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Ozonolyses of Cycloalkenes: Trapping of Carbonyl Oxide by Trifluoroacetophenone

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Ozonolysis reactions of cyclic olefins **1a-c** and norbornene **1n** in the presence of trifluoroactophenone **6** provided the corresponding cross-ozonides **7a-c** and **7n**. Further reactions of ozonides **7a-c** and **7n** with the independently prepared carbonyl oxide **11** gave diozonides of structure **10a-c** and **10n**. The ozonolysis of 1-methylcyclopentene **12a** and 1-methylcyclohexene **12b** in the presence of trifluoroactophenone **6** provided exclusively ozonide **15** and **16** derived from capture of carbonyl oxide **13**. All of the new ozonides have been isolated as pure substances and characterized by their ^1H NMR and ^{13}C NMR spectra.

Introduction

Ozonolyses of cycloalkenes in aprotic solvents result in formation of polymeric peroxides, because of the intramolecular cycloaddition of carbonyl oxide with aldehyde is much slower than that of intramolecular process.[1-3]

Ozonolyses of certain cycloolefins **1** in methanol, however, revealed a partially anomalous behavior as compared to acyclic olefins. A priori, one would have expected that the primary intermediates of type **2** are trapped by methanol to give compounds of type **4**. But in addition to **4**, variable amounts of the isomeric product of type **5** were obtained.[4,5]

Ozonolyses of Cycloalkenes

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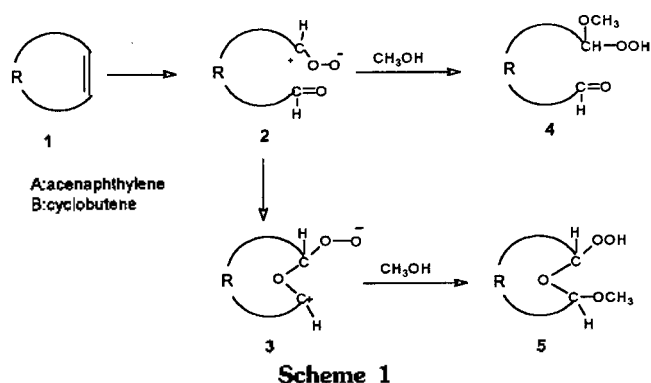
Scheme 1

This was explained by an intramolecular reaction between the carbonyl oxide moiety and the aldehyde group of **2** to give intermediate **3**, which is subsequently trapped by methanol to give **5** (Scheme 1).

In the present work, we are interested to find out whether the carbonyl oxide moieties in intermediates of type **2** can be trapped by added carbonyl compounds **6** to give mono-ozonides of type **7**.[5-9] Such ozonides would represent functionalized ozonides which could undergo subsequent reactions at the aldehyde groups. To predict the regioselectivity in the cleavage of the primary ozonides from the unsymmetrical cycloalkenes, we have conducted ozonolyses of 1-methylcycloalkenes in the presence of **6**.

Results and Discussion

In pursuit of our goals, we have ozonized the cyclic olefins **1a-c** and norbornene **1n** in inert solvents in the presence of two molar equivalents of a trifluoroacetophenone **6**. Ozonolyses of cylopentene **1a**, cyclohexene **1b**, cycloheptene **1c** and norbornene **1n** in the presence of trifluoroacetophenone **6** as a good dipolarophile[10,11] afforded in each case the corresponding ozonides **7**, whereas in this reactions no evidence was found the formation of ozonides of type **9** or peroxidic products **8** as outlined in Scheme 2.

Ozonolyses of **1a, 1b, 1c** and **1n** in the presence of **6** gave the corresponding type **7** in yields between 38 and 57%. All of the peroxidic products have been isolated by column chromatography on silica gel. The unsymmetrically substituted ozonides **7a-c** and **7n** were mixtures of two stereoisomers, each. The structures of all isolated ozonides were established by ¹H- and ¹³C NMR spectroscopy, and their reduction with triphenylphosphine (TPP) to give the

