Reaction of Ozonide with $SbCl_5$ or $ClSO_3H$. Participation of $SbCl_5$-Complexed or Protonated Carbonyl Oxide

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Abstract: The reactions of 11 kinds of 1,2,4-trioxolanes (ozonides) with $SbCl_5$ or $ClSO_3H$ in methylene chloride have been investigated. Depending on the substituents, the reaction paths seem to vary. We have proposed the mechanism that heterolytic fission of the C-O bond of the peroxide bridge affords 3,6-dialkyl-1,2,4,5-tetroxane and/or 1,4-dialkyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane. The reaction of methylcyclopentene ozonide with $SbCl_5$ or $ClSO_3H$ gave stereoselectively 1-methyl-2,3,5,6,11-pentaoxa-4-*exo*-(4-ketopentyl)bicyclo[5.3.1]undecane, which rearranged to *trans*-3,6-bis(4-ketopentyl)-1,2,4,5-tetroxane. A similar result was obtained in the reaction of phenylcyclopentene ozonide with $ClSO_3H$. In contrast, the reaction with $SbCl_5$ afforded stereoselectively *cis*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane. By cleavage of the ether bridge, however, a mixture of ketone (aldehyde) and ester (carboxylic acid) is obtained in a molar ratio of 1:1. The reaction of some ozonides with liquid sulfur dioxide has been performed.

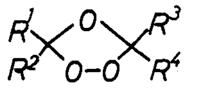
Introduction

Acid-catalyzed decomposition of some ozonides (1,2,4-trioxolanes) has been examined, but the mechanism has not been elucidated because of the lack of systematic studies. Bernatek and his co-workers[1,2] have found that decomposition of ozonides by means of formic acid, or acetic acid plus perchloric acid, yielded performic acid or peracetic acid with the expected carbonyl compounds, and a mechanism was suggested involving a initial protonation and cleavage at the more basic ether oxygen. However, a different mechanism was proposed to explain the reaction of 5-decene ozonide in acetic acid in the presence of catalytic amounts of *p*-toluenesulfonic acid:[3] catalysis at a peroxidic oxygen occurs to give an aldehyde and a protonated carbonyl oxide. The latter decomposes to a carboxylic acid. As evidence for this mechanism, it was cited that a small amount of acyloxyalkyl hydroperoxide was obtained. It is also known that the reaction of 2-phenylskatole ozonide with sulfuric acid in the presence of acetic anhydride in ether gave the rearranged product, *N*-benzoyl-*O*-acetyl-*o*-aminophenol.[4] To explain the result, a mechanism involving O-O bond fission in the first step of the reaction was suggested.

In light of these results, we have examined the reaction of 11 kinds of ozonides with $SbCl_5$ or $ClSO_3H$ in methylene chloride, and now report that heterolytic fission of the C-O bond of the peroxide bridge affords 3,6-dialkyl-1,2,4,5-tetroxane **3** and/or 1,4-dialkyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane **2**. By cleavage of the ether bridge, however, a mixture of ketone (aldehyde) and ester (carboxylic acid) is obtained in a molar ratio of 1:1.

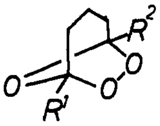
Results and Discussion

When 1-methylcyclopentene-1 ozonide (**1a**) was allowed to react with 0.03 molar equiv of $SbCl_5$ in methylene chloride at room temperature for 30 min, 1-methyl-2,3,5,6,11-pentaoxa-4-*exo*-(4-ketopentyl)bicyclo[5.3.1]undecane (**2a**) was obtained in a yield of 32% along with a 29% yield of *trans*-3,6-bis(4-ketopentyl)-1,2,4,5-tetroxane (**3a**) (see Table I). The fact that 44% of **2a** rearranges to **3a** in the presence of 0.06 molar equiv of $SbCl_5$ for the period up to 30 min suggests that **2a** forms from **1a** almost exclusively in the first stage of the reaction (see Table II). We suggest the mechanism in Scheme I to explain the stereoselective formation of **2a**. The first step involves heterolytic fission of the C-O bond of the peroxide bridge, followed by electron migration to give the $SbCl_5$-complexed carbonyl oxide **4**. Because of steric reasons, **4** should be the anti form.[5] Then the positive carbon of **4** attacks the oxygen of the peroxide bridge of another ozonide from the endo direction to give the zwitterionic intermediate **5**, which is followed by nucleophilic attack of the oxygen attached to $SbCl_5$ at C_2 to afford **2a**.[6] Attack of **4** from the exo direction seems to be improbable because of the large interaction between the methyl group of an ozonide and the oxygen attached to $SbCl_5$. In connection with the above mechanism, it should be pointed out that the participation of BF_3-complexed pinacolone oxide has been postulated by Bartlett, Baumstark, and Landis[7] to explain the formation of cyclic pinacolone diperoxide from tetramethyl-1,2-dioxetane. They suggested that a reasonable first step involves the initial coordination of BF_3 with the dioxetane, followed by rearrangement of the complex to BF_3-complexed carbonyl oxide. The carbonyl oxide formed by elimination of BF_3 is subsequently dimerized into the diperoxide. Considering the fact that **2a** is the precursor of **3a** in our reaction, however, **3a** does not seem to come from the dimerization of the corresponding carbonyl oxide, but rather forms from the intermediate **6** by nucleophilic attack of the



