Reaction of 13 with Sodium 2,2,2-Trifluoroethoxide. Method A. To a stirred solution of 0.52 g (1.08 mmol) of **13** in 2 mL of benzene-d_6 was added, at 10 °C, 0.26 g (2.15 mmol) of sodium 2,2,2-trifluorethoxide and 0.57 g (2.15 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. The following spectral data were obtained after 5 min of stirring: ^{31}P (C_6D_6) δ −155.7 (82%), −159 (18%). The ^{19}F NMR spectrum has a major resonance at δ −80.01 (J_{FCCH} = 10 Hz) and two triplets at δ −74.85 (J_{FCCH} = 8.5 Hz) and −75.00 (J_{FCCH} = 10.6 Hz).

Method B. To a stirred solution of 0.52 g (1.08 mmol) of **13** in 2 mL of hexamethylphosphorictriamide, at 10 °C, was added 0.33 g (2.7 mmol) of sodium 2,2,2-trifluoroethoxide in 2 mL of the same solvent. Immediately after mixing the ^{31}P NMR spectral data were obtained: ^{31}P NMR (external lock, 7 °C) δ −161.3.

Reaction of 14 with Sodium 2,2,2-Trifluoroethoxide. To a stirred solution of 0.24 g (0.52 mmol) of **14** in 2 mL of benzene-d_6 was added, at 10 °C, 0.13 g (1.04 mmol) of sodium 2,2,2-trifluoroethoxide and 0.28 g (1.04 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. The progress of the reaction was monitored by observing the ^{31}P NMR spectrum in C_6D_6: 2 days at room temperature, δ −58.5; 1 day at 36 °C, δ 24.7 (triphenylphosphine oxide, 10%), δ −58.5 (90%); 2 days at 36 °C, δ 24.7.

Reaction of 15 with Sodium 2,2,2-Trifluoroethoxide. To a stirred solution of 0.43 g (1.1 mmol) of **15** in 2 mL of benzene-d_6 was added, 10 °C, 0.27 g (2.2 mmol) of sodium 2,2,2-trifluoroethoxide and 0.58 g (2.2 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. After 10 min of stirring, the only absorption in the ^{31}P NMR spectrum was at δ −128.0.

Reaction of 16 with Sodium 2,2,2-Trifluoroethoxide. To a stirred solution of 0.4 g (1.6 mmol) of **16** in 2 mL of benzene-d_6 was added, at room temperature, 0.39 g (3.2 mmol) of sodium 2,2,2-trifluoroethoxide and 0.85 g (3.2 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. After 30 min of stirring at room temperature the ^{31}P NMR spectrum (C_6D_6) showed two absorptions at δ −102.2 (33%) and −105.9 (67%). The ^{13}C NMR spectrum shows strong absorptions for the 18-crown-6 ether and excess salt as well as complicated multiplets due to coupling to fluorine; however there are three equal-sized doublets which are well resolved. A possible assignment is δ 59.2 (d, J_{COP} = 15.7 Hz) and δ 59.5 (d, J_{COP} = 22 Hz) for the methylene carbons of the cis isomer and δ 59.6 (d, J_{COP} = 11.6 Hz) for the methylene carbons of the trans isomer. In a similar experiment, using toluene-d_8 as the solvent, conducted at −23 °C the following spectral data were obtained: ^{31}P NMR (toluene-d_8) δ −102.2 (50%) and δ −105.9 (50%). After the reaction mixture was warmed to room temperature overnight, the relative precentages became 33:66.

Acknowledgment. This research has been supported by the National Science Foundation and by Public Health Service Research Grant GM 26428. We also wish to thank the Mobil Chemical Co. for funds which aided in the purchase of NMR equipment.

Formation of the Crossed Product 1,4-Disubstituted 2,3,5,6,11-Pentaoxabicyclo[5.3.1]undecane from a Mixture of Two Kinds of Ozonides in the Presence of an Acid Catalyst. Elucidation of the Intermediates in the Acidolysis of an Ozonide

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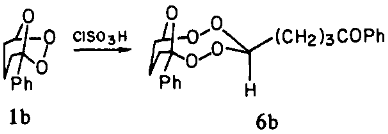
Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan, and the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan. *Received July 7, 1980*

Abstract: The reaction of a mixture of two kinds of ozonides in the presence of an acid catalyst gives the crossed 2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane derivative. When a mixture of 3-phenylindene ozonide (**1a**) and stilbene ozonide (**1e**), for example, was treated with 0.03 mol equiv of $ClSO_3H$ or $SbCl_5$, 1,4-diphenyl-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**18**) was obtained. Consistent with this result, the reaction of **1e** with a zwitterionic intermediate **3a** (prepared by treating **1a** with 1 mol equiv of $SbCl_5$) gave **18** in a yield of 10%. These results have been explained by considering a mechanism which involves the initial attack of **3a** (when the catalyst is $SbCl_5$) or a similar intermediate **2a** with a carboxonium ion structure (in the case of $ClSO_3H$) on another ozonide. However, the reaction of a mixture of 1-phenylcyclopentene ozonide (**1b**) and 1-methylcyclopentene ozonide (**1c**) gave 1-methyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**20**) as the sole crossed product. Consistent with this, the reaction of **1c** with a zwitterionic intermediate **3b** (prepared by treating **1b** with 1 mol equiv of $SbCl_5$) gave the same product **20**. The participation of the $SbCl_5$-complexed carbonyl oxide **5b** (when the catalyst is $SbCl_5$) or the protonated carbonyl oxide **4b** (in the case of $ClSO_3H$) has been postulated to explain the result. As the model species for these postulated intermediates, the carboxonium ion **2m** and the protonated carbonyl oxide **4m** have been investigated with an ab initio SCF-MO method.

Because of its unique structure, the chemistry of an ozonide (1,2,4-trioxolane) is expected to be promising. However, the synthetic use has been limited hitherto to the syntheses of ring-contraction products by thermolysis or photolysis.[2] Recently we have reported that the reaction of 1-phenylcyclopentene ozonide (**1b**) with catalytic amounts of $ClSO_3H$ gave 1-phenyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**6b**) (eq 1);[3,4] this result seems to be novel because not only does the



(1)

peroxide **6b** fall into a new category of cyclic peroxides[5] but also the formation of an eight-membered ring by cyclization is well-known to be quite difficult.[6] To explain the formation of **6b**, we

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(1) (a) Osaka University. (b) Institute for Molecular Science.

(2) (a) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1. (b) Kobayashi, Y.; Kumadaki, F.; Ohsawa, A.; Hanzawa, Y.; Harada, M.; Iitake, Y. *Tetrahedron Lett.* **1975**, 3001. (c) Story, P. R.; Morrison, W. H. III; Butler. J. M. *J. Am. Chem. Soc.* **1968**, *90*, 817.

(3) Miura, M.; Nojima, M. *J. Chem. Soc., Chem. Commun.* **1979**, 467.

(4) Miura, M.; Nojima, M. *J. Am. Chem. Soc.* **1980**, *102*, 288.

(5) Swern, D. "Organic Peroxides"; Wiley: New York, 1970, Vol. 1; 1971, Vol. 2; 1973, Vol. 3.

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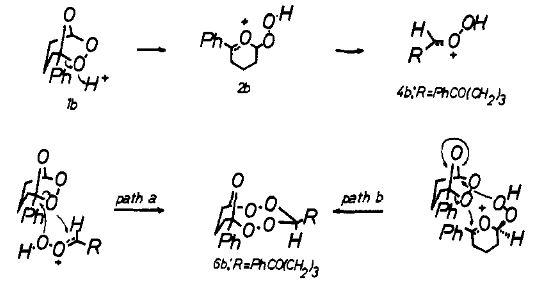
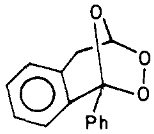
Scheme I

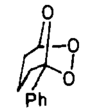


have tentatively suggested a mechanism which involves the participation of a protonated carbonyl oxide **4b** as the key intermediate;[4] the first step of the reaction involves heterolytic fission of one of the C–O bonds of the peroxide bridge to give a fairly stable intermediate **2b** with a carboxonium ion structure which is followed by electron migration to afford a protonated carbonyl oxide **4b**. Subsequently, attack of **4b** on another ozonide **1b** occurs to yield **6b** (path a in Scheme I). However, we later noticed that the same compound **6b** would have been formed by the action of an intermediate **2b** on **1b** (path b in Scheme I).

