

Pyrolytic syn elimination

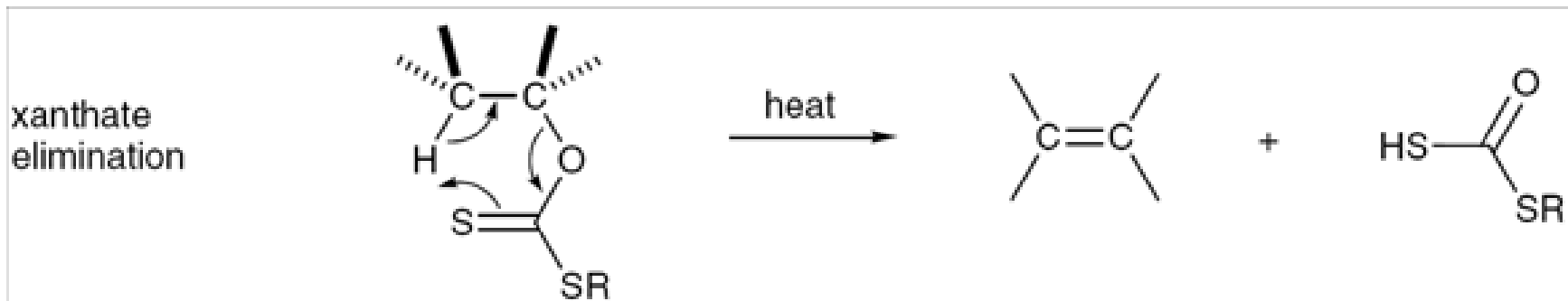
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Associate Professor

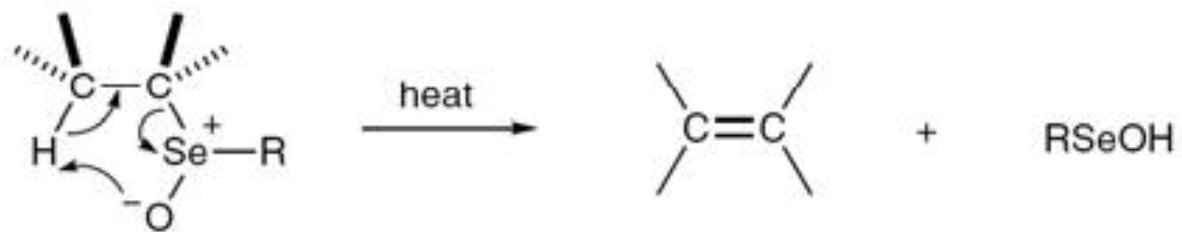
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Introduction

- Pyrolysis is a process in which chemical decomposition of organic materials have been occurred at elevated temperature
- It takes place in a concerted manner (via cyclic TS) with syn stereochemical relationship in which the hydrogen atom and the leaving group depart from the same side of the incipient double bond: Examples are-

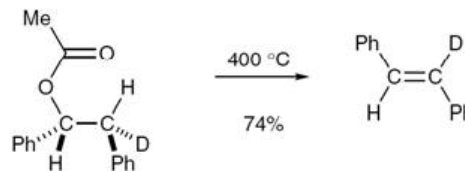
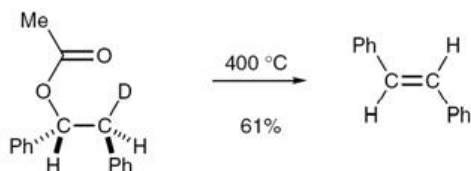


