H), 2.37 (m, 2 H), 2.50 (m, 2 H), 6.11 (dd, 1 H), 6.83 (dt, 1 H), 9.49 (d, 1 H), 9.76 (s, 1 H)].

(Z)-6-(1,2,4-Trioxolan-3-yl)-2-hexenal (10cf): Colorless liquid. ^1H NMR: δ = 1.70 (m, 2 H), 1.81 (m, 2 H), 2.68 (m, 2 H), 5.06 (s, 1

H), 5.17 (t, $J = 5.16$ Hz, 1 H), 5.19 (s, 1 H), 6.00 (dd, $J = 11.23$ and 6.41 Hz, 1 H), 6.59 (dt, $J = 11.23$ and 7.36 Hz, 1 H), 10.06 (d, $J = 7.72$ Hz, 1 H). – ^{13}C NMR: $\delta = 23.65, 27.96, 30.92, 94.49, 103.58, 131.08, 152.13, 191.13$. – $\text{C}_8\text{H}_{12}\text{O}_4$ (172.2): calcd. C 55.80, H 7.02; found C 55.63, H 6.93.

Reduction of (Z)-10cf with TPP gave 2-heptene-1,7-dial.

Ozonolysis of 5c in the Presence of 3g: Ozonolysis of 5c (0.28 g, 3.0 mmol) and 3g (0.41 g, 6.0 mmol) gave a liquid residue, from which (Z)-10cg (0.47 g, 2.22 mmol, 74%) was isolated.

(Z)-3-Methyl-5-[6-oxohex-4-enyl]-1,2,4-trioxolane-3-carbonitrile (10cg): Colorless liquid (a mixture of two diastereoisomers at the ozonide ring). ^1H NMR: $\delta = 1.75$ (m, 2 H), 1.87 (s, 3 H), 1.95 (m, 2 H), 2.72 (m, 2 H), [5.28 (t, $J = 4.43$ Hz), 5.64 (t, $J = 4.43$ Hz)] (1 H), 6.02 (dd, $J = 11.26$ and 6.17 Hz, 1 H), 6.59 (dt, $J = 11.26$ and 5.34 Hz, 1 H), 10.06 (d, $J = 7.82$ Hz, 1 H). – ^{13}C NMR: $\delta = 21.28, 23.01, 23.47, 27.69, 27.89, 29.24, 33.45, 98.81, 106.28, 106.33, 116.42, 116.98, 131.11, 151.71, 191.10$. – $\text{C}_{10}\text{H}_{13}\text{NO}_4$ (211.2): calcd. C 56.87, H 6.20; found C 56.64, H 6.27.

Reduction of (Z)-10cg with TPP gave 2-heptene-1,7-dial and acetyl cyanide.

Ozonolysis of 5d in the Presence of 3f: Ozonolysis of 5d (0.32 g, 3.0 mmol) and 1 mL of 3f gave a liquid residue, from which (Z)-10df (0.41 g, 2.3 mmol, 74.1%) was isolated.

(Z)-7-(1,2,4-Trioxolan-3-yl)-2-heptenal (10df): Colorless liquid. ^1H NMR: $\delta = 1.56$ (m, 4 H), 1.78 (m, 2 H), 2.64 (t, $J = 7.36$ Hz, 2 H), 5.03 (s, 1 H), 5.14 (t, $J = 4.73$ Hz, 3 H), 5.17 (s, 1 H), 5.97 (dd, $J = 15.86$ and 8.12 Hz, 1 H), 6.62 (dt, $J = 15.86$ and 6.94 Hz, 1 H), 10.07 (d, $J = 8.12$ Hz, 1 H). – ^{13}C NMR: $\delta = 23.59, 28.09, 31.20, 94.36, 103.74, 130.67, 152.93, 191.13$. – $\text{C}_9\text{H}_{14}\text{O}_4$ (186.2): calcd. C 58.05, H 7.58; found C 58.26, H 7.44.

Reduction of (Z)-10df with TPP gave 2-octene-1,8-dial [^1H NMR: $\delta = 1.69$ (m, 4 H), 2.35 (m, 2 H), 2.49 (m, 2 H), 6.12 (dd, 1 H), 6.83 (dt, 1 H), 9.52 (d, 1 H), 9.78 (s, 1 H)].

Ozonolysis of 5d in the Presence of 3g: Ozonolysis of 5d (0.32 g, 3.0 mmol) and 3g (0.41 g, 6.0 mmol) gave a liquid residue, from which (Z)-10dg (0.57 g, 2.53 mmol, 84%) was isolated.