Scheme 2
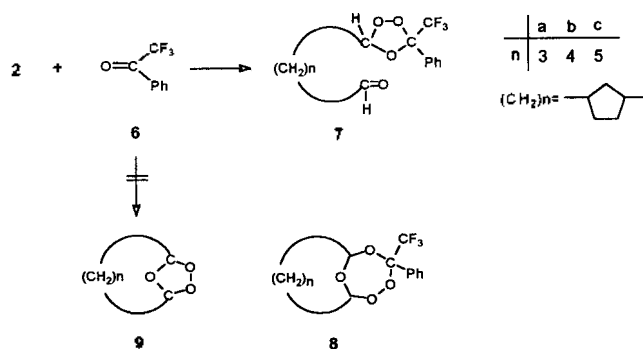
expected fragments, *viz.* dialdehydes of structure O=CH-R-CH=O and the corresponding trifluoroacetophenone **6**. Characteristic signals in the ¹H NMR spectra of all ozonides of type **7** were those for the R-C-H groups in the ozonide rings and the -CH=O groups in the side chains. The R-C-H signals and -CH=O signals for ozonides **7a-c** and **7n** appeared in the range of δ=5.06-5.61 and 9.55-9.78, respectively.

Characteristic signals in the ¹³C NMR spectra of all ozonides of structure **7** were those of the magnetically nonequivalent (R,H)C-atoms and (CF₃,Ph)C-atoms in the ozonide rings and of the C=O atoms in the side chains. The signals for the C-atoms in the ozonide rings appeared in the range of δ=103.9 and δ=109.1, respectively. The C=O signals of ozonides appeared in the range of δ=201.0-202.5.

In an attempt to make use of the functionalized ozonides of type **7**, we have generated formaldehyde-O-oxide **11** in the presence of ozonides **7** on purpose to induce a cycloaddition reaction between **11** and the aldehyde group in **7**. To this end, isopropenyl acetate[12] has been ozonized in the presence of one half molar equivalent of one of the ozonides in dichloromethane at -78 °C. Ozonolyses of **7a**, **7b**, **7c** and **7n** in the presence of formaldehyde-O-oxide **11** affected ozonide **10a** (48%), **10b** (68%), **10c** (51%) and **10n** (47%), respectively. All of the diozonides have been isolated by column chromatographic methods. They were obtained as mixtures of the correspponding *cis*- and *trans*-isomer, each.
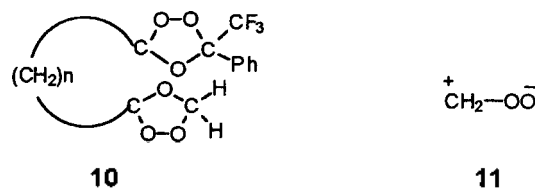
The structrural assignments of diozonides are based on their reduction with TPP to give formaldehyde, the corresponding dialdehyde O=CH-R-CH=O and trifluoroacto-phenone **6**. Characteristic signals in the ¹H NMR spectra were those of the CH₂ and CH groups in the ozonide ring appearing in the range of δ=5.02-5.60 for ozonides **10a-c** and **10n**. Characteristic signals in the ¹³C NMR spectra were those in the range of δ=94.0-109.8 for all diozonides.

Cycloreversion process of primary ozonides can provide two possible different intermediates, **13** and **14**, in the case of unsymmetrically substituted alkenes. Ozonolysis of 1-methylcyclopentene **12a** in the presence of trifloroaceto-phenone **6** did not provide the corresponding ozonide **17a**. Instead, ozonide **15a** and **16a** were obtained in yields of 43% and 10%, respectively.[15] By contrast, ozonolysis of 1-methylcyclohexene **12b** in the presence of the above mentioned carbonyl compound did provide exclusibly the corresponding ozonides **16b**. Ozonolyses of **12a** and **12b** in the presence of **6** gave exclusively the cross-ozonide **16a** and **16b**, suggesting the formation of methyl substituted carbonyl oxide moiety **13** rather than **14** is favored. The formation of ozonide **15a** in ozonolysis of **12a** is in line with the known fact that 5-membered cycloolefins[13,14] give high yields of ozonides, *i.e.* intramolecular reaction of the carbonyl oxide in **13a** can compete with intermolecular reaction with trifluoroacetophenone **6** (Scheme 3).
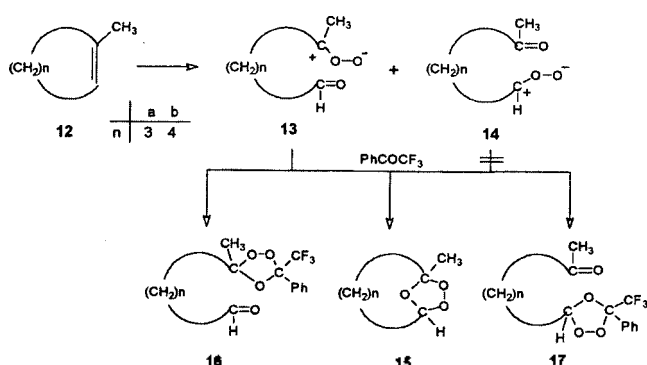
Scheme 3

