University of Tikrit
College of Science
Dept. of Chemistry

# *SNi substitution nucleophilic internal pyrolytic eliminations*

**By Doctoral Students**

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# *SNi substitution nucleophilic internal*

In a few reactions *nucleophilic substitution proceeds with retention of configuration, even where there is no possibility of a neighboring- group effect.*

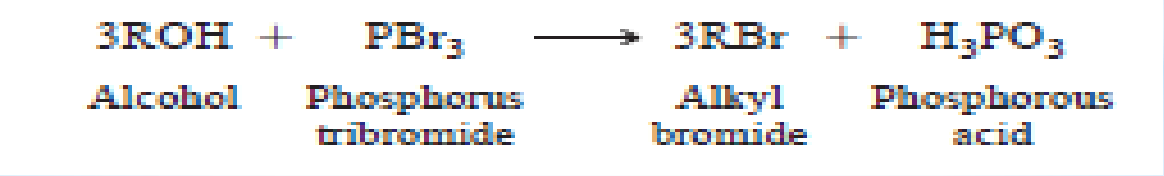
*Follows second order kinetics.*

*Rare*

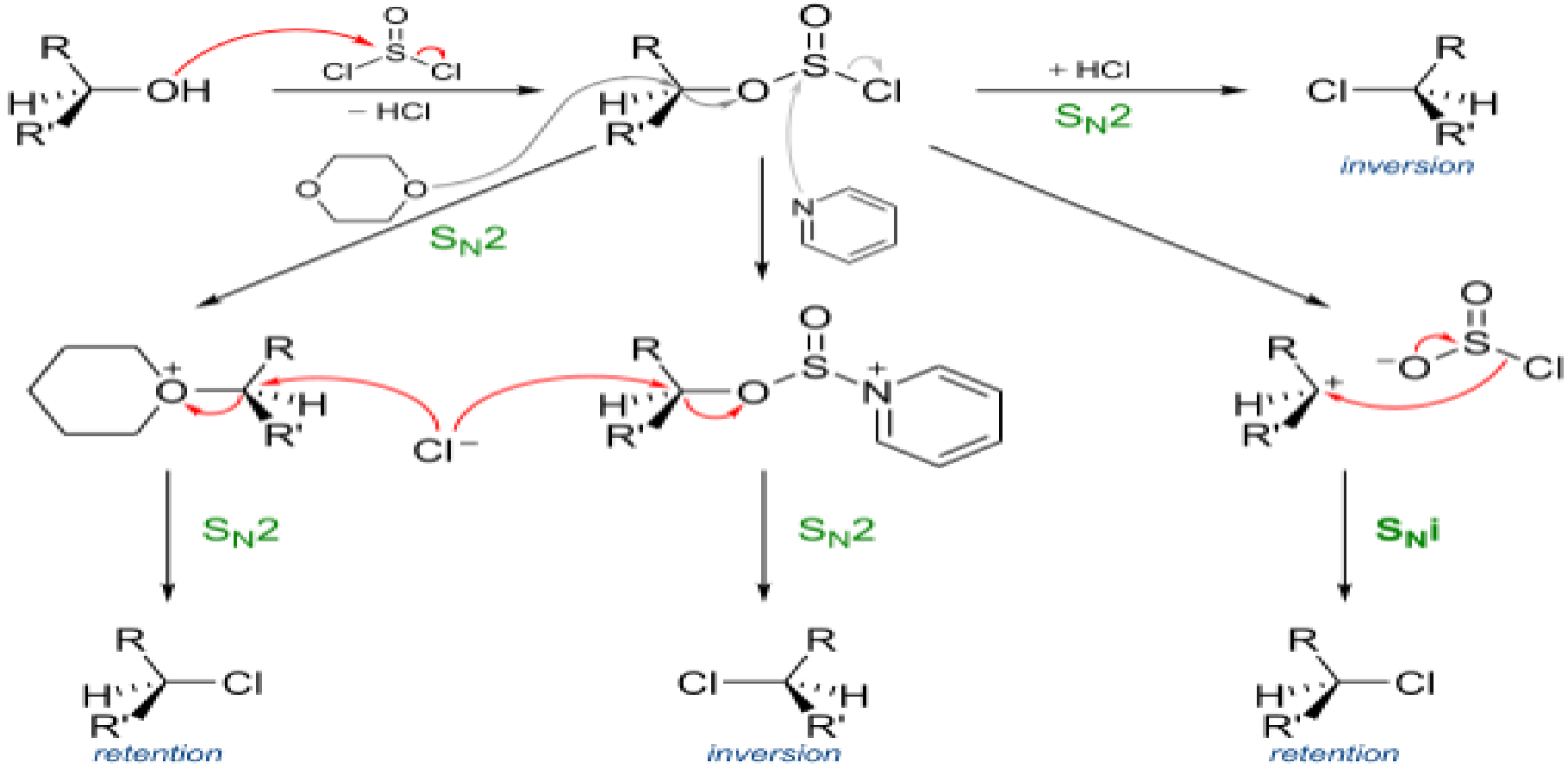
This kind of *reaction is seen only in one situation between alcohols and thionyl chloride or phosphorus tribromide has been studied exclusively.*

