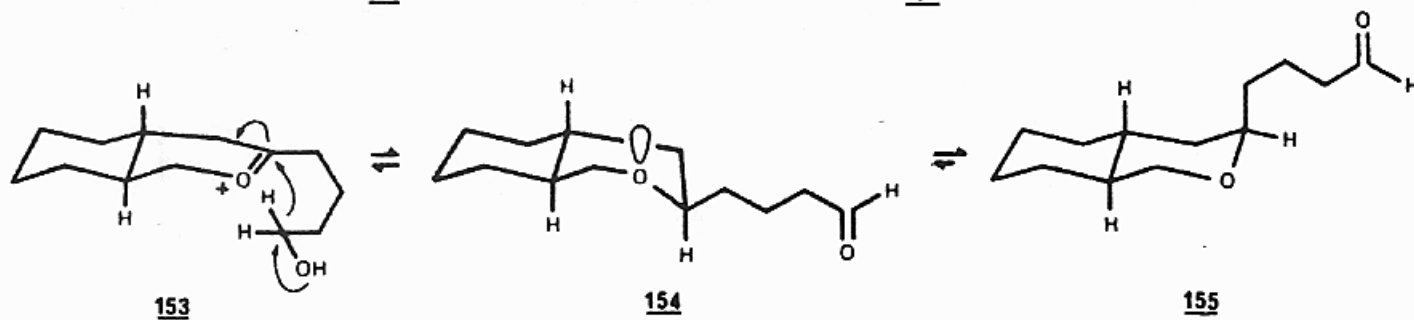
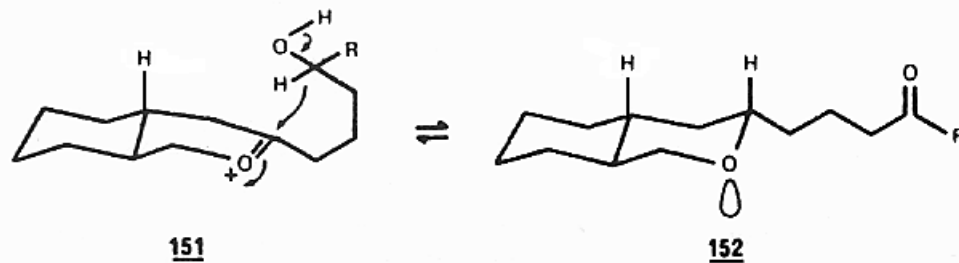
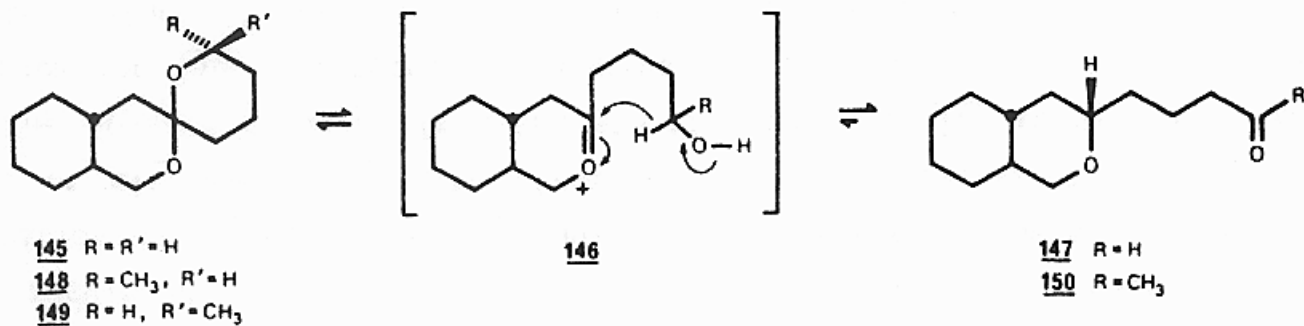


