

# THALLIUM(III) NITRATE

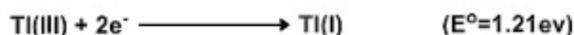
## Introduction [1]:-

- Name:- Thallium(III) Nitrate trihydrate
- Abbreviation:- TTN
- Melting point:- 102-105 °C.
- Solubility:- water, organic solvents.
- General information:-
  - Oxidizing agent; Lewis acid.
  - All thallium compounds are extremely toxic to inhalation, skin contact, and ingestion. Toxicity is cumulative. Extreme caution should be used when handling these materials. Use in a fume hood.

Thallium nitrate is a selective and versatile oxidizing agent, generally accompanied by reduction of Tl(III) to Tl(I). Thallium nitrate is electrophilic in character, so it reacts with alkenes & alkynes to give addition products.

It is very effective oxidizing agent because:-

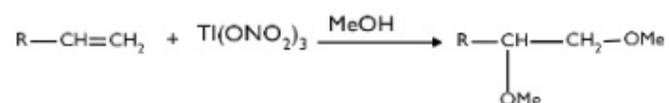
- (i) Reduction potential of this half cell reaction is positive and high.



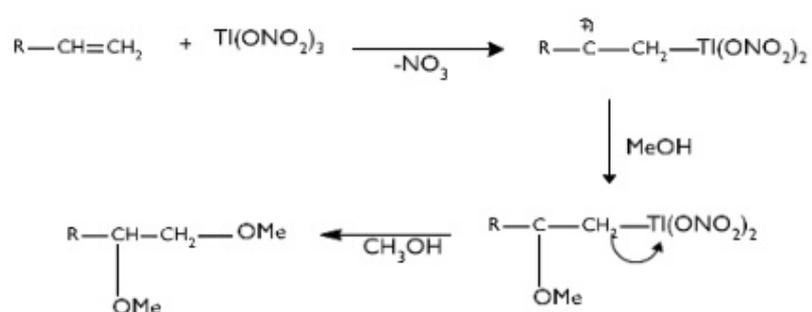
- (ii) Carbon-Tl(III) bond is very weak, so it undergoes heterolytic cleavage very readily and forms carbocation easily.
- (iii) Nitrate-ion is not a very good nucleophile, so the solvent may participate selectively as a nucleophile in the reaction.

**Oxidation of alkenes<sup>[1]</sup>-**

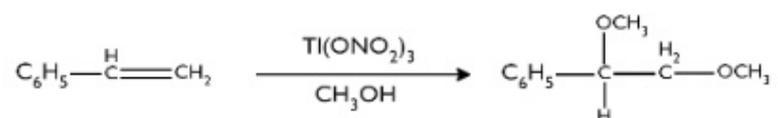
Thallium nitrate react with alkenes in methanol solution to give carbonyl or 1,2- glycol dimethyl ether.