selenoxide
elimination



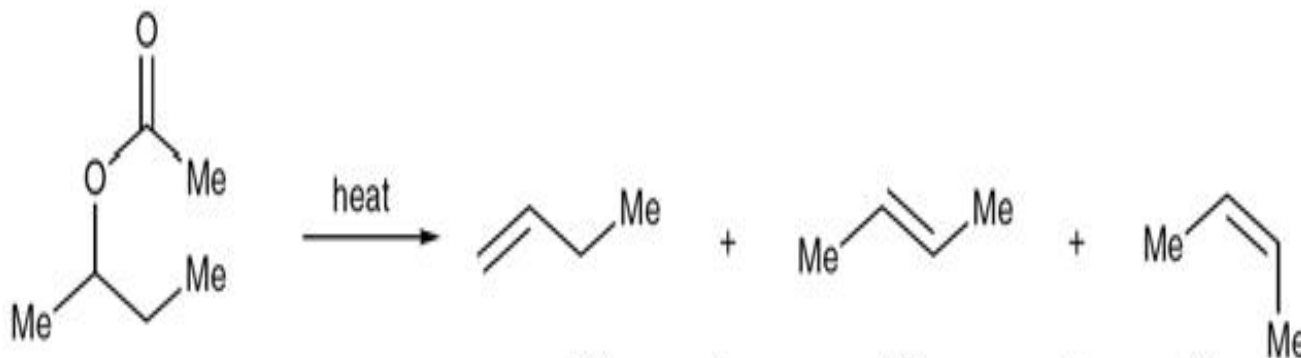
Pyrolysis of Esters

- ✓ Usually effected at 300-500°C (Very high; Limitation of its usefulness !)
- ✓ Carried out by simple heating if bp is high enough,
- ✓ Carried out by passing the vapor through a heated tube
- ✓ The absence of solvents and other reactants simplifies the isolation of the product
- ✓ Effective for the preparation of sensitive or reactive alkenes due to the absence of acidic or basic reagents
- ✓ Passing through 6-membered cyclic Transition State

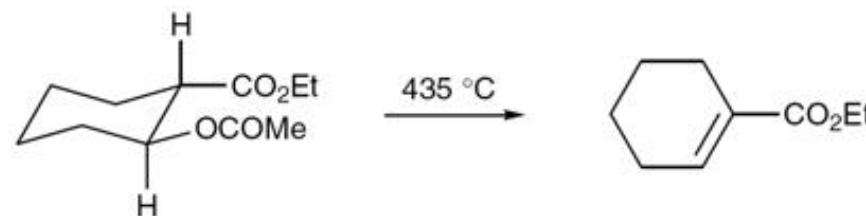
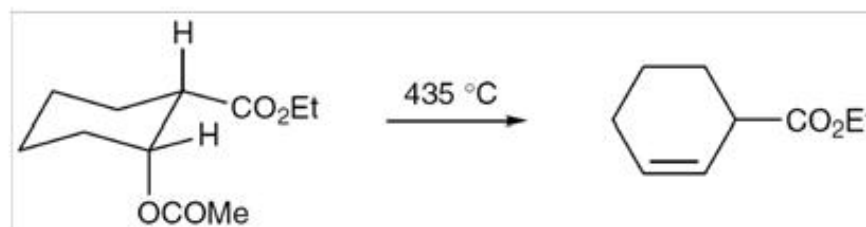


Regioselectivity and stereoselectivity

- ✓ In acyclic compounds, the regioselectivity is often poor
- ✓ The composition of the products is determined mainly by the number of H atoms on each β -carbon



In cyclic compounds ring conformation is important



- ✓ If there is a conjugating substituent in the β -position, elimination occurs predominantly to give the conjugated alkene

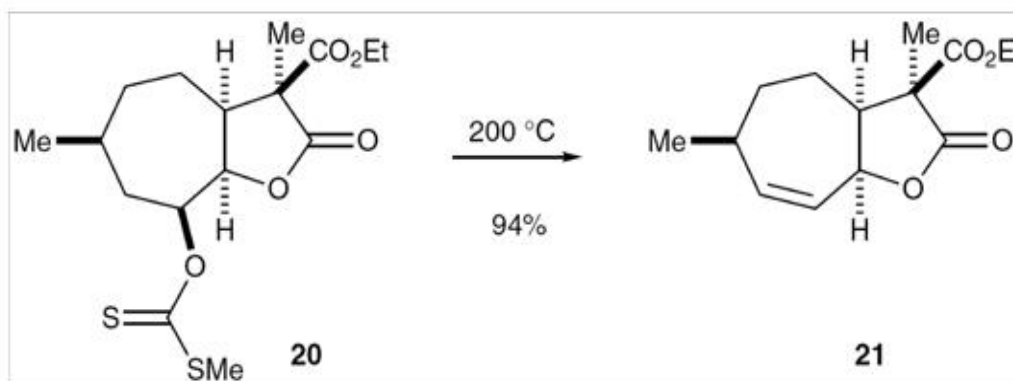
Pyrolysis of Xanthates

- Introduction

- ✓ Takes place in the region of 150-250°C (Much lower T; 300-500°C in ester)
- ✓ Separation of the alkene product from sulfur-containing by-products can sometimes be troublesome

