

Detailed of Course Structure

Name of the Department: Chemistry

Name of the Programme (U.G./P.G./Ph.D.): Post Graduate

Semester: II-Semester

Name of the paper/course (unit or title if there are multiple files of the same paper): Principle of Organic Synthesis and Organic Spectroscopy

Name of the teacher: Dr. Biswajit Maji

Sl No	Unit No	Topic	Remark
1	Unit I	Principles of Organic Synthesis	Completed
2	Unit II	Rearrangement and Organometallic Reactions	Undergoing
3	Unit III	Ultraviolet and Infrared Spectroscopy	Completed
4	Unit IV	Nuclear Magnetic Resonance and Mass Spectroscopy	Completed
5	Unit V	Structure Determination of Organic Compounds	Not completed

Topic enclosed herewith Unit II-Rearrangement Reactions

Disclaimer: There is no claim of the originality of the material and it is given only for the students to study

References:

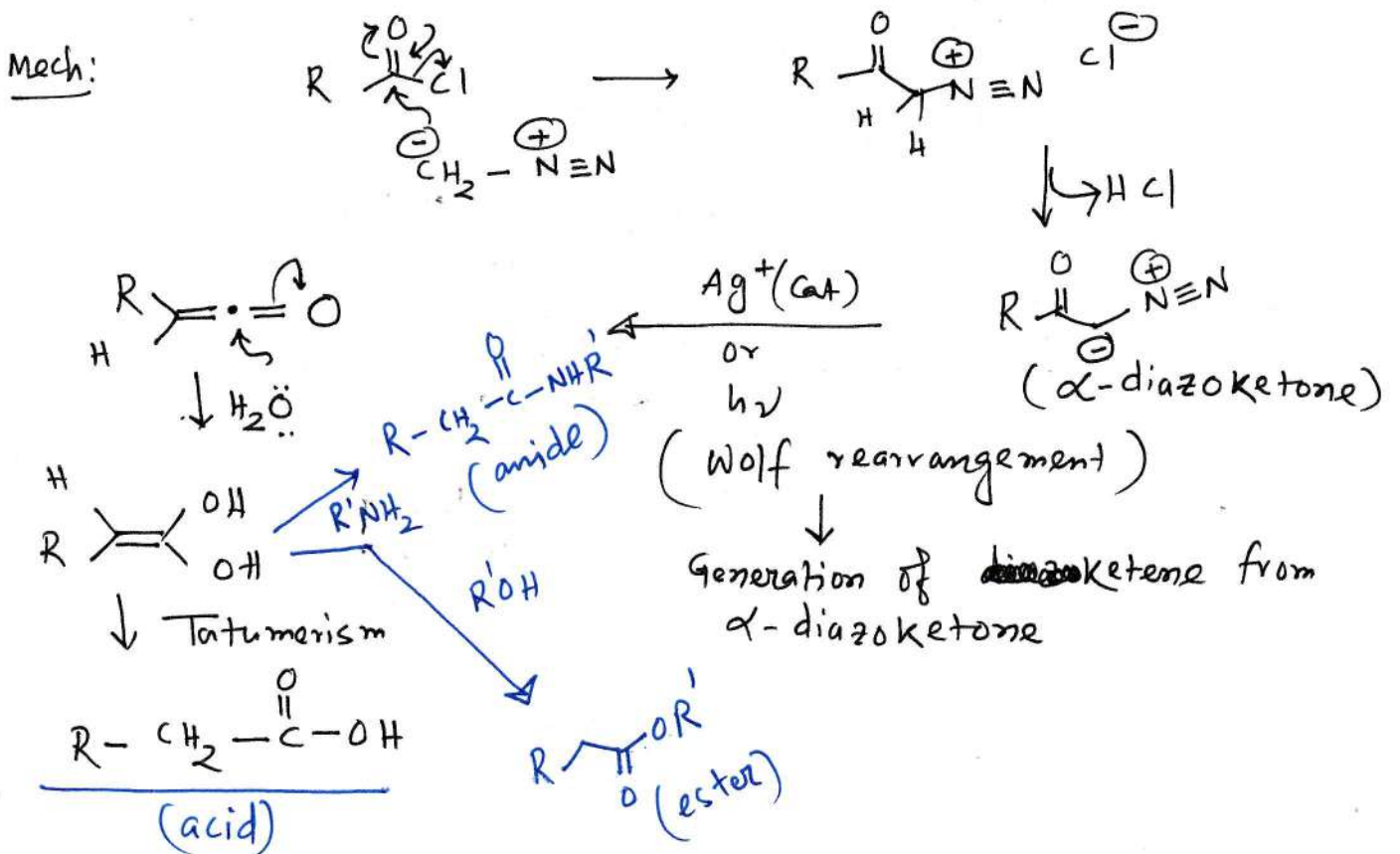
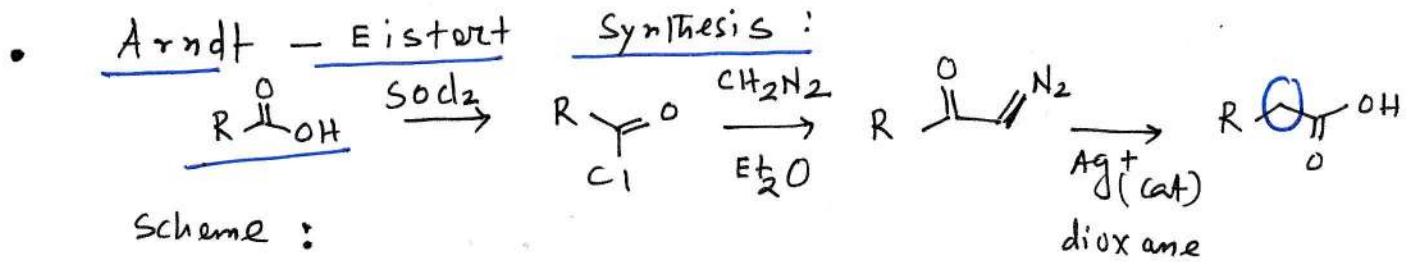
1. Organic Chemistry II-Edition by J. Clayden, N. Greeves and S. Warren.
2. Name Reactions: A Collection of Detailed Reaction Mechanisms (Springer) by J. J. Li
3. Organic Chemistry Portal: <https://www.organic-chemistry.org/namedreactions/>
4. Research Journals: Organic Letter, The Journal of Organic Chemistry, The Journal of American Chemical Society, Macromolecules link: <https://pubs.acs.org/>
5. Research Journals: Tetrahedron Letters, Tetrahedron Link: <https://www.sciencedirect.com/journal/>