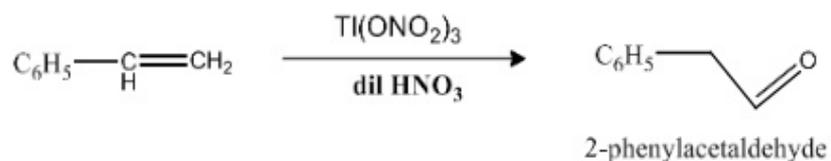
Mechanism:-

**For example:-**

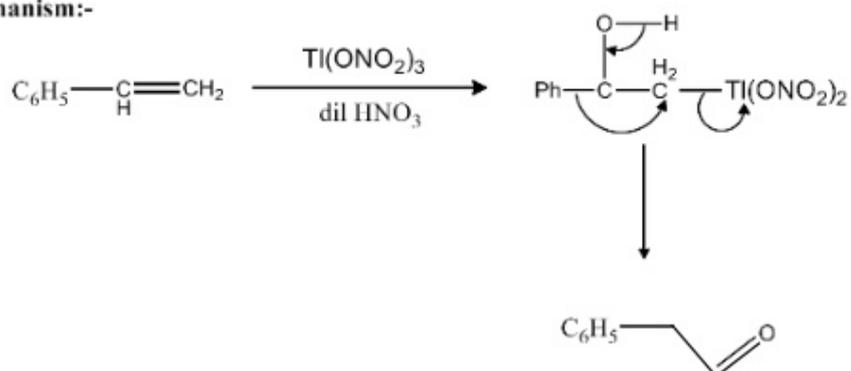
Styrene forms 1, 2 dimethyl derivative when treated with  $\text{Ti}(\text{ONO}_2)_3$  in  $\text{CH}_3\text{OH}$



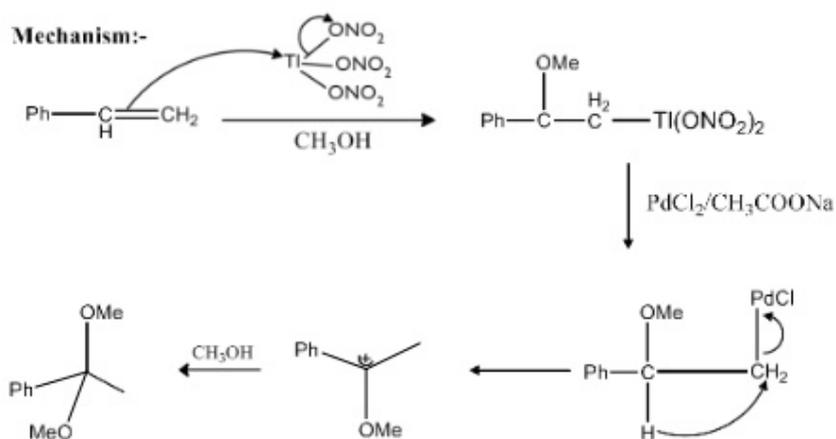
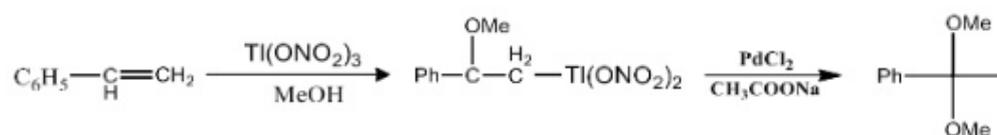
If the above reaction is carried out in dil  $\text{HNO}_3$  then arylacetaldehyde is obtained in high yield.



**Mechanism:-**

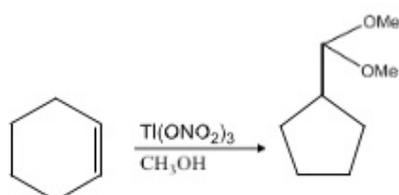
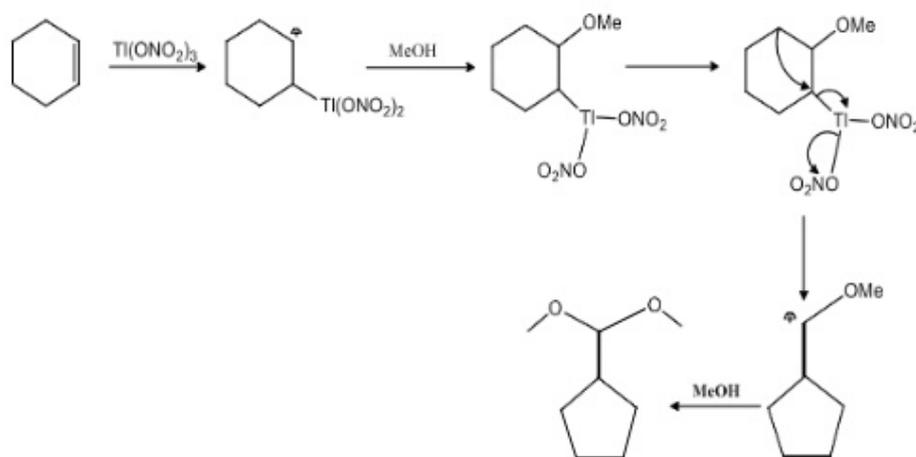


Oxidation of alkenes into ketones / ketals can be obtained in the presence of catalytic amount of PdCl<sub>2</sub>/CH<sub>3</sub>COONa in methanol.