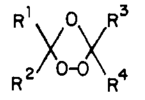
In the light of these results, we have examined the acid-catalyzed cross coupling of ozonides **1a–h**. Synthesis of a crossed



1a



1b, R = Ph
1c, R = Me



1d, $R^1 = R^2 = R^3 = Ph; R^4 = H$
1e, $R^1 = R^3 = Ph, R^2 = R^4 = H$
1f, $R^1 = R^2 = Ph, R^3 =$ pentyl, $R^4 = H$
1g, $R^1 = Ph, R^3 =$ pentyl, $R^2 = R^4 = H$
1h, $R^1 = R^3 =$ pentyl, $R^2 = R^4 = H$

product with a unique structure is of value.[7-9] In addition, the intermediates, which participate in the cyclization reaction, may be elucidated on the basis of the structure of the product together with the reactivity order of ozonides in the acidic conditions.[10]

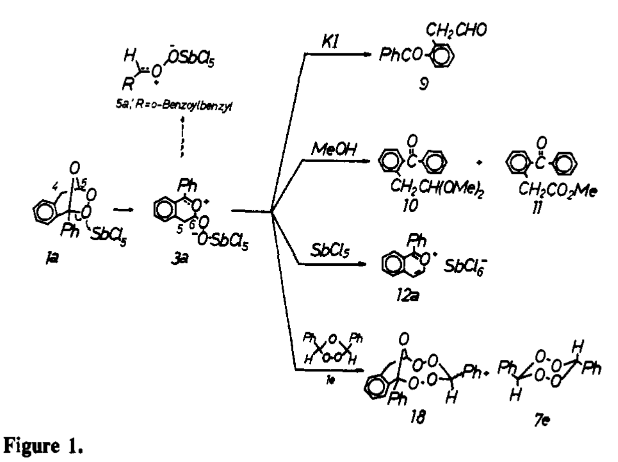


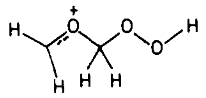
Figure 1.

Table I. Formation of Pyrylium Salt from Ozonide[a]

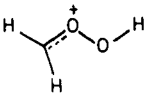
ozonide	pyrylium salt			
		% yield	UV abs, nm[b]	mp,[b] °C
1a[c]	12a	35[d]	400, 333, 248, 220	214–215
1i	12i	45	416, 333, 253, 222	255–256
1j[e]	12j	26[f]	400, 338, 236, 222[g,h]	i
1k	12k	57	452, 307, 265, 215	245–246[j]

[a] The pyrylium salt was obtained by the reaction of an ozonide with 2 mol equiv of $SbCl_5$, the gegenanion of which exchanged by treating it with perchloric acid in acetic acid. [b] Data of the perchlorate salt unless otherwise noticed. [c] UV absorption of 3a appeared at 338, 250, and 225 nm. [d] o-Benzoylphenylacetic acid was isolated in 23% yield. [e] UV absorption of 3j appeared at 337, 249, and 225 nm. [f] 1-Methyl-1-o-benzoylphenylacetic acid (30%) and 1j (17%) were also isolated. [g] Data of the hexachloroantimonate salt. [h] The perchlorate salt formed in solution, but was not isolate in the solid state. [i] The antimonate salt did not give an exact melting point. [j] Melting point in the literature is 244–245 °C: Shiner, R. L.; Knox, W. R. *J. Org. Chem.* 1951, *16*, 1064.

As an approach to elucidate the intermediates, we have examined the isolation of a reactive intermediate from an equimolar mixture of an ozonide and $SbCl_5$ in CCl_4 and its reaction with another ozonide. As the model species for the intermediates which may participate in the coupling reaction of ozonides, an ab initio SCF–MO calculation has been carried out on the carboxonium ion **2m** and the protonated carbonyl oxide **4m**. Of relevance to



2m



4m

4m, the participation of BF_3-complexed carbonyl oxide has been postulated by Bartlett, Baumstark, and Landis[11] to explain the formation of cyclic pinacolone diperoxide from tetramethyl-1,2-dioxetane.

Results and Discussions

Isolation and Reaction of Zwitterionic Intermediate 3. When a solution of 3-phenylindene ozonide (**1a**) (2 mmol) in CCl_4 (10 mL) was added to a solution of $SbCl_5$ (1 mol equiv) in CCl_4 (20 mL), a yellow precipitate separated immediately. Because of its hygroscopic character and lability in solution,[12] the precipitate could not be purified. However, the following facts suggest that

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(6) A clear-cut maximum of the activation free energy in the 8- and 11-membered ring region in the ring formation from o-ω-bromoalkoxy phenoxide and o-ω-bromoalkyl phenoxide is displayed by the enthalpy of activation, as the result of an overall medium effect, due to combination of bond angle deformation, bond opposition force, and transannular interactions: Illuminati, G.; Mandoloni, L.; Masci, B. *J. Am. Chem. Soc.* **1977**, *99*, 6308.

(7) Recently the syntheses of new cyclic peroxides have attracted greater notice because of their unique properties including chemiluminescence[8] and their biological activities.[9]

(8) (a) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366. (b) Adam, W. *Ibid.* **1979**, *12*, 390; (c) *Adv. Heterocycl. Chem.* **1977**, *21*, 437. (d) Wasserman, H. H.; Murray, R. W. "Singlet Oxygen"; Academic Press: New York, 1979.

(9) (a) Nicolaou, K. C.; Gasic, G. P.; Brnette, W. E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 293. (b) Adam, W.; Birke, A.; Cadiz, C.; Diaz, S.; Rodriguez, A. *J. Org. Chem.* **1978**, *43*, 1978. (c) Salomon, R. G.; Salomon, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 3051. (d) Porter, N. A.; Gilmore, D. W. *Ibid.* **1977**, *99*, 3503.

(10) The reactivity order of ozonides, as estimated by periodic measurement of the NMR spectra of a mixture of the ozonide and $ClSO_3H$ in CD_3OD, is as follows: **1a**, **1b** > **1c** > **1d**, **1e**, **1f**, **1g** > **1h**. It was also confirmed that the reaction proceeds via heterolytic fission of one of the C–O bonds of peroxide bridge, from which the more stable carbonium ion forms, to give the corresponding α-methoxy hydroperoxide and the compounds derived from it: Miura, M.; Nojima, M.; Kusabayashi, M. *J. Chem. Soc., Perkin Trans. 1*, in press. The relative reactivity between **1a** and **1b** could not be obtained by these experiments. Taking account the difference in stability between **2a** and **2b**, however, it seems that **1a** is more reactive than **1b** (molecular models suggest that the mutual interactions of vicinal hydrogens of the methylene chain is considerably large in **2b**. Furthermore, the positive carbon of **2a** is stabilized by two phenyl rings).

(11) Bartlett, P. D.; Baumstark, A. L.; Landis, M. E. *J. Am. Chem. Soc.* **1977**, *99*, 1890.

(12) At low temperature the solubility of **3a** in CH_2Cl_2 is quite low. When the solution is warmed to room temperature, the absorption of the pyrylium ion starts to appear gradually.

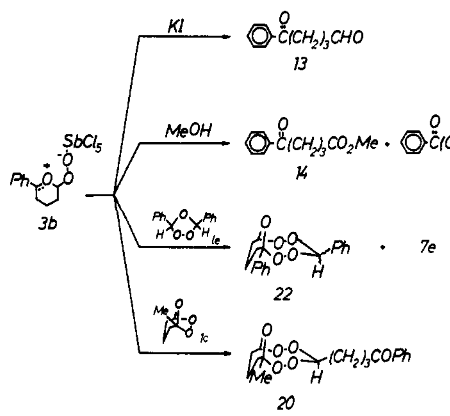
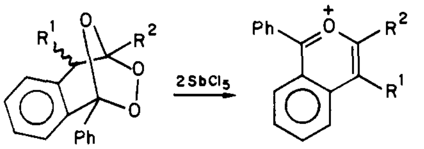


Figure 2.

