anilines show subtle differences for the inversion mechanism in these two classes of compounds.

Acknowledgment. We thank Frank M. Michaels and Sandra M. Finn of the Analytical Technology Division of Eastman Kodak Co. for their help in measuring and interpreting NMR and IR spectra, respectively. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japanese Government (No. 60540337) for which we are grateful.

Registry No. 12a, 117985-07-6; 12b, 117985-08-7; 12c, 117985-05-4; 12d, 117985-06-5; 14a, 111955-89-6; 14b, 117985-09-8.

Supplementary Material Available: Tables of rate constants for the isomerization of 12a, 13, and 14b in various solvents and at various pressures (3 pages). Ordering information is given on any current masthead page.

Ozonolysis of Tetrasubstituted Ethylenes, Cycloolefins, and Conjugated Dienes on Polyethylene

Karl Griesbaum,* Willi Volpp, Reinhard Greinert, Hans-Joachim Greunig, Jürgen Schmid, and Henning Henke[1]

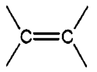
Engler-Bunte-Institut, Bereich Petrochemie, Universität Karlsruhe (TH), D-7500 Karlsruhe, Germany

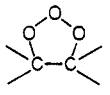
Received August 8, 1988

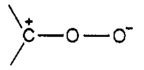
Ozonolyses of four tetrasubstituted ethylenes (**7a–d**), of two medium-sized cycloolefins (**10a,b**), and of norbornene (**14**) on polyethylene gave the corresponding ozonides, which could not be obtained by ozonolyses in solution. Ozonolyses of three conjugated dienes (**25a,b**, **28**) on polyethylene gave the corresponding diozonides, as the first examples of this class of ozonides. The thermal decomposition of some of the ozonides has been studied.

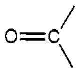
Introduction

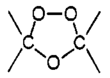
Ozonides (**5**) can be prepared by ozone treatment of olefins, by oxygenation of olefins, oxiranes, or furans, and by oxygenation of diazoalkanes in the presence of aldehydes.[2] Since the scope of the application of oxygenation reactions is limited by certain structural prerequisites such as the presence of aromatic substituents in olefin or oxirane substrates, the ozonolysis of olefins (**1**) in aprotic solvents represents the most versatile method for the preparation of ozonides. Nevertheless, this method failed when applied to a variety of substrates such as most tetrasubstituted ethylenes, monocyclic olefins except for those having four- to six-membered rings, certain bicyclic olefins, and certain acyclic conjugated dienes. While such reactions do proceed according to the Criegee mechanism[3a] in the initial steps to give the primary ozonides **2** and the initial fragments of types **3** and **4**, the latter do not undergo [3 + 2]-cycloadditions to give ozonides **5**. The failure of tetrasubstituted ethylenes to afford the corresponding ozonides **5** has been attributed to the low reactivity of the ensuing ketone fragments **4**, as opposed to aldehyde fragments, in 1,3-dipolar cycloadditions;[3b] in the case of medium-sized cycloolefins, it has been argued that the chances for intramolecular ring closures are not as good with the Criegee intermediates of larger cycloolefins as with those derived from four-, five-, or six-membered cycloolefins.[3c] Hence, in either case, the carbonyl oxide fragments **3** undergo side reactions which often lead to peroxidic materials other than ozonides, particularly acyclic and cyclic oligomers of **3**, such as dimers of structure **6**.

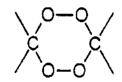

1


2


3


4


5


6

In an attempt to prevent such side reactions, ozonolyses of olefins adsorbed on silica gel have been examined[4,5] with the goal of immobilizing the primary fragments **3** and **4** at the places of their origin and thus favoring [3 + 2]-cycloadditions to give ozonides **5**. It was reported that this method provided higher yields of the ozonides of cyclopentene and of 2-pentene than ozonolysis in solution and that no cross-ozonides were formed from 2-pentene.[4] But to our knowledge, it was in no case possible to obtain an ozonide from a substrate that did not afford an ozonide in solution. In fact, it was reported that in the ozonolysis of 1-decene, *cis*-6-decene, and 1-methylcyclohexene on silica gel, "the results showed a marked similarity with ozonation in non-participating solvents".[5] In pursuit of this concept, we have carried out ozonolyses of olefins on solid organic polymers, and it was found that powdered polyethylene can be superior to silica gel. In the following, we report results from the application of this method to the ozonolysis of the tetrasubstituted ethylenes **7a–d**, the cycloolefins **10a,b** and **14**, and the conjugated dienes **25a,b** and **28**.

Results and Discussion

Tetrasubstituted Ethylenes (7a–d). Ozonolyses of **7a**,[3d] **7b**,[6] and **7d**[7] in aprotic solvents have been reported to give no or at best trace amounts (in the case of **7d**) of the corresponding ozonides **8**, whereas to our knowledge the ozonolysis of **7c** has not yet been examined. Nevertheless, ozonides **8c** and **8d** are known. They have been prepared via alternate routes, viz., **8c** from electron transfer

---

[1] Institut für Anorganische Chemie, Universität Karlsruhe (TH).

[2] Griesbaum, K. In Houben-Weyl *Methoden der organischen Chemie*; Georg Thieme Verlag: Stuttgart; Vol. E 13/2, in press.

[3] Bailey, P. S. In *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. I, (a) p 11; (b) p 25; (c) p 87; (d) p 34; (e) p 140ff; (f) p 159ff; (g) p 191ff.

[4] Den Besten, I. E.; Kinstle, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 5969.

[5] Aronowitch, C.; Tal, D.; Mazur, Y. *Tetrahedron Lett.* **1982**, *23*, 3623.

[6] Murray, R. W.; Lin, J. W. P.; Grumke, D. A. *Adv. Chem. Ser.* **1972**, *112*, 9.

[7] Criegee, R.; Korber, H. *Chem. Ber.* **1971**, *104*, 1812.

photooxygenation of 2,3-dimethyl-2,3-diphenyloxirane[8] and **8d** from ozonolysis of tetraphenylethylene in acetone.[7] The latter method had been also attempted, however without success, for the preparation of **8a** by ozonolysis of **7a** in acetone.[3c] Hence, ozonide **8a** has remained unknown despite many and varied attempts to prepare it.[3d]

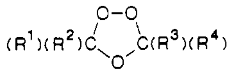
Ozonolysis of **7a**, **7b** (cis:trans ca. 1:1), **7c** (cis:trans ca. 1:1), and **7d** on polyethylene afforded the corresponding ozonides **8a**,[9] **8b** (cis:trans ca. 1:1), **8c** (cis:trans ca. 1:1.3), and **8d** in yields of ca. 8, 16, 29, and 30%, respectively. Individual ozonolyses of *cis*-**7c** and of *trans*-**7c** gave in each case mixtures of *cis*-**8c** and *trans*-**8c**, albeit in different ratios of 1:0.8 and of 1:3.9, respectively.

The hitherto unknown ozonides **8a** and **8b** have been isolated and characterized by spectroscopic means, elemental analysis, and reduction with triphenylphosphine to give acetone and butanone, respectively. Ozonides **8c** and **8d** have been identified by comparison of pertinent analytical data with those reported in the literature. In line with a prediction of Criegee,[7] ozonide **8a** is unusually stable: It could be heated to 80 °C in $CDCl_3$ for 36 h without any detectable decomposition; at room temperature it was not reduced by dimethyl sulfide and only slowly reduced by sodium iodide in acetic acid or by triphenylphosphine, and even at 80 °C, complete reduction with triphenylphosphine in $CDCl_3$ required 36 h. Ozonides **8b–d** are also stable compounds.

