

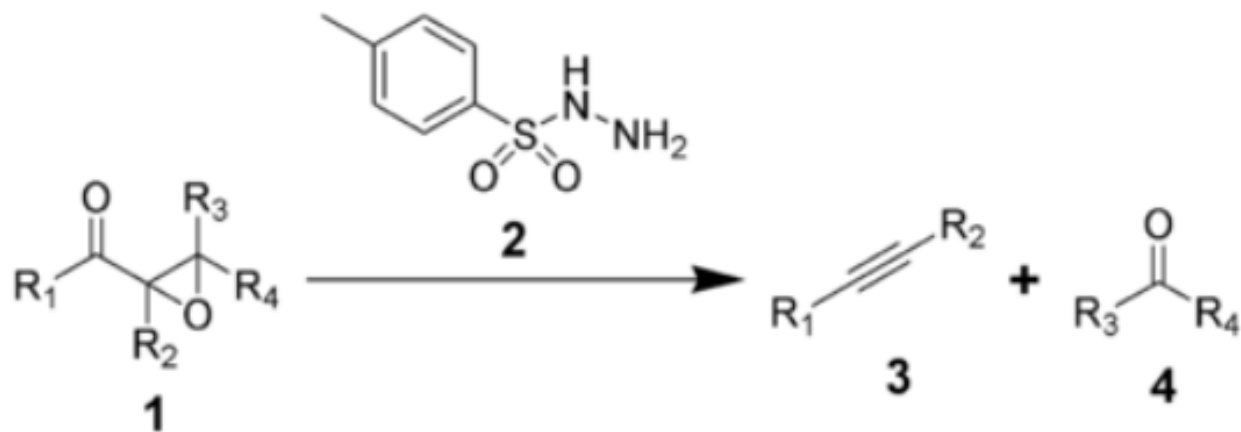
# **Eschenmoser(埃申莫瑟) - Tanabe fragmentation**

Lirong Cai

March 31th 2015

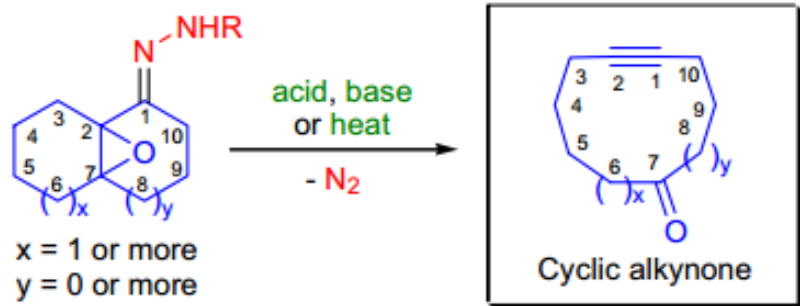
# Eschenmoser fragmentation

---

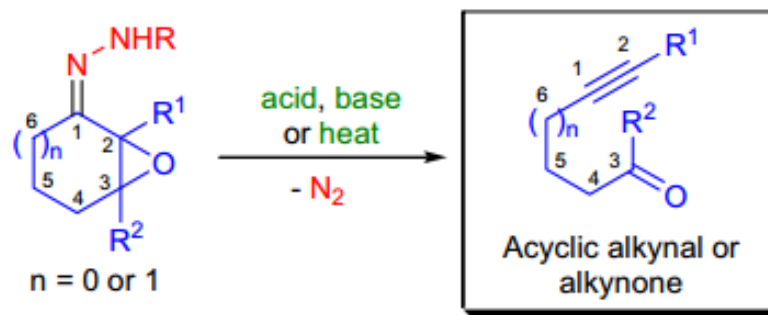


# Eschenmoser fragmentation

Synthesis of cyclic alkynesones:



Synthesis of acyclic alkynones and alkynals:

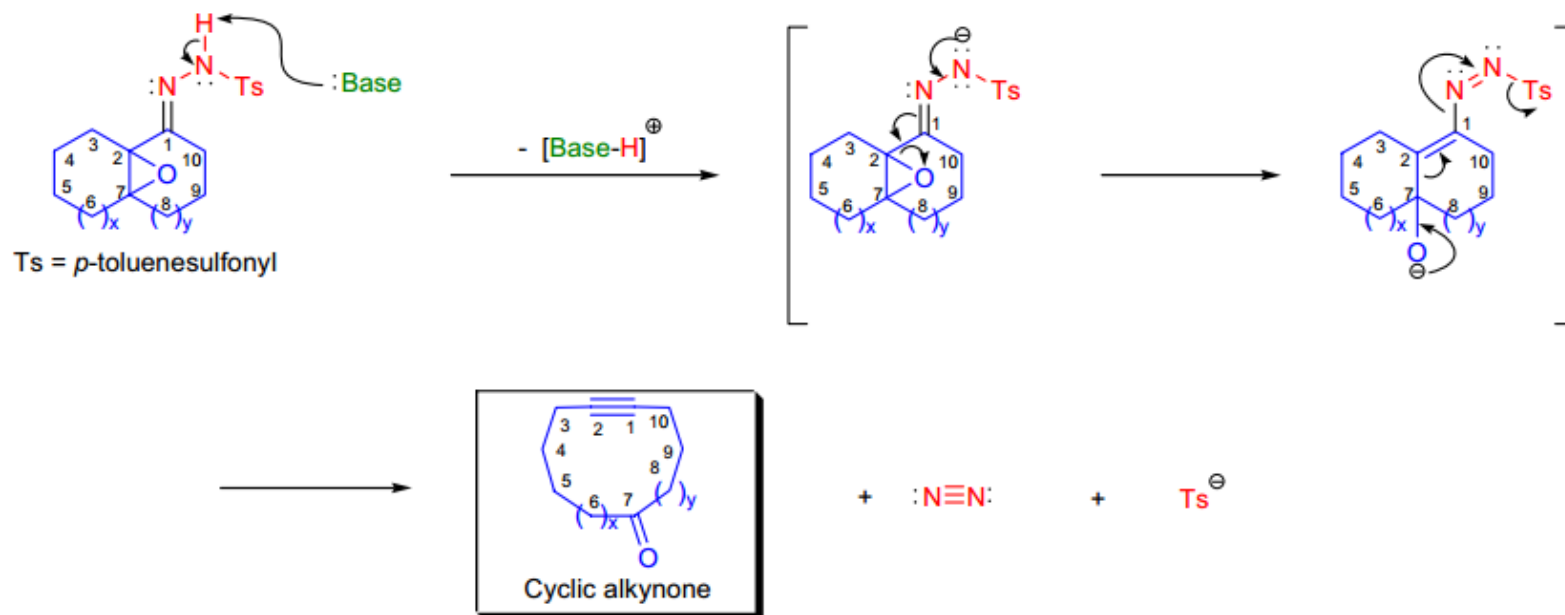


R = tosyl, 2,4-dinitrophenyl; R<sup>1-2</sup> = H, alkyl; when R<sup>2</sup> = H, then the product is an alkynal, and when R<sup>2</sup> = alkyl, then it is an alkynone