## **SECTION 5**

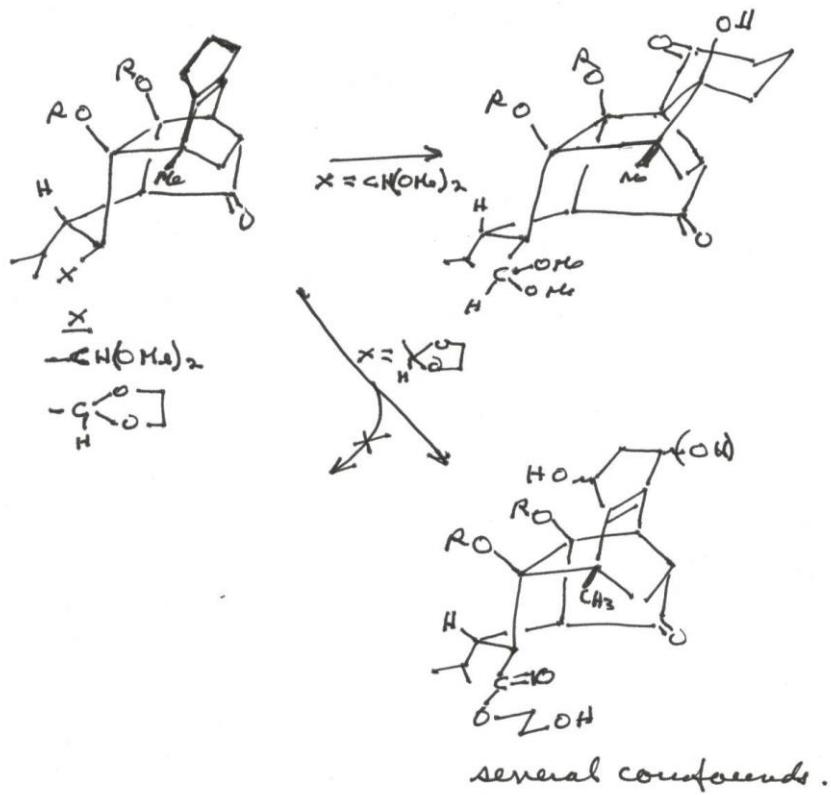
# **Stereoelectronic Effects (S.E.) in Other Reactions of Acetals**

*(2018)*

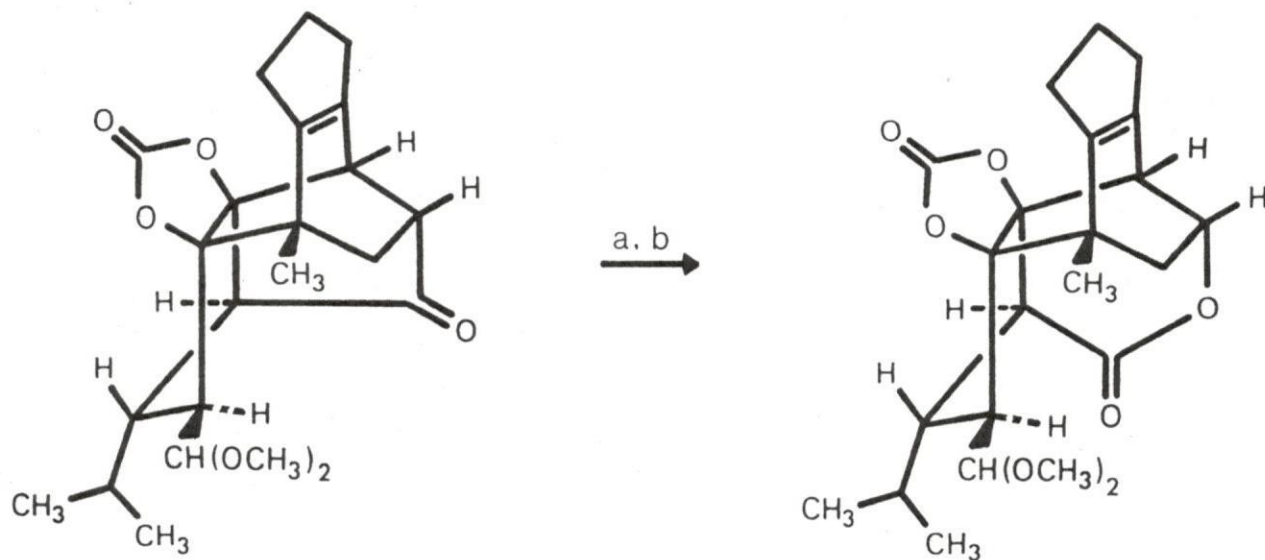
# Hydride Transfer to Cyclic Oxenium Under Acidic Conditions (antiperiplanar lone pair)



