Eschenmoser(埃申莫瑟）-Tanabe fragmentation

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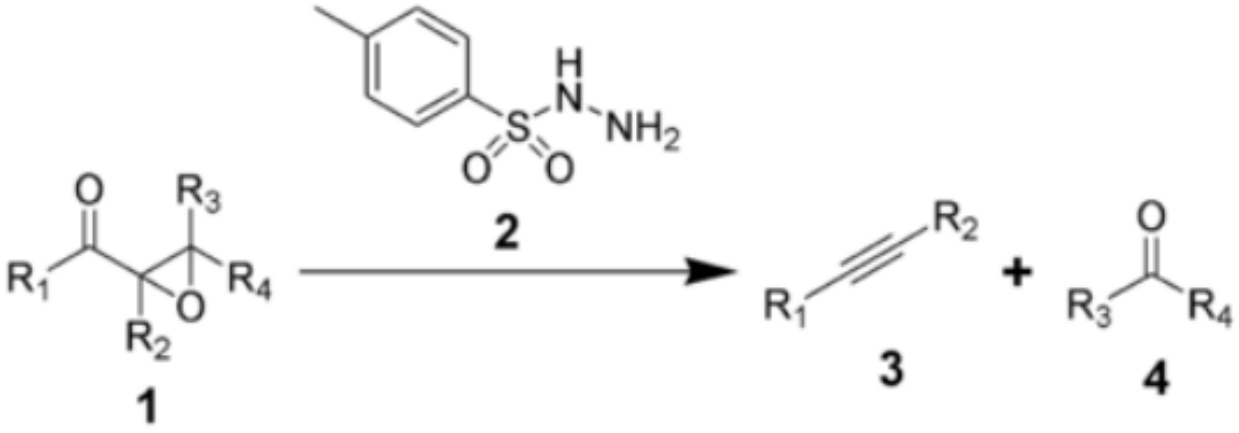
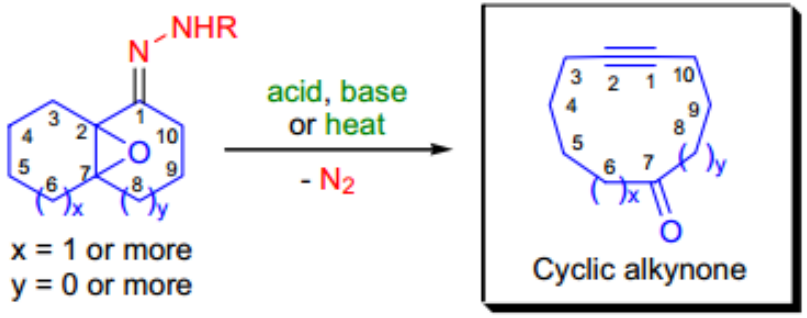
Eschenmoser fragmentation

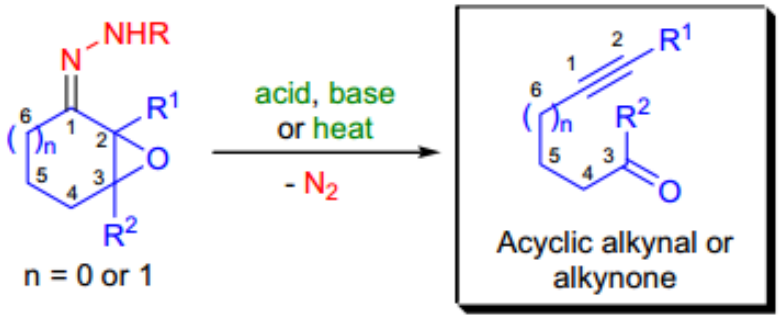


Eschenmoser fragmentation

Synthesis of cyclic alkynones:



Synthesis of acyclic alkynones and alkynals:

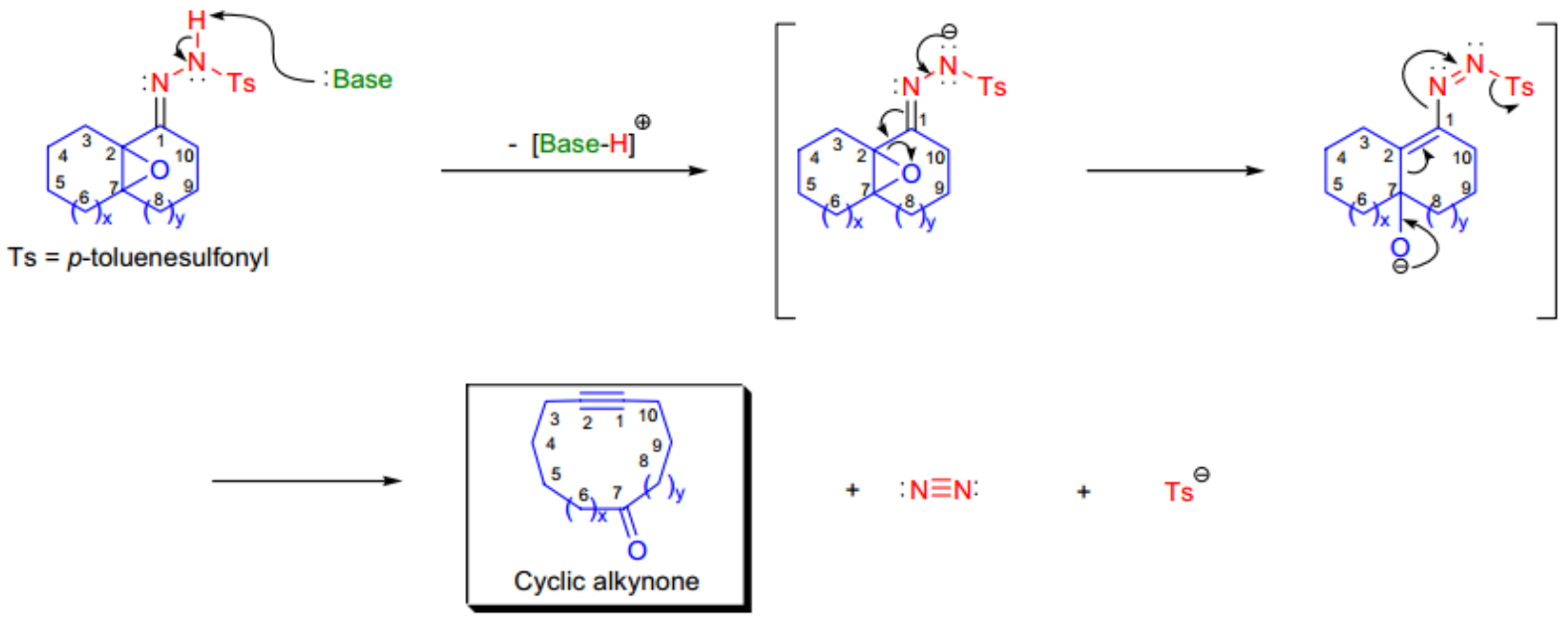


R = tosyl, 2,4-dinitrophenyl; R^{1-2} = H, alkyl; when R^2 = H, then the product is an alkynal, and when R^2 = alkyl, then it is an alkynone

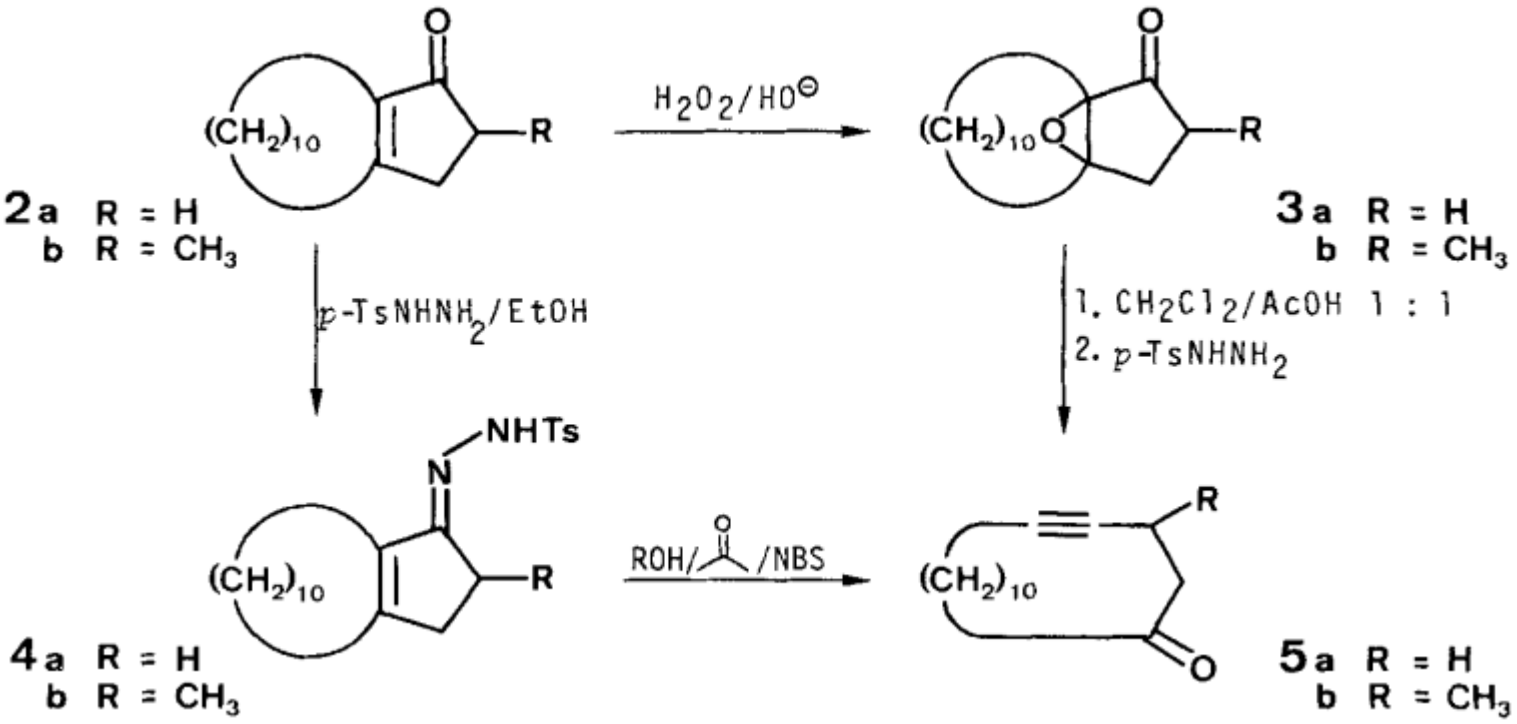
Advantages of the Eschenmoser-Tanabe fragmentationare the following:

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

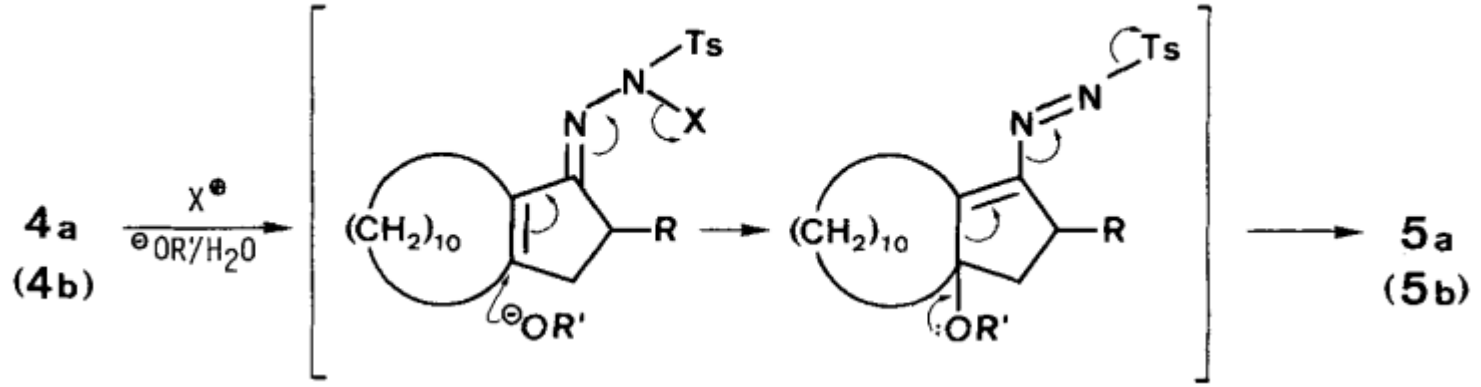
Eschenmoser fragmentation



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 alkynones.