(Z)-3-Methyl-5-[7-oxohept-5-enyl]-1,2,4-trioxolane-3-carbonitrile (10dg): Colorless liquid (a mixture of two diastereoisomers at the ozonide ring). ^1H NMR: $\delta = 1.46$ (m, 4 H), 1.76 (s, 3 H), 2.54 (t, $J = 6.23$ Hz, 2 H), [5.16 (t, $J = 4.61$ Hz), 5.53 (t, $J = 4.61$ Hz)] (1 H), 5.84 (dd, $J = 9.68$ and 7.23 Hz, 1 H), 6.50 (dt, $J = 9.68$ and 3.18 Hz, 1 H), 9.96 (d, $J = 8.08$ Hz, 1 H). – ^{13}C NMR: $\delta = 21.17, 23.13, 23.36, 28.01, 28.84, 29.09, 29.64, 33.75, 98.24, 98.67, 106.52, 116.42, 117.04, 130.69, 152.8, 191.16$. – $\text{C}_{11}\text{H}_{15}\text{NO}_4$ (225.2): calcd. C 58.66, H 6.71; found C 58.46, H 6.65.

Reduction of (Z)-10dg with TPP gave 2-octene-1,8-dial and acetyl cyanide.

Isomerization of (Z)-Ozonides 10bf, 10cf, 10df, 10bg, 10cg and 10dg: Solutions of 3.0 mL of an ozonide in 10 mL of dichloromethane were kept at room temperature for several weeks. The solvent was evaporated at room temperature and reduced pressure and the formed (E)-ozonides were isolated by flash chromatography.

(E)-5-(1,2,4-Trioxolan-3-yl)-2-pentenal (10bf): Colorless liquid. Yield 71%. ^1H NMR: $\delta = 1.97$ (m, 2 H), 2.52 (m, 2 H), 5.08 (s, 1 H), 5.23 (s, 1 H), 5.25 (t, $J = 4.54$ Hz, 1 H), 6.01 (dd, $J = 8.16$ and 3.14 Hz, 1 H), 6.83 (dt, $J = 8.16$ and 3.02 Hz, 1 H), 9.50 (d,

$J = 7.82$ Hz, 1 H). – ^{13}C NMR: $\delta = 22.73, 32.95, 94.57, 102.80, 133.67, 157.25, 194.64$. – $\text{C}_7\text{H}_{10}\text{O}_4$ (158.2): calcd. C 53.14, H 6.37; found C 53.36, H 6.32. Reduction with TPP gave 2-hexenedial.

(E)-6-(1,2,4-Trioxolan-3-yl)-2-hexenal (10cf): Colorless liquid. Yield 74%. ^1H NMR: $\delta = 1.79$ (m, 4 H), 2.40 (m, 2 H), 5.06 (s, 1 H), 5.16 (t, $J = 4.08$ Hz, 1 H), 5.19 (s, 1 H), 6.15 (dd, $J = 10.84$ and 7.83 Hz, 1 H), 6.82 (dt, $J = 10.84$ and 4.58 Hz, 1 H), 9.51 (d, $J = 7.78$ Hz, 1 H). – ^{13}C NMR: $\delta = 22.33, 30.99, 32.55, 94.47, 103.56, 133.82, 157.58, 194.28$. – $\text{C}_8\text{H}_{12}\text{NO}_4$ (172.2): calcd. C 55.80, H 7.02; found C 55.96, H 6.94. Reduction with TPP gave 2-heptene-1,6-dial.

(E)-7-(1,2,4-Trioxolan-3-yl)-2-heptenal (10df): Colorless liquid. Yield 85%. ^1H NMR: $\delta = 1.55$ (m, 4 H), 1.76 (m, 2 H), 2.37 (m, 2 H), 5.05 (s, 1 H), 5.14 (t, $J = 4.78$ Hz, 1 H), 5.18 (s, 1 H), 6.11 (dd, $J = 13.75$ and 7.83 Hz, 1 H), 6.82 (dt, $J = 13.75$ and 7.28 Hz, 1 H), 9.50 (d, $J = 7.28$ Hz, 1 H). – ^{13}C NMR: $\delta = 23.68, 27.95, 31.28, 32.80, 94.42, 103.81, 133.63, 158.19, 194.27$. – $\text{C}_9\text{H}_{14}\text{O}_4$ (186.2): calcd. C 58.05, H 7.58; found C 58.24, H 7.47. Reduction with TPP gave 2-octene-1,8-dial.

