M. MURAKAMI, K. SAKITA, K. IGAWA, K. TOMOOKA\* (TOKYO INSTITUTE OF TECHNOLOGY, JAPAN) Stereoselective Oxy-Functionalization of  $\gamma$ -Silyl Allylic Alcohols with Ozone: A Facile Synthesis of Silyl Peroxide and Its Reactions

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## **1,2,3-Triols: Partial Oxidation of** γ-Silyl Allylic Alcohols with Ozone



**Significance:** In a unique oxidation of an alkene with ozone, the vinylsilane moiety does not undergo the normal cleavage of the double bond. The solvent is the key to the unusual reaction since a 1:1 mixture of **2**:(usual ozonolyzed product) was observed in  $CH_2Cl_2$ . The reaction is chemoselective since an alkene was oxidized in presence of an alkyne group. The authors noted that the silyl peroxides are stable and require no special handling (slow degradation above 80 °C).

**Comment:** In situ IR monitoring failed to detect any intermediates, suggesting a very short-lived ozonide. The study demonstrates that in ethyl acetate, at the ozonide stage, the silyl group migrates faster than the normal ozonide rearrangement, preventing C–C-bond cleavage. The silyl peroxide function can be converted into the corresponding ketone in 73% under a simple base treatment (not shown here). The reaction tolerates the free alcohol or the silylated allylic alcohol.

## Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

## Key words

ozonolysis

alkene oxidation

1,2,3-triols

allylic alcohol functionalization

silyl peroxide

diastereoselective alkylation

peroxide reduction

syn-1,2-diol



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