this compound is zwitterion **3a** (Figure 1). (a) ^{1}H NMR spectrum in CD_2Cl_2 showed two doublets centered at δ 3.70 ($\sim$1 H, the separation of the peaks = 5.6 Hz) and 4.03 ($\sim$1 H, the separation of the peaks = 8.0 Hz) due to protons attached to C-5[13] and the absorption of H-6 in the region of aromatic protons. Thus, these protons were strongly deshielded compared with the corresponding protons of **1a** [δ 3.03 (2 d, J = 18.4 and 0.5 Hz, 1 H, H-4), 3.38 (2 d, J = 18.4 and 1.8 Hz, 1 H, H-4), and 6.20 (2 d, J = 1.8 and 0.5 Hz, 1 H, H-5)]. These data suggest that the precipitate is not a 1:1 donor–acceptor complex between the catalyst and **1a** coordinated at the peroxidic oxygen but the zwitterion **3a**.[14] (b) The UV absorption (λ_{max} 338 nm) in CH_2Cl_2 may be reasonably attributed to **3a** on the basis of the fact that a solution of 2-phenyl-1-oxonia-1-cyclopentene hexachloroantimonate in CF_3CO_2H shows absorption at 292 nm.[14a] (c) When the precipitate was treated with potassium iodide in acetic acid, iodine was liberated immediately. From a reaction mixture, *o*-benzoylphenylacetaldehyde (**9**) was isolated in a yield of 69%.[15] (d) The reaction with methanol gave a mixture of 1,1-dimethoxy-*o*-benzoylphenylethane (**10**) and methyl *o*-benzoylphenylacetate (**11**) in yields of 14% and 17%, respectively.[10] (e) When the precipitate was treated with 1 mol equiv of $SbCl_5$ in CH_2Cl_2, 2-phenyl-3,4-benzopyrylium hexachloroantimonate (**12a**) was obtained (Figure 1). This result and the NMR data[16] strongly suggest that the precipitate is not the $SbCl_5$-complexed carbonyl oxide **5a**. The reactions of **1a**, **1i**, **1j**, and **1k** with 2 mol equiv of $SbCl_5$ gave the corresponding pyrylium salts **12a**, **12i**, **12j**, and **12k**, respectively (eq 2 and Table I). A similar zwitterionic intermediate **3b** was isolated from **1b** (Figure 2). The structure was also assigned on the basis of spectral and chemical properties: (a) ^{1}H NMR [δ 1.88–2.32 (m, 2 H), 2.40–2.76 (m, 2 H), 2.92–3.24 (m, 2 H), 5.98 (t, J = 5.8 Hz, 1 H, H-6), 7.36–7.72 (m, 3 H), and 7.84–8.04 (m, 2 H)] is consistent with the proposed structure.[16] (b) Treatment with KI in acetic acid gave 5-benzoylbutyraldehyde (**13**) in 68% yield. (c) When the precipitate was allowed to react with methanol, a mixture of methyl 4-benzoylbutylate (**14**) and 1,1-dimethoxy-4-benzoylbutane (**15**) was obtained in yields of 8% and 45%, respectively (Figure 2). Other ozonides **1c–h** did not give, however, the similar zwitterionic intermediates in a stable form.



(2)

1a, $R^1 = R^2 = H$
1i, $R^1 = Ph, R^2 = H$
1j, $R^1 = Me, R^2 = H$
1k, $R^1 = H, R^2 = Ph$

12a, $R^1 = R^2 = H$
12i, $R^1 = Ph, R^2 = H$
12j, $R^1 = Me, R^2 = H$
12k, $R^1 = H, R^2 = Ph$

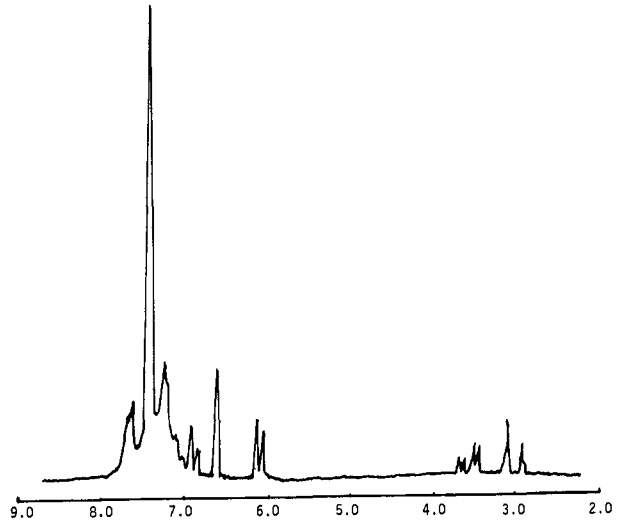


Figure 3. ^{1}H NMR spectrum of **18** in $CDCl_3$.

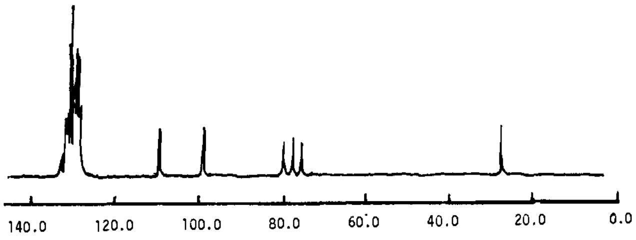


Figure 4. ^{13}C NMR spectrum of **18** in $CDCl_3$.

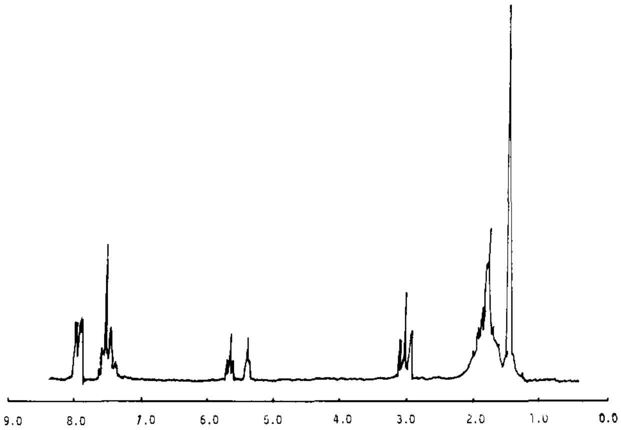


Figure 5. ^{1}H NMR spectrum of **20** in $CDCl_3$.

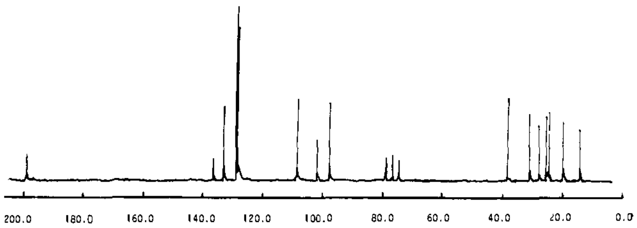


Figure 6. ^{13}C NMR spectrum of **20** in $CDCl_3$.

The reaction of **3a** with stilbene ozonide (**1e**) was performed at −60 to −20 °C, and the products were isolated by column

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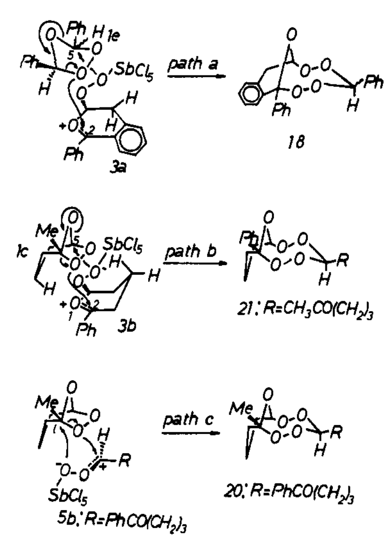
(13) The signal should be appeared as two quartets because of the geminal coupling and the coupling with H-6. Because of the low solubility of **3a** in CD_2Cl_2, however, other signals could not be distinguished form the noise.

(14) (a) Ward, H. R.; Scherman, P. D., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3812. (b) Olah, G. A.; Calin, M.; O'Brien, D. H. *Ibid.* **1967**, *89*, 3582. (c) *Ibid.* 3586. (d) Olah, G. A.; Bollinger, J. M. *Ibid.* **1967**, *89*, 2993. (e) Perst, H. *Carbonium Ions 5*, 1961–2047.

(15) In this reaction and the continuing reactions the yields of the products were calculated on the basis of ozonide used.

(16) One of the reviewers has suggested that the NMR data may be assignable to **5a**. If this were true, the equivalent methylene protons should have been appeared as a doublet. In the case of **5b**, the methylene protons attached to benzoyl group should be appeared as a triplet. However, the data are not consistent with the above expectations.

Scheme II



chromatography on silica gel. 1,4-Diphenyl-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**18**), a cross-coupling product, was obtained in a yield of 5% along with a 8% yield of *trans*-3,6-diphenyl-1,2,4,5-tetroxane (**7e**) (Figure 1).[17] When **3b** was treated with the same ozonide, **1e**, a mixture of **22** and **7e** was obtained in yields of 10% and 7%, respectively (Figure 2). The identity of **18** was determined by its spectra characteristics [see Experimental Section, Figures 3 (^{1}H NMR), and 4 (^{13}C NMR)]. We suggest the following mechanism (path a in Scheme II) to explain the result. The first step involves the attack of the C-2 of **3a** on the peroxidic oxygen of **1e**, followed by electron migration and the subsequent attack of the oxygen coordinated by SbCl$_5$ on the C-5 of **1c** from the backside to give **18**.

The reaction of **3b** with 1-methylcyclopentene ozonide (**1c**) afforded 1-methyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**20**) as the sole crossed product (Figure 2). The structure of **20** was assigned on the basis of its spectral properties [see Experimental Section, Figures 5 (^{1}H NMR), and 6 (^{13}C NMR)]. The attack of the C-2 of **3b** on **1c** in the first step of the reaction (path b in Scheme II), however, would afford not **20** but a 1-phenyl-4-*exo*-(4-ketopentyl) derivative **21**. In contrast, a mechanism which involves the participation of the SbCl$_5$-complexed carbonyl oxide **5b** seems to explain the result very well: the SbCl$_5$-complexed carbonyl oxide **5b**, formed from **3b** by electron migration, attacks first the peroxidic oxygen of **1c** from the endo direction, which is followed by electron migration and the subsequent attack of the oxygen coordinated by SbCl$_5$ on the C-1 of **1c** from the front side to give **20** (path c in Scheme II).