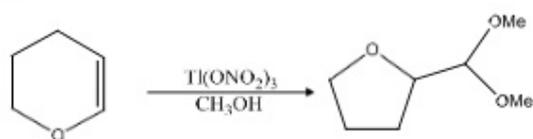
**Oxidation of cyclic ketones<sup>(1)</sup>:-**

Cycloalkenes undergo oxidative rearrangement with the reagent; oxidative rearrangement takes place via ring-contraction.

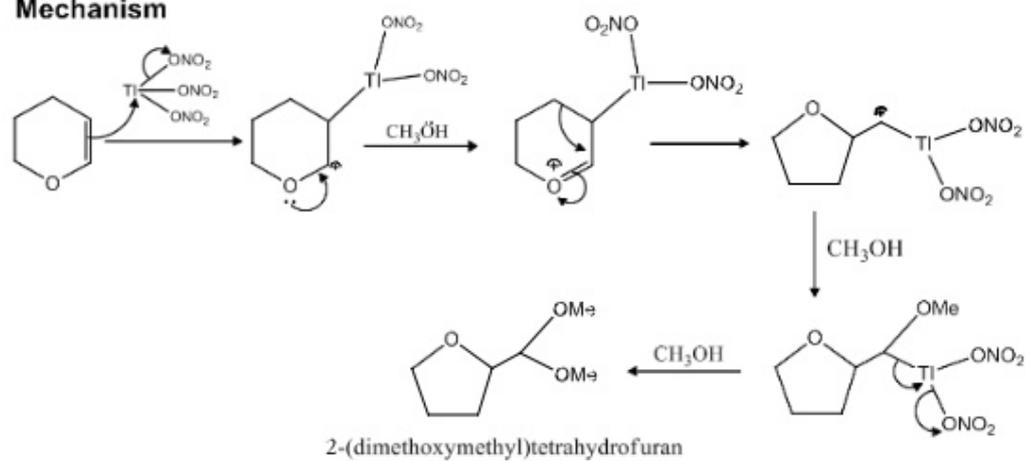
**Mechanism:-**

This reaction is also applied to heterocyclic compounds.

**For example<sup>(1)</sup>**:-



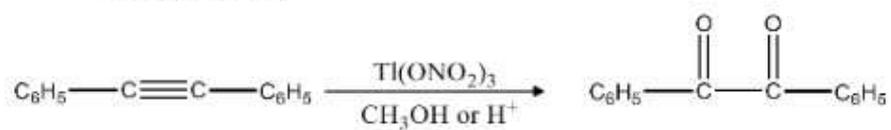
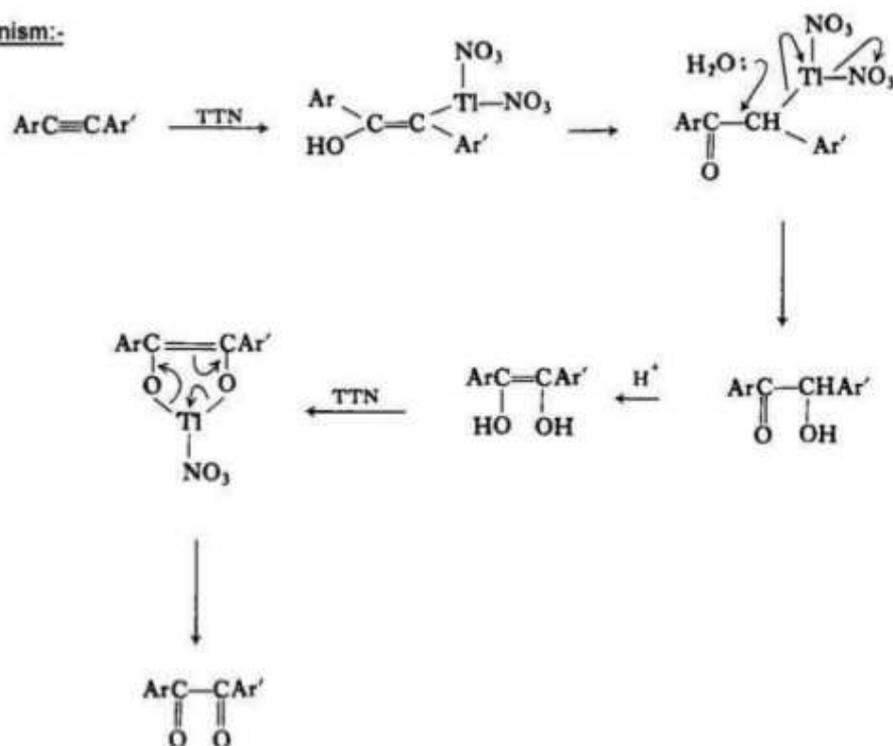
### Mechanism