In the ozonolysis of **7a**, the cyclic peroxides **9a** and **9b** were also formed, and in the ozonolysis of **7d**, ca. 2% of the cross-ozonide **8a** was also formed. This demonstrates that the fragments of types **3** and **4** are not rigidly fixed at the places of their origin, but can undergo a certain degree of migration. The present results do not reveal, however, whether this migration occurs at −78 °C or during the warm-up period after the completion of the ozone treatment.

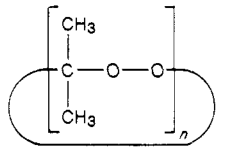
$(R^1)(R^2)C{=}C(R^3)(R^4)$

7



8

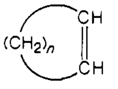
a: $R^1 - R^4 = CH_3$
b: $R^1 = R^3 = CH_3$, $R^2 = R^4 = C_2H_5$
c: $R^1 = R^3 = CH_3$, $R^2 = R^4 = C_6H_5$
d: $R^1 = R^2 = CH_3$, $R^3 = R^4 = C_6H_5$



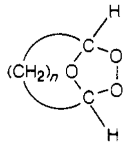
9

a: $n = 2$
b: $n = 3$

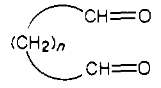
Cyclooctene (10a), Cyclodecene (10b), and Norbornene (14). Ozonolyses of cyclooctene (**10a**)[10] and of norbornene (**14**)[11] in aprotic solvents have failed to produce the corresponding ozonides. Moreover, to our knowledge, ozonides of cycloolefins with larger than six-membered rings have not been isolated, but only claimed in some cases as "in situ ozonides" without any proof of even a transient existence.[12] By contrast, ozonolyses of cyclooctene (**10a**), cyclodecene (**10b**), and norbornene (**14**) on polyethylene in this work produced the corresponding ozonides **11a**, **11b**, and **15** in yields of ca. 8, 40, and 14%, respectively. They have been isolated and identified by spectroscopic means as well as by reduction to the corresponding dialdehydes **12a**, **12b**, and **16**, respectively. Ozonides **11a** and **11b** have been additionally reduced with $LiAlH_4$ to give the corresponding diols **13**.



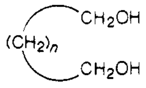
10



11

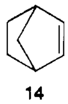


12

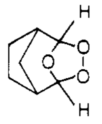


13

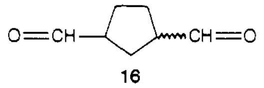
a: $n = 6$; b: $n = 8$



14

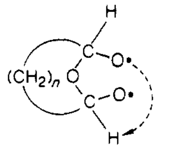


15

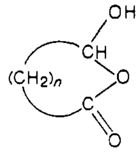


16

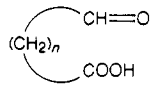
Ozonides **11a** and **11b** were stable at room temperature, whereas at temperatures of ⩾60 °C they decomposed to give 83% of **19a** and 79% of **19b**, respectively. The decomposition of **11b** gave additionally ca. 1% of cyclooctane. By analogy with previously observed ozonide decompositions,[3e] these results can be rationalized by homolytic cleavage of the peroxide bond in **11** to give **17**, which in turn undergoes an intramolecular hydrogen abstraction to give **18**, followed by the formation of **19**. Alternatively, radical **17b** may split off formic anhydride to give diradical **20**, which undergoes ring closure to give cyclooctane.



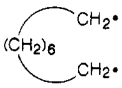
17



18



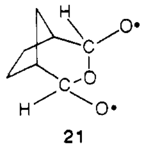
19



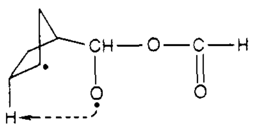
20

a: $n = 6$; b: $n = 8$

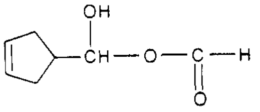
Ozonide **15** was unstable at room temperature and decomposed slowly to give nearly quantitatively **24** and formic acid. This is again explained by homolytic cleavage of the peroxide bond in **15**. However, due to steric restraints,[3e] the ensuing diradical **21** does not abstract hydrogen as in the case of **17**, but undergoes fragmentation to give diradical **22**. The latter, in turn, abstracts hydrogen to give **23**, which is subsequently converted into **24** and formic acid.



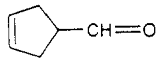
21



22



23



24

Isoprene (25a), 2,3-Dimethyl-1,3-butadiene (25b), and 2,3,4,5-Tetramethyl-2,4-hexadiene (28). In previous

---

(8) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Sandison, M. *Tetrahedron* **1985**, *41*, 2229.

(9) Preliminary communication: Griesbaum, K.; Volpp, W.; Greinert, R. *J. Am. Chem. Soc.* **1985**, *107*, 5309.

(10) Habib, R. M.; Chiang, C.-Y.; Bailey, P. S. *J. Org. Chem.* **1984**, *49*, 2780 and literature cited therein.

(11) Perry, R. H. *J. Org. Chem.* **1959**, *24*, 829.

(12) Kropf, H.; Müller, E.; Weickmann, A. In Houben-Weyl *Methoden der organischen Chemie*, 4th Ed.; Georg Thieme Verlag: Stuttgart; Vol. IV/1a, p 27.

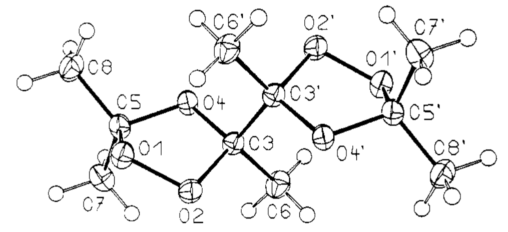
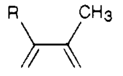
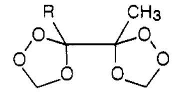


Figure 1. ORTEP view[32] of *meso*-**29** with thermal ellipsoids drawn at the 50% probability density level. Hydrogen atoms are represented as open circles. Primes label the second half of the molecule generated by inversion. The torsional angles of the five-membered ring are as follows: C5-O1-O2-C3, -41.6°; O1-O2-C3-O4, +24.6°; O2-C3-O4-C5, +1.6°; C3-O4-C5-O1, -27.8°; O4-C5-O1-O2, +42.0°.

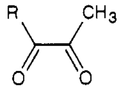
investigations, we found that treatment of the above substrates with ca. 1 molar equiv of ozone in pentane gave the corresponding monoozonides of **25a**[13] and **25b**,[14] yet no ozonide of **28**.[13] By contrast, ozonolyses of the same dienes on polyethylene in the present work afforded the diozonides **26a**, **26b**, and **29**[15] in yields of 40, 27, and 37%, respectively, whereas no monoozonides could be detected even at very low levels of conversion.