Lecture Note — On
Rearrangement Reaction

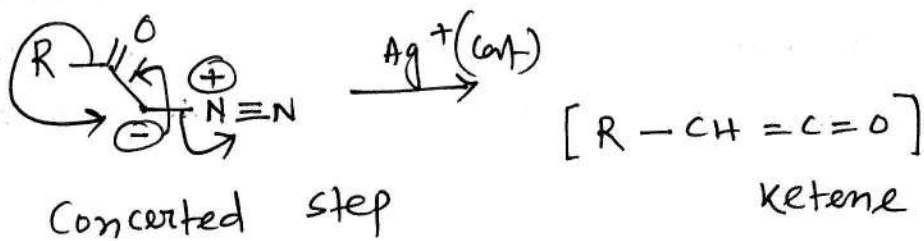
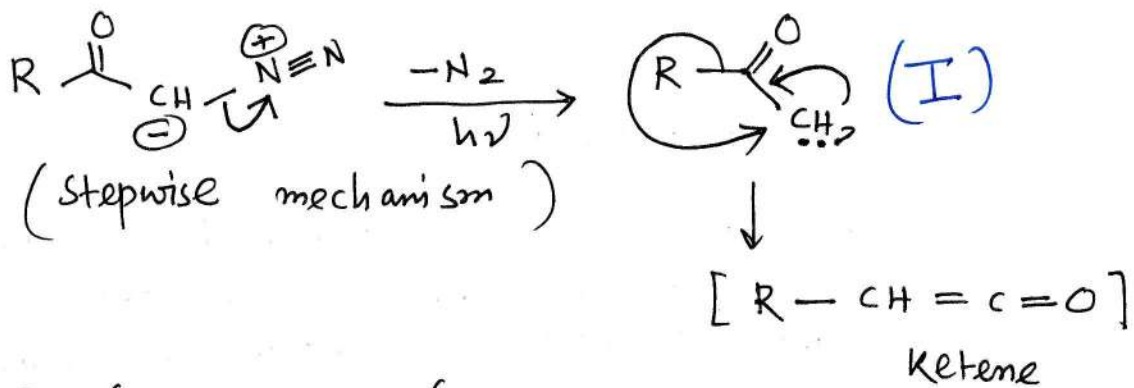
• Rearrangement Reaction :

A rearrangement reaction is a type of organic reaction involves a rearrangement of an atom or a group of atoms (substituents) occurs through a one atom to another atom. i.e. skeletal rearrangement occurs ~~throughout~~ in the reactions.