(E)-3-Methyl-5-[5-oxopent-3-enyl]-1,2,4-trioxolane-3-carbonitrile (10bg): Colorless liquid. Yield 73%. ^1H NMR: $\delta = 2.14$ (m, 2 H), 2.16 (s, 3 H), 2.58 (m, 4 H), 5.39 (t, $J = 6.24$ Hz, 1 H), 6.19 (dd, $J = 11.13$ and 5.82 Hz, 1 H), 6.82 (dt, $J = 11.13$ and 8.07 Hz, 1 H), 9.53 (d, $J = 7.58$ Hz, 1 H). – ^{13}C NMR: $\delta = 27.92, 30.85, 94.23, 106.11, 116.72, 134.46, 154.10, 194.46$. – $\text{C}_9\text{H}_{11}\text{NO}_4$ (197.2): calcd. C 56.87, H 6.20; found C 56.11, H 6.29. Reduction with TPP gave 2-hexene-dial and acetyl cyanide.

(E)-3-Methyl-5-[6-oxohex-4-enyl]-1,2,4-trioxolane-3-carbonitrile (10cg): Colorless liquid (a mixture of diastereoisomers at the ozonide ring). Yield 65%. ^1H NMR: $\delta = 1.75$ (m, 2 H), 1.86 (s, 3 H), 1.95 (m, 2 H), [5.28 (t, $J = 4.46$ Hz), 5.64 (t, $J = 4.46$ Hz)] (1 H), 6.16 (dd, $J = 6.28$ and 3.04 Hz, 1 H), 6.82 (dt, $J = 6.28$ and 3.20 Hz, 1 H), 9.51 (d, $J = 7.82$ Hz, 1 H). – ^{13}C NMR: $\delta = 21.29, 21.79, 27.91, 29.27, 32.45, 98.87, 106.32, 116.72, 117.08, 131.17, 151.43, 194.26$. – $\text{C}_{10}\text{H}_{13}\text{NO}_4$ (211.2): calcd. C 56.87, H 6.20; found C 57.04, H 6.14. Reduction with TPP gave 2-heptene-dial and acetyl cyanide.

(E)-3-Methyl-5-[7-oxohept-5-enyl]-1,2,4-trioxolane-3-carbonitrile (10dg): Colorless liquid. Yield 81%. ^1H NMR: $\delta = 1.51$ (m, 4 H), 1.78 (s, 3 H), 1.83 (m, 2 H), 2.18 (m, 2 H), 5.19 (t, $J = 4.64$ Hz, 1 H), 6.05 (dd, $J = 10.63$ and 6.42 Hz, 1 H), 6.76 (dt, $J = 10.63$ and 3.28 Hz, 1 H), 9.44 (d, $J = 7.82$ Hz, 1 H). – ^{13}C NMR: $\delta = 21.31, 23.21, 27.93, 29.79, 32.69, 98.64, 106.62, 116.74, 133.73, 157.83, 194.24$. – $\text{C}_{11}\text{H}_{15}\text{NO}_4$ (225.2): calcd. C 58.66, H 6.71; found C 58.42, H 6.84. Reduction with TPP gave 2-octene-1,8-dial and acetyl cyanide.

Ozonolysis of 6a in the Presence of 3f: Ozonolysis of 6a (0.32 g, 3.0 mmol) and 1 mL of 3f gave a liquid residue, from which (Z)-11f (0.17 g, 0.91 mmol, 30%), 16f (0.1 g, 0.75 mmol, 25%), 12f (0.08 g, 0.45 mmol, 15%) and 14 (0.02 g, 0.24 mmol, 8%) were isolated.

(Z)-7-(1,2,4-Trioxolan-3-yl)-4-heptenal (11f): Colorless liquid. ^1H NMR: $\delta = 1.68$ (m, 2 H), 2.12 (m, 2 H), 2.27 (m, 2 H), 2.40 (m, 2 H), 4.95 (s, 1 H), 5.04 (t, $J = 5.11$ Hz, 1 H), 5.08 (s, 1 H), 5.31 (m, 2 H), 9.67 (t, $J = 1.51$ Hz, 1 H). – ^{13}C NMR: $\delta = 20.28, 21.98, 31.36, 43.87, 94.34, 103.45, 129.01, 129.67, 202.24$. – $\text{C}_9\text{H}_{14}\text{O}_4$ (186.2): calcd. C 58.05, H 7.58; found C 59.97, H 7.46.

Reduction of (Z)-11f with TPP gave 4-octene-1,8-dial. [^1H NMR: $\delta = 2.27$ (m, 4 H), 2.40 (m, 4 H), 5.31 (t, 2 H), 9.67 (s, 2 H)].