25

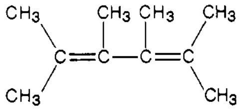


26

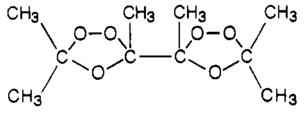


27

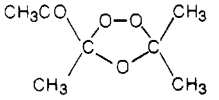
a: R = H; **b**: R = CH_3



28



29

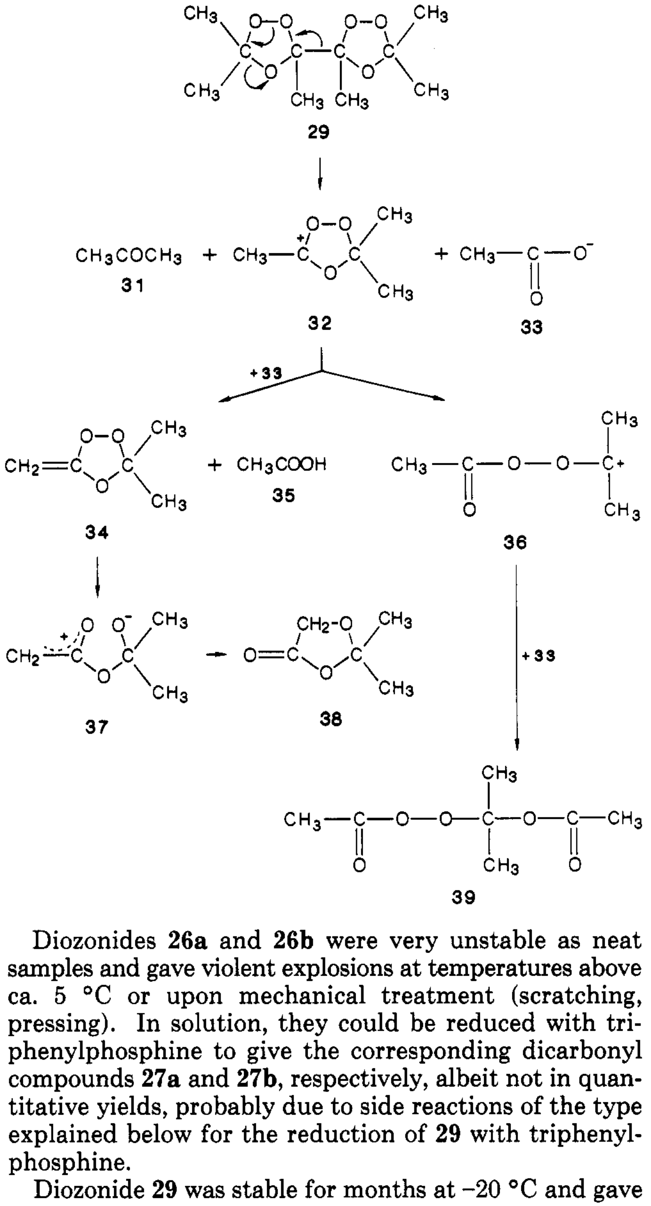


30

Diozonides **26a**, **26b**, and **29** consisted of two diastereomers each. They have been separated by chromatographic methods in each case. In the case of **29**, the isomer having the shorter retention time has been shown to be the meso form by single-crystal X-ray diffraction. The assignment is based on the fact that the molecule has a crystallographic center of symmetry between the two asymmetric carbon atoms C3 and C3′. One should note the increased distance between C3 and C3′ of 1.556 (2) Å, since, as discussed below, cleavage of this bond is involved in the thermal decomposition of **29**. On the basis of the observed torsional angles (Figure 1), the ozonide rings have an envelope conformation[16] with the peroxidic oxygen atoms O1 and O1′ occupying the out-of-plane positions.[17]

Due to their instability, the diastereomers of diozonides **26a** and **26b** have not been characterized by X-ray diffraction analysis. By analogy with the diastereomers of **29**, the isomers having the shorter retention times have been tentatively assigned the (*R*,*S*) (*S*,*R*) racemate of **26a** and the meso form of **26b**, respectively.

Scheme I



Diozonides **26a** and **26b** were very unstable as neat samples and gave violent explosions at temperatures above ca. 5 °C or upon mechanical treatment (scratching, pressing). In solution, they could be reduced with triphenylphosphine to give the corresponding dicarbonyl compounds **27a** and **27b**, respectively, albeit not in quantitative yields, probably due to side reactions of the type explained below for the reduction of **29** with triphenylphosphine.

Diozonide **29** was stable for months at -20 °C and gave only ca. 10% decomposition when it was kept at room temperature for 15 days. Reduction of **29** with lithium aluminum hydride gave 2-propanol and the two diastereomers of 2,3-butanediol. Reduction of **29** with triphenylphosphine at room temperature afforded a mixture of acetone, 2,3-butanedione (**27b**), and acetic anhydride in molar proportions of 9:3.2:1. We assume that the reduction of **29** occurs stepwise via **30**, which, in line with the known instability of α-keto ozonides,[3f] undergoes fragmentation to give acetone and acetic anhydride[18] in competition with its reduction to give 2,3-butanedione (**27b**). This assumption derives support from the fact that reduction of **29** with triphenylphosphine at -30 °C gave a product mixture, in which ca. 5% of **30**, which is more stable at this low temperature, could be detected with the help of an authentic sample.[18] Attempts to produce larger proportions of **30** by reduction of **29** with a deficient amount of triphenylphosphine failed, however, since the second reduction step (i.e., **30** → **27b**) is approximately 20 times faster than the first step (i.e., **29** → **30**).

Deliberate thermal decomposition of neat diozonide **29** at 40 °C gave acetone (**31**), acetic acid (**35**), lactone **38**, and

---

(13) Griesbaum, K.; Zwick, G. *Chem. Ber.* **1985**, *118*, 341.

(14) Griesbaum, K.; Keul, H.; Agarwal, S.; Zwick, G. *Chem. Ber.* **1983**, *116*, 409.

(15) Preliminary communication: Griesbaum, K.; Volpp, W. *Angew. Chem.* **1986**, *98*, 108; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 81.

(16) Hendrickson, J. B. *J. Am. Chem. Soc.* **1961**, *83*, 4537.

(17) By contrast, *cis*-3,5-difluoro-1,2,4-trioxolane has been reported to have an envelope conformation in which the ether oxygen atom occupies the out-of-plane position: Hillig, K. W.; Kuczkowski, R. L.; Cremer, D. *J. Phys. Chem.* **1984**, *88*, 2025.

(18) Volpp, W. Unpublished results.

peroxide **39** in relative amounts of 42, 29, 6, and 23%, respectively. Decomposition reactions of **29** in $CDCl_3$ at 50 °C gave the same products, albeit in different proportions. The structure of the hitherto unknown peroxide **39** has been assigned on the basis of the spectral data and by reduction with $LiAlH_4$ to give ethanol and 2-propanol.

The results of the thermal decomposition of **29** are rationalized by the reaction sequence depicted in Scheme I: In the first step, **29** is fragmented by cleavage of one of the two adjacent ozonide rings and by additional cleavage of the C–C bond that connects the two ozonide rings, to give **31** to **33**. Either the postulated ozonide cation **32** can be deprotonated, e.g., by attack of **33**, to give the allenic ozonide **34** and acetic acid (**35**), or it can undergo ring opening to give cation **36**, which in turn is trapped by acetate ion (**33**) to give peroxide **39**. Ozonide **34** could not be detected in the reaction mixture. This is not surprising, though, since in the past all attempts at preparing ozonides from allenic substrates have been futile.[3g] We assumed that **34** is spontaneously cleaved to give lactone **38** via the allylic cation **37**. In order to test this possibility, we have ozonized 1,1-dimethylallene on polyethylene. Again, ozonide **34** could not be detected, but lactone **38** was formed as a minor product and could be isolated.

The results reported in this paper demonstrate that the ozonolysis of olefins on polyethylene is widely applicable for the preparation of ozonides. In particular, it extends the scope of the formation of ozonides to types that have not been accessible by the hitherto available preparation methods such as ozonides of tetraalkylated ethylenes, medium-sized cycloolefins, and bicyclic olefins. In addition, the possibility of preparing thermally labile ozonides and studying their mode of decomposition provides new insight into peroxide chemistry.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Bruker WP 60 or WM 250, ^{13}C NMR spectra on a Bruker WM 250, IR spectra on a Beckman 4260 or Acculab 1, and GC/MS spectra on a Hewlett-Packard 5985 B instrument. GLC analyses were performed on a Shimadzu GC-6A or a Hewlett-Packard 5880 instrument. Preparative gas chromatographic (PGC) separations were carried out on a Perkin-Elmer F 21 instrument.