*Hence this reaction can be explained neither by* SN1 nor by SN2

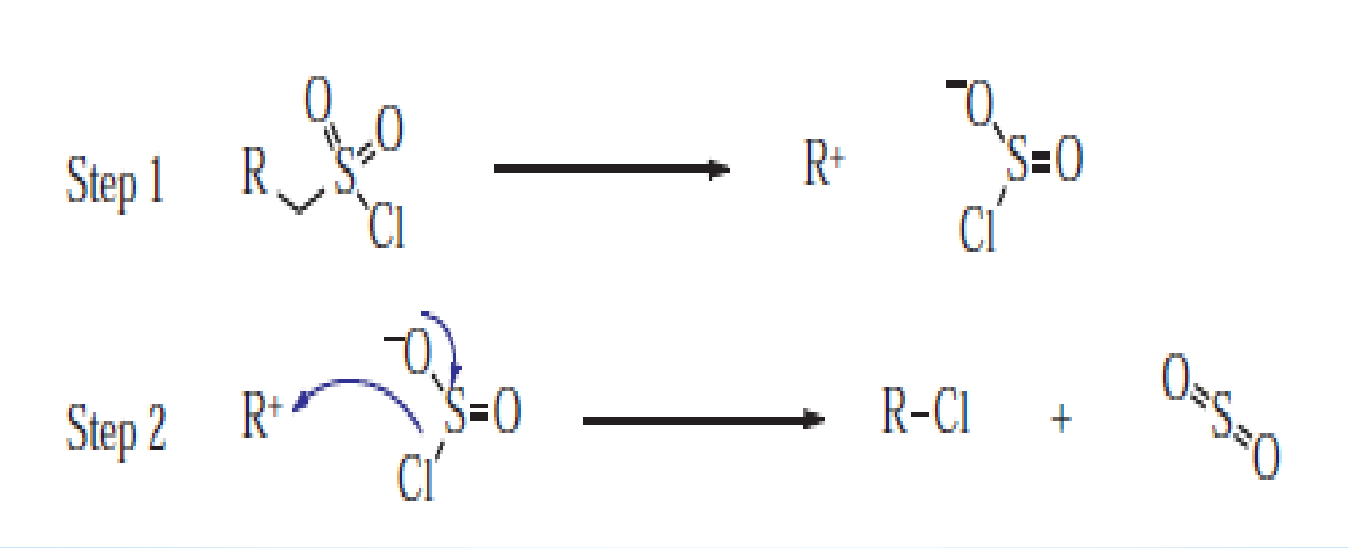
*Example*

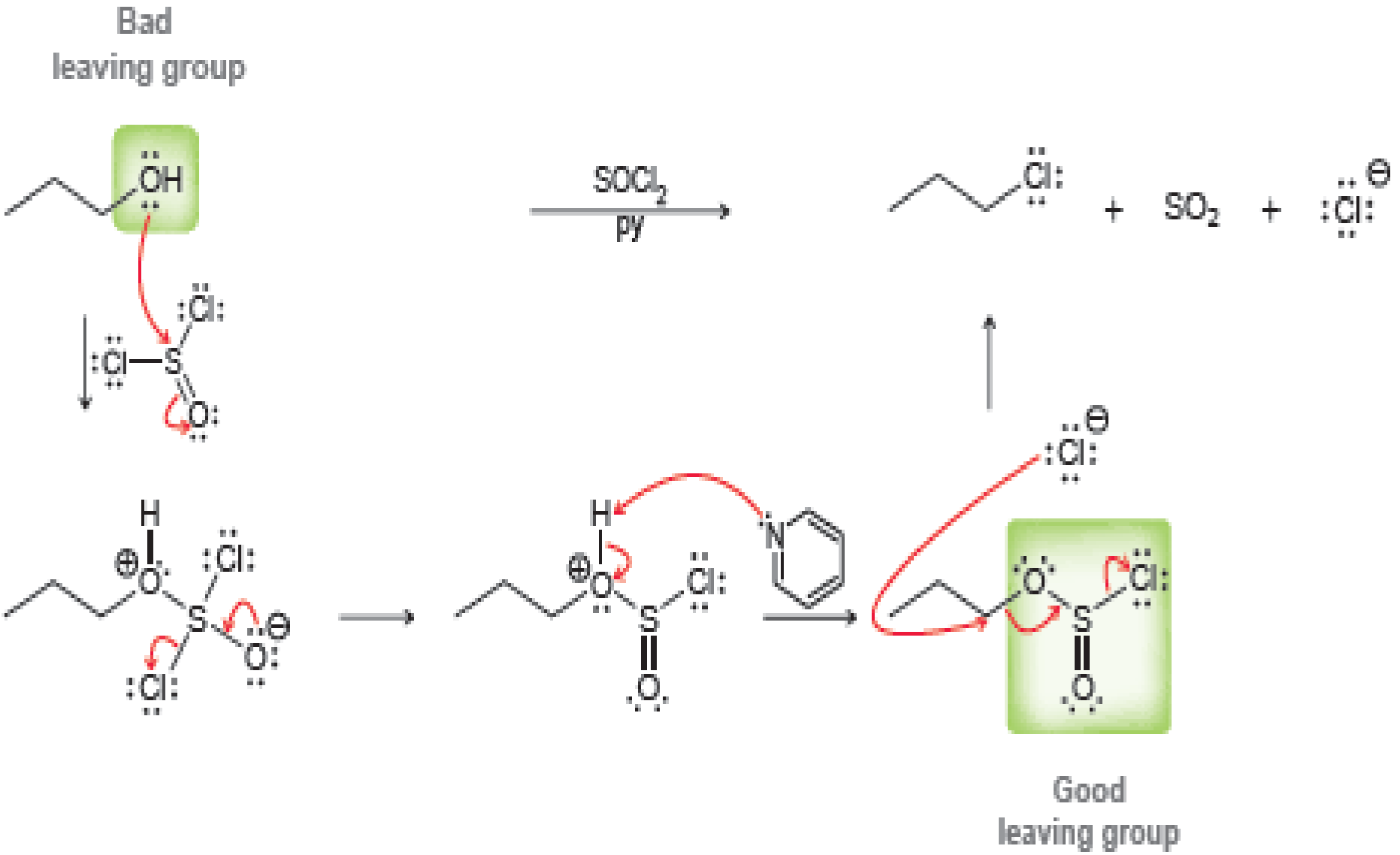
The principle mechanism of SNi reactions is based on the assumption that addition of pyridine to the reaction leads to inversion configuration, Hence if the solvent added in the medium of this reaction is pyridine, then the reaction will no longer remain SNi as the mechanism will change to that of SN2, When the solvent is also a nucleophile such as dioxane two successive SN2 reactions take place and the stereochemistry is again retention.