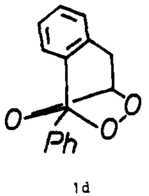
1

e; $R^1=R^2=C_6H_5$, $R^3=CH_3(CH_2)_4$, $R^4=H$
f; $R^1=C_6H_5$, $R^3=CH_3(CH_2)_4$, $R^2=R^4=H$
g; $R^1=R^3=CH_3(CH_2)_4$, $R^2=R^4=H$
h; $R^1=R^2=R^3=R^4=C_6H_5$
i; $R^1=R^2=R^3=C_6H_5$, $R^4=H$
j; $R^1=R^3=C_6H_5$, $R^2=R^4=H$



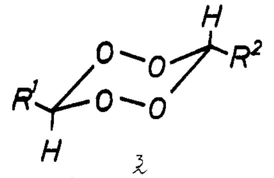
1

a; $R^1=CH_3$, $R^2=H$
b; $R^1=(CH_3)_2CH$, $R^2=H$
c; $R^1=C_6H_5$, $R^2=H$
k; $R^1=R^2=C_6H_5$



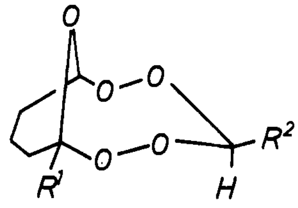
1d

0002-7863/80/1502-0288$01.00/0



1

a; $R^1 = R^2 = CH_3COCH_2CH_2CH_2$
b; $R^1 = R^2 = (CH_3)_2CHCOCH_2CH_2CH_2$
c; $R^1 = R^2 = C_6H_5COCH_2CH_2CH_2$
d; $R^1 = R^2 =$ o-Benzoylbenzyl
f; $R^1 = C_6H_5$, $R^2 = CH_3CH_2CH_2CH_2CH_2$
g; $R^1 = R^2 = CH_3CH_2CH_2CH_2CH_2$
j; $R^1 = R^2 = C_6H_5$



2

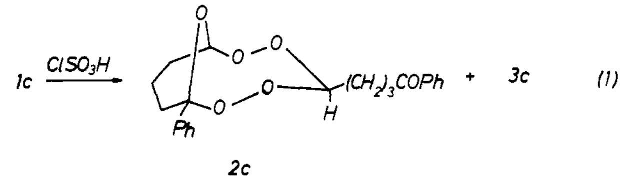
a; $R^1 = CH_3$, $R^2 = CH_3COCH_2CH_2CH_2$
b; $R^1 = (CH_3)_2CH$, $R^2 = (CH_3)_2CHCOCH_2CH_2CH_2$
c; $R^1 = C_6H_5$, $R^2 = C_6H_5COCH_2CH_2CH_2$

$RCOCH_2CH_2CH_2CO_2H$

9; $R = CH_3$
10; $R = (CH_3)_2CH$
11; $R = C_6H_5$

oxygen coordinated by $SbCl_5$ at C_6 from the front side (Scheme I). The reaction with $ClSO_3H$ gave **2a** (45%). In this reaction the protonated carbonyl oxide should be the key intermediate, which attacks another ozonide in the absence of a nucleophilic solvent. From the reaction of 1-isopropylcyclopentene-1 ozonide (**1b**) with $SbCl_5$ the mixture of 1-(2-methylethyl)-2,3,5,6,11-penta-oxa-4-*exo*-(4-keto-5-methylhexyl)bicyclo[5.3.1]undecane (**2b**) and *trans*-3,6-bis(4-keto-5-methylhexyl)-1,2,4,5-tetroxane (**3b**) was obtained.