The results in this study provide ample evidences that carbonyl oxides which are formed in the ozonolysis of cyclic olefins can be readily trapped by "foreign" carbonyl compounds like trifluoroacetophenone to give cross-ozonides. This opens a convenient short-path synthesis for ozonides which bear aldehyde groups and which are, thus, capable of further reactions. As one of several conceiveable aldehyde reactions, the cycloaddition with formaldehyde-O-oxide was realized to give a variety of diozonides. This represents another new short-path synthesis for ozonides which were not known previously.

Experimental

All NMR spectra were recored with Bruker FT-NMR (300 MHz), using TMS as an internal reference. The ozonide was isolated by flash chromatography on 80 g silica gel using diethyl ether/n-pentane in a ratio of 1 : 2.

Ozonolyses Reactions

Unless mentioned otherwise, the following procedure was used: The ozonolyses reaction was carried out in methylene chloride at − 78 °C until the solution turned blue. Residual ozone was flashed out with nitrogen, the solvent was distilled off at room temperature under reduced pressure, and the residue was separated by flash chromatography.

Reduction of Ozonides with Triphenylphosphine.
A solution of the ozonide in CDCl₃ was mixed with triphenylphosphine in a NMR tube, and the reaction was monitored by ¹H- and ¹³C NMR spectroscopy.

Ozonolysis of 1a and 6

Ozonolysis of 0.40 g (6 mmol) of 1a and 2.08 g (12 mmol) of trifluoroacethophenone in 50 mL of methylene chloride, followed by distillation of the solvent under reduced pressure gave a liquid residue. From which 0.78 g (2.7 mmol, 46%) of 7a was isolated by Flash chromatography [solvent : diethyl ether/n-pentane, 1 : 2].

(5-Phenyl-5-trifluoromethyl-1,2,4-trioxolan-3-yl)-butanal(7a). Colorless liquid (a 1 : 1 mixture of two isomers): ¹H NMR (CDCl₃) δ 1.71-1.95 (m, 4H), 2.42-2.70 (m, 2H), [5.27 (t, *J*=3.5 Hz), 5.61 (t, *J*=3.5 Hz)](1H), 7.40-7.60 (m, 5H), [9.68 (s), 9.77 (s)](1H). ¹³C NMR (CDCl₃); δ 16.15, 28.22, 29.81, 42.96, 103.7 (q, *J*=33 Hz), 105.5, 106.6, 120.4 (q, *J*=292 Hz), 122.7, 126.6, 128.3, 130.5, 132.2, 135.5, 201.0. Anal. Calcd. for C₁₃H₁₃O₄F₃: C, 53.80; H, 4.51. Found C, 53.64; H, 4.46.

Reduction of 7a with TPP gave 1,5-pentanedial [δ

1.90 (quin., *J*=4 Hz, 2H), 2.47 (t, *J*=4 Hz, 4H), 9.72 (s, 1H)] and corresponding carbonyl compound 6 which was identified on the basis of its ¹³C NMR data with those reported.[16]

Ozonolysis of 1b and 6

Ozonolysis of 0.25 g (3 mmol) of 1b and 1.04 g (6 mmol) of trifluoroacethophenone in 50 mL of methylene chloride, followed by distillation of the solvent under reduced pressure gave a liquid residue. From which 0.52 g (1.7 mmol, 57%) of 7b was isolated [solvent : diethyl ether/n-pentane, 1 : 2].

(5-Phenyl-5-trifluoromethyl-1,2,4-trioxolan-3-yl)-pentanal (7b). Colorless liquid (a 1 : 2 mixture of two isomers): ¹H NMR (CDCl₃) δ 1.45-1.76 (m, 6H), 2.38-2.49 (m, 2H), [5.27 (t, *J*=3.0 Hz), 5.59 (t, *J*=3.0 Hz)](1H), 7.41-7.59 (m, 5H), [9.72 (s), 9.79 (s)](1H): ¹³C NMR (CDCl₃); δ 21.61, 23.23, 28.78, 30.36, 43.46, 103.7 (q, *J*=33 Hz), 105.8, 106.9, 120.5 (q, *J*=290 Hz), 122.8, 126.7, 128.4, 130.6, 132.4, 201.7. Anal. Calcd. for C₁₄H₁₅O₄F₃: C, 55.26; H, 4.97. Found C, 55.56; H, 4.71.