- Transitions State

- ✓ 6-Ring TS with *syn*-relationship of H and X

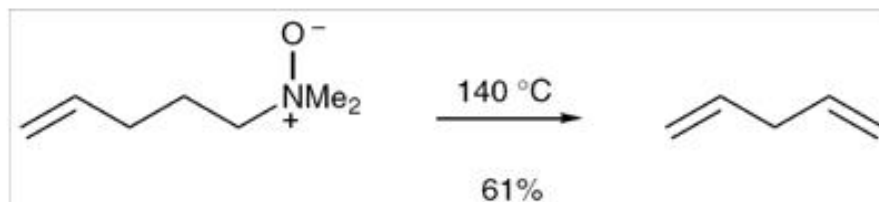


In acyclic compounds (E) isomer generated predominantly

- ✓ In acyclic compounds, regioselectivity is often poor

Pyrolysis of amine oxides (Cope elimination)

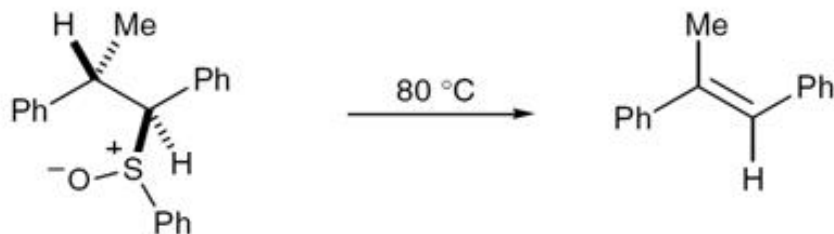
- ✓ Prepared by oxidation of *tert*-amine (with H₂O₂ or mCPBA)
- ✓ Alternative way to the Hofmann elimination of quaternary ammonium salt
- ✓ Takes place under relatively mild reaction conditions (100-200°C)
- ✓ Allow generation of C=C bond without subsequent migration into the conjugation systems



- ✓ 5-Ring TS with *syn*-relationship of H and X

Pyrolysis of sulfoxides

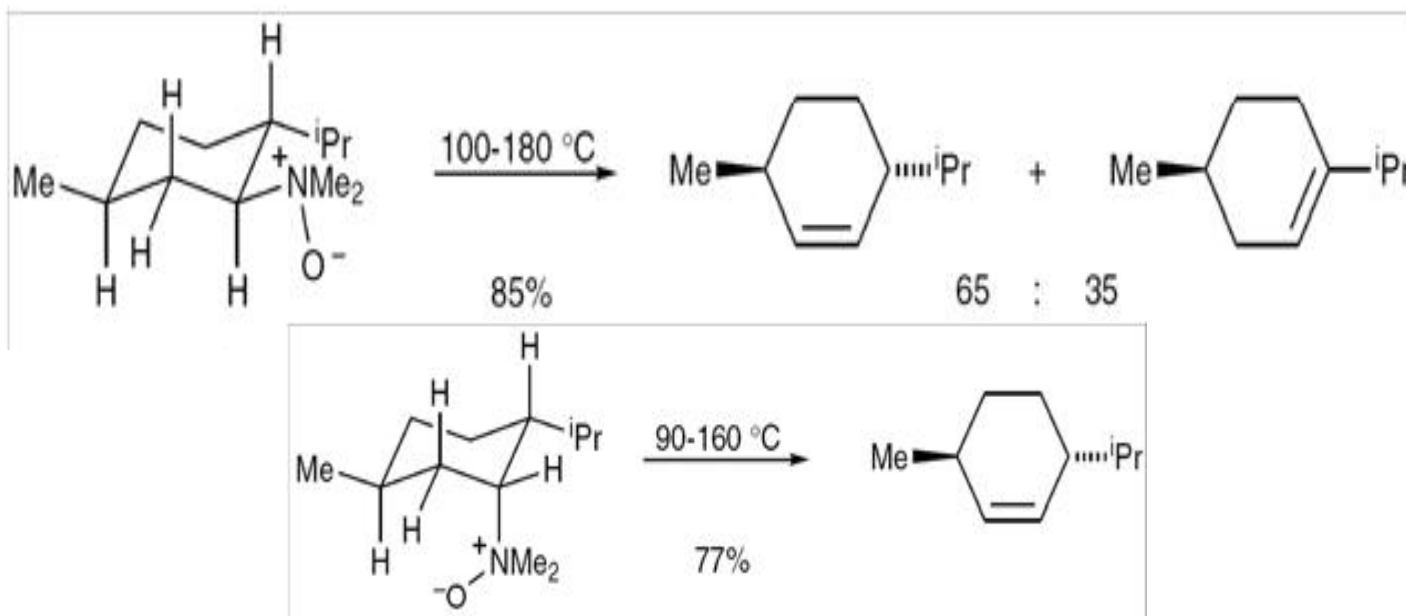
- ✓ Readily obtained by oxidation of sulfides (mCPBA or NaIO₄)
 - ✓ Sulfoxides with a β-hydrogen atom readily undergo *syn*-elimination on pyrolysis
 - ✓ Take place with a high *syn*-stereoselectivity
 - ✓ Another useful method for making C=C bonds
-
- ✓ 5-Ring TS with *syn*-relationship of H and X