When the reaction of 1-phenylcyclopentene-1 ozonide (**1c**) was performed with 0.03 molar equiv of $ClSO_3H$, 1-phenyl-2,3,5,6,11-pentaoxa-4-*exo*-(3-benzoylpropyl)bicyclo[5.3.1]undecane (**2c**) was obtained in a yield of 55% along with a 7% yield of *trans*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**3c**) (eq 1). In contrast, the reaction of **1c** with 0.03 molar equiv of $SbCl_5$ for 30 min gave a mixture of *cis*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**3c'**, 35%) and the trans isomer **3c** (20%). The following facts suggest that **3c'** forms from **1c** stereoselectively. In the presence of 0.06 molar equiv of $SbCl_5$, 40% of **3c'** rearranges to the trans isomer **3c** during 30 min. When **2c** was allowed to react under the same conditions, only the trans isomer **3c** was obtained in a yield of 89%, which suggests that **2c** is not the precursor of **3c'**. The reaction of **1c** with $SbCl_5$ for 5 min afforded predominantly **3c'** (37%) with **3c** (9%). To explain the stereoselective formation of **3c'** the mechanism in Scheme II is suggested. The positive carbon of the $SbCl_5$-complexed carbonyl oxide **7** attacks the oxygen of the peroxide bridge of an ozonide from the endo direction[8] to give the zwitterionic intermediate **8**, which is followed by nucleophilic attack of the oxygen coordinated by $SbCl_5$ from the direction opposite to the C–O bond of the ether bridge to afford **3c'**. The remarkable difference of the $SbCl_5$-catalyzed reaction of **1c** from that with $ClSO_3H$ may be due to the fact that the oxygen coordinated by $SbCl_5$ in the intermediate **5** is bulkier than the protonated one, compelling attack of the $SbCl_5$-coordinated oxygen at C_2, which is highly crowded by the bulky phenyl group, to be difficult. In the $SbCl_5$-catalyzed reaction a part of the ozonide **1a** or **1b** may react following the mechanism in Scheme II, but we failed to isolate the corresponding cis tetroxane. The reaction of 3-phenylindene-1