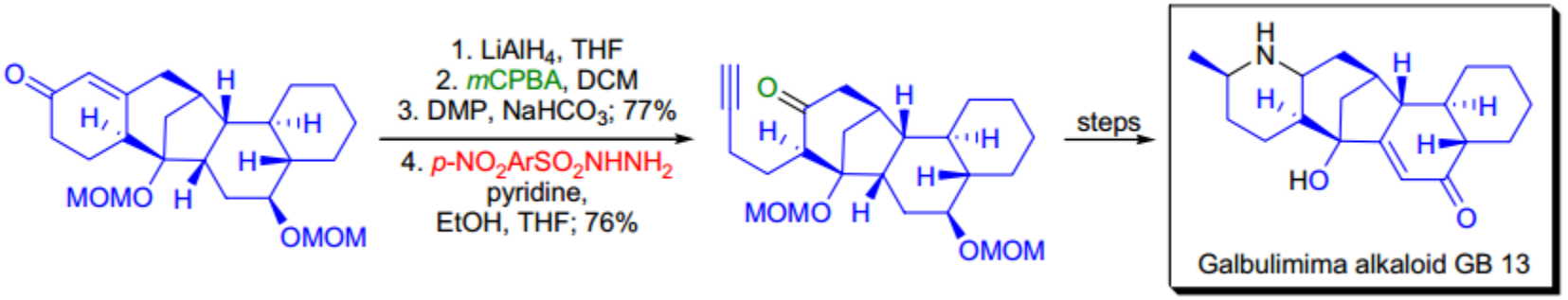


Scheme 3. *Vinylogous fragmentation reaction*

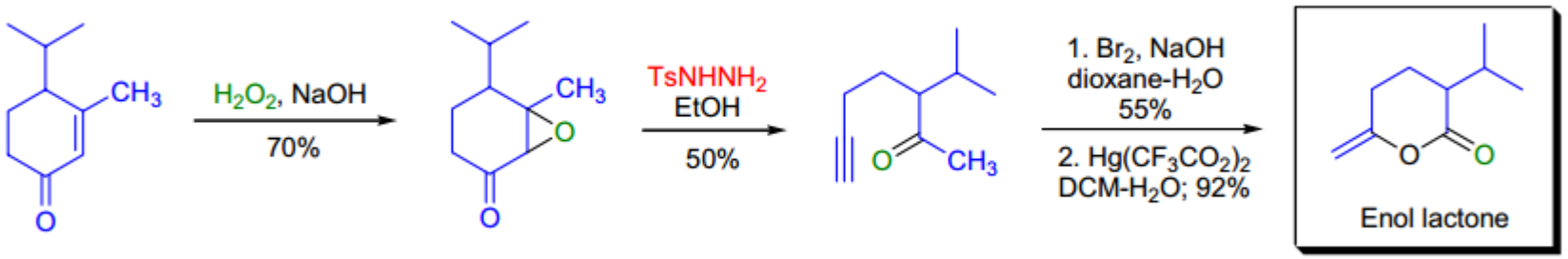


Helv. Chim. Acta **1979**, 62, 2655-2660.

Eschenmoser fragmentation

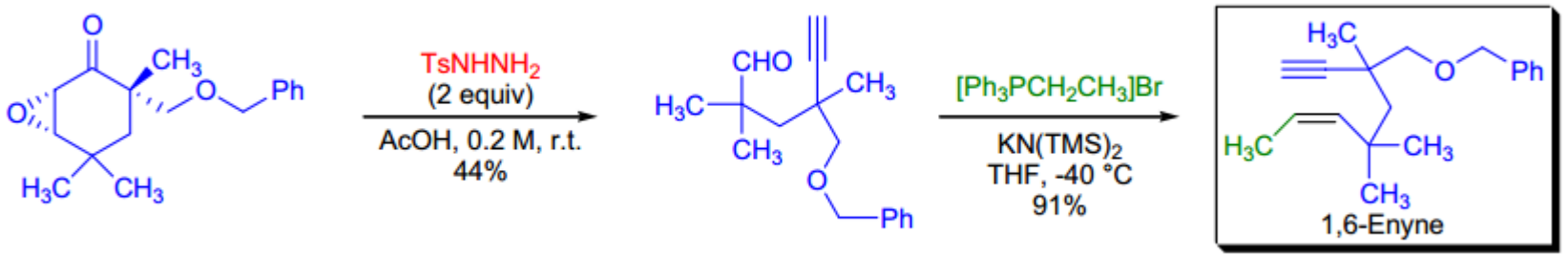


J. Am. Chem. Soc. **2003**, 125, 2400-2401.

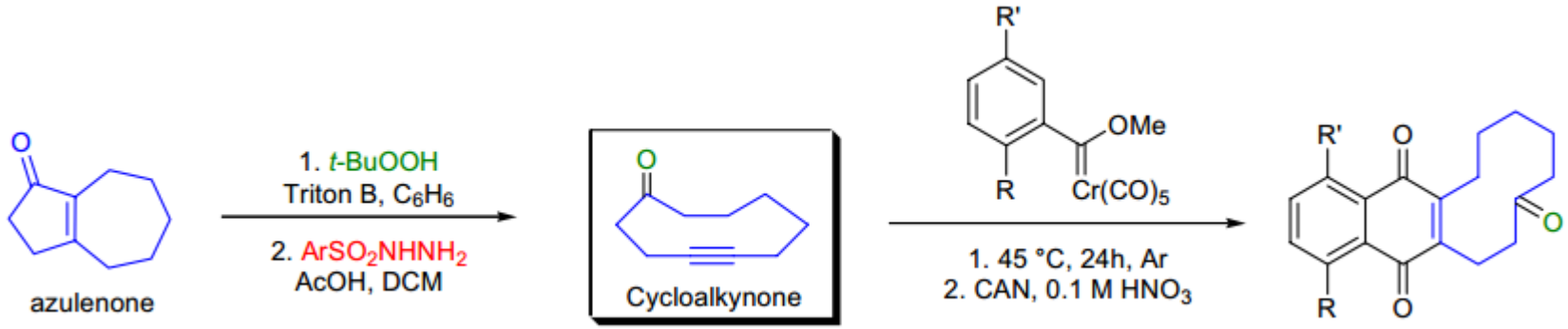


J. Org. Chem. **1993**, 58, 1900-1908.

Eschenmoser fragmentation



Synthesis **1993**, 824-832.



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