From steric reasons the configuration of the SbCl$_5$-complexed carbonyl oxide is supposed to be anti; alkoxy carbenium ions, which have analogous structures with **5b**, exist mainly as anti forms.[14b-e]

MO Approach to the Carboxonium Ion 2m and the Protonated Carbonyl Oxide 4m. As the model species for the two postulated intermediates in the cross cyclization of ozonides, **2m** and **4m** (plus formaldehyde) were investigated with the ab initio SCF–MO method. The geometries of these species were fully optimized by the energy gradient method[18] with the STO-3G basis set.[19] The energies at the optimized geometries were calculated with the 4-31G basis set.[20] The equilibrium geometry (in angstroms and degrees) for **2m** is shown in Figure 7. The atoms C-1, O-2, C-3, O-4, O-5, and H-1 of **2m** are on the same plane, while the position of H-5 is slightly below this plane. The energy obtained was −302.339 hartrees. For the protonated carbonyl oxide **4m**, we examined the planar and the cyclic forms.[21,22] The energies of

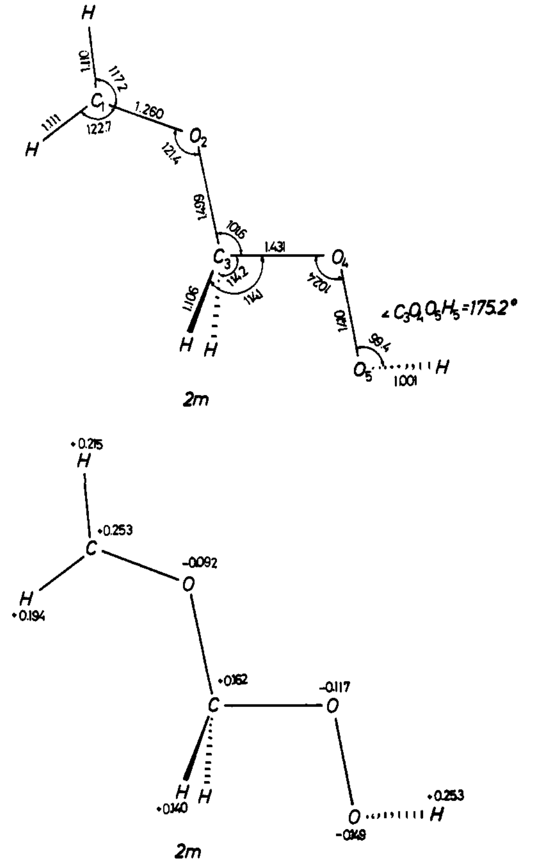


Figure 7.

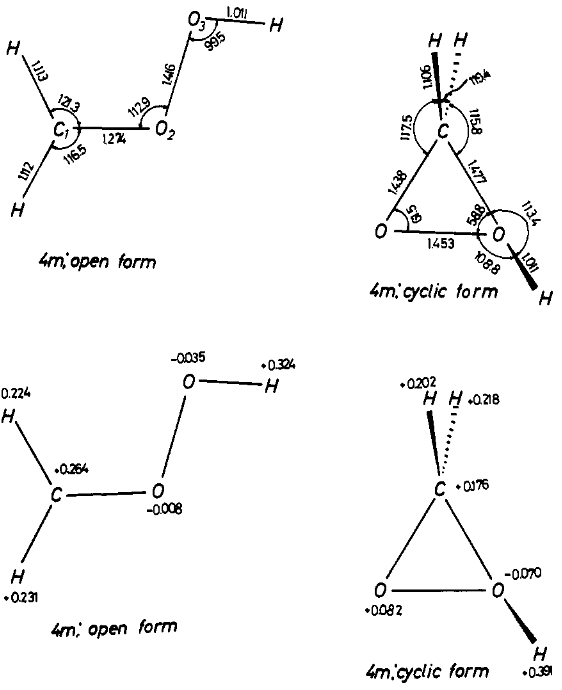


Figure 8.

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[17] As the byproducts, a large amount of complex mixture which contained *o*-benzoylphenylacetaldehyde and benzaldehyde was obtained. The acid products were the mixture of *o*-benzoylphenylacetic acid and benzoic acid. These results seem to be reasonable by considering the fact that the peroxidic products are decomposed easily in the presence of 1 mol equiv of SbCl$_5$: Miura, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1*, **1980**, 1950.

[18] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

[19] Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 575.

[20] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

these forms were calculated to be −188.6240 and −188.5605 hartrees, respectively, the open form being more stable than the cyclic form (Figure 8). Finally, the energy of formaldehyde was −113.6917 hartrees at the equilibrium geometry of $r_{C=O}$ = 1.217 Å, r_{C-H} = 1.101 Å, and ∠HCH = 114.5°.

The information obtained by these calculations reveals the following. (a) The carboxonium ion intermediate **2m** is more stable than the protonated carbonyl oxide **4m** plus formaldehyde in a value of 15.1 kcal/mol. If the entropy term is taken into account (+40 eu by dissociation in the gas phase, which corresponds to 12 kcal/mol at 300 K),[23] the energy difference becomes as small as 3.1 kcal/mol. (b) The charge density on C-3 of **2m** (+0.16) is significantly large, and approach of nucleophile to this position is quite probable, though the C-1 of **2m** (+0.25) and the C-1 of **4m** (+0.26) may be more reactive for a nucleophile. (c) The proton attached to the peroxidic oxygen in **2m** (+0.25) and also that in **4m** (+0.33) are quite acidic, and the proton transfer from these species to a nucleophile is expected to be very easy.

On the basis of these data we would like to discuss **2b** and **4b**. For the following reasons the difference in the energy between **2b** and **4b** is expected to be larger than that of the model species considered above. (a) Conformational reasons lead to the well-known fact that the six-membered carboxonium ion is more stable than the open form.[24] (b) Stabilization due to the increase of entropy by ring opening is ca. 7 kcal/mol in the gas phase.[25] Furthermore, the effect of the entropy term is smaller in solution compared with that in gas phase.[23] Thus, **2b** is more stable than **4b** by more than 8 kcal/mol, which suggests that **4b** does not seem to exist as a stable intermediate.[26] This conclusion is consistent with the fact that the reaction of **1b** with $SbCl_5$ in CCl_4 gave **3b** in a stable form. These facts, however, do not seem to exclude the possibility that **4b** formed from **2b** by electron migration works as a transient species in the favorable conditions.

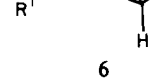
Acid-Catalyzed Cross Coupling of Ozonides. The ozonides 3-phenylindene ozonide (**1a**), 1-phenylcyclopentene ozonide (**1b**), 1-methylcyclopentene ozonide (**1c**), triphenylethylene ozonide (**1d**), stilbene ozonide (**1e**), 1,1-diphenylheptene 1-ozonide **1f**), 1-phenylheptene 1-ozonide (**1g**), and dodecene 6-ozonide (**1h**) were used for the objective reaction. For the formation of the crossed 2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane derivative, it was necessary to use a bicyclic ozonide (**1a**, **1b** or **1c**) paired to another ozonide.[27] Thus, we investigated the reactions for 17 kinds of combinations of the ozonides (Table II). The reaction was performed as follows. To a CH_2Cl_2 solution containing two kinds of ozonides in the molar ratio of 1:1 was added 0.03 mol equiv of a catalyst ($SbCl_5$ or $ClSO_3H$) in CH_2Cl_2 in one portion, and the reaction mixture was kept at 20 °C for an appropriate time. After conventional workup the products were isolated by column chromatography on silica gel.