Scheme I

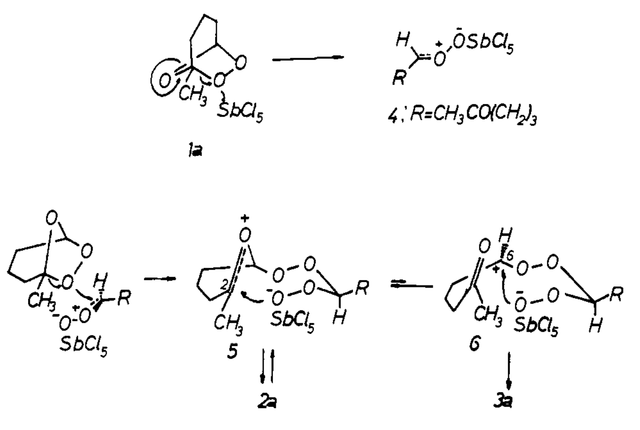


Table I. Reaction of Ozonides with $SbCl_5$ or $ClSO_3H$

ozonide	catalyst (proportion)	reaction time, min	product (% yield[a])
1a	$SbCl_5$ (0.3)	30	**3a** (61), **9** (10)
1a	$SbCl_5$ (0.03)	45	**2a** (32), **3a** (29), **9** (2)
1a	$ClSO_3H$ (0.03)	30	**2a** (45), **9** (4)[b]
1b	$SbCl_5$ (0.03)	30	**2b** (28), **3b** (32), **10** (12)
1c	$SbCl_5$ (0.3)	15	**3c** (19), **3c'**, (11), **11** (31)
1c	$SbCl_5$ (0.03)	30	**3c** (20), **3c'** (35), **11** (10)
1c	$SbCl_5$ (0.03)	5	**3c** (9), **3c'**, (37), **11** (14)
1c	$ClSO_3H$ (0.03)	30	**2c** (55), **3c** (7), **11** (6)
1d	$SbCl_5$ (0.3)	30	**3d** (2), **12** ((64)
1d	$SbCl_5$ (0.03)	30	**3d** (30), **12** (17)
1d	$ClSO_3H$ (0.03)	80	**3d** (9), 12d**12,** (42)[c]
1e	$SbCl_5$ (0.03)	30	**3g** (41), **13** (82), **18** (8)
1f	$SbCl_5$ (0.03)	30	**3f** (4), **3g** (27), **3j** (13), **16** (9), **18** (5), **17**[d]
1g	$SbCl_5$ (0.03)	30	**3g** (35), **18** (3), **17**[d]
1h	$SbCl_5$ (0.3)	30	**13** (98), **14** (90)
1h	$SbCl_5$ (0.03)	30	**13** (98), **14** (99)
1i	$SbCl_5$ (0.3)	30	**13** (88), **14** (11), **15** (71), **16** (11)
1j	$SbCl_5$ (0.3)	30	**3j** (5), **15** (80), **16** (78)
1j	$SbCl_5$ (0.03)	40	**3j** (40), **15** (60), **16** (68)
1j	$ClSO_3H$ (0.03)	30	**3j** (41), **15** (30), **16** (57)[c]
1k	$SbCl_5$ (0.3)	30	**19** (48), **20** (45)
1k	$SbCl_5$ (0.03)	30	**19** (49), **20** (39)

[a] The yield of the tetroxane was calculated by considering that 1 mol of tetroxane forms from 2 mol of ozonide. Yields of other products show mol % yield. [b] The starting material was recovered in a yield of 14%. [c] Polymeric products were isolated. [d] The yield of hexylaldehyde was not investigated.

Table II. Reaction of **2a**, **2b**, and **2c** with $SbCl_5$

substrate	proportion of catalyst	reaction time, min	product (% yield)
2a	0.6	15	**3a** (66)
2a	0.06	30	**3a** (32), **2a** (30)
2b	0.6	30	**3b**, (84)
2c	0.6	30	**3c** (81)
2c	0.06	30	**3c** (89)

Table III. Reactions of Ozonides with Liquid Sulfur Dioxide

ozonide	reaction time, h	product (% yield[a])
1h	12	**13** (95), **14** (90)
1i	24	**13** (82), **14** (14), **15** (59), **16** (14)
1j	24	**15** (82), **16** (91)
1k	4	**19** (35), **20** (44)

[a] The yield shows mol % yield.

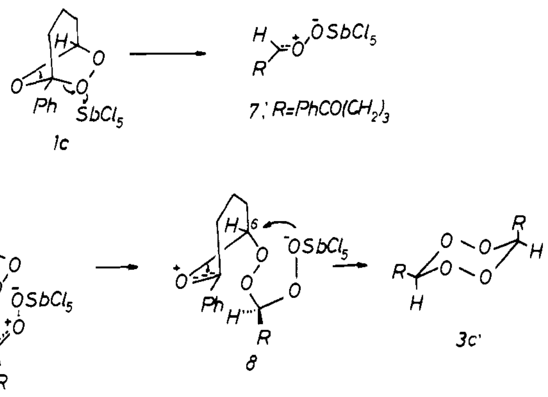
ozonide (**1d**) with $SbCl_5$ gave a mixture of *trans*-3,6-bis(*o*-benzoylbenzyl)-1,2,4,5-tetroxane (**3d**) and *o*-benzoylphenylacetic acid (**12**).