Procedures for Ozonolyses of Olefins on Polyethylene. (a) Pretreatment of Polyethylene. Polyethylene (Microthene FN 500 from Serva Feinbiochemica, Heidelberg, Germany; spherical particles, maximum size 20 μm) was continuously extracted with ether for 24 h to remove soluble components. Subsequently, it was dried at room temperature and 10^{-3} Torr for 24 h.

(b) Loading of the Olefin. Two procedures have been used, depending on the volatility of the olefinic substrate. In the case of volatile liquid olefins, the dried polyethylene was placed into a cylindrical adsorption tower of the appropriate capacity, and the olefin was placed into a reservoir. Then, dried nitrogen was successively passed through the reservoir and the adsorption tower at room temperature until the desired amount of olefin was loaded. In the case of nonvolatile liquid or solid olefins, the dried polyethylene was placed into a round-bottom flask and admixed with so much of a low-boiling solvent (e.g., diethyl ether or *n*-pentane) that the resulting suspension could be stirred. Then the olefin was added, the mixture was stirred for ca. 15 min, the solvent was removed by suction at room temperature, and the loaded polyethylene was transferred into an adsorption tower.

(c) Ozonolysis of the Olefin. The loaded adsorption tower was placed into a bath that had the desired temperature, and an O_3/O_2 stream (ca. 1 mmol of O_3/L of gas) was passed through the tower at a rate of ca. 20 L/h. After completion of the ozonolysis, dried nitrogen was passed through the tower until residual ozone was removed, the tower was warmed up to room temperature, and the polyethylene was transferred into a round-bottom flask and repeatedly extracted with an appropriate solvent.

Ozonolysis of 2,3-Dimethyl-2-butene (7a). Compound **7a** (2.11 g, 25 mmol) was loaded on 60 g of polyethylene in a stream of nitrogen and ozonized for 3 h at −78 °C. The products were extracted with ether, and the combined extracts were distilled at room temperature and 15 Torr to leave 1.19 g of a semisolid peroxidic residue. The distillate was collected at −78 °C, and the ether was distilled off through a 20-cm Vigreux column at normal pressure to leave 1.6 g of a peroxidic liquid residue. GLC analysis (glass column, 0.3 × 300 cm, 2.5% OV 101 on Chromosorb G; 60–160 °C at 4 °C/min) showed the presence of ca. 17% of **8a** (t_R = 7.9 min), corresponding to a minimum yield of ca. 8%. From the combined liquid residues of four ozonolysis reactions, 524 mg (4%) of pure ozonide **8a** has been isolated by PGC (glass column, 0.7 × 300 cm, 5% OV 101 on Chromosorb G; 80 °C).

The semisolid residue was dissolved in pentane, and the solution was stored at −20 °C for 14 h to give a solid precipitate. ^1H NMR analysis ($CDCl_3$, Me_4Si) showed that it consisted of **9a** (δ 1.20–1.53 and 1.53–1.90, br s, each)[19] and **9b** (δ 1.47, s).[19]

3,3,5,5-Tetramethyl-1,2,4-trioxolane (8a): colorless liquid; ^1H NMR, ^{13}C NMR, and MS data have been reported previously;[9] IR (film) 3000, 2940, 1470, 1375, 1265, 1245, 1215, 1115, 1005, 875, 860, 845 cm^{-1}. Anal. Calcd for $C_6H_{12}O_3$: C, 54.52; H, 9.16. Found: C, 54.42; H, 8.96.

Reduction of 8a. A solution of **8a** and triphenylphosphine in $CDCl_3$ was kept at room temperature for 3 days. ^1H NMR analysis showed that no reduction of **8a** had occurred. Then, the sample was heated to 80 °C in a closed NMR tube. ^1H NMR analysis after 36 h showed no residual **8a** but the presence of acetone (89%; δ 2.15) and of chloroacetone (16%; δ 2.29 and 4.13). This was verified by GLC analysis with the help of authentic samples.

Ozonolysis of 3,4-Dimethyl-3-hexene (7b). A 1:1 mixture (2.0 g, 17.9 mmol) of *cis*- and *trans*-**7b**[20] was loaded on 100 g of polyethylene in a stream of nitrogen and ozonized at −77 °C for 20 h. The mixture was evacuated with an oil pump at ambient temperatures, and the reaction product (1.7 g) was collected in a trap cooled with liquid nitrogen. ^1H NMR analysis showed the presence of butanone (δ 2.14, s, CH_3CO; 47%), *cis*- and *trans*-**8b** (δ 1.41 and 1.43, s, CH_3C; 47%), and unreacted **7b** (6%). A sample of ozonide **8b** was isolated by PGC (glass column, 0.7 × 500 cm, 5% Carbowax 20 M on Chromosorb G; 80 °C).

3,5-Dimethyl-3,5-diethyl-1,2,4-trioxolane (*cis*- and *trans*-8b): colorless liquid; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.97 and 0.98 (t, each, J = 7.57 Hz), 1.41 and 1.43 (s, each), 1.74 and 1.76 (q, each); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.42 and 8.52 [CH_3 (CH_2)], 22.21 (CH_3), 30.71 and 30.82 (CH_2), 110.59 (C); CI-MS, m/e (relative intensity) 161 (3) $(MH)^+$; EI-MS, m/e (relative intensity) 145 (1) $[M - CH_3]^+$, 131 (30) $[M - C_2H_5]^+$, 72 (11) $[CH_3COC_2H_5]^+$, 57 (17) $[C_2H_5CO]^+$, 43 (100) $[CH_3CO]^+$. Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 60.00; H, 10.02.

Reduction of 8b. To a solution of **8b** in $CDCl_3$ was added solid triphenylphosphine at room temperature. ^1H NMR analysis after 48 h showed the signals of butanone at δ 1.05 (t, J = 7.33 Hz), 2.14 (s), and 2.59 (q), whereas those of **8b** had disappeared.

Ozonolysis of 2,3-Diphenyl-2-butene (7c). A 1:1 mixture (1.0 g, 4.8 mmol) of *cis*- and *trans*-**7c**[21] was loaded on 100 g of polyethylene from an ether solution and ozonized for 24 h at −77 °C. The products were extracted with ether, and the ether was evaporated to leave 1.3 g of a liquid residue. ^1H NMR analysis ($CDCl_3$, Me_4Si) of this residue showed the presence of 12% of *cis*-**8c** (δ 1.87, s)[8] and 16% of *trans*-**8c** (δ 1.65, s),[8] corresponding to a crude yield of 29%. GC/MS analysis by chemical ionization confirmed the structure of **8c**: m/e 257 $(MH)^+$, 241 $(M - CH_3)^+$, 225 $(MH - O_2)^+$, 137 $(MH - CH_3COC_6H_5)^+$.

Ozonolysis of *cis*-7c. Compound *cis*-**7c** (1.0 g, 4.8 mmol) on 100 g of polyethylene was ozonized at −77 °C for 24 h, and the product was worked up as described above. ^1H NMR analysis ($CDCl_3$, Me_4Si) showed the presence of 12% of *cis*-**8c** and 10% of *trans*-**8c**, corresponding to a cis:trans ratio of 1:0.8.