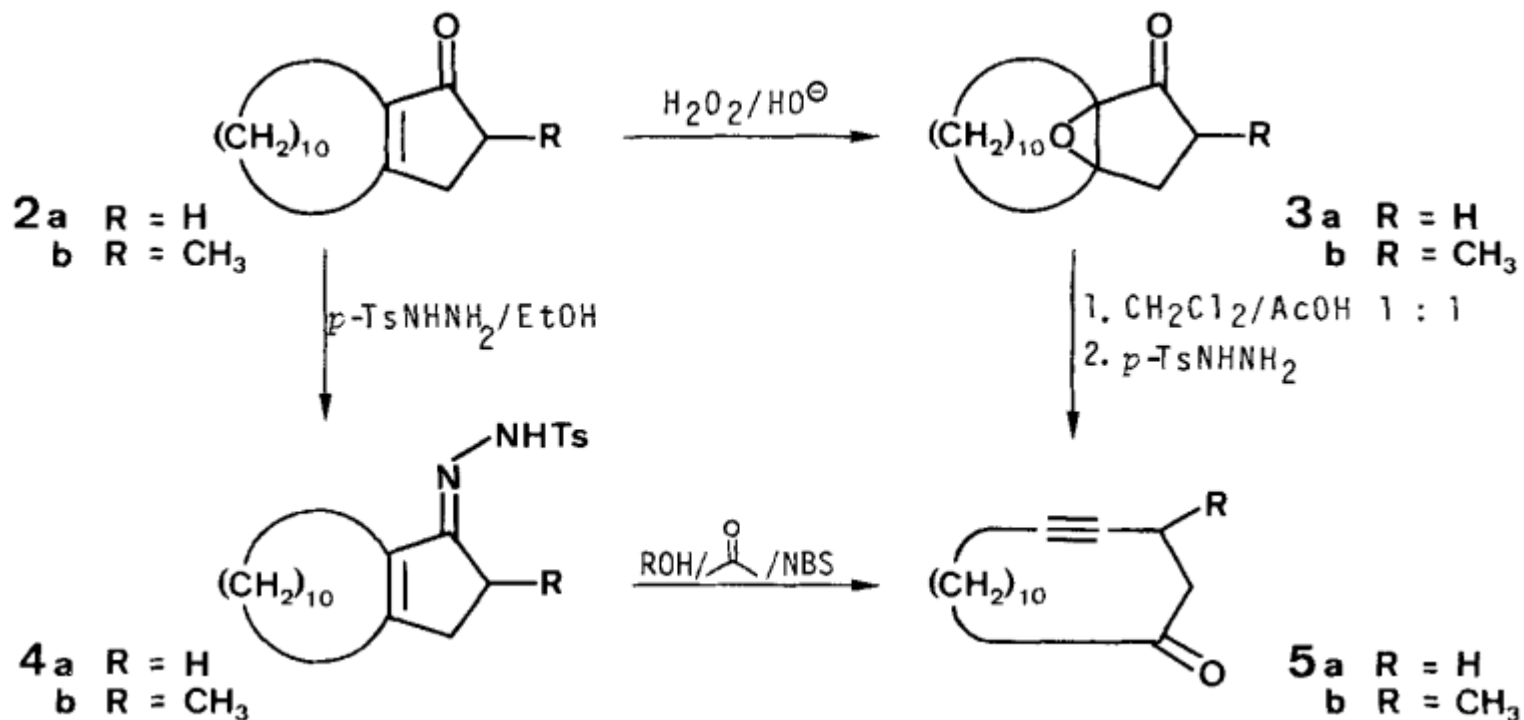
Advantages of the Eschenmoser-Tanabe fragmentation are the following:

- 1) easy access to medium-sized cyclic ketones;
- 2) both terminal and disubstituted alkynes can be prepared;
- 3) the fragmentation is not limited to the use of aromatic sulfonylhydrazones.