When 1,1-diphenylheptene-1 ozonide (**1e**) was allowed to react with $SbCl_5$, a mixture of *trans*-3,6-dipentyl-1,2,4,5-tetroxane (**3g**) and benzophenone (**13**) was obtained, which suggests that selective cleavage of one of the C–O bonds of the peroxide bridge, from which the more stable carbenium ion forms, occurs. The reaction of 1-phenylheptene-1 ozonide (**1f**) with $SbCl_5$ afforded *trans*-3-phenyl-6-pentyl-1,2,4,5-tetroxane (**3f**) with **3g** and *trans*-3,6-diphenyl-1,2,4,5-tetroxane (**3j**), suggesting the formation of both benzaldehyde oxide and hexylaldehyde oxide complexed with $SbCl_5$. From dodecene-6 ozonide (**1g**) the tetroxane **3g** was obtained in good yield. A reasonable first step involves heterolytic C–O bond fission of the peroxide bridge, which is followed by elimination of hexylaldehyde to form the $SbCl_5$-complexed hexylaldehyde oxide. Then this reactive intermediate may attack the oxygen of the peroxide bridge of another ozonide, which is followed by the subsequent reactions shown in Scheme III to give predominantly the thermodynamically more stable trans tetroxane **3g.** Of course, a part of **3g** may be formed from the corresponding cis tetroxane or 3,6,8-tripentyl-1,2,4,5,7-pentaoxacyclooctane as in the case of the rigid ozonide. We cannot discount a different process from that shown in Scheme III for the formation of **3g;** hexylaldehyde oxide, formed from the $SbCl_5$-complexed carbonyl oxide by elimination of the catalyst, may dimerize. However, since ozonolysis of disubstituted ethylene gives polymeric products as the main byproducts,[9] we prefer to regard the mechanism in Scheme III as more probable to explain the formation of the tetroxane in good yield. Dimerization of the $SbCl_5$-complexed carbonyl oxide does not seem to be probable in the presence of excess **1g**.

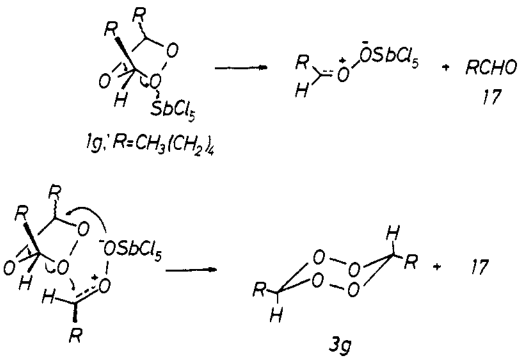
Some of the ozonides seem to react differently. When the reaction of tetraphenylethylene ozonide (**1h**) with 0.3 molar equiv of $SbCl_5$ was performed at room temperature for 30 min, a mixture of benzophenone (**13**) and phenyl benzoate (**14**) was obtained in a molar ratio of 1:1. The same result was obtained in the reaction with 0.03 molar equiv of the catalyst. The reaction of triphenylethylene ozonide (**1i**) gave **13** and phenol **15** with small amounts of **14** and benzaldehyde (**16**). We suggest paths a and b in Scheme IV to explain this result. A first step involves the initial coordination of $SbCl_5$ with the ether oxygen, followed by concerted cleavage of bonds to afford the mixture of **13** and **15** (path a) or that of **14** and **15** (path b). Alternatively $SbCl_5$ could coordinate, however, with the peroxide oxygens to yield the same products. From 1,2-diphenylcyclopentene ozonide (**1k**), phenyl 4-benzoylbutylate (**19**) and 1,3-dibenzoylpropane (**20**) were obtained. The formation of the diketone **20** can be accounted for by reduction of the intermediate ($SbCl_5$-complexed) carbonyl oxide by adventitious water.[7]

The reaction of **1h, 1i,** and **1j** with liquid sulfur dioxide, a mild Lewis acid,[10] gave a mixture of the corresponding ester and ketone (aldehyde) in a molar ratio of 1:1 (see Table III). From **1k** a mixture of **19** and **20** was obtained. The reactions of other ozonides with sulfur dioxide gave only complex mixtures.

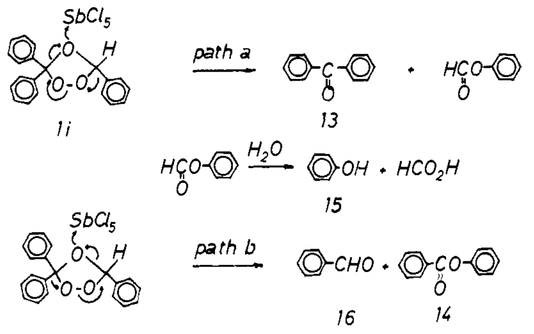
Scheme II



Scheme III



Scheme IV



Experimental Section

General. ^1H NMR spectra were obtained with a JNM-PS-100 spectrometer, ^{13}C NMR spectra with a JEOL FX-60 at 15.03 Hz in $CDCl_3$ at 21 °C using the pulse Fourier transfer technique, mass spectra with a Hitachi RMU-6H spectrometer, and infrared spectra with a Hitachi 215 spectrometer. Molecular weights were measured by a Hitachi Perkin-Elmer 115 vapor pressure osmometer. Ozonolyses were carried out using a Nippon Ozone Model 0-1-2 ozonator.