Reduction of 7b with TPP gave 1,6-hexanedial [δ 1.66 (t, *J*=4 Hz, 4H), 2.33 (t, *J*=4 Hz, 4H), 9.72 (s, 1H)] and corresponding carbonyl compound 6.[16]

Ozonolysis of 1c and 6

Ozonolysis of 0.29 g (3 mmol) of 1c and 1.04 g (6 mmol) of trifluoroacethophenone in 50 mL of methylene chloride, followed by distillation of the solvent under reduced pressure gave a liquid residue. From which 0.39 g (1.2 mmol, 40%) of 7c was isolated [solvent : diethyl ether/n-pentane, 1 : 2].

(5-Phenyl-5-trifluoromethyl-1,2,4-trioxolan-3-yl)-hexanal (7c). Colorless liquid (a 1 : 1 mixture of two isomers): ¹H NMR (CDCl₃) δ 1.33-1.75 (m, 8H), 2.38-2.47 (m, 2H), [5.26 (t, *J*=5.0 Hz), 5.58 (t, *J*=5.0 Hz) (1H), 7.26-7.60 (m, 5H), [9.74 (s), 9.78 (s)](1H). ¹³C NMR (CDCl₃); δ 21.68, 23.48, 28.69, 30.21, 43.61, 103.6 (q, *J*=33 Hz), 105.9, 107.0, 122.7 (q, *J*=289 Hz), 126.7, 128.3, 130.5, 132.4, 202.3. Anal. Calcd. for C₁₅H₁₇O₄F₃: C, 56.6; H, 5.38. Found C, 56.98; H, 5.21.

Reduction of 7c with TPP gave 1,7-heptanedial [δ 1.36 (quin., *J*=4 Hz, 2H), 1.63 (quin., *J*=4 Hz, 4H), 2.45 (t, *J*=4 Hz, 4H)] and corresponding carbonyl compound 6.

Ozonolysis of 1n and 6

Ozonolysis of 0.56 g (6 mmol) of 1n and 2.08 g (12 mmol) of trifluoroacethophenone in 50 mL of methylene chloride, followed by distillation of the solvent under reduced pressure gave a liquid residue. From which 0.72 g (2.28 mmol, 38%) of 7n was isolated [solvent : diethyl ether/ n-pentane, 1 : 2].

(5-Phenyl-5-trifluoromethyl-1,2,4-trioxolan-3-yl)-cyclopentanecarbaldehyde (7n). Colorless liquid (a 1 : 2 mixture of two isomers): ¹H NMR (CDCl₃) δ 1.18-2.67 (m, 8H), [5.16 (d, *J*=4.0 Hz), 5.49 (d, *J*=4.0 Hz), (1H)] 7.31-7.50 (m, 5H), [9.49 (s), 9.55 (s)](1H). ¹³C NMR (CDCl₃); δ 26.28, 27.29, 39.14, 40.58, 51.38, 103.9 (q, *J*=33 Hz), 108.0, 109.1, 122.7 (q, *J*=290 Hz), 126.8, 128.4, 129.2, 130.1, 132.2, 135.6, 202.5. Anal. Calcd. for C₁₅H₁₅O₄F₃: C, 56.96; H, 4.78. Found C, 56.87; H, 4.68.

Reduction of 7n with TPP gave cyclopentanedicarb-aldehyde [δ 1.86-2.26 (m, 6H), 2.83 (m, 2H)] and corresponding carbonyl compound 6.

Ozonolysis of 7a and Isopropenyl Acetate

Ozonolysis of 0.73 g (2.4 mmol) of **7a** and 0.48 g (4.8 mmol) of isopropenyl acetate in 40 mL of methylene chloride gave a liquid residue, from which 0.38 g (1.15 mmol, 48%) of **10a** was isolated [solvent: diethyl ether/n-pentane, 1:4].