Ozonolysis of *trans*-7c. Compound *trans*-**7c** (1.0 g, 4.8 mmol) on 100 g of polyethylene was ozonized at −77 °C for 24 h as

---

[19] McGarrity, J. F.; Prodolliet, J. *J. Org. Chem.* **1984**, *49*, 4465.

[20] Lenoir, D. *Synthesis* **1977**, 553.

[21] Brasen, W. R.; Kantor, S. W.; Skell, P. S.; Hauser, C. R. *J. Am. Chem. Soc.* **1957**, *79*, 397.

described above to give a mixture containing 7% of *cis*-**8c** and 18% of *trans*-**8c**, corresponding to a cis:trans ratio of 1:3.9.

Ozonolysis of 1,1-Diphenyl-2-methylpropene (7d). Compound **7d**[22] (2.0 g, 9.6 mmol) was loaded on 100 g of polyethylene from a solution in ether and ozonized at −77 °C for 24 h. The product was extracted with ether, the combined extracts were evaporated at room temperature and ca. 15 Torr, and the distillate was collected in a cold trap at −78 °C. From the semisolid residue (2.6 g), ozonide **8d** was isolated by column chromatography (silica gel, pentane/diethyl ether, 95:5) and recrystallized from aqueous methanol: yield 730 mg (29.6%); mp 59 °C (lit.[7] mp 60–61 °C); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.54[23] (s, 6 H), 7.33 (m, 6 H), 7.49 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.7, 109.8, 110.7, 126.9, 128.1, 128.6, 139.7.

The distillate was redistilled through a 20-cm Vigreux column at normal pressure to remove most of the ether. GLC and GC/MS analysis (capillary column, 50 m, SE 54, 50–180 °C at 7 °C/min) of the liquid residue (2 mL) showed the presence of ozonide **8a** [t_R = 8.6 min; *m/e* 132 $(M)^+$, 117 $(M - CH_3)^+$, 74 $(M - CH_3COCH_3)^+$, 43 $(CH_3CO)^+$]. The assignment was confirmed by coinjection of authentic **8a**.

Ozonolysis of Cyclooctene (10a). Compound **10a** (1.8 g, 16.4 mmol) was loaded on 75 g of polyethylene in a stream of nitrogen and ozonized for 3.5 h at −75 °C. The product was extracted with ether, ether was removed in a rotary evaporator at ambient temperatures and ca. 15 Torr, and from the liquid residue was isolated 200 mg (7.7%) of ozonide **11a** by flash chromatography on silica gel (pentane/diethyl ether, 50:1).

2,3,11-Trioxabicyclo[6.2.1]undecane (11a): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.47–2.03 (m, 6 H), 5.19 (t, *J* = 2.67 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 19.05, 27.86, 31.63, 102.93; CI-MS, *m/e* (relative intensity) 159 (3) $(MH)^+$; EI-MS, *m/e* (relative intensity) 125 (8), 97 (48), 69 (60), 57 (44), 55 (62), 43 (48), 41 (100); IR (film) 2960, 2920, 2870, 1455, 1335, 1120, 1055, 1035, 1020, 975, 915, 825, 725 cm^{-1}. Anal. Calcd for $C_8H_{14}O_3$: C, 60.72; H, 8.94; O, 30.34. Found: C, 61.16; H, 9.10; O, 29.59.

Reduction of 11a. (a) Reduction with Triphenylphosphine. A solution of **11a** and triphenylphosphine in $CDCl_3$ was kept at room temperature for 18 h. ^{1}H NMR analysis showed the presence of octanedial (**12a**) (δ 1.42–1.76, m; 2.14–2.44, m; 9.76, t, *J* = 1.65 Hz) as the sole product.

(b) Reduction with LiAlH$_4$. To a suspension of 200 mg (5 mmol) of $LiAlH_4$ in 20 mL of diethyl ether was added a solution of 110 mg (0.7 mmol) of **11a** in 5 mL of ether slowly with stirring. After the reaction was completed, diluted aqueous hydrochloric acid was added, and the organic layer was separated, dried over magnesium sulfate, filtered, and concentrated in a rotary evaporator at ambient temperatures and 15 Torr to leave 90 mg (0.61 mmol) of solid 1,8-octanediol (**13a**). It was identified on the basis of the identity of its GLC retention time (19.95 min; 50-m capillary column, SE 54) and MS data [*m/e* 116 (1), 99 (3), 95 (7), 82 (72), 67 (100), 55 (91), 41 (81)] with those of an authentic sample.

Thermal Decomposition of 11a. A solution of **11a** in $CDCl_3$ was kept at room temperature for 14 days. ^{1}H NMR analysis showed the spectrum of **11a** and gave no indication for the presence of decomposition products. Then the solution was heated to 60 °C in a closed NMR tube for 12 days. ^{1}H NMR analysis showed the signals of **19a**: δ 1.32–1.96 (m), 2.24–2.99 (m), 8.3–9.4 (br s), 9.73 (t, *J* = 1.62 Hz). Heating of neat **11a** at 50 °C for 8 days afforded quantitatively **19a**.

Ozonolysis of Cyclodecene (10b). Compound **10b** (1.75 g, 12.7 mmol) was loaded on 80 g of polyethylene from a pentane solution, ozonized for 6.5 h at −50 °C, and worked up as described above to give 945 mg (40%) of ozonide **11b**.

2,3,13-Trioxabicyclo[8.2.1]tridecane (11b): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.19–1.80 (m, 7 H), 1.90–2.06 (m, 1 H), 5.29–5.33 (m, X part of an ABX system, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 19.73, 23.47, 24.75, 28.80, 104.34; CI-MS, *m/e* (relative intensity) 187 (7) $(MH)^+$; EI-MS, *m/e* (relative intensity) 186 (0.4) $(M)^+$, 153 (4), 135 (27), 125 (25), 97 (39), 83 (50), 81 (100), 69 (48), 67 (63), 55 (74), 41 (43); IR (film) 2970, 2940, 2880, 1475, 1450, 1395, 1380, 1360, 1350, 1130, 1115, 1065, 1050, 1005, 970, 925, 705 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.52; H, 9.68; O, 25.80. Found: C, 64.82; H, 9.14; O, 25.70.

Reduction of 11b. (a) Reduction with Triphenylphosphine. A solution of **11b** and triphenylphosphine in $CDCl_3$ was kept at ambient temperature for 12 h. ^{1}H NMR analysis showed the presence of decanedial (**12b**): δ 1.31–1.88 (m), 2.33–2.57 (td, *J* = 6.60 and 1.65 Hz), 9.78 (t, *J* = 1.65 Hz).

(b) Reduction with LiAlH$_4$ was carried out as described above for **11a** to give 545 mg (3.1 mmol) of 1,10-decanediol (**13b**). It was assigned on the basis of the identity of the GLC retention time (24.95 min; conditions as above) and MS data [*m/e* 147 (1), 126 (1), 109 (9), 95 (25), 82 (48), 68 (65), 67 (68), 55 (100)] with those of an authentic sample.

Thermal Decomposition of 11b. A solution of **11b** in $CDCl_3$ was heated to 60 °C for 10 days in a closed NMR tube. ^{1}H NMR analysis showed the signals of **19b**: δ 1.32–1.92 (m), 2.24–2.79 (m), 9.77 (t, *J* = 1.65 Hz), 10.1–10.9 (br s). GLC (conditions as above) and GC/MS analysis and comparison of the data obtained with those of authentic samples showed additionally the presence of minor amounts of formic acid (t_R = 5.5 min) and ca. 1% of cyclooctane (t_R = 10.38 min). Heating of neat **11b** at 50 °C for 5 days afforded nearly quantitatively **19b**.