Discovery of the Ozonolysis of acetals



P. Derlong chaents, C. Morace  
 Can. J. Chem. 1971, 49, 2465

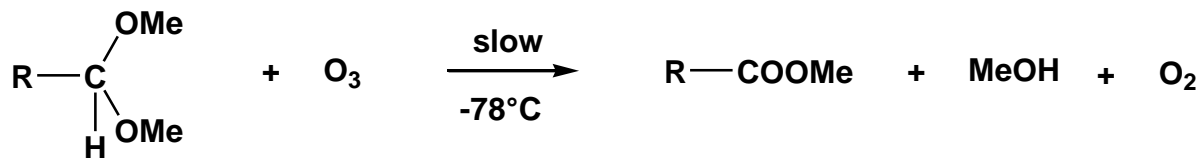
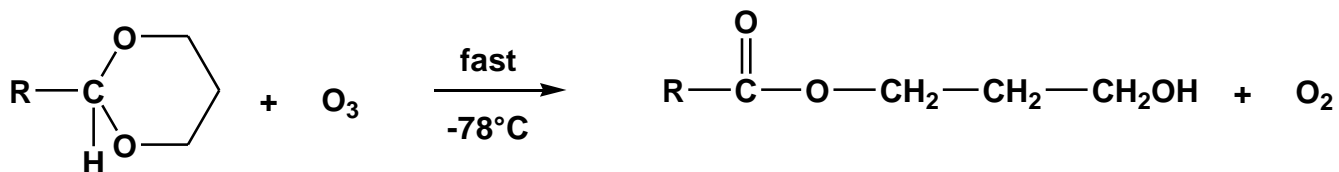
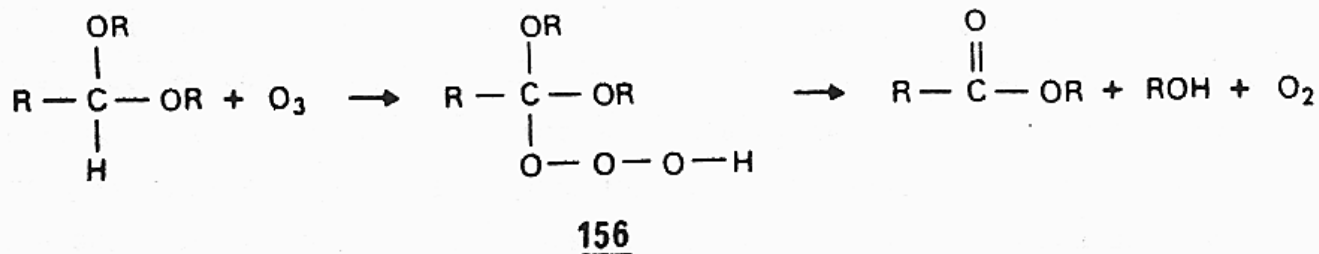



---

a)  $\text{CH}_3\text{CO}_3\text{H}$ , NaOAc;    b)  $\text{WCl}_6 + 2n\text{-BuLi}$ , THF