**Oxidation of alkynes** <sup>[1][2]</sup>:-

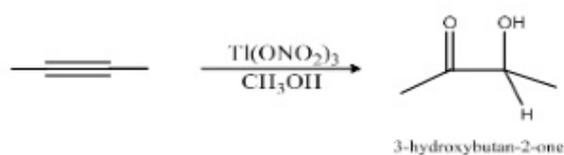
With the alkynes the product obtained depends on the structure of alkynes, i.e.:-

- a) Diaryl alkynes react with  $Tl(ONO_2)_3$  in  $CH_3OH$  or in acidic solution gives benzils in high yields.

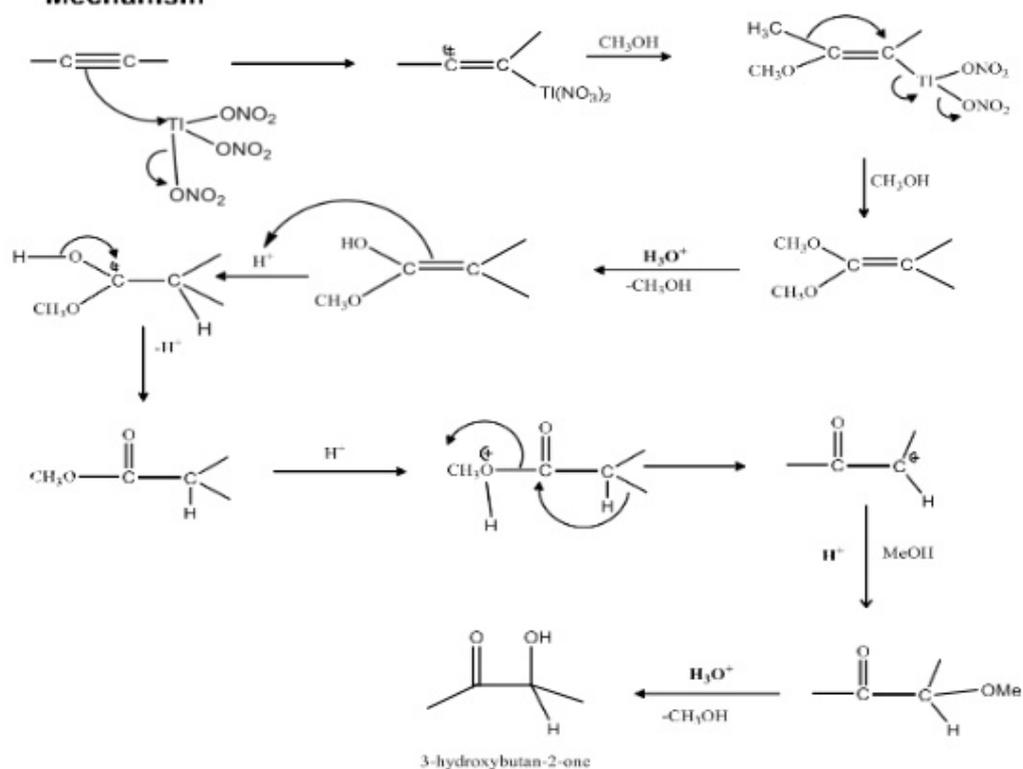
**For example** <sup>[2]</sup>:-**Mechanism:-**