- ✓ A convenient method for introducing unsaturation at the position α- to carbonyl compounds
- ✓ The (*E*)-isomer usually predominates in reactions leading to 1,2-disubstituted alkenes

Regioselectivity and stereoselectivity

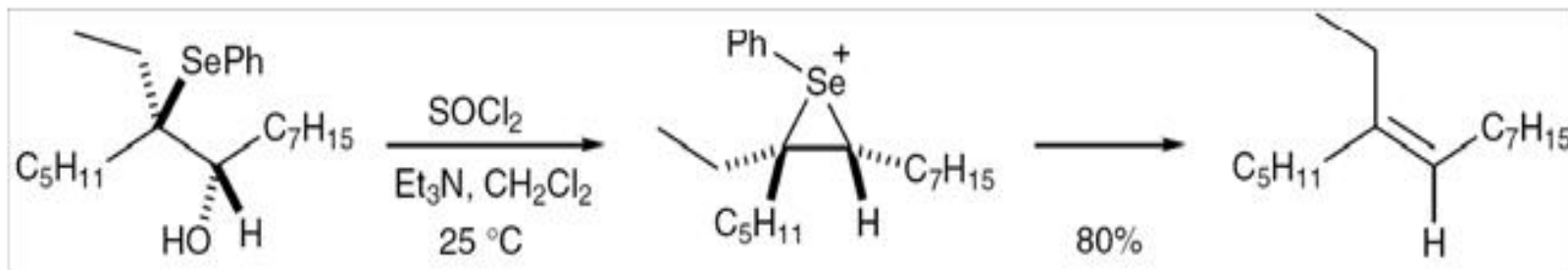
- ✓ In acyclic compounds, the configuration of tertiary amine oxide determines the stereochemistry of the alkene
- ✓ In cyclic compounds, ring conformation is very important



- ✓ The Cope elimination is reversible
- ✓ The intramolecular reverse Cope elimination, involving the addition of a tethered hydroxylamine to an alkene, has found recent application for the stereocontrolled preparation of cyclic amines

Pyrolysis of β -Hydroxy selenides

- ✓ High yields of di-, tri- or tetrasubstituted alkenes can be obtained
- ✓ Alternative route to the Wittig reaction when the phosphonium salt cannot be readily obtained
- ✓ Proceeds under the action of MsCl , SOCl_2 , or other appropriate activating conditions
- ✓ Proceeds by stereospecific *anti*-elimination to the episelenonium ion, and then by *syn*-elimination of the episelenonium ion to the alkene



Summary.....