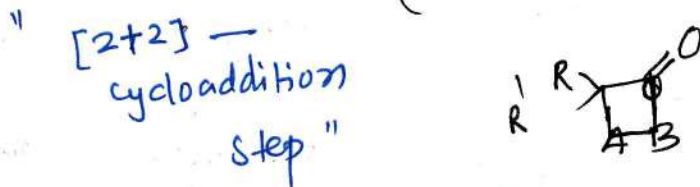
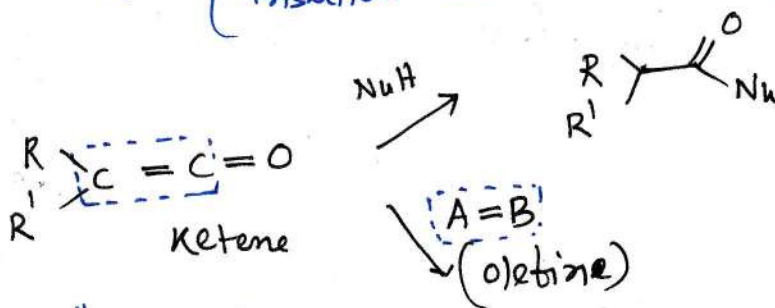
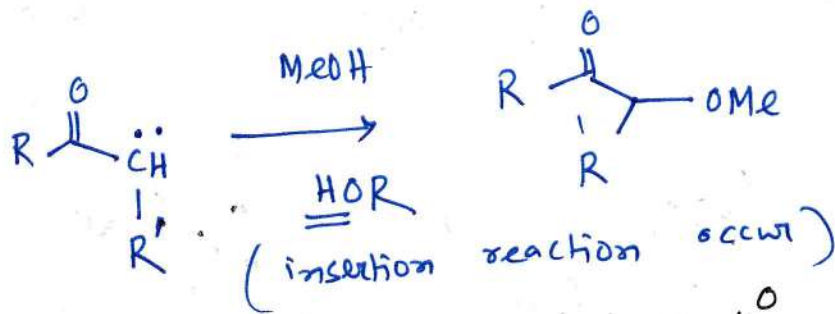
• Let us start discussion on a series of Rearrangement reactions : —



Mechanism of Wolff rearrangement i.e.



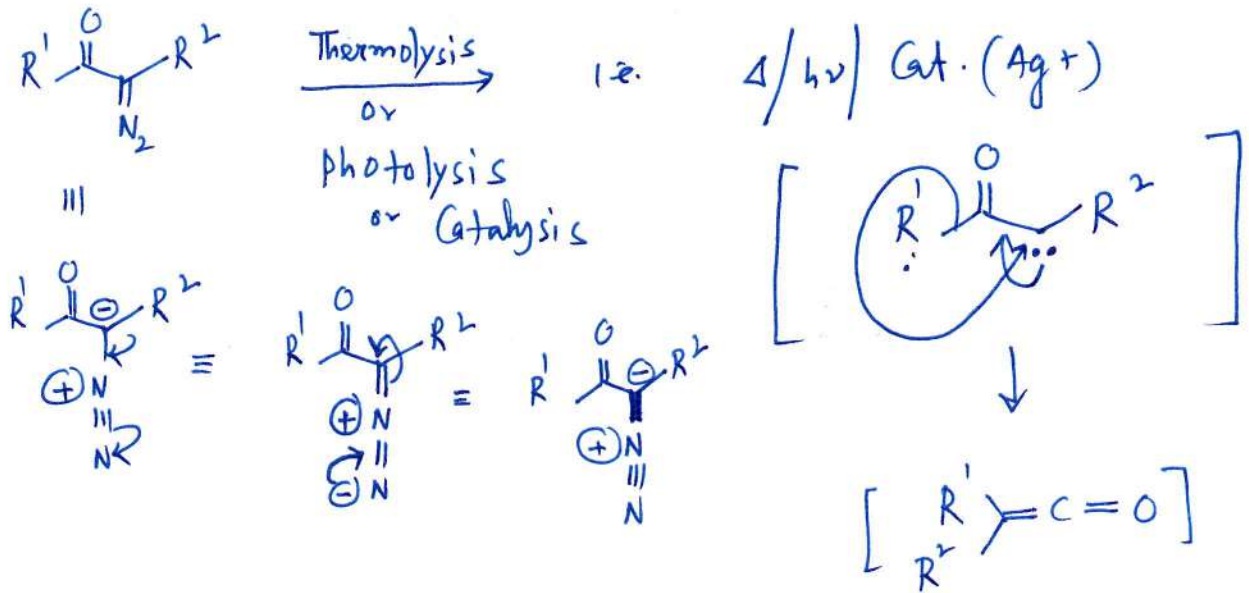
Wolff-rearrangement conducted in MeOH as solvent then the side product derived from an MeOH insertion to the carbene (I) intermediate was observed...