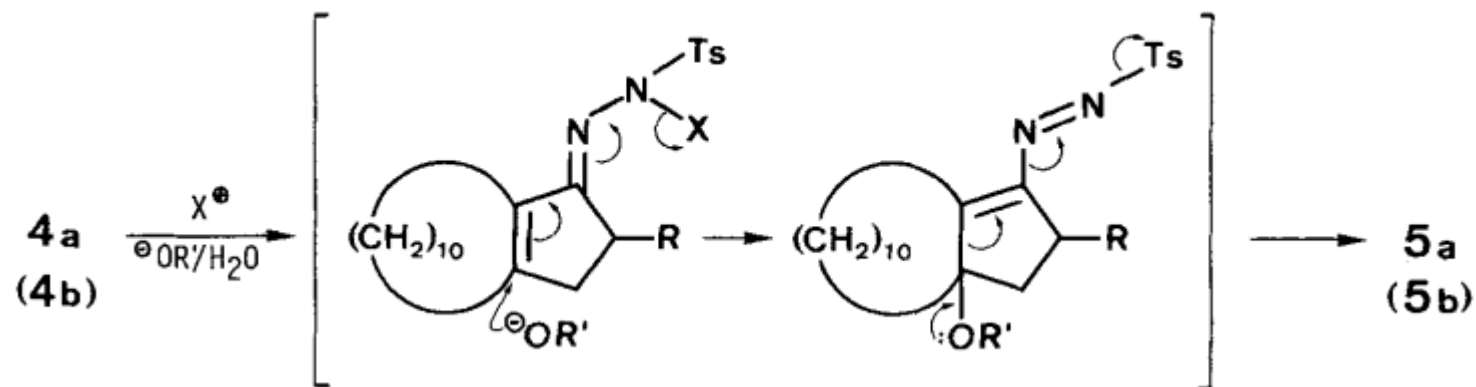
# Eschenmoser fragmentation



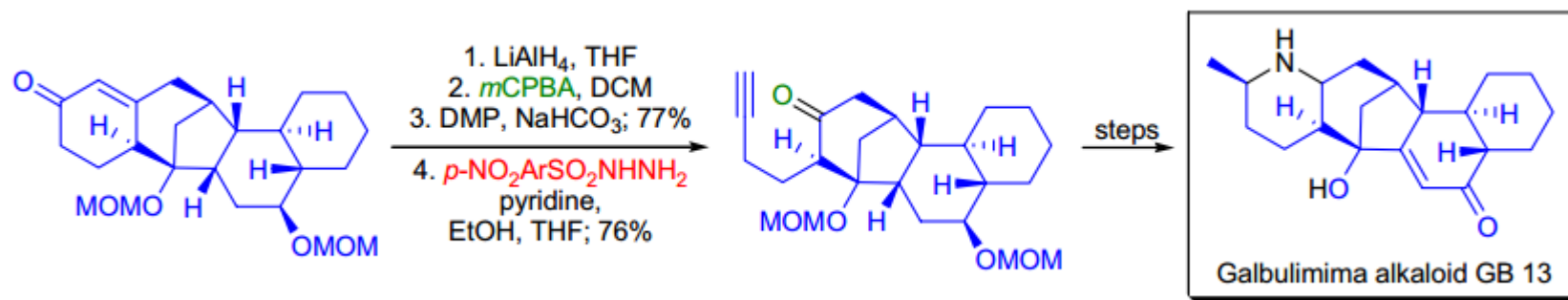
When the preparation of the epoxy ketone is not possible or has to be avoided, treatment of the unsaturated hydrazones with excess NBS in methanol leads directly to the desired alkyne.



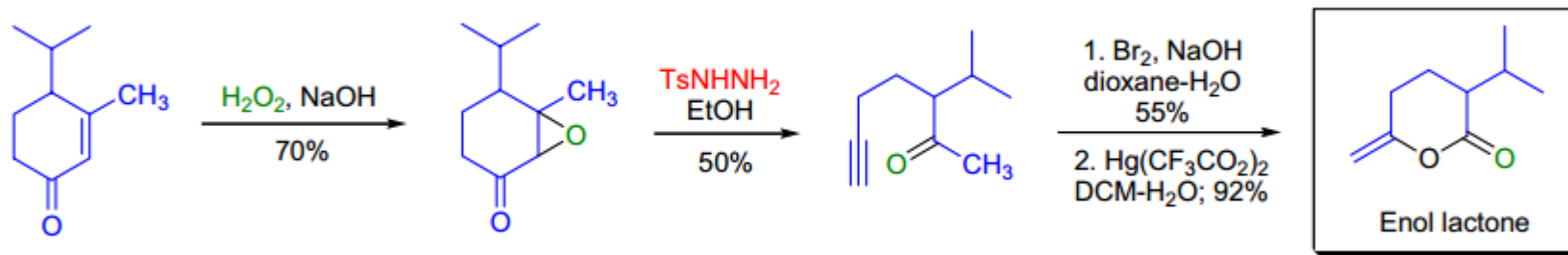
Scheme 3. Vinylogous fragmentation reaction