# Oxidation of Acetals by Ozone

## Reactions



P. Deslongchamps, C. Moreau. *Can. J. Chem.* **1971**, *49*, 2465.

P. Deslongchamps, C. Moreau, D. Fréhel, P. A. Atlani. *Can. J. Chem.* **1972**, *50*, 3402.

P. Deslongchamps, C. Moreau, D. Fréhel, R. Chênevert. *Can. J. Chem.* **1975**, *53*, 1204.

# Explanation of Reactivity: Two Lone Pairs Antiperiplanar to C-H Bond

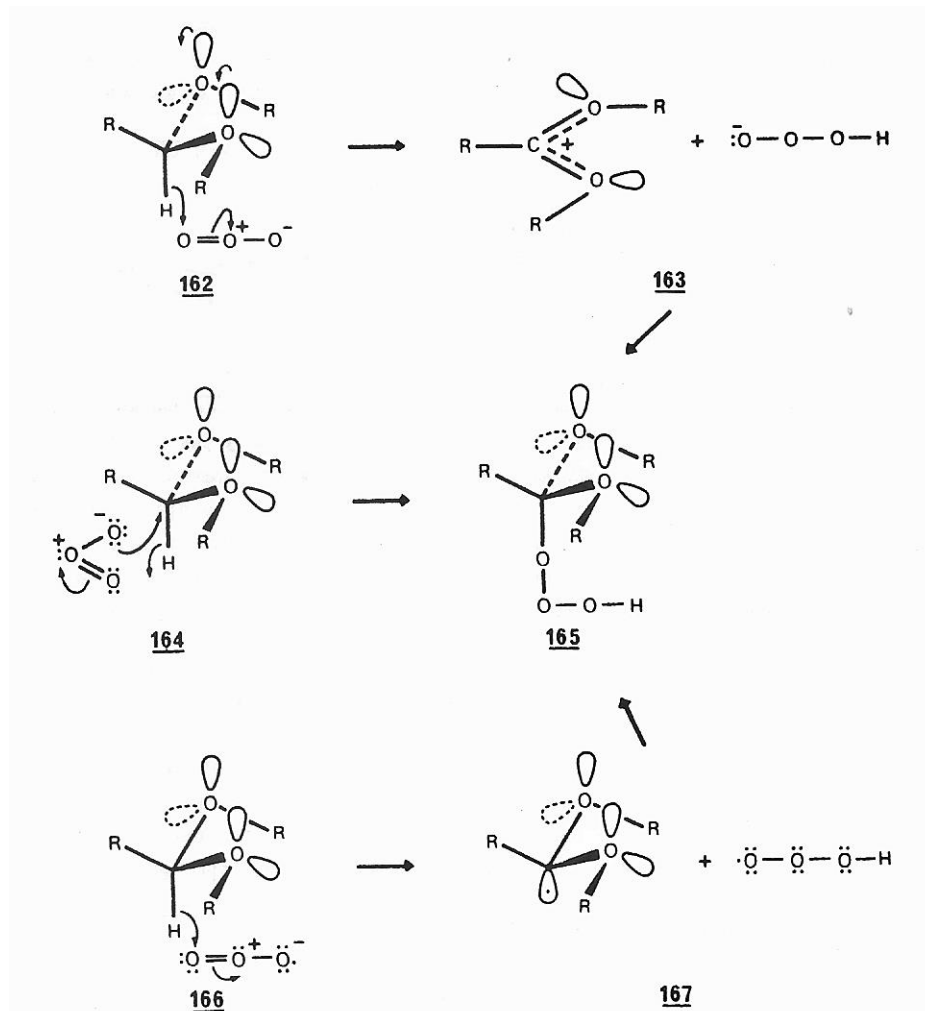
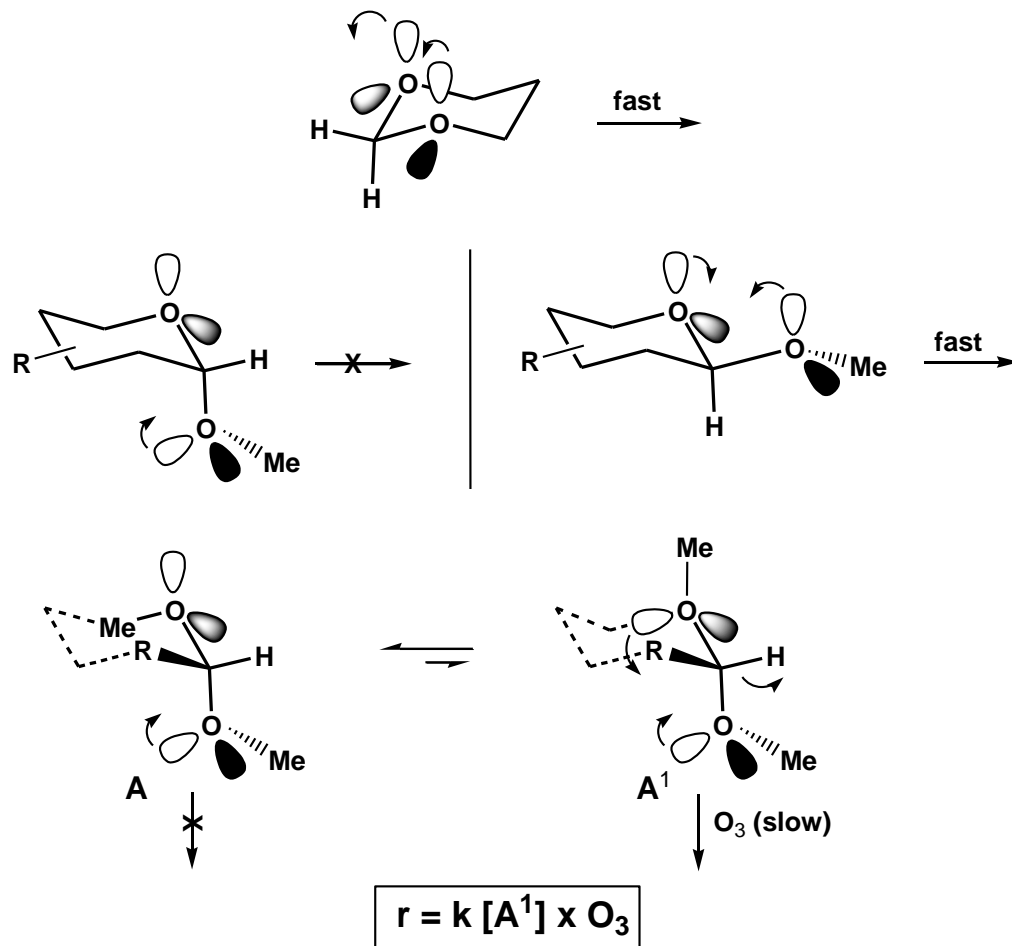