Ozonolysis Procedure. From 5 to 10 mmol of olefins, dissolved in 30 mL of CCl_4, was ozonized by passing a slow stream of ozone (1 molar equiv) through the mixture. The excess ozone was removed by flushing the solution with a slow stream of nitrogen for several minutes. The pure ozonide was obtained by column chromatography on silica gel.

From 1,1-diphenylheptene-1 the ozonide (**1e**) was obtained: a liquid; NMR ($CDCl_3$) δ 5.46 (t, J = 5.4 Hz, 1 H); IR 1450, 1260, 1210, 1100, 1050, 755, 695 cm^{-1}. Anal. ($C_{19}H_{22}O_3$) C, H. The ozonolysis of 1-phenylheptene-1 gave a mixture of the ozonides **1f** and **1g**, which were separated by repeated column chromatography. The ozonide **1f** was a liquid: NMR ($CDCl_3$) δ 0.86 (t, J = 5.4 Hz, 3 H), 1.12–1.96 (m, 8 H), 5.42 (t, J = 3.8 Hz, 1 H), 5.96 (s, 1 H), 7.10–7.60 (m, 5 H); IR 1460, 1380, 1316, 1220, 1110, 1060, 1015, 760, 700 cm^{-1}. Anal. ($C_{13}H_{18}O_3$) C, H. The ozonide **1g** was a liquid: NMR ($CDCl_3$) δ 0.88 (t, J = 5.4 Hz, 6 H), 1.08–1.84 (m, 16 H), 5.12 (t, J = 3.8 Hz, 2 H);

IR 1475, 1390, 1110, 920 cm^{-1}. Anal. ($C_{12}H_{24}O_3$) H; C: calcd, 66.63; found, 65.80. From 1-isopropylcyclopentene the ozonide **1b** was obtained: a liquid; NMR δ 1.03 (d, J = 7.5 Hz, 6 H), 1.40–2.48 (m, 7 H), 5.50 (br s, 1 H); IR 1460, 1345, 1095 cm^{-1}. Anal. ($C_8H_{14}O_3$) C, H.

Ozonides **1a**,[11] **1c**,[12] **1d**,[13] **1h**,[14] **1i**,[12] **1j**,[12] and **1k**[13] were prepared according to the reported methods.

Reaction of 1-Methylcyclopentene Ozonide (1a), 1-Isopropylcyclopentene Ozonide (1b), 3-Phenylindene Ozonide (1d), and 1,2-Diphenylcyclopentene Ozonide (1k) with $SbCl_5$. To a solution of **1a** (2 mmol) in methylene chloride (20 mL) was added $SbCl_5$ (0.06 mmol) in methylene chloride (20 mL) in one portion. The reaction was continued at room temperature for 30 min. After workup the neutral products were chromatographed on silica gel using 4:1 benzene–ether. The first fraction contained 1-methyl-2,3,5,6,11-pentaoxa-4-*exo*-(4-ketopentyl)bicyclo[5.3.1]undecane (**2a**): a liquid; NMR δ 1.48–2.04 (m, 10 H), 1.46 (s, 3 H, CCH_3), 2.12 (s, 3 H, $COCH_3$), 2.46 (t, J = 6.8 Hz, 2 H, $COCH_2$), 5.34 (br s, 1 H, H-7), 5.54 (t, J = 5.1 Hz, 1 H, H-4); IR 1720, 1380, 1235, 1160, 1110, 1055, 940 cm^{-1}. Anal. ($C_{12}H_{20}O_6$) C, H (for the assignment of the structure see that of **2c**). The second fraction contained *trans*-3,6-bis(4-ketopentyl)-1,2,4,5-tetroxane (**3a**): mp 79.5–81.0 °C; mol wt 238 (calcd for $C_{12}H_{20}O_6$, 260); NMR ($CDCl_3$) δ 2.16 (s, 6 H, $COCH_3$), 2.48 (t, J = 6.2 Hz, 4 H, $COCH_2$), 5.85 (t, J = 5.1 Hz, 2 H, H-3 and H-6); IR 1715, 1390, 1260, 1170, 1105, 1060, 1000 cm^{-1}. Anal. ($C_{12}H_{20}O_6$) C, H. From the acid layer 5-ketohexanoic acid (**9**) was isolated, bp 120–121 °C (1 mm) (lit.[15] 141–149 °C (2 mm)).