Table II. Acid-Catalyzed Cross Coupling of Ozonides[a]

pair of ozonides	catalyst	product (% yield)
1a	$ClSO_3H$	7a (9)[c,l]
1a	$SbCl_5$	7a (30)[d,l]
1a + 1b	$ClSO_3H$[e]	16 (15), 6b (29)
1a + 1b	$SbCl_5$[f]	16 (12), 7b (10)
1a + 1c	$ClSO_3H$	17 (4), 6c (46)
1a + 1c	$SbCl_5$[e]	17 (8), 6c (27), 7a (35)
1a + 1d	$ClSO_3H$	18 (25), 26 (88)
1a + 1e	$ClSO_3H$	18 (25), 7e (2)
1a + 1e	$SbCl_5$	18 (4), 7e (7)
1a + 1f	$ClSO_3H$	19 (25), 26 (85)
1a + 1g	$ClSO_3H$[g]	18 (20), 19 (13), 1g (20)
1a + 1h	$ClSO_3H$	1h (64)
1a + 1h	$SbCl_5$	19 (3), 7a (28), 1h (58)
1b	$ClSO_3H$	6b (45)[h,l]
1b	$SbCl_5$	8b (35), 7b (20)[l]
1b	$SbCl_5$[i]	6b (48)[j]
1b + 1c	$ClSO_3H$	20 (14), 6b (25), 6c (31)
1b + 1c	$SbCl_5$	20 (34), 6b (2), 6c (25), 7b (3)
1b + 1d	$ClSO_3H$	22 (13), 6b (47), 26 (84)
1b + 1e	$ClSO_3H$	22 (19), 6b (27), 7e (3)
1b + 1e	$SbCl_5$	22 (6), 7b (18), 7e (6)
1b + 1f	$ClSO_3H$	23 (11), 6b (40), 1f (17), 26 (73)
1b + 1g	$ClSO_3H$	22 (8), 23 (12), 6b (34), 1g (29)
1b + 1g	$SbCl_5$	7b (25), 7h (32)
1b + 1h	$ClSO_3H$	6b (52), 1h (85)
1b + 1h	$SbCl_5$	8b (8), 7b (14), 7h (18)
1c	$ClSO_3H$	6c (45)[k,l]
1c	$SbCl_5$	6c (32), 7c (29)[k,l]
1c + 1e	$ClSO_3H$	23 (10), 6c (29), 1c (19), 1e (25)
1c + 1f	$ClSO_3H$	6c (44), 1f (12), 26 (74)
1c + 1g	$ClSO_3H$	24 (5), 25 (5), 6c (42), 1g (36)
1c + 1h	$ClSO_3H$	6c (53), 1h (82)

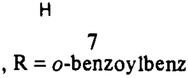
[a] A mixture of ozonides was treated with 0.03 mol equiv of the catalyst in CH_2Cl_2 at 20 °C. The reaction with $ClSO_3H$ was performed for 1 h, and, in contrast, the reaction with $SbCl_5$ was performed for 30 min unless otherwise specified. [b] The yield of the peroxide products was calculated by considering that 1 mol of the product forms from 2 mol of ozonide. Yields of other products show mole percent yield. [c] *o*-Benzoylphenylacetic acid was obtained in 42% yield along with the polymeric products. [d] The byproduct was *o*-benzoylphenylacetic acid (17%). [e] The reaction was performed for 10 min. [f] The reaction mixture was kept at 20 °C for 5 min. [g] The reaction was performed for 2 h. [h] 4-Benzoylbutanoic acid (10%) was isolated as the byproduct. [i] The reaction was performed at −30 °C for 1 h. [j] 4-Benzoylbutyraldehyde (14%) and 1b (20%) were isolated. [k] 5-Ketohexanoic acid was the byproduct. [l] Data taken from ref 4.

The reaction of a mixture of **1a** and **1e** in the presence of $ClSO_3H$ gave **18** (25%) along with **7e** (2%). It should be noted that **18** was obtained by the reaction of **1e** with **3a** which had been



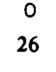
6

6b, R^1 = Ph, R^2 = $PhCO(CH_2)_3$
6c, R^1 = Me, R^2 = $MeCO(CH_2)_3$



7

7a, R = *o*-benzoylbenzyl
7b, R = $PhCO(CH_2)_3$
7c, R = $MeCO(CH_2)_3$
7e, R = Ph
7h, R = pentyl



26

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(21) Highly relevant with **4m**, the structure and the properties of carbonyl oxide (peroxymethylene) have attracted great attention. By the MO calculations, peroxymethylene is shown to be more stable in the cyclic form than the open form.[22a,b,c] Really, dioxirane (the cyclic form) has been identified in the reaction of ozone with ethylene at low temperature.[22d] It was claimed, however, that the carbonyl oxide with a zwitterionic character is the real species in solution.[2a,22e] As for *syn* and *anti*-alkylperoxymethylenes, an equilibrium in solution phase ozonolysis is excluded.[22b,d] From steric reasons, the anti form is expected to be more stable than the syn form. However, the more sophisticated calculations suggest that the syn form of methylperoxymethylene is more stable by 3–4 kcal/mol than the anti form in the nonpolar solvent.[22c,f]

(22) (a) Hiberty, P. C.; Leforeister, C. *J. Am. Chem. Soc.* **1978**, *100*, 2012. (b) Harding, L. B.; Goddard, W. A.; III. *Ibid.* **1978**, *100*, 7180. (c) Cremer, D. *Ibid.* **1979**, *101*, 7199. (d) Suerram, R. D.; Lovas, F. J. *Ibid.* **1978**, *100*, 5117. (e) Bailey, P. S.; Ferrell, T. M. *Ibid.* **1978**, *100*, 899. (f) Bailey, P. S.; Ferrell, T. M.; Rustaiyan, A.; Seyhan, S.; Unruh, L. E. *Ibid.* **1978**, *100*, 894.

(23) Schaleger, L. L.; Long, F. A. *Adv. Phys. Org. Chem.* **1963**, *1*, 1–33.

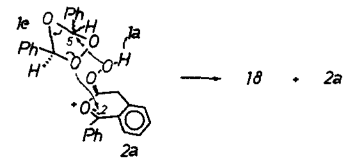
(24) Pasto, D. J.; Serve, M. P. *J. Am. Chem. Soc.* **1965**, *87*, 1515.

(25) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; pp 65–66.

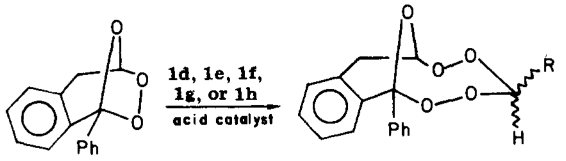
(26) Of course, there is some uncertainity when extrapolating the conclusions from the calculations of simple molecules **2m** and **4m** to the large compounds **2b** and **4b**. In addition, **2b** and **4b** are polar species, and solvent effects can be energically important and different for two species, altering the relative energy difference between them. In connection with the above, a reviewer has suggested that **2b** and **4b** may readily interconvert (or be in equilibrium). If they are so, the proportion of **2b** in equilibrium should be, however, very high.

(27) The reaction of a monocyclic ozonide in the presence of an acid catalyst only gives the corresponding 1,2,4,5-tetroxane.[4]

Scheme III



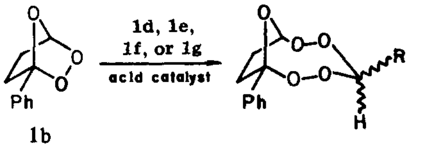
previously isolated (Figure 1). The reaction of **1a** with **1d** also gave **18**. The peroxide **19** was obtained by the reaction of a mixture of **1a** and the monocyclic ozonide **1f** or **1h**. The reaction of **1a** with **1g** gave a mixture of **18** and **19** (eq 3 and Table II).



(3)

18, R = Ph
19, R = pentyl

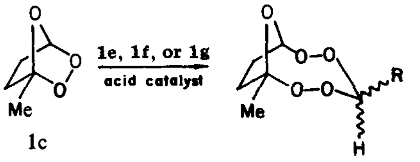
When **1b** was treated with a monocyclic ozonide (**1d–g**), we obtained **22** and/or **23** (eq 4 and Table II). The reaction of **1c** with a monocyclic ozonide (**1d–g**) gave **24** and/or **25** (eq 5 and Table II). Considering the higher reactivity of a bicyclic ozonide compared with a monocyclic ozonide,[10] the C–O bond of a bicyclic ozonide must be cleaved predominantly in the first step of the reaction to form a carboxonium ion intermediate. Attack of **2a** on **1e** is reasonably expected to give **18** (Scheme III): It is possible to bring the intermediate **2a** and the ozonide **1e** into positions favorable to ring closure. In other words, cleavage of the C–O bond of **1e** by the attack of the SP^2 carbon of **2a** on **1e** may be assisted by the nucleophilic attack of the peroxidic oxygen of **2a** on the slightly charge-developed C-5 of **1e**. In addition, a proton or SbCl$_5$ attached to a peroxidic oxygen of **2a** and a proton or SbCl$_5$ to that of **3a**, respectively, may be transferred to an ozonide in excess before cyclization to increase the nucleophilicity of the peroxidic oxygen and also to decrease the steric hindrance in the ring closure. This may be a part of the reason that the reaction of the isolated intermediate **3a** with 1 mol equiv of **1e** gave **18** in lower yield compared with the reaction of a mixture of **1a** and **1e** in the presence of catalytic amounts of an acid. In the former case there is not an excess of ozonide. An oxygen atom effect may be also a reason for the smooth formation of a crossed product with an eight-membered ring. The bond opposite force and transannular interaction in the cyclic compound containing five oxygen atoms are expected to be significantly small compared with the case of cyclooctane. The influence of the oxygen atom on ease of ring closure has been observed in the cyclization of *o*-ω-bromoalkoxy phenoxide and *o*-ω-bromoalkyl phenoxide; $k_{\text{intra}}^{\text{diether}}/k_{\text{intra}}^{\text{monoether}}$ ratio at 50 °C for the formation of an eight-membered ring is 6.42.[6] The byproduct **7e** may come from unreacted **1e** in the first stage of the reaction.[4]