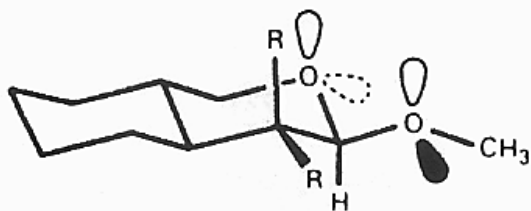
Fig. 20

# Relative Rate of Oxidation and Acetal Conformation

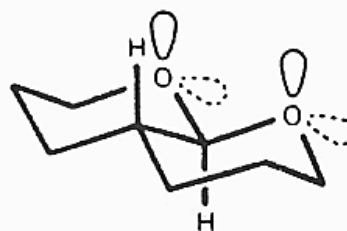


**N.B.** Ozonolysis of dimethoxyacetal is slow because it is a bimolecular process. The rate depends on the concentration of the reactive conformation A<sup>1</sup> (small population) and the O<sub>3</sub> concentration.

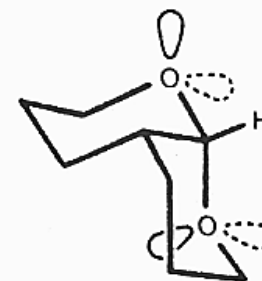
# Oxidation by Ozone



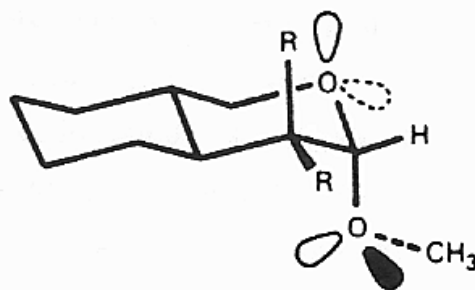
**157** R = CH<sub>3</sub> ✓



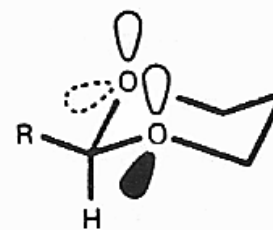