5-Phenyl-5-trifluoromethyl-3-[3-(1,2,4-trioxolane-3-yl)-propyl]-1,2,4-trioxolane (10a). Colorless liquid (a 1:2 mixture of two isomers): ^{1}H NMR (CDCl$_3$): δ 1.71-2.03 (m, 6H), 5.02 (d, J=5 Hz, 1H), 5.10 (m, 1H), 5.14 (d, J=5 Hz, 1H), [5.25 (t, J=5 Hz), 5.60 (t, J=5 Hz)] (1H), 7.45-7.73 (m, 5H). ^{13}C NMR (CDCl$_3$): δ 20.35, 29.45, 38.29, 101.5, 103.7 (q, J=33 Hz) 115.5, 117.8, 120.5 (q, J=291 Hz) 126.6, 128.4, 129.1, 130.1, 135.5. Anal. Calcd. for C$_{14}$H$_{15}$O$_6$F$_3$: C, 50.00; H, 4.50. Found C, 49.76; H, 4.37.

Reduction of 10a with TPP gave 1,5-pentanedial and corresponding carbonyl compound **6**. ·

Ozonolysis of 7b and Isopropenyl Acetate. Ozonolysis of 0.32 g (1.05 mmol) of **7b** and 0.21 g (2.1 mmol) of isopropenyl acetate in 40 mL of methylene chloride gave a liquid residue, from which 0.25 g (0.71 mmol, 68%) of **10b** was isolated [solvent: diethyl ether/n-pentane, 1:4].

5-Phenyl-5-trifluoromethyl-3-[4-(1,2,4-trioxolan-3-yl)-butyl]-1,2,4-trioxolane (10b). Colorless liquid (a 1:1 mixture of two isomers): ^{1}H NMR (CDCl$_3$): δ 1.47-1.79 (m, 8H), 5.04 (d, J=5 Hz, 1H), 5.13 (m, 1H), 5.19 (d, J=5 Hz, 1H), [δ 5.27 (t, J=5 Hz), 5.59 (t, J=5 Hz)] (1H), 7.45-7.63 (m, 5H). ^{13}C NMR (CDCl$_3$): δ 23.86, 29.17, 30.71, 31.25, 94.43, 103.8 (q, 33 Hz), 106.2, 107.3, 120.1 (q, 290 Hz), 123.9, 127.1, 128.8, 130.7, 131.2, 132.8. Anal. Calcd. for C$_{15}$H$_{17}$O$_6$F$_3$: C, 51.43; H, 4.89. Found C, 51.67; H, 4.65.

Reduction of 10b with TPP gave 1,6-hexanedial and corresponding carbonyl compound **6**.

Ozonolysis of 7c and Isopropenyl Acetate Ozonolysis of 0.32 g (1.0 mmol) of **7c** and 0.21 g (2.1 mmol) of isopropenyl acetate in 40 mL of methylene chloride gave a liquid residue, from which 0.19 g (0.51 mmol, 51%) of **10c** was isolated [solvent: diethyl ether/n-pentane, 1:4].

5-Phenyl-5-trifluoromethyl-3-[5-(1,2,4-trioxolan-3-yl)-propyl]-1,2,4-trioxolane (10c). Colorless liquid (a 1:2 mixture of two isomers): ^{1}H NMR (CDCl$_3$): δ 1.26-1.76 (m, 10H), 5.03 (d, J=6 Hz, 1H), 5.15 (m, 1H), 5.19 (d, J= 6 Hz, 1H), [5.27 (t, J=5 Hz), 5.57 (t, J=5 Hz)](1H), 7.42-7.60 (m, 5H). ^{13}C NMR (CDCl$_3$): δ 23.50, 28.88, 30.85, 94.00, 95.57, 103.6 (q, 33 Hz), 107.1, 120.4, 122.7 (q, 289 Hz), 126.7, 128.4, 130.5, 132.8. Anal. Calcd. for C$_{16}$H$_{19}$O$_6$F$_3$: C, 52.75; H, 5.26. Found C, 64.89; H, 5.14.

Reduction of 10c with TPP gave 1,7-heptanedial and corresponding carbonyl compound **6**.

Ozonolysis of 7n and Isopropenyl Acetate Ozonolysis of 1.52 g (4.8 mmol) of **7n** and 0.97 g (9.7 mmol) of isopropenyl acetate in 40 mL of methylene chloride gave a liquid residue, from which 0.82 g (2.26 mmol, 47%) of **10n** was isolated [solvent: methylene chloride/n-pentane, 15:4].