Ozonolysis of Norbornene (14). Compound **14** (1.8 g, 19.1 mmol) was loaded on 80 g of polyethylene from a pentane solution, ozonized for 7 h at −75 °C, and worked up as described above to give 380 mg (14%) of ozonide **15**.

2,3,9-Trioxatricyclo[4.2.1.1^{5,8}]decane (15): colorless solid; mp ca. 55 °C dec; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.74 (dt, *J* = 10.76 and 2.84 Hz, 1 H), 1.33–1.39 (m, 2 H), 1.56 (dm, *J* = 10.76 Hz, 1 H), 1.93–1.99 (m, 2 H), 2.58–2.63 (m, 2 H), 5.82 (d, *J* = 6.27 Hz, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.77, 25.71, 40.77, 99.73; CI-MS, *m/e* (relative intensity) 143 $(MH)^+$; EI-MS, *m/e* (relative intensity) 142 (1) $(M)^+$, 110 (5), 95 (10), 79 (28), 67 (100), 53 (19), 41 (69); IR (CCl_4) 3000, 2970, 2890, 1480, 1460, 1455, 1330, 1310, 1255, 1185, 1090, 1070, 1010, 930, 875, 570, 520 cm^{-1}.

Reduction of 15. A solution of **15** and trimethyl phosphite in $CDCl_3$ was kept at room temperature for 3 h. ^{1}H NMR analysis showed the presence of cyclopentane-1,3-dicarbaldehyde (**16**): δ 1.7–2.3 (m, 3 H), 2.5–3.1 (m, 1 H), 9.64 (d, *J* = 2.02 Hz, 1 H). The spectrum was identical with that of an authentic sample of **16**.

Decomposition of 15. A solution of **15** in $CDCl_3$ was kept at room temperature for 7 days. ^{1}H NMR analysis showed the presence of only formic acid (δ 8.05) and **24**. Neat **15** gave the same products when kept at room temperature for 1 week, and even at −20 °C, partial decomposition occurred within 20 days. Aldehyde **24** was isolated by PGC (glass column, 0.7 × 400 cm, 5% Carbowax 20 M on Chromosorb G; 90 °C for 10 min, then 90–180 °C at 15 °C/min).

4-Formylcyclopentene (24): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.52–2.76 (m, 4 H), 3.03–3.15 (m, 1 H), 5.67 (s, 2 H), 9.66 (d, 2 H, *J* = 2.04 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 32.92, 48.95, 129.12, 202.92; EI-MS, *m/e* (relative intensity) 96 (86) $(M)^+$, 95 (57) $(M - H)^+$, 67 (100) $(M - CHO)^+$, 66 (30) $(M - HCHO)^+$, 65 (36) $(C_5H_5)^+$, 41 (29) $(C_3H_5)^+$, 39 (33) $(C_3H_3)^+$.

Synthesis of 24. A solution of 17.0 g (0.12 mol) of 4-bromocyclopentene[24] in 50 mL of dry ether was added dropwise to a mixture of 2.8 g of magnesium and 30 mL of dry ether, and the mixture was stirred for 5 h at room temperature. The product was poured on dry ice, and the mixture was allowed to reach room temperature. It was acidified with 2 N sulfuric acid. Then, the organic phase was separated, the aqueous phase was extracted with ether, and the combined extracts and organic phase were sequentially washed with a saturated aqueous solution of sodium chloride and a 10% aqueous solution of sodium carbonate. The latter extract was acidified with hydrochloric acid and extracted with ether. The extract was washed with water, dried over magnesium sulfate, and evaporated at reduced pressure at room temperature to give 8.82 g (66%) of 3-cyclopentene-1-carboxylic acid. It was dissolved in 50 mL of ether and added dropwise to a slurry of 6.0 g (16 mmol) of lithium aluminum hydride in 50 mL of ether. The mixture was refluxed for 3 h and hydrolyzed at room temperature by the sequential addition of 25 mL of water and 5 mL of 3 N aqueous sodium hydroxide. The ether phase

---

[22] Brodhag, A.; Hauser, L. R. *J. Am. Chem. Soc.* **1955**, *77*, 3024.

[23] In ref 7, a δ value of 1.44 was reported. We have prepared ozonide **8d** by the procedure reported,[7] and we have found a δ value of 1.54.

[24] Maercker, A.; Geuss, R. *Chem. Ber.* **1973**, *106*, 773.

was separated, and ether was evaporated to leave 6.8 g (87%) of 4-(hydroxymethyl)cyclopentene. To a slurry of 12.15 g of pyridinium dichromate in 30 mL of dichloromethane was added 2.11 g (21.5 mmol) of 4-(hydroxymethyl)cyclopentene, and the mixture was stirred at room temperature for 36 h. Then 50 mL of pentane was added, the precipitate was filtered off, and the filtrate was sequentially washed with 5 N hydrochloric acid and water and dried over magnesium sulfate. The solvent was evaporated, and the residue was purified by chromatography (column, 2 × 60 cm; 80 g of silica gel; pentane/diethyl ether, 5:1) to give 350 mg (17%) of **24**. The ^{1}H NMR, ^{13}C NMR, and mass spectra were identical with those reported above for the sample of **24** that had been obtained from the decomposition of ozonide **15**.

Ozonolysis of Isoprene (25a). Compound **25a** (0.2 g, 2.9 mmol) was loaded on 20 g of polyethylene in a stream of nitrogen and ozonized for 15 h at −78 °C. The products were extracted with ether, and ether was partly removed in a rotary evaporator at ambient temperature and ca. 15 Torr. From the liquid residue (3 mL),[25] the two diastereomers of diozonide **26a** were isolated by chromatography (column, 1.2 × 30 cm; 20 g of silica gel 60; pentane/diethyl ether, 6:1, at a rate of 8 mL/min).

3-Methyl-3-(1,2,4-trioxolan-3-yl)-1,2,4-trioxolane (26a): IR ($CDCl_3$) of the mixture of the diastereomers 2967, 2932, 2896, 2255, 1718, 1457, 1387, 1369, 1290, 1271, 1210, 1173, 1140, 1122, 1089, 1058, 1007, 988, 971, 927 cm^{-1}.

(a) (*R*,*S*) (*S*,*R*) racemate: colorless liquid; elution time = 12.2–16.5 min; yield 40 mg (20%); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.51 (s, 3 H), 5.04 (s, 1 H), 5.08 (s, 1 H), 5.21 (s, 1 H), 5.27 (s, 1 H), 5.35 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si, −40 °C) δ 14.6 (q, J = 130.3 Hz), 94.2 (dd, J = 173.0 and 168.4 Hz), 94.7 (dd, J = 176.3 and 166.1 Hz), 99.8 (d, J = 118.9 Hz), 106.5 (s).

(b) (*R*,*R*) (*S*,*S*) racemate: colorless liquid; elution time = 16.5–23.3 min; yield 40 mg (20%); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.50 (s, 3 H), 5.04 (d, J = 0.48 Hz, 1 H), 5.05 (d, J = 0.38 Hz, 1 H), 5.21 (s, 1 H), 5.31 (t, J = 0.60 Hz, 1 H), 5.36 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si, −40 °C) δ 14.4 (q, J = 130.1 Hz), 94.0 (dd, J = 174.6 and 168.8 Hz), 94.5 (dd, J = 176.4 and 166.0 Hz), 99.6 (d, J = 175.7 Hz), 106.4 (s).