In SNi reaction, we have retention of configuration.
But this is different from SN1 reactions as there is no formation a racemic mixture over here.
This is also different from SN2 reactions as in SN2, there is inversion of configuration, whereas over here, the stereochemistry of the reactant and the product is nearly the same.
Hence this reaction can be explained neither by SN1 nor by SN2.

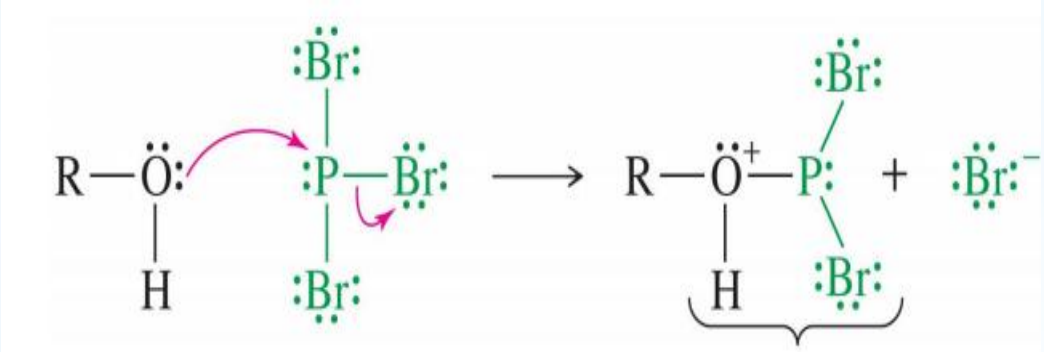


# Convert propan-1-ol to 1-chloropropane

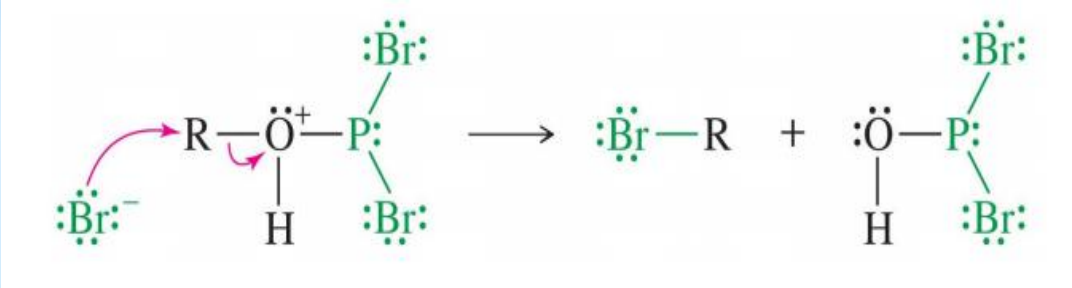


# *Mechanism Reaction of a Primary Alcohol with PBr3*

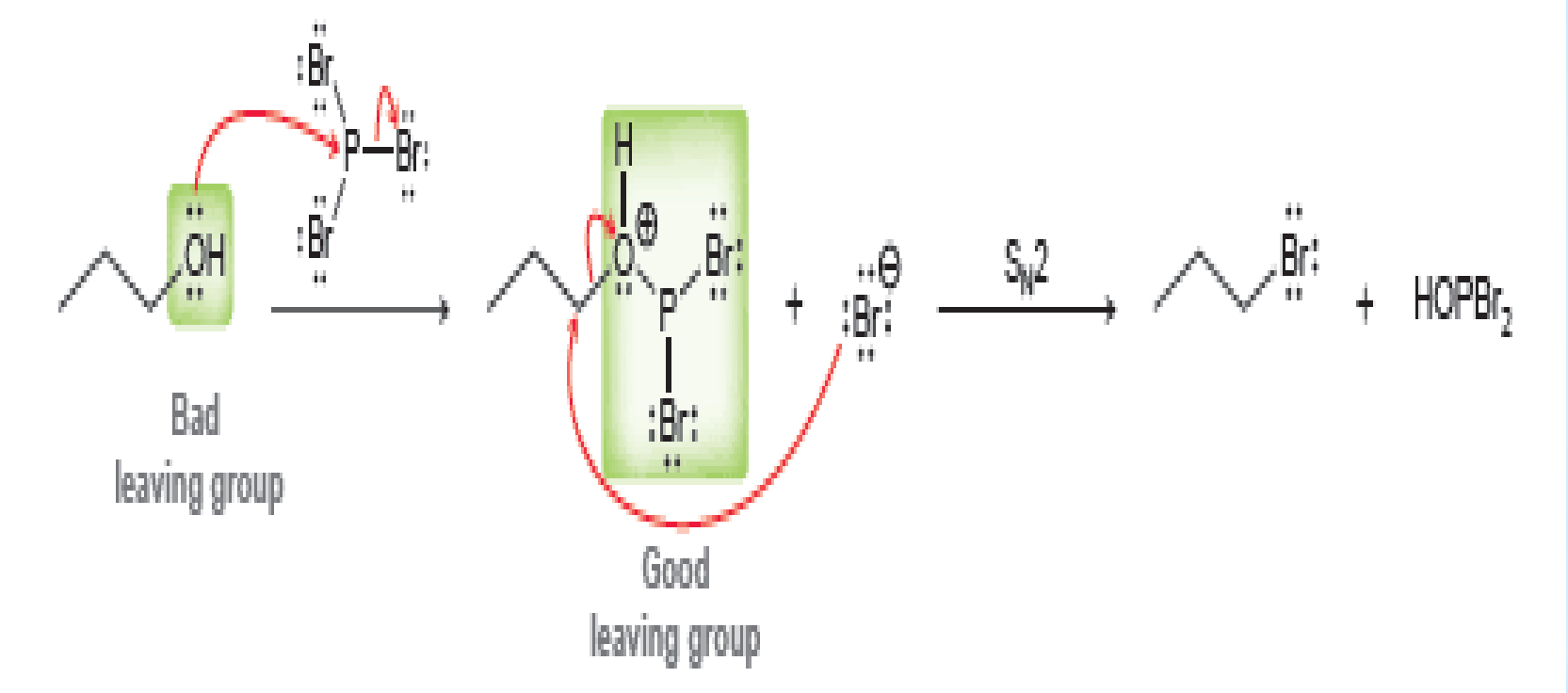
The hydroxyl oxygen displaces a halide (good leaving group) from the Phosphorous.