(4)

1b

22, R = Ph
23, R = pentyl



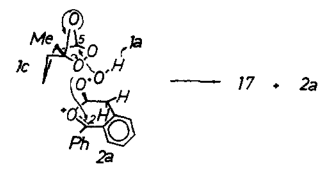
(5)

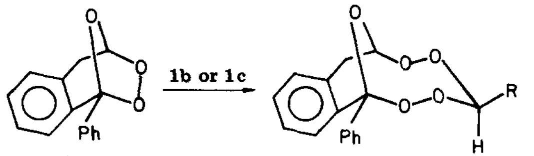
1c

24, R = Ph
25, R = pentyl

When a mixture of **1a** and **1b** was allowed to react with 0.03 mol equiv of ClSO$_3$H for 10 min, 1-phenyl-4-*exo*-(3-benzoylpropyl)-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**16**) was obtained in a yield of 15% along with a 29% yield of **6b**. Similarly, the reaction of a mixture of **1a** and **1c** yielded **17** (eq 6). If the assumption is valid that **1a** is more reactive than **1b** and **1c**,[10] the key intermediate in the above reactions should be **2a**. The formation of **16** or **17** is reasonably explained by considering the attack of the C-2 of **2a** on **1b** and **1c**, respectively (Scheme IV). In contrast, the reaction of a mixture of **1b** and **1c** in the presence of ClSO$_3$H gave 1-methyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**20**) as the sole crossed product in a yield of 14% along with **6b** (25%) and 1-methyl-4-*exo*-(4-ketopentyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**6c**) (31%) (eq 7). When SbCl$_5$ was used as the catalyst, **20** was obtained in a yield of 34% along with **6b** (2%), **6c** (25%), and *trans*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**7b**) (3%): No evidence was obtained, however, for the formation of **21**, the compound which would be formed by the attack of the C-2 of **3b** on **1c** (path b in Scheme II). It should be noticed that **20** was obtained by the reaction of **1c** with the zwitterion **3b** previously isolated, too (Figure 2). As mentioned before, a mechanism which involves the attack of a SbCl$_5$-complexed carbonyl oxide **5b** on **1c** (path c in Scheme II) seems to be most probable to explain the result. The question then arises why the reaction of a mixture of **1b** and **1c** proceeds differently. The molecular models suggest that the approach of a carboxonium ion **3b** to **1c** from the endo direction (path b in Scheme II) is quite difficult because of the large interaction between the methylene group of **3b** and the peroxidic oxygen of **1c** along with the interaction between the methylene group of **1c** and the O-1 of **3b**. The former interaction does not exist in the reaction of **3a** with **1c** (Scheme IV). These may be the reasons why **3b** reacts with **1c** via the less stable **5b**: approach of the peroxidic oxygen of **1c** to the electrophilic C-6 of **3b** may render cleavage (or weakening[28]) of the C–O bond of **3b** and change the hybrid of C-6 to sp^2 to form **5b**. From the view of steric hindrance, this intermediate or, more likely, transition state **5b**, compared with **3b**, attacks more easily the crowded peroxidic oxygen of **1c**. Thus, the formation of a C–O bond between **5b** and **1c** occurs which is accompanied by the attack of the terminal oxygen of **5b** on the highly electrophilic C-1 of **1c** to give **20**.

Scheme IV

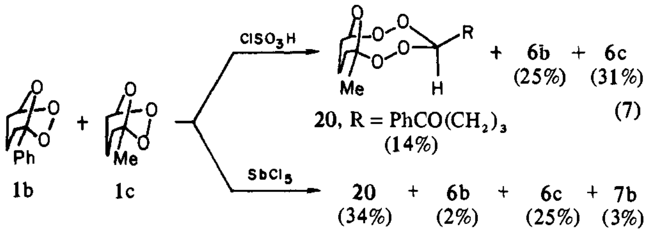




(6)

1a

16, R = PhCO(CH$_2$)$_3$
17, R = MeCO(CH$_2$)$_3$



(7)

(8)

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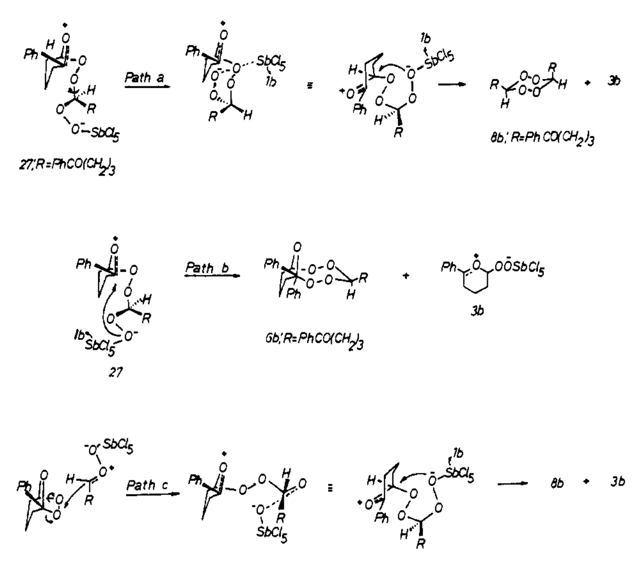
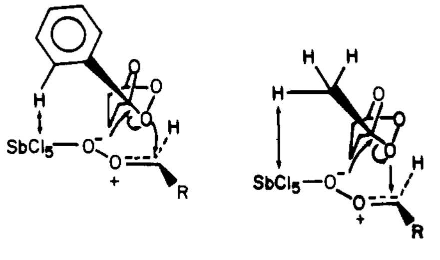
[28] The protonated carbonyl oxide, the positive carbon of which is stabilized by carbonyl oxygen participation, may be close to the true species of **4b**.

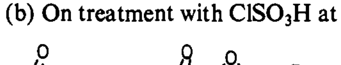
Scheme V



In the reaction of a mixture of **1b** and **1c**, the dependency of the product composition on catalyst is remarkable. The **20**/(**6b** + **7b**) ratio found in the reaction with $SbCl_5$, which is considered to be the ratio of **1c** to **1b** attacked by **5b**, is ca. 7. In contrast, the **20**/**6b** ratio is ca. 0.6 when $ClSO_3H$ is the catalyst. These results strongly suggest that the $SbCl_5$-complexed carbonyl oxide **5b**, compared with the protonated carbonyl oxide **4b**, is prone to attack the less reactive ozonide **1c**. The existence of a large interaction between the phenyl ring of **1b** and $SbCl_5$, attached to the peroxidic oxygen of **5b**, may not allow **5b** to occupy a favorable position to attack the peroxidic oxygen of **1b** with simultaneous cyclization (the structure of a possible intermediate may be shown as **27** in Scheme V). In contrast, the interaction of the methyl of **1c** with $SbCl_5$ of **5b** is not so large, and the cyclization reaction is expected to proceed smoothly to afford **20**. In the case of **4b** such an interaction is small, and this species attacks predominantly the more reactive ozonide **1b** to give **6b**.



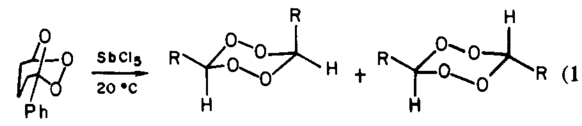
Of relevance to the above results, the product composition in the reaction of **1b** depends remarkably on reaction temperature and catalyst. (a) The reaction with $SbCl_5$ at −30 °C gave **6b** in a yield of 48% (eq 9). (b) On treatment with $ClSO_3H$ at 20 °C, **6b** was



(9)

6b, R = $PhCO(CH_2)_3$

obtained in a yield of 45%.[4] (c) When the reaction with $SbCl_5$ was performed at 20 °C, however, a mixture of *cis*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**8b**) and the trans isomer **7b** was obtained in yields of 35% and 20%, respectively (eq 10).[4] It was



(10)

8b, R = $PhCO(CH_2)_3$ 7b, R = $PhCO(CH_2)_3$

also confirmed that **6b** is not the precursor of **8b**. The mechanism in Scheme V may be the most probable explanation of these results. The $SbCl_5$-complexed carbonyl oxide **5b** attacks **1b** from the endo direction to form the intermediate **27**. At 20 °C the rotation of the C–O bond may occur first; this is followed by the transfer of $SbCl_5$ to another ozonide and the subsequent ring closure to afford **8b** (path a in Scheme V).[29] In contrast, the rotation of the C–O bond is slowed down at −30 °C and, as the result, the transfer of $SbCl_5$ to another ozonide occurs first and is followed by ring closure to yield **6b** (path b in Scheme V). The less bulky protonated carbonyl oxide **4b** seems to be able to hold an advantageous position to attack the peroxidic oxygen of **1b** with simultaneous ring closure. A mechanism which involves attack of **5b** on **1b** from the exo direction (path c in Scheme V) has been tentatively proposed to explain the formation of **8b**.[4] However, paths a and b in Scheme V seem to explain the results more rationally.