The reaction of **1b** with $SbCl_5$ gave a mixture of **2b** and **3b**, which were separated by column chromatography on silica gel. 1-(2-Methylethyl)-2,3,5,6,11-pentaoxa-4-*exo*-(4-keto-5-methylhexyl)bicyclo[5.3.1]undecane (**2b**) was a liquid: NMR ($CDCl_3$) δ 0.86 (d, J = 5.1 Hz, 3 H, CCH_3), 0.94 (d, J = 5.1 Hz, 3 H, CCH_3), 1.07 (d, J = 7.0 Hz, 6 H, $COC(CH_3)_2$), 1.20–2.12 (m, 11 H), 2.38 (septet, J = 7.0 Hz, COCH), 2.43 (t, J = 6.8 Hz, 2 H, $COCH_2$), 5.24 (br s, 1 H, H-7), 5.44 (t, J = 4.5 Hz, 1 H, H-4); IR 1705, 1470, 1385, 1250, 1115, 1015, 995 cm^{-1}. Anal. ($C_{16}H_{28}O_6$) C, H. *trans*-3,6-Bis(4-keto-5-methylhexyl)-1,2,4,5-tetroxane (**3b**) was a solid: mp 68–69 °C; NMR ($CDCl_3$) δ 1.10 (d, J = 6.9 Hz, 12 H, CCH_3), 1.40–1.88 (m, 8 H), 2.36–2.72 (m, 6 H), 5.85 (t, J = 4.5 Hz, 2 H, H-3 and H-6); IR 1705, 1470, 1385, 1250, 1115, 1015, 995 cm^{-1}. Anal. ($C_{16}H_{28}O_6$) C, H. As an acid product 5-keto-6-methylheptanoic acid (**10**) was obtained, bp 145–146 °C (10 mm) (lit.[16] 147–148 °C (10 mm)).

From **1d** *trans*-3,6-bis(*o*-benzoylbenzyl)-1,2,4,5-tetroxane (**3d**) was isolated: mp 154–155 °C; NMR ($CDCl_3$) δ 2.80–3.56 (m, 4 H), 5.72 (t, J = 6.0 Hz, 2 H, H-3 and H-6), 6.60–7.88 (m, 18 H); IR 1665, 1450, 1270, 1120, 1005, 930, 755, 710 cm^{-1}. Anal. ($C_{30}H_{24}O_6$) C, H. The acid product was *o*-benzoylphenylacetic acid (**12**), mp 130–131 °C (lit.[17] 130–131 °C).

The reaction of **1k** gave, with 1,3-dibenzoylpropane (**20**), phenyl 4-benzoylbutylate (**19**) which was hydrolyzed to give 4-benzoylbutanoic acid (**11**), mp 127–128 °C (lit.[18] 127–128 °C).

Reaction of 1-Phenylcyclopentene Ozonide (1c) with $SbCl_5$. The reaction of the ozonide **1c** (6 mmol) with the catalyst (0.18 mmol) was performed at room temperature for 30 min. Trituration of the neutral product with ether gave *trans*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**3c**): mp 147–148 °C; mol wt 388 (calcd for $C_{22}H_{24}O_6$, 384); NMR ($CDCl_3$) δ 1.48–2.08 (m, 8 H), 2.98 (t, J = 6.8 Hz, 4 H, $COCH_2$), 5.88 (t, J = 5.1 Hz, 2 H, H-3 and H-6); IR 1680, 1265, 1210, 1010 cm^{-1}. Anal. ($C_{22}H_{24}O_6$) C, H. After evaporation of ether, the mother liquor was triturated with aqueous methanol to afford *cis*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**3c′**): mp 106–107 °C; mol wt 410 (calcd for $C_{22}H_{24}O_6$, 384); NMR ($CDCl_3$) δ 1.48–2.16 (8 H, m), 2.98 (t, J = 6.8 Hz, 4 H, $COCH_2$), 5.47 (br s, 1 H, H-3, eq), 5.68 (t, J = 5.4 Hz, 1 H, H-6, ax); IR 1690, 1680, 1380, 1260, 1205, 1010 cm^{-1}. Anal. ($C_{22}H_{24}O_6$) C, H. As an acid product **11** was obtained.