The positively charged oxygen is a good leaving group
The liberated halide performs an SN2 type attack on the back side of the R group.



# Convert propan-1-ol to 1-Bromopropane




Notice the similarity among all of the SN2 processes that we have seen in this section. All involve the conversion of the hydroxyl group into a better leaving group followed by nucleophilic attack. If any of these reactions occurs at a chirality center, inversion of configuration is to be expected.

## *Hence we can draw four important inferences:*

1-In ether medium, the reaction follows the rules of SNi mechanism.
2-If pyridine is added as the medium solvent to this reaction, it will form a strong nucleophile in pyridinium chloride, which will cause a backward attack on the system, eliminating sulphur dioxide from it.
3-This type of reaction will be termed as SN2 because there is inversion of configuration. In case of pyridine, the nature of the reaction changes from SNi to SN2.
4- In case of SNi reactions, the rate of the reaction is dependent on the concentration of both the alcohol and the thionyl chloride.
As opposed to the case of SN1 and SN2 reactions.

# pyrolytic eliminations

The pyrolytic eliminations occur most commonly via the Ei mechanism involving a cyclic transition state, which may comprise of four–, five– or six–membered transition states. It is a concerted mechanism, and is almost exclusively a *syn* elimination (the hydrogen atom and the leaving group depart from the same side of the resulting double bond). Evidences for this mechanism are:

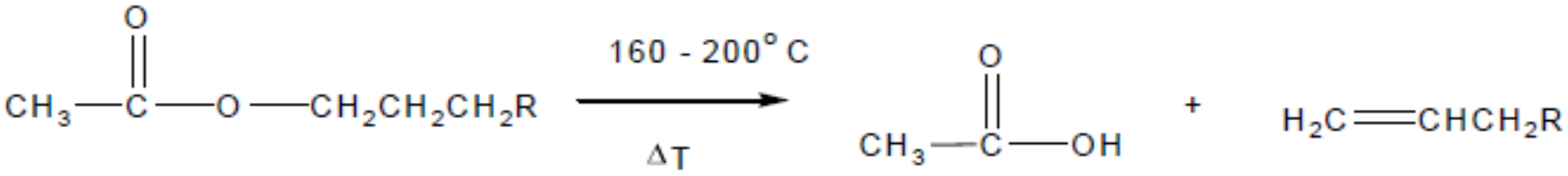
1. First order reaction kinetics.
2. No reaction intermediate has been isolated, suggesting it to be a concerted mechanism.
3. Free radical inhibitors show no effect on the reaction (no free radical mechanism involved).
4. Moreover, these eliminations show a negative entropy of activation which advocates that the transition state has a more restricted geometry (consequences of a cyclic transitionstate).

# Pyrolytic elimination

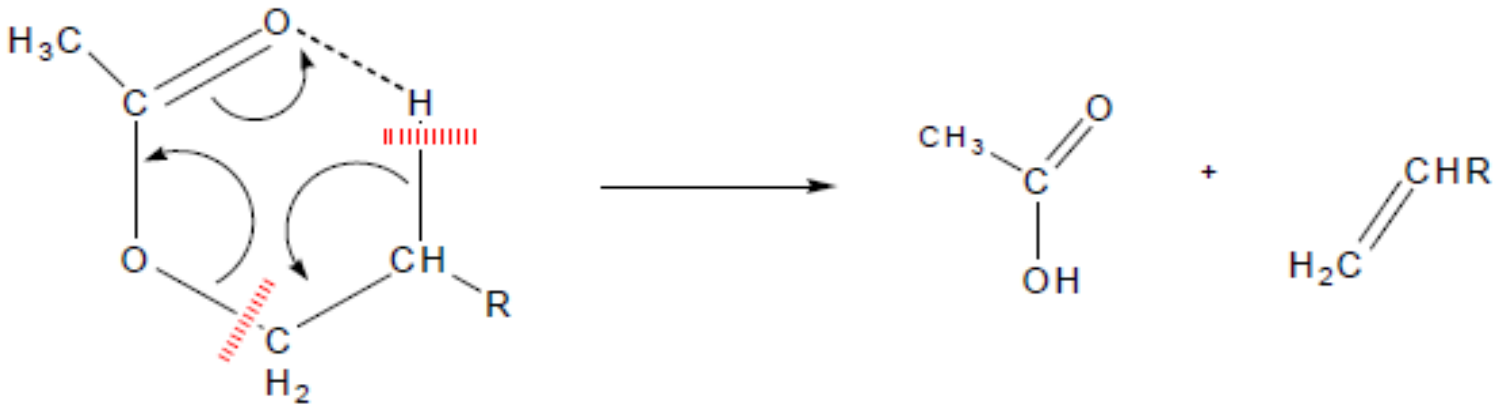
Reactions are characteristic for acetates or xanthates –Chugaev reaction and *t*-aminoxides – Cope elimination