3-[2-(1,2,4-Trioxolane-3-yl)ethyl]-1,2,4-trioxolane (12f): Colorless liquid. ^1H NMR: δ = 1.84 (s, 4 H), 5.07 (s, 2 H), 5.17 (s, 2 H), 5.29 (t, J = 4.82 Hz, 2 H). – ^{13}C NMR: δ = 25.96, 94.54, 103.10. – $\text{C}_6\text{H}_{10}\text{O}_6$ (178.1): calcd. C 40.45, H 5.66; found C 40.32, H 5.68.

3-(1,2,4-Trioxolane-3-yl)propanal (16f): Colorless liquid. ^1H NMR: δ = 2.02 (m, 2 H), 2.49 (t, J = 6.10 Hz, 2 H), 4.96 (s, 1 H), 5.06 (s, 1 H), 5.16 (t, J = 5.23 Hz, 1 H), 9.67 (s, 1 H). – ^{13}C NMR: δ = 21.95, 37.80, 94.47, 102.52, 200.96. – $\text{C}_5\text{H}_8\text{O}_4$ (132.1): calcd. C 45.46, H 6.10; found C 45.57, H 5.83.

1,4-Butandial (14): Colorless liquid. ^1H NMR: δ = 2.81 (s, 4 H), 9.77 (s, 2 H). – ^{13}C NMR: δ = 36.34, 200.32.

Ozonolysis of 6a in the Presence of 3g: Ozonolysis of **6a** (0.32 g, 3.0 mmol) and **3g** (0.41 g, 6.0 mmol) gave a liquid residue, from which (**Z**)-**11g** (0.17 g, 0.75 mmol, 25%), **16g** (0.14 g, 0.82 mmol, 27%), **12g** (0.11 g, 0.43 mmol, 14%) and **14** (0.02 g, 0.24 mmol, 8%) were isolated.

(Z)-3-Methyl-5-[7-oxohept-3-enyl]-1,2,4-trioxolane-3-carbonitrile (11g): Colorless liquid (a mixture of two diastereoisomers at the ozonide ring). ^1H NMR: δ = 1.86 (s, 3 H), [1.71 (m), 1.95 (m)] (2 H), [2.15 (m), 2.27 (m)] (2 H), 2.39 (m, 2 H), 2.51 (t, J = 5.42 Hz, 2 H), [5.25 (t, J = 5.23 Hz), 5.62 (t, J = 5.23 Hz)] (1 H), 5.42 (m, 2 H), 9.77 (s, 1 H). – ^{13}C NMR: δ = 20.32, 21.30, 21.43, 21.64, 29.91, 33.74, 43.85, 98.35, 98.68, 106.24, 106.38, 116.26, 117.04, 128.97, 129.62, 202.16. – $\text{C}_{11}\text{H}_{15}\text{NO}_4$ (225.2): calcd. C 58.66, H 6.71; found C 58.42, H 6.53.

Reduction of (**Z**)-**11g** with TPP gave 4-octene-1,8-dial and acyl cyanide.

3-Methyl-5-(3-oxopropyl)-1,2,4-trioxolane-3-carbonitrile (16g): Colorless liquid. ^1H NMR: δ = 1.87 (s, 3 H), 1.68 (s, 3 H), [2.03 (m), 2.23 (m)] (1 H), [2.61 (t, J = 7.21 Hz), 2.73 (t, J = 7.21 Hz)] (1 H), [5.32 (t, J = 5.42 Hz), 5.75 (t, J = 5.42 Hz)] (1 H), [9.83 (s), 10.08 (s)] (1 H). – ^{13}C NMR: δ = 20.87, 21.07, 22.04, 26.70, 37.05, 37.75, 98.40, 98.99, 105.47, 105.86, 116.93, 200.28, 200.57. – $\text{C}_7\text{H}_9\text{NO}_4$ (171.2): calcd. C 49.14, H 5.30; found C 48.97, H 5.37.

5-Cyano-3-[2-(5-cyano-5-methyl-1,2,4-trioxolane-3-yl)ethyl]-5-methyl-1,2,4-trioxolane (12g): Colorless liquid (a mixture of diastereoisomers at the ozonide ring). ^1H NMR: δ = 1.86 (s, 6 H), 1.75 (m, 4 H), [5.31 (m), 5.72 (m)] (2 H). – ^{13}C NMR: δ = 21.11, 23.22, 23.96, 27.84, 28.39, 98.47, 99.00, 105.43, 116.21, 116.84. – $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_6$ (256.2): calcd. C 46.88, H 4.72; found C 46.64, H 4.69.