Reduction of 26a. A solution of **26a** and triphenylphosphine in $CDCl_3$ was kept at 0 °C for 10 min. ^{1}H NMR analysis of the yellow solution showed the presence of **27a** (δ 9.19, s, 1 H; 2.41, s, 3 H), along with monomeric (δ 9.72) and oligomeric formaldehyde (δ 4.91–4.97) as well as minor byproducts.

Ozonolysis of 2,3-Dimethyl-1,3-butadiene (25b). Compound **25b** (2.0 g, 24.4 mmol) was loaded on 100 g of polyethylene in a stream of nitrogen and ozonized for 15 h at −78 °C. The products were extracted with ether, and ether was removed in a rotary evaporator at ambient temperature and ca. 15 Torr. From the semisolid residue (1.6 g), the two diastereomers of diozonide **26b** were isolated by chromatography (column, 2.7 × 60 cm; 150 g of silica gel 60; pentane/diethyl ether, 5:1, at a rate of 13 mL/min).

CAUTION: A sample of isolated **26b** exploded violently when it was touched with a metal spatula at ca. 5 °C.

3-Methyl-3-(3-methyl-1,2,4-trioxolan-3-yl)-1,2,4-trioxolane (26b). (a) *meso*-26b: colorless solid; mp ca. 10 °C; elution time = 21.3–25.3 min; yield 0.2 g (10%); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.53 (s, 6 H), 5.14 (s, 2 H),[26] 5.23 (s, 2 H);[26] ^{13}C NMR ($CDCl_3$, Me_4Si) δ 18.8 (q, J = 129.0 Hz), 94.4 (t, J = 85.0 Hz), 108.5 (m, J = 4.2 Hz).

(b) *rac*-26b: colorless liquid; elution time = 25.3–31.5 min; yield 0.34 g (17%); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.52 (s, 6 H), 5.15 (s, 2 H),[26] 5.23 (s, 2 H).[26]

Reduction of 26b. A solution of **26b** and triphenylphosphine in $CDCl_3$ was kept at 0 °C for 10 min. ^{1}H NMR of the yellow solution showed the presence of **27b** (δ 2.34, s) along with oligomeric formaldehyde as well as minor byproducts.

Ozonolysis of 2,3,4,5-Tetramethyl-2,4-hexadiene (28). Compound **28**[27,28] (2.0 g, 14.5 mmol) was loaded on 98 g of polyethylene in a stream of nitrogen and ozonized at −75 °C for 4 h. The products were extracted with ether, and the ether was evaporated through a rotary evaporator at room temperature and reduced pressure to leave 2.5 g of a liquid residue. It was separated by column chromatography (water-cooled column, 200 g of silica gel, pentane/diethyl ether, 20:1) to give 1.2 g of a mixture of *meso*- and *rac*-**29**. This was further separated by HPLC (column, 3.2 × 12 cm, Li Chrosorb Si 60; pentane/diethyl ether, 19:1) to give *meso*-**29** (t_R = 21.0–21.8 min) and *rac*-**29** (t_R = 22.9–24.5 min).

***rac*-3,5,5-Trimethyl-3-[3,5,5-trimethyl-1,2,4-trioxolan-3-yl]-1,2,4-trioxolane (29)**: colorless liquid; ^{1}H NMR (C_6D_6, Me_4Si) δ 1.30 (q, J = 0.61 Hz), 1.40 (q, J = 0.61 Hz), 1.52 (s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 20.13, 23.41, 24.93, 108.88, 109.76; CI-MS, *m/e* (relative intensity) 235 (56) $(MH)^+$, 177 (83) $(MH - CH_3COCH_3)^+$, 117 (42) $(M/2)^+$, 75 (100) $[(CH_3)_2COOH]^+$. Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.74. Found: C, 51.44; H, 7.74.

***meso*-3,5,5-Trimethyl-3-[3,5,5-trimethyl-1,2,4-trioxolan-3-yl]-1,2,4-trioxolane (29)**: colorless solid; mp 51 °C; ^{1}H NMR (C_6D_6, Me_4Si) δ 1.30 (q, J = 0.64 Hz), 1.43 (q, J = 0.64 Hz), 1.52 (s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 20.16, 23.12, 24.94, 108.98, 109.60; CI-MS, *m/e* (relative intensity) 235 (46), 177 (93), 117 (100), 75 (79). Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.74. Found: C, 51.40; H, 7.78.

X-ray Analysis of *meso*-29. Suitable single crystals were grown from an *n*-pentane/ether (20:1) solution. Crystal data: $C_{10}H_{18}O_6$, M_r 234.25, monoclinic, $P\,2_1/n$ (No. 14), a = 5.947 (4) Å, b = 13.442 (7) Å, c = 7.484 (5) Å, β = 100.11 (5)°, temperature −106(±3) °C, V = 589.0 Å^3, Z = 2, D_{calcd} = 1.321 mg mm^{-3}, D_{measd} = 1.28 (2) mg mm^{-3} obtained by flotation at room temperature, μ = 0.07 mm^{-1} for Mo Kα radiation. The data collection was carried out on a Siemens/Stoe diffractometer equipped with the low-temperature attachment LT-1 of Nicolet. Cooling of the crystal was essential in view of the low melting point. Up to a 2θ-limit of 60°, the intensities of 1692 independent reflections were measured with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Scan mode: 40 steps with $\Delta\omega = \Delta 2\theta = 0.04°$, extra steps for α_1/α_2 dispersion, background determined from 6 points each at the beginning and at the end of a reflection profile, counting time between 0.5 and 1.5 s per step depending on $I/\sigma(I)$. Three standard reflections were recorded at regular intervals for scaling purposes; the overall loss of intensity was less than 2.2%. Corrections were applied for background intensity and Lorentz and polarization effects.

The structure was solved with the aid of the direct-methods program MULTAN 80.[29] Parameter refinement with SHELX 76[30] included anisotropic temperature factors. All hydrogen atoms appeared in a difference Fourier synthesis. Their positions were refined with the thermal B value kept at a fixed level (see supplementary material). The final $R = \sum|F_o| - |F_c|/\sum|F_o|$ was 0.037 [101 parameters, full-matrix refinement, 1597 reflections with $I > 3\sigma(I)$]. At this stage a difference Fourier map showed no feature above 0.3 e/Å^3.

Reduction of 29 with $LiAlH_4$. To a stirred solution of 5 drops of **29** (mixture of racemic and meso) in 10 mL of dry ether was added $LiAlH_4$. The mixture was stirred for 30 min, subsequently refluxed for 1 h, cooled, sequentially admixed with water and diluted sulfuric acid, and extracted with ether. The extract was dried over magnesium sulfate. GLC analysis (glass column, 0.3 × 500 cm, 5% Carbowax 20 M on Chromosorb G; 60–180 °C at 4 °C/min) showed the presence of 2-propanol (t_R = 6.20 min) and the two diastereomers of 2,3-butanediol (t_R = 25.77 and 26.75 min), as confirmed by injection of authentic samples.

Reduction of 29 with Triphenylphosphine at Room Temperature. A solution of 20 mg (0.085 mmol) of **29** (mixture of racemic and meso) in 8 drops of dichloromethane was admixed with 56 mg (0.21 mmol) of triphenylphosphine and left standing for 7 h at room temperature. ^{1}H NMR analysis ($CDCl_3$, Me_4Si) showed the presence of **27b** (δ 2.33, s), **31** (δ 2.17, s), and acetic anhydride (δ 2.23, s) in a molar ratio of 9:3.2:1. GLC analysis

---

[25] **CAUTION**: Further removal of ether is not advisable, since a solution containing ca. 50 vol % of **26a** in ether decomposed spontaneously when it was poured on the chromatography column.