## Acetates pyrolysis

Reactions are *cis*- stereospecific and regiospecific

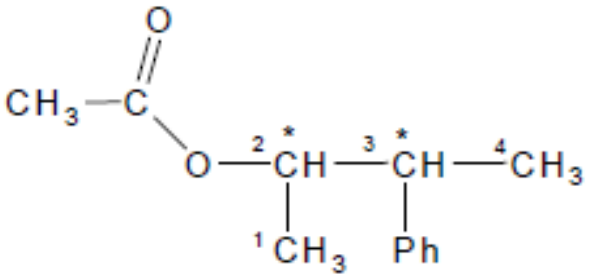


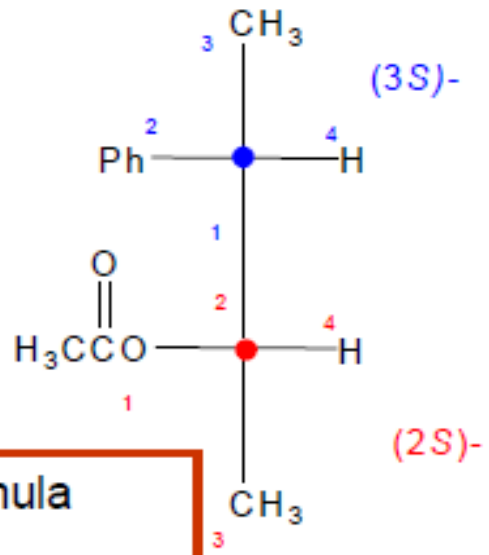

## Reaction proceeds via cyclic intermediate

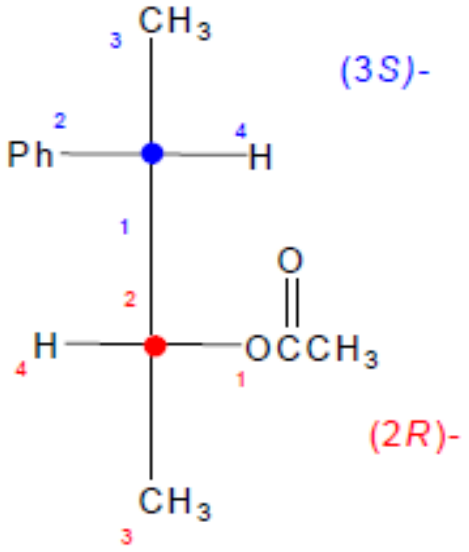


# Pyrolytic elimination

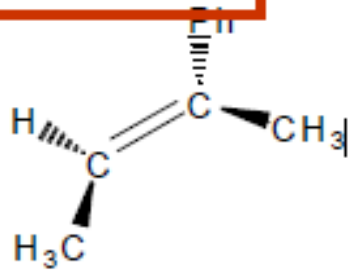
What is the product of (2*R*,3*S*)-2-(3-phenylbutyl)acetate?



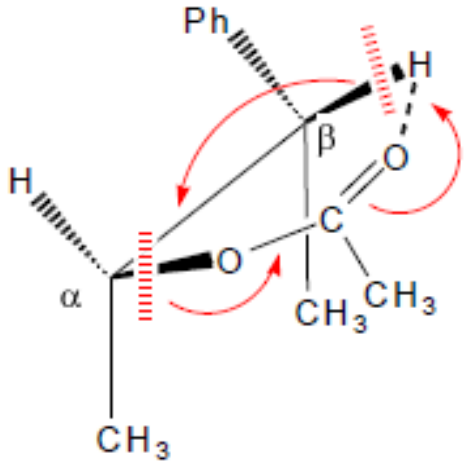



1. Composition of corresponding formula
2. Configuration determination
3. Transformation into perspective formula
4. *Cis*- *(syn*-) elimination
5. Determination of olefine configuration
6. Composition of proper name

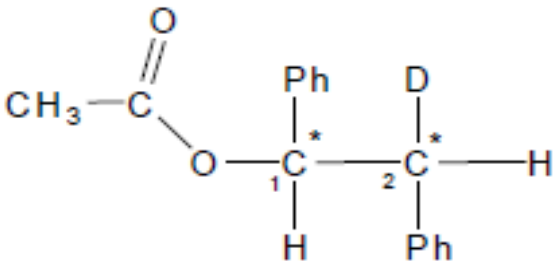


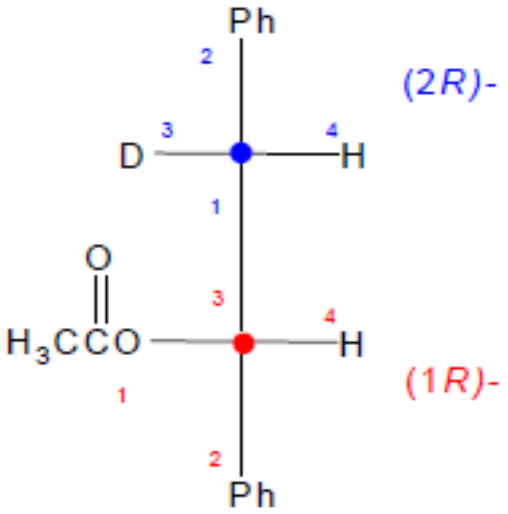
(*E*)-2-phenylbut-2-ene



# Pyrolytic elimination

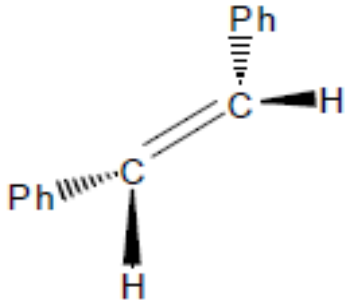
What is the product of pyrolysis of (1*R*,2*R*)-1,2-diphenyl-2-deuterioethylacetate?