- b) **Dialkyl-alkynes** react with  $Ti(ONO_2)_3$  in  $CH_3OH$  or in acidic solution gives acyloin in high yields.

For example:-

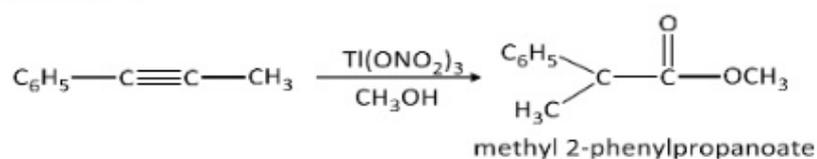


### Mechanism

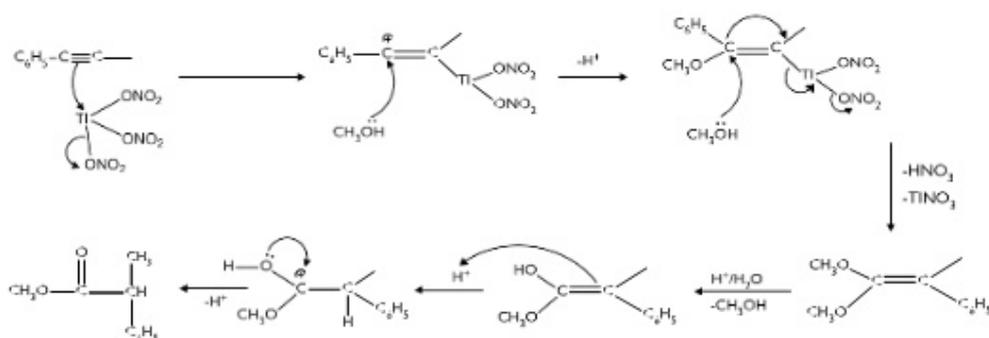


- c) **Alkyl-aryl alkynes** in acidic solution give mixture of product, but in  $\text{CH}_3\text{OH}$  give methyl ester of  $\alpha$ -alkyl-aryl acetic acid.

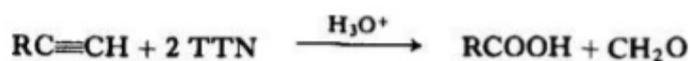
For example:-



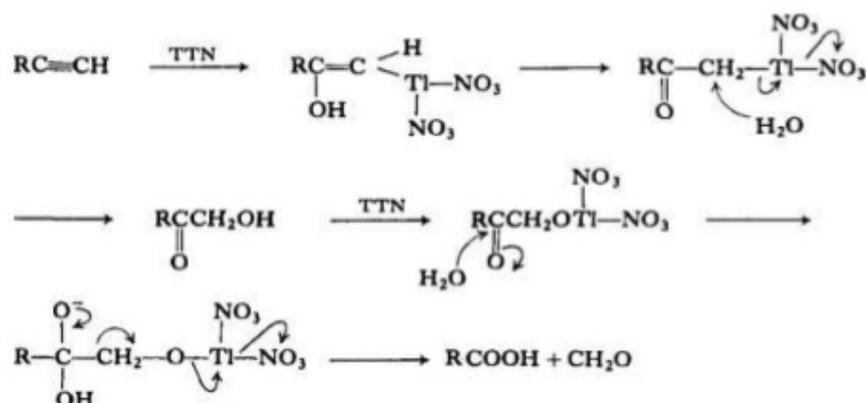
**Mechanism:-**



- d) Terminal alkynes reacts with  $\text{Ti}(\text{ONO}_2)_3$  in acidic medium, yields acids with the loss of one carbon<sup>[2]</sup>.