The data seem to contain some additional information. (a) In spite of the possibility of formation of two configurationally isomeric products, only one isomer was isolated in all the reactions. The coupling constants of H-4 suggest that **16**, **17**, **19**, **20**, **23**, and **25** are the compounds with an exo configuration.[4] Scheme IV suggests that the reaction of **1a** with **1c** gives the product **17** with an exo configuration. The crossed compound **20** is also expected to be formed stereoselectively from the proposed reaction scheme (path c in Scheme II).

However, the reason is obscure why the reaction of **1a** with a flexible ozonide **1h**, for example, gives only the exo isomer **19**. Of course the compound with an exo configuration is expected to be more stable than the endo isomer from steric reasons. (b) As is expected from the relative stability of carbonium ions, one of the C–O bonds of the peroxide bridge of **1d** seems to be cleaved selectively by the carboxonium ion **2**. Thus, the reaction of a mixture of **1a** and **1d**, for example, affords **18** in a yield of 25% along with a 88% yield of benzophenone (**26**). Similarly, **19** is the sole crossed product in the reaction of a mixture of **1f** and **1a**. However, the reaction of **1g** with **1a** gave both **18** (20%) and **19** (13%). As is expected from the poor reactivity, the coupling product was obtained in low yield when **1h** was used to pair to another ozonide.

Experimental Section

General Procedures. ^1H NMR spectra were obtained with a JNM-PS-100 spectrometer in $CDCl_3$, ^{13}C NMR with a JEOL-EX-60 at 15.03 MHz in $CDCl_3$ at 21 °C with the use of pulse Fourier transfer technique, MS with a Hitachi RMU-6H spectrometer, and infrared spectra with a Hitachi 215 spectrometer. Ozonolyses were carried out with use of a Nippon Ozone Model 0-1-2 ozonator.

Ozonolysis. The procedure has been described previously.[4] From 1,3-diphenylindene, the ozonide **1j** was obtained: mp 103–104 °C (from methanol); NMR δ 4.16 (s, 1 H), 5.92 (s, 1 H), 6.68–7.68 (m, 14 H); IR (KBr) 1480, 1455, 1320, 1285, 1200, 1110, 1010, 970, 760, 700 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_3$: C, 79.93; H, 5.10. Found: C, 79.62; H, 4.82. The ozonolysis of 1-methyl-3-phenylindene gave the ozonide **1j**: mp 106–107 °C (from methanol); NMR δ 1.46 (d, J = 7.5 Hz, 3 H), 3.12 (q, J = 7.5 Hz, 1 H), 5.96 (s, 1 H), 6.64–7.72 (m, 9 H); IR (KBr) 1450, 1320, 1205, 1030, 970, 760 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.42; H, 5.42. Ozonides **1a**,[30] **1b**,[31] **1c**,[32] **1d**,[31] **1e**,[31] **1f**,[4] **1g**,[4] **1h**,[4] and **1k**[33] were prepared according to the reported methods.

Isolation and Reaction of Zwitterionic Intermediate. To a solution of $SbCl_5$ (2 mmol) in CCl_4 (20 mL) was added a solution of 3-phenylindene ozonide (**1a**) (2 mmol) in CCl_4 (10 mL) at −20 °C in one portion, and the mixture was stirred for 5 min. The precipitate **3a** was filtered and washed with chilled CCl_4. The salt **3b** was prepared similarly.

The reaction of the salt **3a** was performed as follows. To methanol (30 mL) kept at −60 °C was added the precipitate **3a** (from 2 mmol of the ozonide **1a**) in one portion. The mixture was allowed to warm to −20 °C, and the reaction was continued for a further 30 min at this tem-

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[29] Even at 20 °C the process shown as path b in Scheme V seems to compete with that shown as path a in Scheme V: the NMR spectra of the crude products, after treating **1b** with 0.03 mol equiv of $SbCl_5$ for 5 min, suggests the existence of **6b**, **7b**, and **8b** in a molar ratio of 5:20:75.

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perature. After conventional workup, the products were isolated by column chromatography on silica gel. Elution with benzene gave 1,1-dimethoxy-2-*o*-benzoylphenylethane (**10**) in a yield of 14%: an oil; IR (KBr) 1660, 1445, 1270, 1120, 1065, 920, 760 cm^{-1}; NMR δ 3.02 (d, J = 6.0 Hz, 2 H), 3.18 (s, 6 H), 4.48 (t, J = 6.0 Hz, 1 H), 7.20–7.88 (m, 14 H); *m/e* 270 (M$^+$). The physical properties were identical with those of an authentic sample prepared by the reaction of *o*-benzoylphenylacetaldehyde (**9**) with methanol in the presence of $ClSO_3H$. Elution with benzene–ether (1:1) gave methyl *o*-benzoylphenylacetate (**11**): mp 70.0–70.5 °C (from methanol) (lit.[34] 70.0–70.5 °C); NMR δ 3.52 (s, 3 H), 3.86 (s, 2 H), 7.16–8.88 (m, 9 H); IR (KBr) 1740, 1660, 1600, 1445, 1270, 1170, 760, 700 cm^{-1}. The reaction of **3b** with methanol gave a mixture of 1,1-dimethoxy-4-benzoylbutane (**15**) (45%) and methyl 4-benzoylbutylate (**14**) (8%). The acetal was an oil: IR (neat) 1685, 1450, 1205, 1065, 755 cm^{-1}; NMR δ 1.52–1.92 (m, 4 H), 2.92 (t, J = 7.5 Hz, 2 H), 3.24 (s, 6 H), 4.32 (t, J = 5.4 Hz, 1 H), 7.20–7.50 (m, 3 H), 7.80–7.92 (m, 2 H). The ester was also an oil: *m/e* 206 (M$^+$); IR (neat) 1730, 1680, 1440, 1205, 745 cm^{-1}; NMR δ 1.80–2.28 (m, 2 H), 2.42 (t, J = 7.5 Hz, 2 H), 3.02 (t, J = 7.5 Hz, 2 H), 3.64 (s, 3 H), 7.20–7.64 (m, 3 H), 7.82–8.40 (m, 2 H).

When the solid **3a** (from 2 mmol of **1a**) was treated with a solution of KI (5 mmol) in CH_3CO_2H (20 mL), the aldehyde **9** was obtained in a yield of 69%: an oil; IR (neat) 1720, 1660, 1480, 1440, 1260, 920, 700 cm^{-1}. The aldehyde was characterized by oxidizing it to *o*-benzoylphenylacetic acid; mp 130–131 °C.[4] The reaction of **3b** in the same conditions afforded 4-benzoylbutyraldehyde (**13**) in a yield of 68%.

To a solution of $SbCl_5$ (2 mmol) in CH_2Cl_2 was added **3a** (from 2 mmol of **1a**) in one portion; the mixture was stirred at 20 °C for 30 min and then triturated with petroleum ether (20 mL). The pyrylium salt **12a** was filtered and dried over $CaCl_2$ in vacuo. The trial to purify the solid by recrystallization failed. However, treatment of the solid with a mixture of perchloric acid (3 mL), acetic acid (10 mL), and ether (10 mL) yielded the pure perchlorate salt.