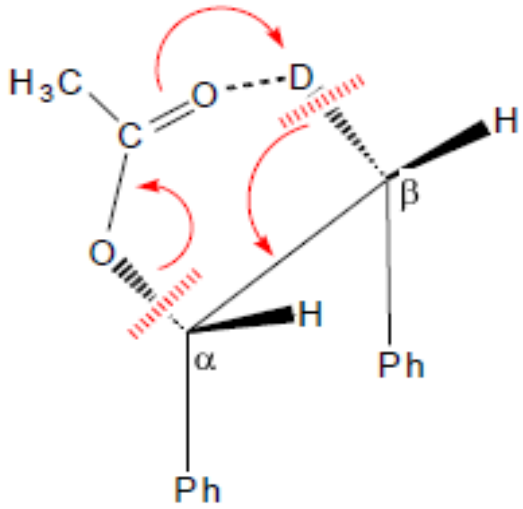




1. Composition of corresponding formula
2. Configuration determination
3. Transformation into perspective formula
4. *Cis- (syn-)* elimination
5. Determination of olefine configuration
6. Composition of proper name

(*Z*)-diphenylethene



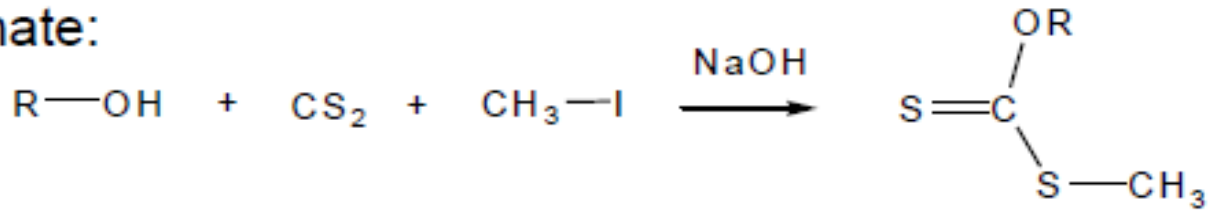

-$CH_3COOD$

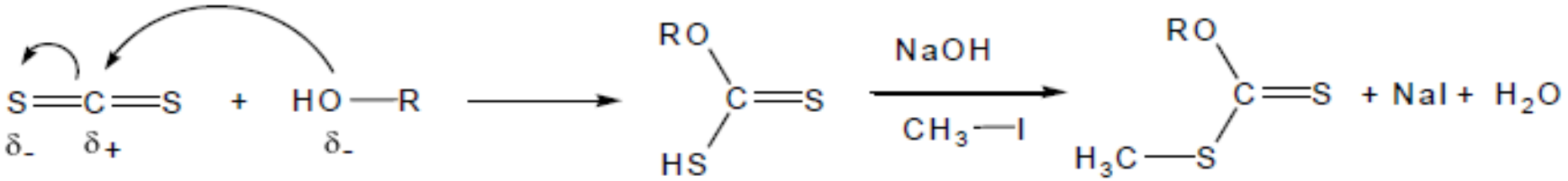


# Pyrolytic elimination – Chugayev reaction

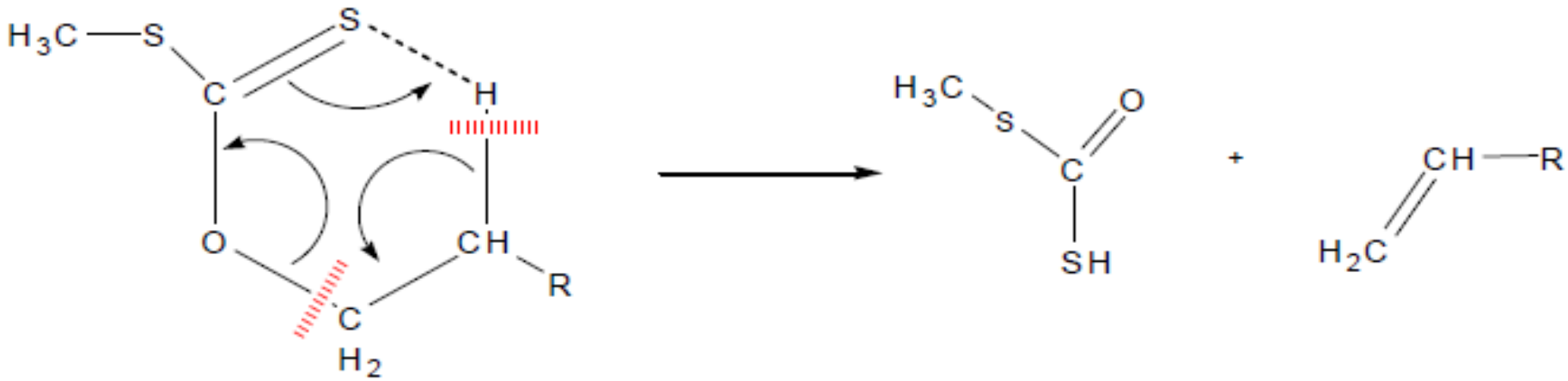
Reactions are *cis*- stereospecific and regiospecific

Preparation of xanthate:



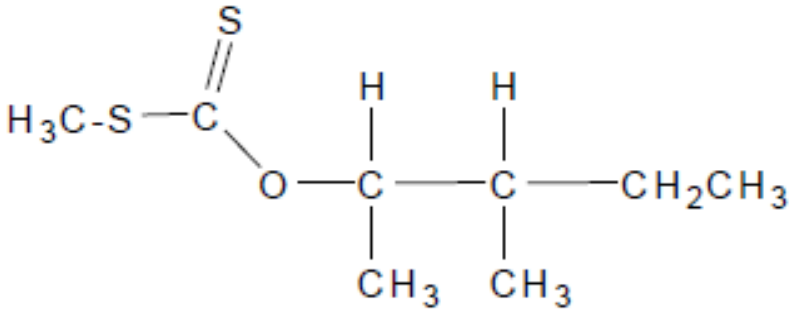



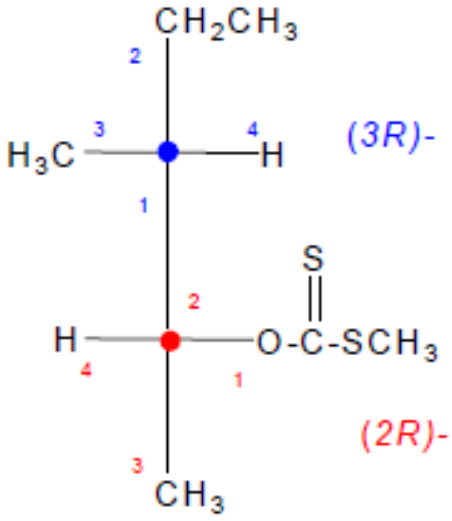

Reactions proceed via cyclic state



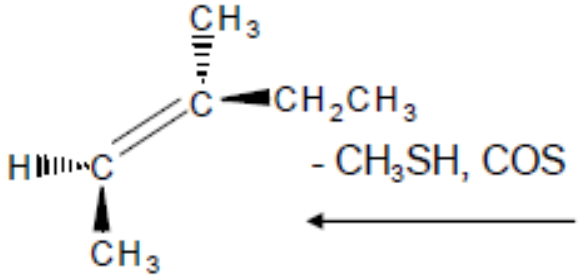
# Pyrolytické eliminace

What is the product of (*S*)-methyl-(2*R*,3*R*)-O-(3-methylpent-2-yl) xanthate pyrolysis?

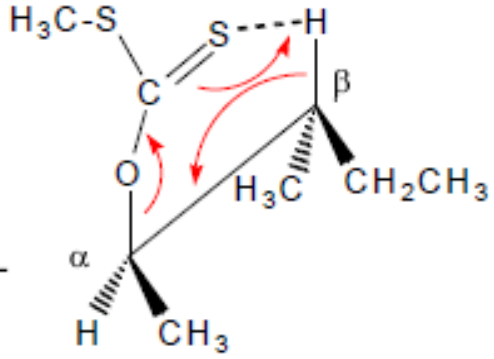



(*Z*)-3-methylpent-2-ene




- $CH_3SH$, COS

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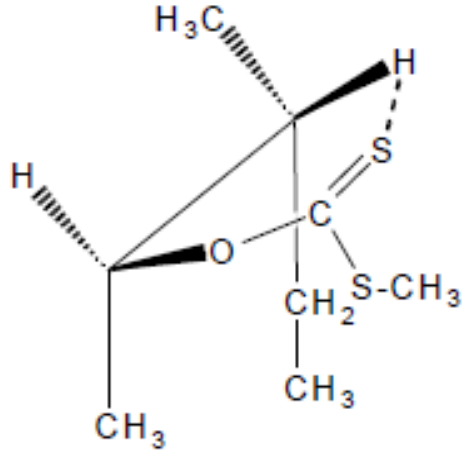
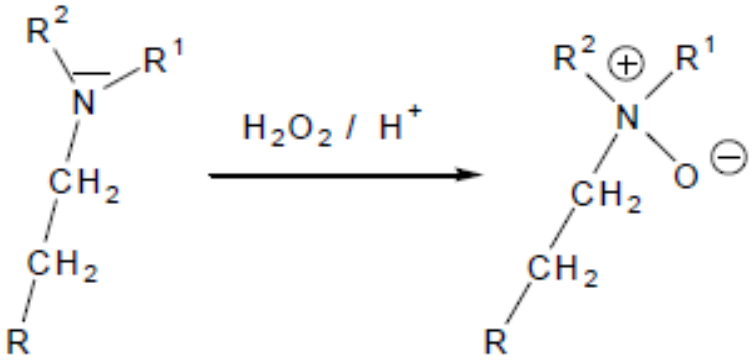


# Pyrolytic elimination – Cope reaction

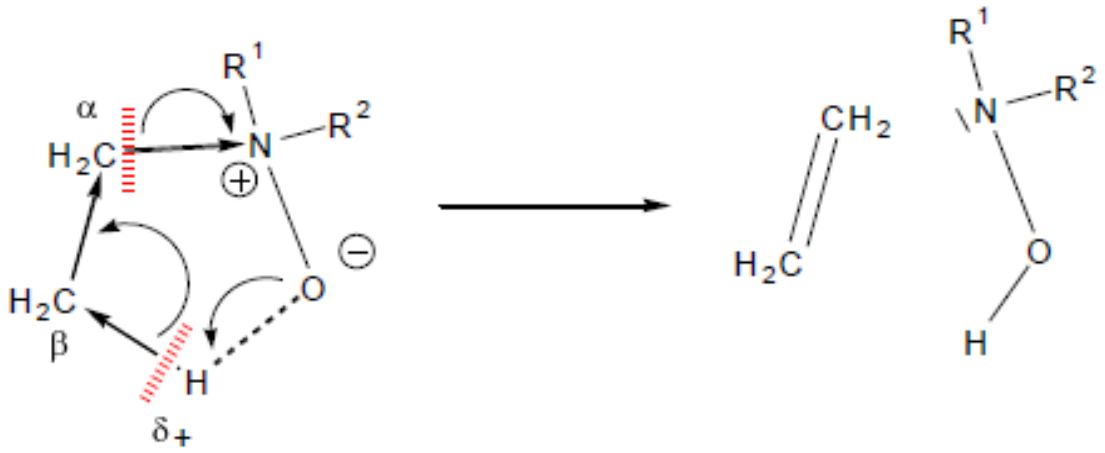
Reactions are *cis*- stereospecific and regiospecific