**158** ✓



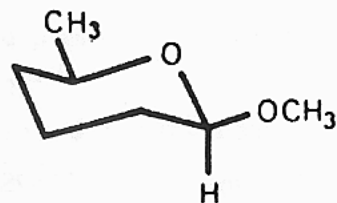
**159** ✗



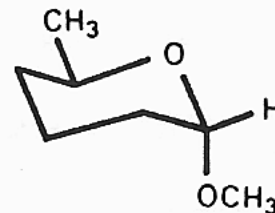
**160** R = CH<sub>3</sub> ✗



**161** ✓



**172** ✓

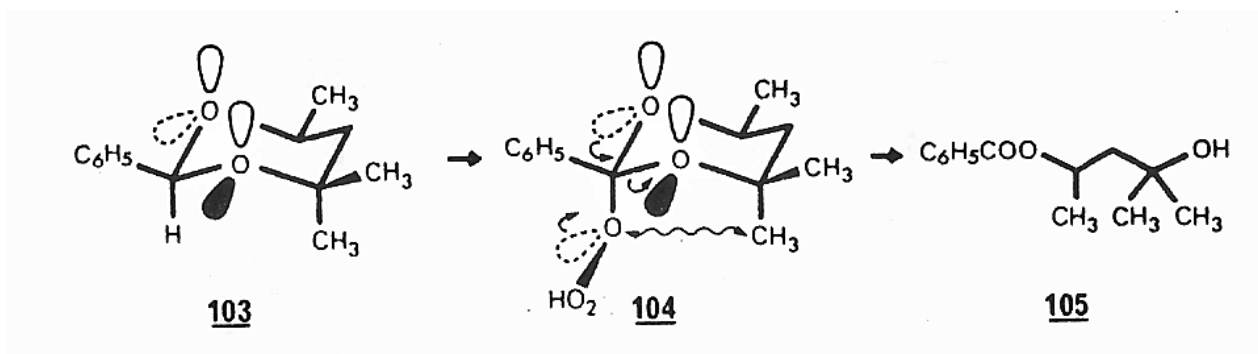


**173** ✗



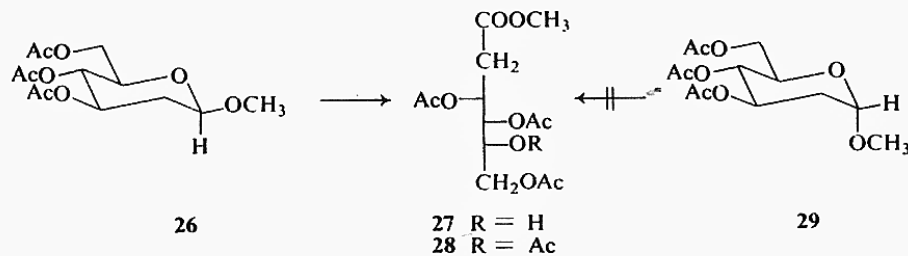
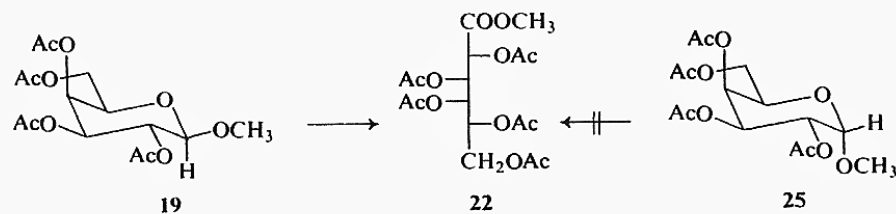
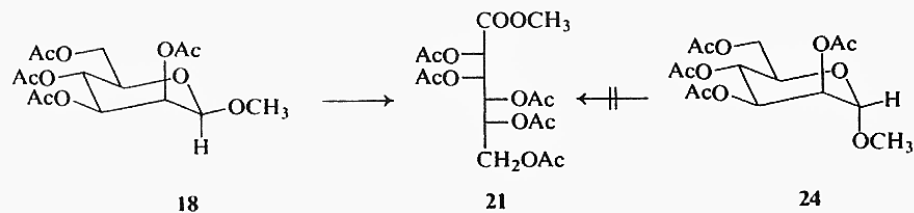
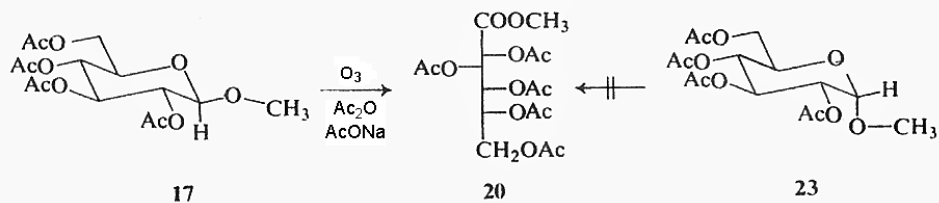
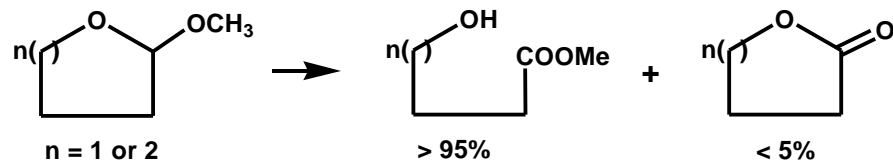
## An Interesting Case of Steric Decompression Effect