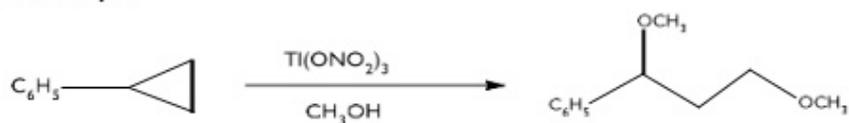
**Mechanism:-**



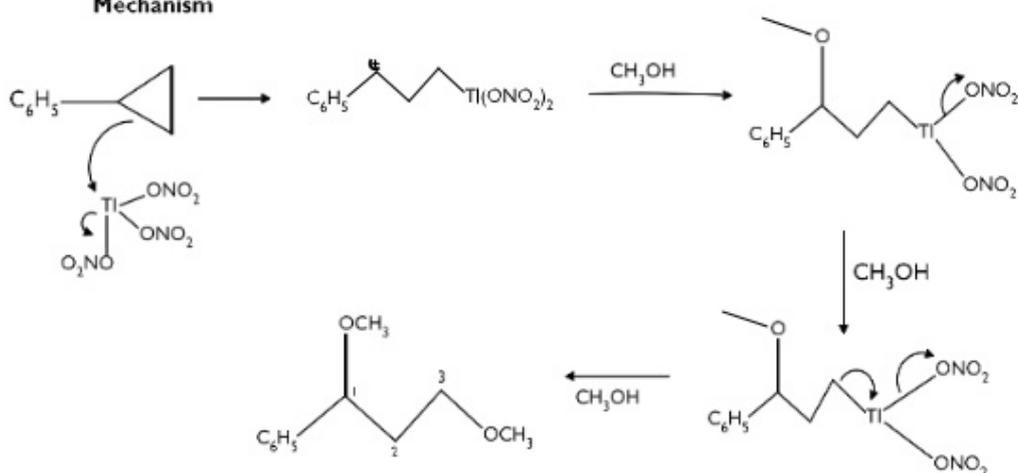
**Oxidation of cyclopropane<sup>(1)</sup>**

Cyclopropane react with  $\text{Ti}(\text{ONO}_2)_3$  in methanol to give mainly 1,3 dimethyl alkanes.