# Eschenmoser fragmentation

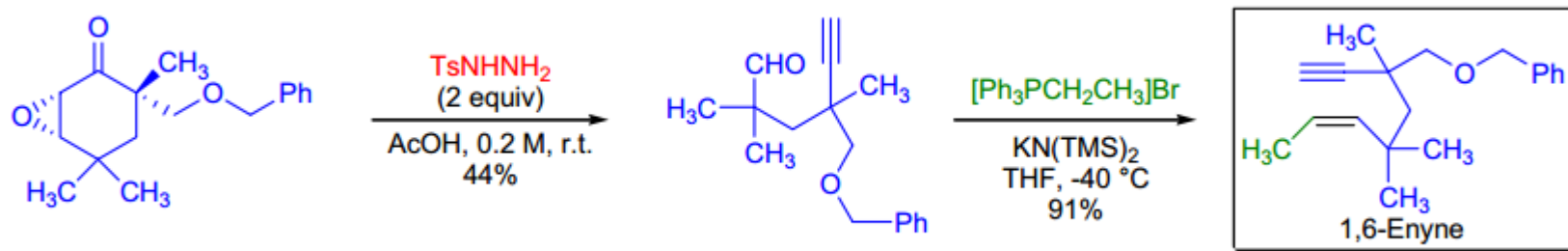


*J. Am. Chem. Soc.* **2003**, 125, 2400-2401.

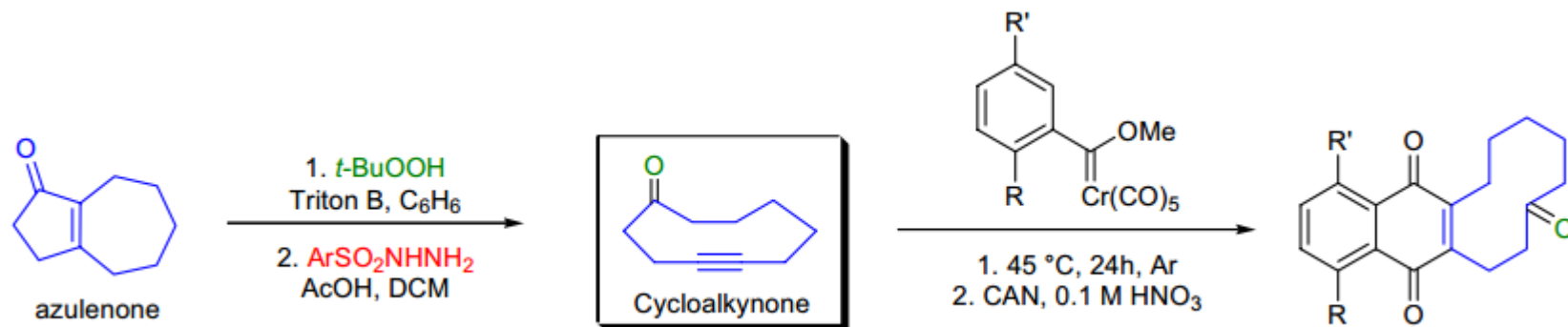


*J. Org. Chem.* **1993**, 58, 1900-1908.

# Eschenmoser fragmentation



*Synthesis* **1993**, 824-832.



*J. Org. Chem.* **1992**, 57, 7052-7055.