Reaction of 1-Phenylcyclopentene Ozonide (1c) with $ClSO_3H$. The mixture of the ozonide **1c** (6 mmol) and $ClSO_3H$ (0.18 mmol) was kept at room temperature for 30 min. The reaction products were triturated with ether, which gave 1-phenyl-2,3,5,6,11-pentaoxa-4-*exo*-(3-benzoylpropyl)bicyclo[5.3.1]undecane (**2c**): mp 144–145 °C; mol wt 365 (calcd for $C_{22}H_{24}O_6$, 384); ^1H NMR ($CDCl_3$) δ 1.40–2.04 (m, 10 H), 2.95 (t, J = 5.7 Hz, 2 H, $COCH_2$), 5.60 (br s, 1 H, H-7), 5.72 (t, J = 5.7 Hz, 1 H, H-4), 7.12–7.70 (m, 8 H), 7.75–7.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.785, 19.363, 24.832, 28.007, 33.995, 37.847 (CH_2), 98.444 (C-4), 103.329 (C-7), 108.910 (C-1), 125.465, 128.014, 128.118, 128.589, 132.962, 136.914, 142.279 (phenyl), 199.337 (CO); MS *m/e* 384 (M^+), 192 ($M^+ - 192$), 177 ($M^+ - 207$), 158 ($M^+ - 226$), 148 ($M^+ - 238$), 146 ($M^+ - 238$), 120 ($M^+ - 264$), 105 ($M^+ - 279$). Anal. ($C_{22}H_{24}O_6$) C, H. The proton attached to C-7 appeared as a broad singlet even in the widened spectrum. The coupling constant of H-5 with the vicinal protons in the bicyclo[3.2.1]octane system is well known to be very small.[19] The H-5 proton of **1c** also appeared as a not-well-resolved triplet ($J \simeq 1.2$ Hz). On the analogy of the structure, H-7 of **2c** is reasonably expected to appear as a broad singlet. Assignment of the ^{13}C NMR spectrum of **2c** depended on the comparison of the spectrum with that of **1c**; δ 16.080, 29.035, and 33.176 (CH_2), 103.672 (C-5), 107.974 (C-1), 125.841, 128.362, 129.415, and 135.997 (phenyl). The exo configuration was assigned on the basis of the similarity of the triplet signal of H-4 with that of the axial proton of **3c** or **3c′**. In contrast, the signal of the equatorial proton of **3c′** is a broad singlet. Column chromatography of the mother liquor on silica gel gave **3c**. From the acid layer **11** was obtained.

Reaction of 1-Phenylheptene-1 Ozonide (1f) with $SbCl_5$. A mixture of **1f** (4 mmol) and the catalyst (0.12 mmol) in methylene chloride (40 mL) was kept at room temperature for 30 min. The neutral products were isolated by column chromatography on silica gel (elution with light petroleum–benzene and then benzene–ether). 3,6-Dipentyl-1,2,4,5-tetroxane (**3g**) was a solid: mp 33–34 °C; NMR ($CDCl_3$) δ 5.68 (t, J = 4.5 Hz, 2 H); IR 1470, 1380, 1360, 1135, 920 cm^{-1}. Anal. ($C_{12}H_{24}O_4$) C, H. 3-Phenyl-6-pentyl-1,2,4,5-tetroxane (**3f**) was a liquid: NMR ($CDCl_3$) δ 6.02 (t, J = 4.8 Hz, 1 H), 6.68 (s, 1 H); IR 1460, 1360, 1010, 920, 755, 695 cm^{-1}. Anal. ($C_{13}H_{18}O_4$) C, H. 3,6-Diphenyl-1,2,4,5-tetroxane (**3j**) was a solid, mp 201–202 °C (lit.[20] 202 °C). As an acid product hexanoic acid (**18**) was isolated.

General Procedure for the Reaction of the Ozonide with Liquid Sulfur Dioxide. Into a high-pressure vessel containing the ozonide (1 mmol), sulfur dioxide (20 mL) was distilled at −70 °C. The vessel was allowed to warm to room temperature, and the reaction was continued for the appropriate time. After conventional workup the products were isolated by column chromatography on silica gel.

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