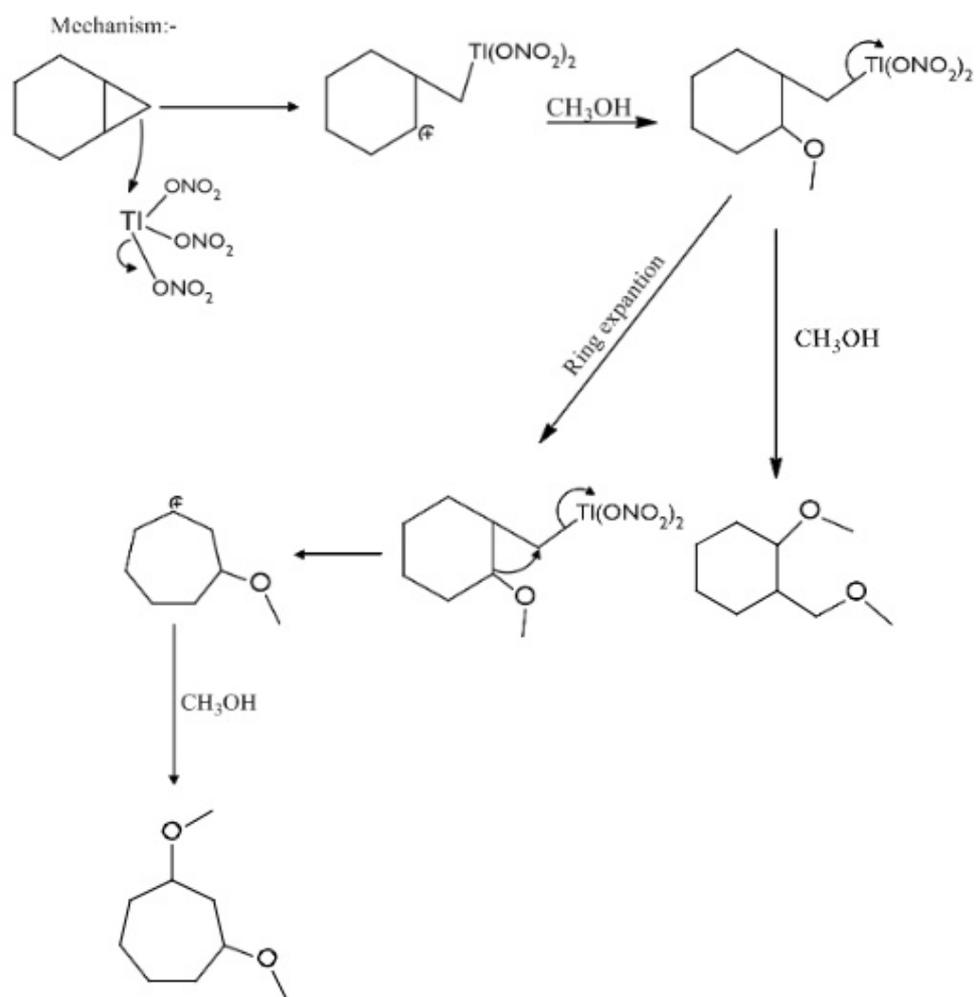
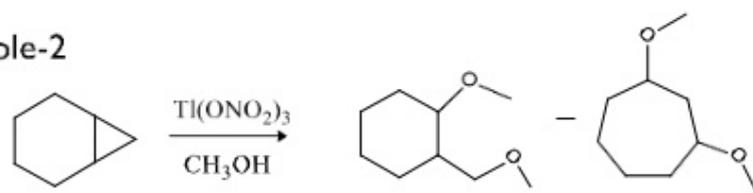
**For example:-**



**Mechanism**



## example-2

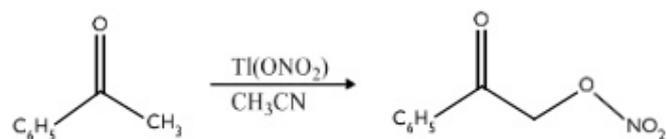
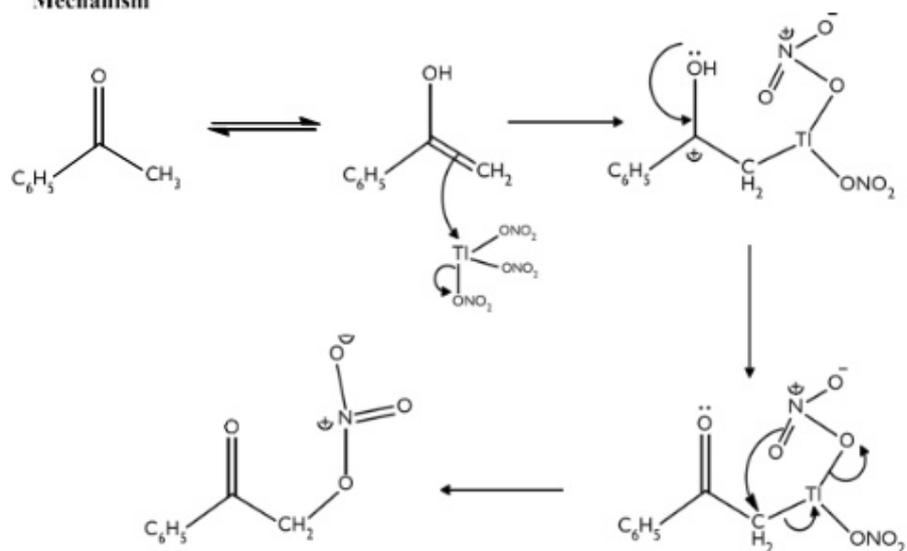