---



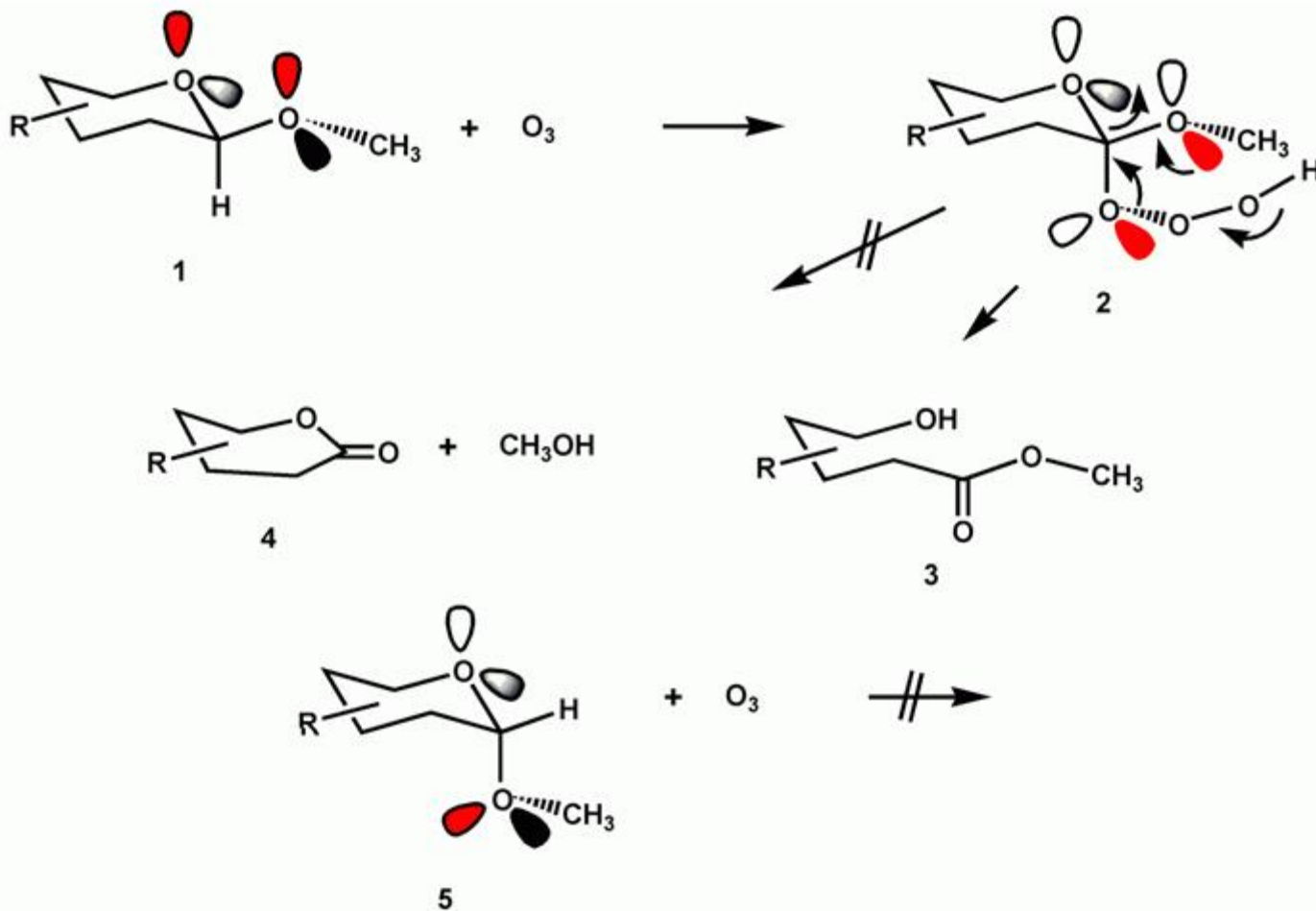
The importance of this effect was verified by carrying out the ozonolysis of acetal **103**. Oxidation of **103** by ozone gave the ester **105** exclusively (33). In this reaction, the hydrotrioxide intermediate **104** has proper electron pair orientation to favor the opening in both directions, but cleavage occurs in only one, yielding **105** because of this steric decompression factor.