Ozonolysis of 6b in the Presence of 3f: Ozonolysis of **11b** (0.41 g, 3.0 mmol) and 1 mL of **3f** gave a liquid residue, from which (**Z**)-**17f** (0.15 g, 0.70 mmol, 23%) and **19f** (0.31 g, 2.0 mmol, 68%) were isolated.

(Z)-4-Methyl-7-(3-methyl-1,2,4-trioxolan-3-yl)-4-heptenal (17f): Colorless liquid. ^1H NMR: δ = 1.46 (s, 3 H), 1.68 (s, 3 H), 1.77 (m, 2 H), 2.12 (m, 2 H), 2.38 (m, 2 H), 2.50 (m, 2 H), 5.03 (s, 1 H), 5.13 (m, 1 H), 5.18 (s, 1 H), 9.77 (s, 1 H). – ^{13}C NMR: δ = 22.68, 23.04, 23.42, 24.59, 37.71, 42.55, 94.41, 109.74, 125.85, 134.20, 202.49. – $\text{C}_{11}\text{H}_{18}\text{O}_4$ (214.3): calcd. C 61.66, H 8.47; found C 61.54, H 8.33.

Reduction of (**Z**)-**17f** with TPP gave 4-methyl-8-oxo-4-nonenal. [^1H NMR: δ = 1.68 (s, 3 H), 2.12 (s, 3 H), 2.38 (m, 4 H), 2.50 (m, 4 H), 5.30 (m, 1 H), 9.77 (s, 1 H)].

3-(3-Methyl-1,2,4-trioxolan-3-yl)propanal (19f): Colorless liquid. ^1H NMR: δ = 1.45 (s, 3 H), 2.14 (m, 2 H), 2.58 (t, J = 6.92 Hz, 2 H), 5.06 (s, 1 H), 5.11 (s, 1 H), 9.75 (s, 1 H). – ^{13}C NMR: δ = 22.94, 30.07, 38.51, 94.46, 109.15, 201.43. – $\text{C}_6\text{H}_{10}\text{O}_4$ (146.1): calcd. C 49.33, H 6.90; found C 49.63, H 6.67.

Ozonolysis of 6b in the Presence of 3g: Ozonolysis of **11b** (0.41 g, 3.0 mmol) and **3g** (0.41 g, 6.0 mmol) gave a liquid residue, from which (**Z**)-**17g** (0.19 g, 0.75 mmol, 25%) and **19g** (0.31 g, 1.81 mmol, 60%) were isolated.

(Z)-3-Methyl-5-[4-methyl-7-oxohept-3-enyl]-1,2,4-trioxolane-3-carbonitrile (17g): Colorless liquid (a mixture of diastereoisomers at the ozonide ring). ^1H NMR: δ = 1.48 (s, 3 H), 1.69 (s, 3 H), 1.83 (s, 3 H), 1.94 (m, 2 H), 2.36 (m, 2 H), 2.76 (m, 2 H), [5.19 (m), 5.33 (m)] (1 H), 9.78 (s, 1 H). – ^{13}C NMR: δ = 21.95, 21.43, 22.86, 23.46, 24.51, 24.59, 24.88, 26.08, 26.69, 36.06, 42.50, 98.71, 113.98, 114.04, 117.29, 124.94, 134.94, 202.51. – $\text{C}_{13}\text{H}_{19}\text{NO}_4$ (253.3): calcd. C 61.64, H 7.56; found C 61.45, H 7.66.

Reduction of (**Z**)-**17g** with TPP gave 4-methyl-8-oxo-4-nonenal and acyl cyanide.

3,5-Dimethyl-5-(3-oxopropyl)-1,2,4-trioxolane-3-carbonitrile (19g): Colorless liquid (a mixture of diastereoisomers at the ozonide ring). ^1H NMR: δ = 1.49 (s, 3 H), 1.86 (s, 3 H), [2.08 (m), 2.29 (m)] (2 H), [2.58 (m), 2.77 (m)] (2 H), [9.77 (s), 9.82 (s)] (1 H). – ^{13}C NMR: δ = 20.92, 21.92, 25.38, 27.50, 31.37, 37.75, 38.75, 98.60, 99.06, 113.47, 113.57, 116.96, 117.20, 200.57. – $\text{C}_8\text{H}_{11}\text{NO}_4$ (185.2): calcd. C 51.88, H 5.99; found C 52.07, H 5.74.

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