[26] NMR samples that were left at room temperature for several hours gave rise to a doublet with J = 0.73 Hz.

[27] Forbes, N. F.; Shilton, R.; Balasubramanian, H. *J. Org. Chem.* **1964**, *29*, 3528.

[28] Criegee, R.; Metz, K. *Chem. Ber.* **1956**, *89*, 1714.

[29] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York, 1980.

[30] Sheldrick, G. M. *SHELX 76. A Program for Crystal Structure Determination*; University of Cambridge, 1976.

(conditions as above) showed the signals of **27b** (t_R = 7.53 min), acetone (t_R = 4.55 min), and acetic anhydride (t_R = 15.93 min), as confirmed by injection of authentic samples.

Reduction of 29 with Triphenylphosphine at -30 °C. A solution of 44 mg (0.188 mmol) of **29** (mixture of racemic and meso) in 70 μL of $CDCl_3$ was admixed with 79 mg (0.30 mmol) of triphenylphosphine at -30 °C and left at this temperature. ^1H NMR analysis ($CDCl_3$, Me_4Si) of samples after 13 and 36 h showed the presence of **27b** (δ 2.33, s), **30** (δ 2.29, s),[18] acetone (δ 2.17, s), and acetic anhydride (δ 2.23, s) in molar ratios of 20:9:49:1 and 31:5:65:1, respectively.

Thermal Decomposition of 29 in Dichloromethane. (a) Isolation of 38 and 39. A solution of 1.2 g (5.1 mmol) of **29** (mixture of racemic and meso) in 10 mL of dichloromethane was heated to 50 °C for 40 h, and the solvent was removed at room temperature and 15 Torr. The liquid residue was dissolved in 30 mL of diethyl ether and washed with aqueous sodium bicarbonate, and the ether was removed at room temperature and 15 Torr to leave 1.88 g of a residue. It was separated by column chromatography (silica gel, pentane/diethyl ether, 4:1) to give 240 mg of **39** and a fraction containing impure **38**. The latter was purified by preparative GLC (glass column, 0.7 × 400 cm, 5% Carbowax 20 M on Chromosorb G; 130 °C for 15 min, 130–180 °C at 16 °C/min).

2,3-Dimethyl-1,3-dioxolan-4-one (38): ^1H NMR ($CDCl_3$, Me_4Si) δ 1.59 (s, 6 H), 4.35 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.90 (q, q, J = 128 and 2.9 Hz), 63.65 (t, J = 153 Hz, 112.67 (br s), 171.37 (t, J = 3.8 Hz); GLC (conditions as above) t_R = 20.50 min. The data agree with those of independently prepared[31] authentic **38**.

Acetyl 1-methyl-1-acetoxyethyl peroxide (39): colorless liquid; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.75 (s, 6 H), 2.06 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.50, 22.02, 23.07, 109.32, 167.56, 168.90. Anal. Calcd for $C_7H_{12}O_5$: C, 47.73; H, 6.87. Found: C, 47.57; H, 6.89.

(b) Determination of Product Distribution. The reactions were carried out in NMR tubes which were closed by ground-glass stoppers, and the products were analyzed by ^1H NMR spectroscopy. The following results were obtained: Heating of 15 mg of **29** in 3 mL of $CDCl_3$ to 40 °C for 2.5 days gave acetone, acetic acid, **38**, and **39** in relative amounts of 42, 29, 6, and 23%. Heating of 93 mg of **29** in 3 mL of $CDCl_3$ to 40 °C for 2.4 days gave the same products in relative amounts of 41, 38, 17, and 4%.

Reduction of 39 with LiAlH$_4$. To 5 drops of **39** in diethyl ether was added solid $LiAlH_4$, and the mixture was left at room temperature for 30 min. Then, water and diluted sulfuric acid were added sequentially, and the mixture was continuously extracted with ether. GLC analysis (glass column, 0.3 × 500 cm, 5% Carbowax 20 M on Chromosorb G; 60 °C) of the extract showed the presence of ethanol (t_R = 8.00 min) and 2-propanol (t_R = 7.63 min). This was confirmed by injection of authentic samples and by GC/MS analysis of the extract: m/e (relative intensity) 46 (29) M^+, 45 (61) $(M - H)^+$, 31 (100) $(M - CH_3)^+$ for ethanol and 59 (3) $(M - H)^+$, 45 (100) $(M - CH_3)^+$ for 2-propanol.

Ozonolysis of 3-Methyl-1,2-butadiene. 3-Methyl-1,2-butadiene (1.9 g, 28 mmol) was loaded on 93 g of polyethylene and ozonized at -75 °C for 4 h. A small sample was extracted with $CDCl_3$. ^1H NMR analysis of the extract showed the presence of acetone and **38** in a molar ratio of 17:1, along with unreacted substrate. The major part of the polyethylene was extracted with diethyl ether, and the ether was distilled off through a 7-cm Vigreux column at normal pressure. From the residue of ca. 1 mL, a sample of pure **38** was isolated by preparative GLC (glass columnm, 0.7 × 400 cm, 5% Carbowax 20 M on Chromosorb G; 120 °C for 13.5 min, 120–180 °C at 18 °C/min).

Supplementary Material Available: Tables 1–3 giving fractional crystallographic coordinates, B values, bond distances and angles, and anisotropic thermal parameters for *meso*-**29** (3 pages). Ordering information is given on any current masthead page.

---

(31) Willstätter, R.; Königsberger, F. *Chem. Ber.* **1923**, *56*, 2108.

(32) Johnson, C. A. *ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*; ORNL-3794, 2nd rev. with supplemental instructions, Oak Ridge National Laboratory, 1979.

Formation of Olefins via Pyrolysis of Sulfonate Esters[1]

E. J. Corey

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Gary H. Posner

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Richard F. Atkinson,* Astrid K. Wingard, Daniel J. Halloran, Donna M. Radzik, and John J. Nash

Grand Valley State University, Allendale, Michigan 49401

Received August 10, 1988

Esters of 8-quinolinesulfonic acid and 2-pyridinesulfonic acid were synthesized from alcohols and the acid chlorides. The secondary esters decomposed cleanly at moderate temperatures to give olefins in high yield. Product studies were consistent with carbocation formation and abstraction by a ring nitrogen to give olefin. The importance of a basic group was confirmed by pyrolysis of a series of para-substituted cyclohexyl benzenesulfonates, p-$XC_6H_4SO_3R$. The compounds with X = NHEt and NHCOMe reacted cleanly to give olefin in good yield. When X = NO_2, Br, CH_3, or OCH_3, olefin was formed in low yield along with considerable amounts of tar.

Although it has been known for many years that heating of sulfonate esters can lead to the formation of olefins,[2] such reactions generally give poor yields and considerable decomposition. We have discovered that secondary esters of 8-quinolinesulfonic acid and 2-pyridinesulfonic acid decompose cleanly at moderate temperatures to give olefins in high yield (eq 1 and 2). In this paper we present examples of this reaction and evidence in support of its mechanism.

The esters were synthesized in good yield by the reaction of alcohols with the corresponding sulfonyl chloride in pyridine or triethylamine except where noted (Table I).

---

(1) This work was supported in part by a grant from the Research and Scholarly Development Committee of Grand Valley State University.

(2) (a) Foldi, Z. *Chem. Ber.* **1927**, *60*, 656. (b) Drahowzal, F.; Klamann, D. *Monatsh. Chem.* **1951**, *82*, 467. (c) Gough, G. A. C.; Hunter, H.; Kenyon, J. *J. Chem. Soc.* **1926**, 2066.

0022-3263/89/1954-0389$01.50/0 © 1989 American Chemical Society