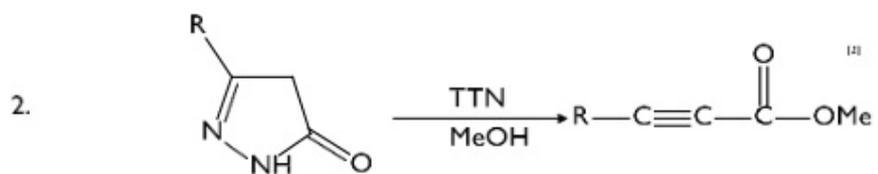
**Oxidation of ketones<sup>[1]</sup>:-**

Treatment of aliphatic/aromatic methyl ketones with thallium nitrate in  $\text{CH}_3\text{CN}$  gives  $\alpha$ -nitratoketones.

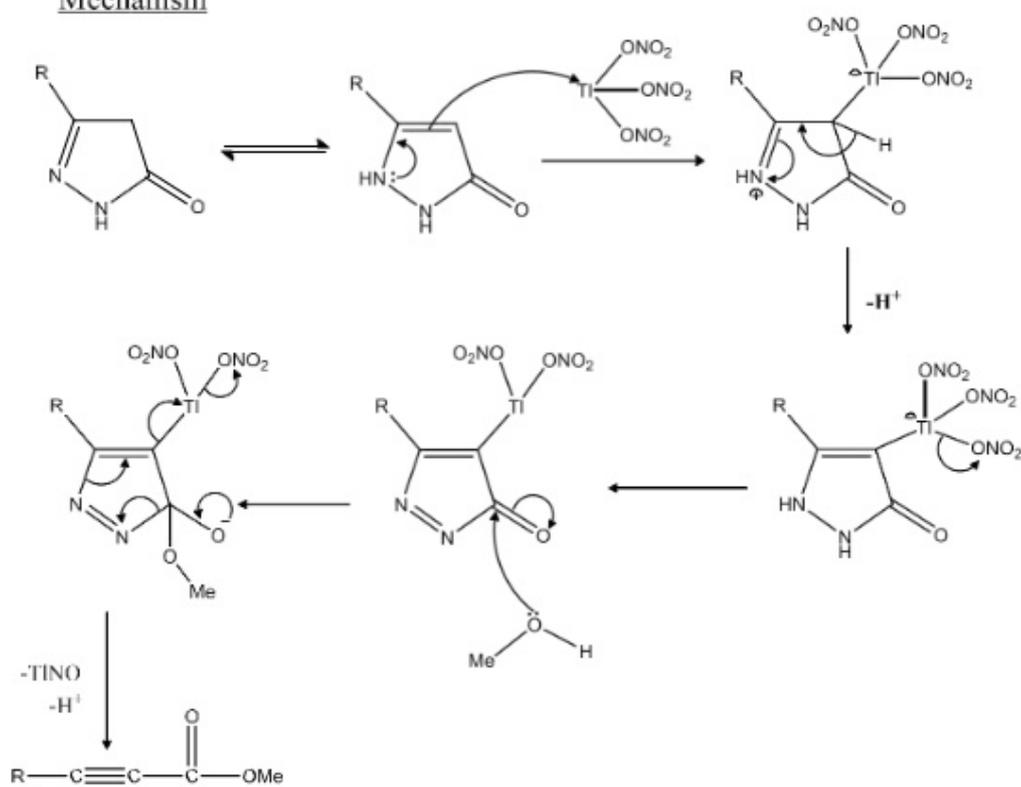
**For example:-**

1.

**Mechanism**



### Mechanism



**Oxidation of  $\alpha, \beta$  unsaturated ketones<sup>[1]</sup>:-**

$\alpha, \beta$  unsaturated ketones, on oxidation give 1,2 diketones in aqueous solution.

**For example****Mechanism**