Preparation of *t*-aminoxide




oxidation of *t*-amines

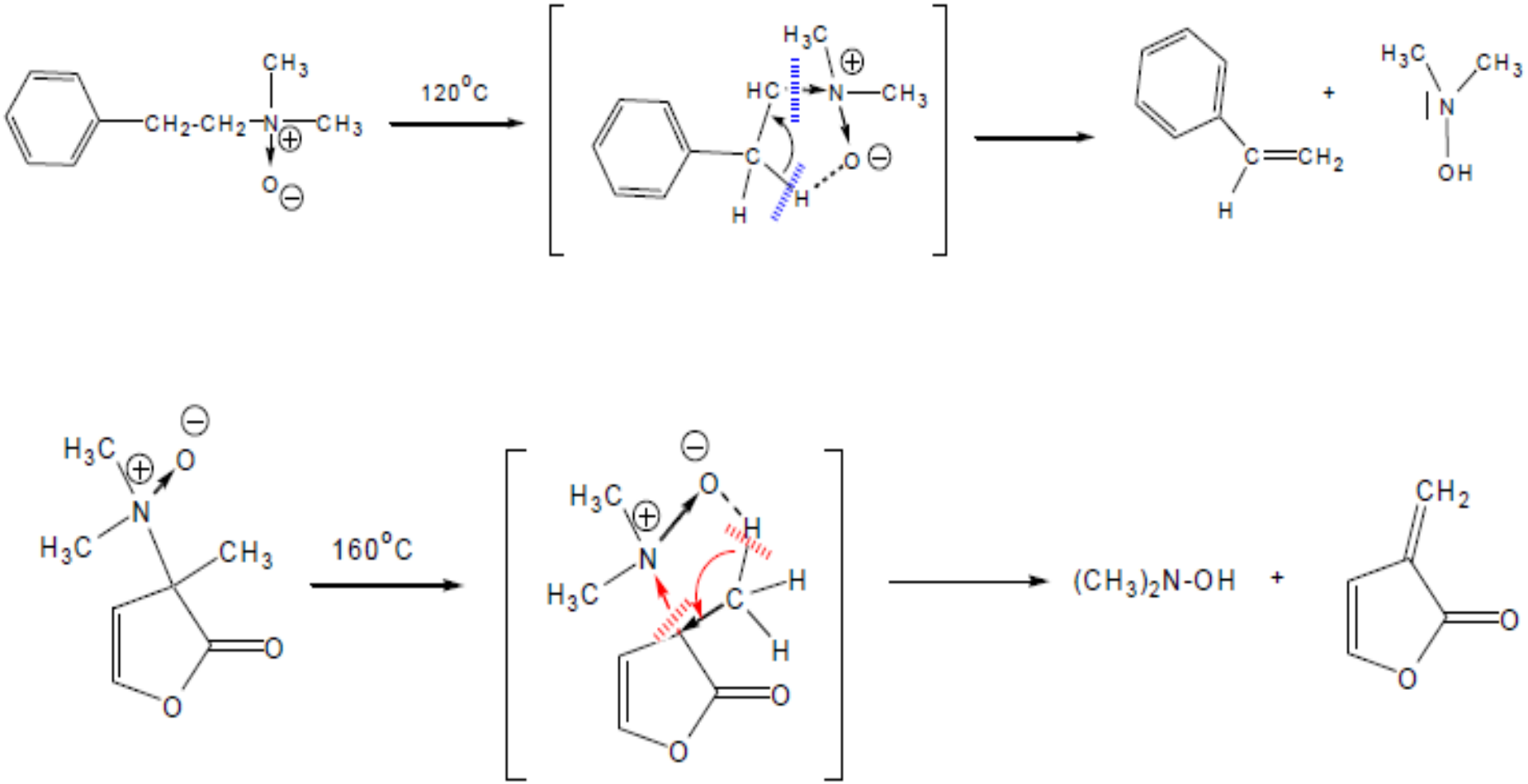
Reactions proceed via cyclic intermediate



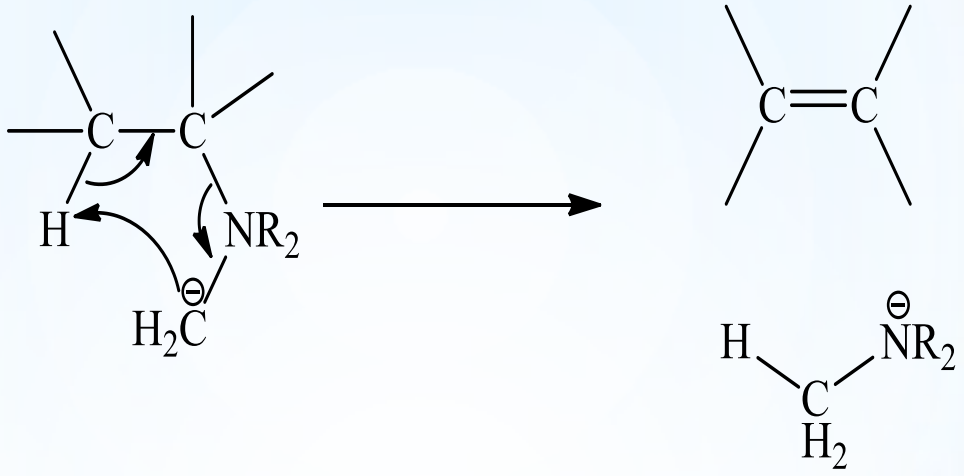

after reaction olefin and substituted hydroxylamin are obtained

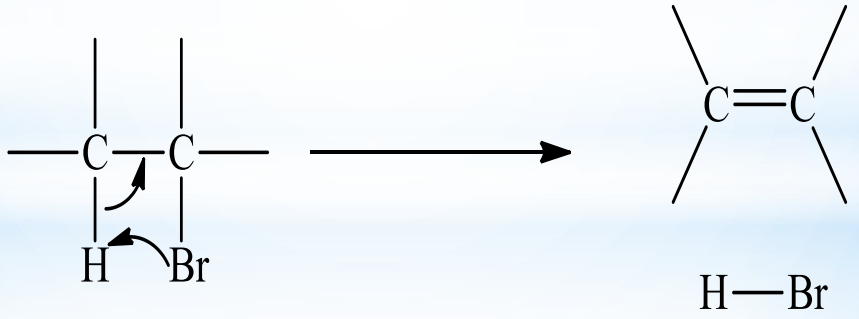
# Pyrolytic elimination

## Cope elimination of N-oxides



**ومن الممكن تكوين حالة انتقالية حلقية رباعية او خماسية حسب نوع التعويض**



# Refrence

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3. William H. Brown, Christopher S. Foote, Brent L. Iverson, Eric V. Anslyn, Bruce M. Novak, Organic Chemistry, $^{6}$Ed, pp(403), (2010).
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