5-Phenyl-5-trifluoromethyl-3-[3-(1,2,4-trioxolan-3-yl)-cyclopentyl]-1,2,4-trioxolane (10n). Colorless liquid (a 1:1 mixture of two isomers): ^{1}H NMR (CDCl$_3$): δ 1.60-2.27 (m, 8H), 5.06 (d, J=5 Hz, 1H), 5.13 (m, 1H), 5.18

(d, J=5 Hz, 1H), [5.06 (d, J=5 Hz), 5.56 (d, J=5 Hz)](1H) 7.45-7.60 (m, 5H). ^{13}C NMR (CDCl$_3$): δ 27.15, 29.44, 40.61, 40.93, 41.17, 94.73, 103.9 (q, J=33 Hz), 106.0, 108.6, 109.8, 122.7 (q, J=290 Hz), 123.9, 127.2, 128.8, 130.7, 132.6. Anal. Calcd. for C$_{16}$H$_{17}$O$_6$F$_3$: C, 53.04; H, 4.73. Found C, 53.31; H, 4.67.

Reduction of 10n with TPP gave cyclopentanedicarbaldehyde and corresponding carbonyl compound **6**.

Ozonolysis of 12a and 6 Ozonolysis of 0.25 g (3 mmol) of **12a** and 1.04 g (6 mmol) of trifluoroacethophenone in 50 mL of methylene chloride, followed by distillation of the solvent under reduced pressure gave a liquid residue. From which 0.16 g (1.3 mmol, 43%) of **15a** and 0.09 g (0.3 mmol, 10%) of **16a** were isolated [solvent: diethyl ether/methylene chloride, 1:15.

1-Methyl-6,7,8-trioxabicyclo[3.2.1]octane (15a). Colorless liquid: ^{1}H NMR (CDCl$_3$): δ 1.43 (s, 3H), 1.60-2.15 (m, 6H), 5.19 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 16.16, 21.31, 29. 26, 33.95, 103.16, 108.05. Ozonide **15a** was identified on the basis of its ^{1}H NMR and ^{13}C NMR data with those reported.[15]

Reduction of 15a with TPP gave 5-oxohexanal [δ 1.71 (quin., J=4 Hz, 2H), 1.96 (s, 3H), 2.30 (t, J=4 Hz, 4H), 9.59 (s, 1H)].

(3-Methyl-5-phenyl-5-trifluoromethyl-1,2,4-trioxolan-3-yl)butanal (16a). Colorless liquid: ^{1}H NMR (CDCl$_3$): δ 1.37 (s, 3H), 1.34-2.56 (m, 6H), 7.24-7.66 (m, 5H), 9.71 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 16.76, 22.71, 36.86, 43.50, 103.42 (q, J=34 Hz), 113.57, 121.54 (q, J=290 Hz), 126.54, 128.30, 130.32, 201.26. Anal. Calcd. for C$_{14}$H$_{15}$O$_5$F$_3$: C, 55.26; H, 4.97. Found C, 55.67; H, 4.85.

Reduction of 16a with TPP gave 5-oxohexanal and corresponding carbonyl compound **6**.

Ozonolysis of 12b and 6 Ozonolysis of 0.2 g (2 mmol) **12b** and 0.7 g (4 mmol) of trifluoroacetophenone in 50 mL of methylene chloride, followed by distillation of the solvent under reduced pressure gave a liquid residue. from which 0.4 g (1.24 mmol, 62%) of **16b** was isolated [solvent: diethyl ether/n-pentane, 1:4].

(3-Methyl-5-phenyl-5-trifluoromethyl-1,2,4-trioxolan-3-yl)-pentanal (16b). Colorless liquid: ^{1}H NMR (CDCl$_3$): δ 1.30 (s, 3H), 1.32-2.61 (m, 8H), 7.23-7.62 (m, 5H), 9.36 (t, J=1.5 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ 21.86, 22.39, 23.34, 35.07, 43.46, 103.40 (q, J=34 Hz), 113.55, 121.53 (q, J=289 Hz), 126.54. 128.24. 128.27, 130.22, 202.2. Anal. Calcd. for C$_{15}$H$_{17}$O$_4$F$_3$: C, 56.59; H, 5.39. Found C, 56.59; H, 5.56.

Reduction of 16b with TPP gave 6-oxoheptanal [δ 1.73 (quin., J=4 Hz, 4H), 1.98 (s, 3H), 2.30 (t, J=4 Hz, 4H), 9.56 (s, 1H)] and corresponding carbonyl compound **6**.

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