To a solution of stilbene ozonide (**1e**) (2 mmol) in CH_2Cl_2 kept at −60 °C was added **3a** (from 2 mmol of **1a**) in one portion; the mixture was allowed to warm to −20 °C in 5 min and was then poured into ice-cold aqueous potassium hydroxide and extracted with ether. After conventional workup the neutral products were isolated by column chromatography on silica gel. Elution with petroleum ether–benzene (1:1) afforded 1,4-diphenyl-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**18**): mp 189–190 °C (from methanol); ^{1}H NMR δ 3.02 (d, J = 19.2 Hz, 1 H, H-8), 3.78 (2 d, J = 19.2 and 6.0 Hz, 1 H, H-8), 6.10 (d, J = 6.0 Hz, 1 H, H-7), 6.60 (s, 1 H, H-4), 6.83–7.92 (m, 14 H) (Figure 3); ^{13}C NMR δ 28.289 (C-8), 98.258 (C-4), 108.584 (C-7) (Figure 4); IR (KBr) 1450, 1260, 1200, 1120, 1020, 1000, 965, 750, 690 cm^{-1}; *m/e* 362 (M$^+$). Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 73.27; H, 4.94. Elution with ether gave only a complex mixture containing **9** and benzaldehyde, and the trial to identify the products failed. The reaction of **3b** with **1e** gave 1,4-diphenyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**22**) (10%) along with **1e** (25%) and **7e** (8%). The compound **22** was a solid: mp 134–135 °C (from methanol); *m/e* 314 (M$^+$); NMR δ 1.40–2.36 (m, 6 H), 5.73 (s, 1 H), 6.62 (s, 1 H), 7.08–7.76 (m, 10 H); IR (KBr) 1490, 1445, 1350, 1310, 1260, 1210, 1120, 1045, 1000, 930, 760, 695 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.75; H, 5.77. Found: C, 68.58; H, 5.70. The reaction of **3b** with **1c** gave a mixture of 1-methyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**20**), **6c**, and **1c** in yields of 14%, 30%, and 10%, respectively. The compound **20** was a solid: mp 92–93 °C (from methanol); *m/e* 322 (M$^+$); ^{1}H NMR δ 1.44 (s, 3 H), 1.52–2.16 (m, 10 H), 3.02 (t, J = 7.5 Hz, 2 H, $PhCOCH_2$), 5.38 (br s, 1 H, H-7), 5.64 (t, J = 5.0 Hz, 1 H, H-4), 7.32–7.68 (m, 3 H), 7.86–8.08 (m, 2 H) (Figure 5); IR (KBr) 1675, 1445, 1375, 1310, 1200, 1150, 1110, 1045, 1000, 930, 880, 730, 690 cm^{-1}; ^{13}C NMR δ 13.929 (CH_3), 19.415, 24.578, 25.223, 28.020, 28.988, 30.870, 37.755 (CH_2), 97.883 (C-4), 102.078 (C-7), 108.584 (C-1), 199.209 (C=O) (Figure 6). Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.36; H, 6.93.

Reaction of 1a with 1b or 1c in the Presence of $ClSO_3H$. To a solution of **1a** (2 mmol) and **1b** (2 mmol) in CH_2Cl_2 (20 mL) was added a solution of $ClSO_3H$ (0.06 mol) in CH_2Cl_2 (20 mL) in one portion, and the reaction was continued at 20 °C for 10 min. After workup the neutral products were chromatographed on silica gel with the use of 10:1 benzene–ether. The first fraction contained 1-phenyl-4-*exo*-(3-benzoylpropyl)-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**16**): mp 109–110 °C (from methanol); *m/e* 432 (M$^+$); NMR δ 1.52–2.12 (m, 4 H), 2.94 (d, J = 18.6 Hz, 1 H), 3.02 (t, J = 7.5 Hz, 2 H), 3.54 (2 d, J = 18.6 and 6.0 Hz, 1 H), 5.72 (t, J = 6.0 Hz, 1 H), 5.96 (d, J = 6.0 Hz, 1 H), 6.74–8.04 (m, 14 H); IR (KBr) 1685, 1450, 1260, 1205, 1120, 1020, 760, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 71.80; H, 5.47. The second fraction contained 1-phenyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**6b**): mp 144–145 °C.[4]

When a mixture of **1a** and **1c** was treated with 0.3 mol equiv of $ClSO_3H$ at 20 °C for 1 h, **17** (4%) and **6c** (46%) were obtained. 1-Phenyl-4-*exo*-(5-ketopentyl)-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**17**) was a solid: mp 107–108 °C (from methanol); *m/e* 370 (M$^+$); NMR δ 1.40–1.88 (m, 4 H), 2.08 (s, 3 H), 2.44 (t, J = 6.0 Hz, 2 H), 2.94 (d, J = 19.5 Hz, 1 H), 3.52 (2 d, J = 19.5 and 6.0 Hz, 1 H), 5.64 (t, J = 4.5 Hz, 1 H), 5.96 (d, J = 6.0 Hz, 1 H), 6.72–7.72 (m, 9 H); IR (KBr) 1710, 1450, 1260, 1120, 1060, 755, 715 cm^{-1}. Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99. Found: C, 67.91; H, 6.01. The compound **6c** was obtained as an oil.[4]

Reaction of a Mixture of 1a and Dodecene 6-Ozonide (1h) with $SbCl_5$. The reaction of a mixture of **1a** (2 mmol) and **1h** (2 mmol) with $SbCl_5$ (0.06 mmol) was performed at 20 °C for 30 min. After workup the neutral products were isolated by column chromatography on silica gel. Elution with benzene–petroleum ether gave **1h** (58%). Elution with benzene afforded 1-phenyl-4-*exo*-pentyl-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**19**): mp 84–85 °C (from methanol); *m/e* 356 (M$^+$); NMR δ 0.84 (t, J = 6.0 Hz, 3 H), 1.04–1.72 (m, 8 H), 2.94 (d, J = 18.0 Hz, 1H), 3.52 (2 d, J = 18.0 and 6.0 Hz, 1 H), 5.64 (t, J = 9.0 Hz, 1 H), 5.96 (d, J = 6.0 Hz, 1 H), 6.72–7.76 (m, 9 H); IR (KBr) 1445, 1260, 1200, 1105, 1010, 750, 695 cm^{-1}. Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 69.80; H, 6.82. Elution with ether–benzene (1:10) gave *trans*-3,6-bis(*o*-benzoylbenzyl)-1,2,4,5-tetroxane (**7a**): mp 154–155 °C.[4]

Reaction of a Mixture of 1b and 1-Phenylheptene 1-Ozonide (1g) with $ClSO_3H$. To a solution of **1b** (4 mmol) and **1g** (4 mmol) in CH_2Cl_2 was added a solution of $ClSO_3H$ in CH_2Cl_2 in one portion, and the reaction was continued at 20 °C for 1 h. After workup the neutral products were isolated by column chromatography on silica gel. Elution with benzene–petroleum ether (1:4) afforded **1g** (29%). Then, the products were eluted with benzene–petroleum ether (1:1). The first fraction contained 1-phenyl-4-*exo*-pentyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**23**): an oil; *m/e* 308 (M$^+$); NMR δ 0.84 (t, J = 6.0 Hz, 3 H), 1.04–2.16 (m, 14 H), 5.62 (s, 1 H), 5.68 (t, J = 4.5 Hz, 1 H), 7.16–7.70 (m, 5 H); IR (neat) 1450, 1350, 1265, 1125, 1100, 1050, 945, 760, 695 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.85. Found: C, 66.24; H, 8.06. The second fraction contained **22**. Elution wiith ether–benzene (1:10) gave **6b** (34%).

Reaction of 1b with 1c in the Presence of $SbCl_5$. The reaction of a mixture of **1b** (4 mmol) and **1c** (4 mmol) with $SbCl_5$ (0.12 mmol) in CH_2Cl_2 (40 mL) was performed at 20 °C for 30 min. The neutral products were isolated by column chromatography on silica gel with the use of ether–benzene (1:10). The first fraction contained **20**. Elution with benzene–ether (3:1) gave *trans*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**7b**): mp 147–148 °C.[4] Then **6c** was eluted.

The reaction of a mixture of **1b** and **1h** gave *cis*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxane (**8b**) (mp 106–107 °C[4]), **7b**, and *trans*-3,6-dipentyl-1,2,4,5-tetroxane (**7h**) (mp 34–35 °C[4]).

Reaction of a Mixture of 1c and 1e with $ClSO_3H$. The neutral products obtained by the reaction of a mixture of **1c** and **1e** were isolated by column chromatography on silica gel with the use of 1:4 benzene–petroleum ether and then 10:1 benzene–ether. The first fraction contained 1-methyl-4-phenyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**24**): mp 87.5–89.0 °C (from methanol); *m/e* 252 (M$^+$); NMR δ 1.52 (s, 3 H), 1.56–2.20 (m, 6 H), 5.48 (s, 1 H), 6.52 (s, 1 H), 7.24–7.60 (m, 5 H); IR (KBr) 1440, 1405, 1215, 1190, 1150, 1100, 1010, 920, 860, 760, 695 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39 Found. C, 62.01; H, 6.22. Elution with ether–benzene (1:3) afforded **6c**.

Reaction of a Mixture of 1c and 1g with $ClSO_3H$. When a mixture of **1c** (2 mmol) and **1g** (2 mmol) was treated with $ClSO_3H$ at 20 °C for 1 h, a mixture of **24**, 1-methyl-4-*exo*-pentyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**25**), and **1g** was obtained. The products were isolated by column chromatography on silica gel. Elution with benzene–petroleum ether (1:4) gave **1g**. Then, the products were eluted with use of benzene–ether (10:1). The first fraction contained **25**: an oil; *m/e* 246 (M$^+$); NMR δ 0.88 (t, J = 4.5 Hz, 3 H), 1.08–2.04 (m, 14 H), 1.44 (s, 3 H), 5.38 (s, 1 H), 5.62 (t, J = 4.5 Hz, 1 H); IR (neat) 1435, 1370, 1225, 1150, 1100, 935 cm^{-u}. From the second fraction, **24** was isolated. Elution with ether–benzene (1:3) gave **6c**.

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