# Ozonolysis of THP-Ether and Glycosides



**DESLONGCHAMPS *et al.***  
 Can. J. Chem.  
 1974, 52, 3651-3664.

# Ozonolysis of acetals

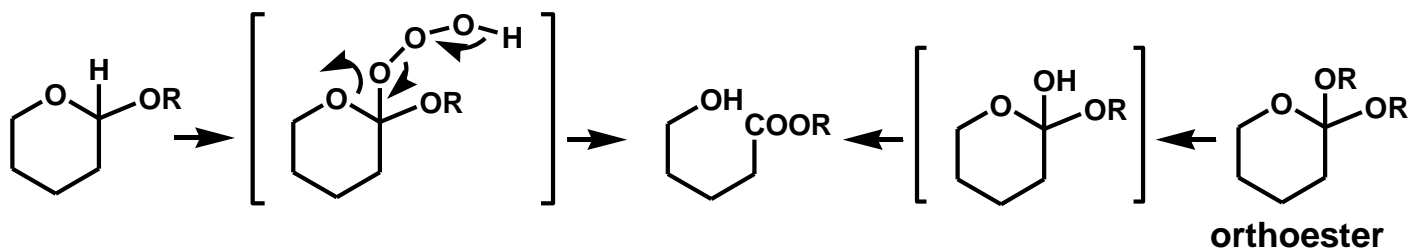


P. DESLONGCHAMPS, C. MOREAU, D. FREHEL, and P. ATLANI.  
The Importance of Conformation in the Ozonolysis of Acetals.  
*Can. J. Chem.* **50**, 3402 (1972).

F. KOVAC, B. PLENISCAR. *J. Am. Chem. Soc.* **101**, 2677 (1979).

# Extension of the Theory of Stereoelectronic Control to Hydrolytic Reactions

1. Ozonolysis of THP ether takes place by formation of a hydrotrioxide intermediate.
2. Formation of the hydrotrioxide intermediate is controlled by two oxygen lone pairs oriented antiperiplanar to the C-H bond.
3. The hypothesis was put forward that cleavage of the hydrotrioxide intermediate can only take place if there are two oxygen lone pairs oriented antiperiplanar to the leaving OR bond (explains formation of hydroxy ester).
4. As the hydrotrioxide intermediate is analogous to a tetrahedral intermediate in hydrolysis reaction, the same stereoelectronic principle should apply in the hydrolysis of cyclic orthoester.



**N.B.** Ozonolysis of THP-ether and glycosides is a reaction of limited scope. However, transposition of what was learned about stereoelectronic effect to further understand the cleavage of tetrahedral intermediates in hydrolytic processes now takes all its importance. Indeed, hydrolytic reactions are important in Nature.