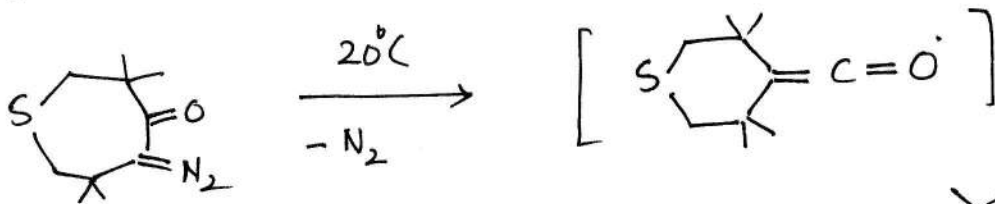
(2)

Details Wolff Rearrangement Reactions :

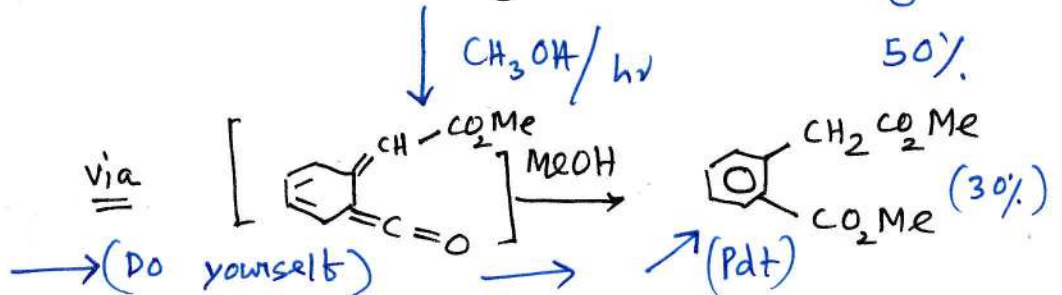
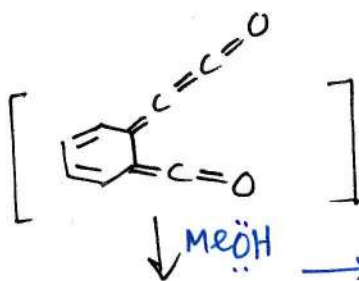
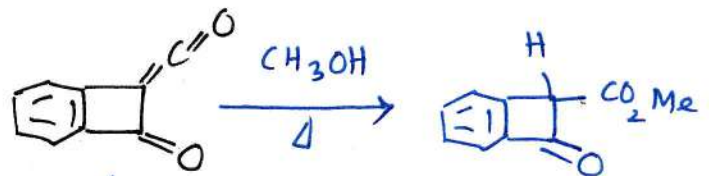
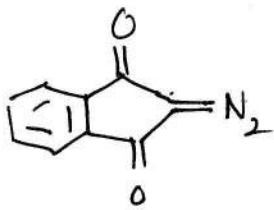
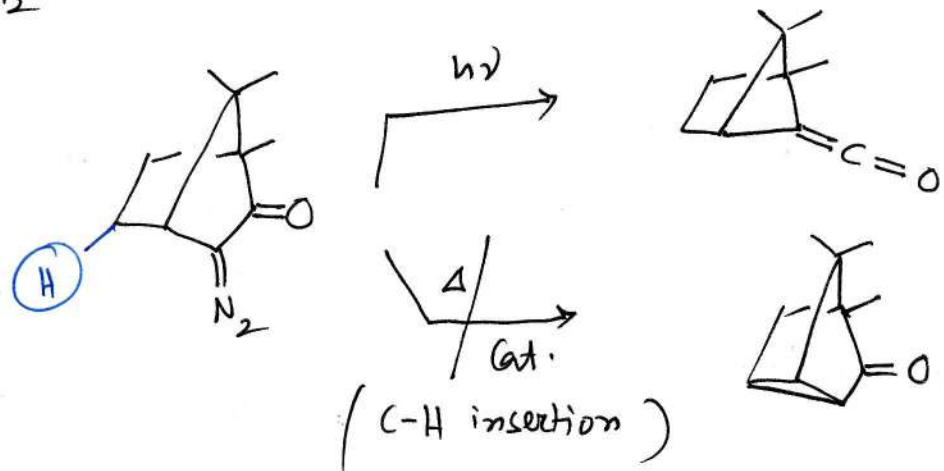
See Ref. Angew. Chem. Int. Ed. 1975, 14, 32-43



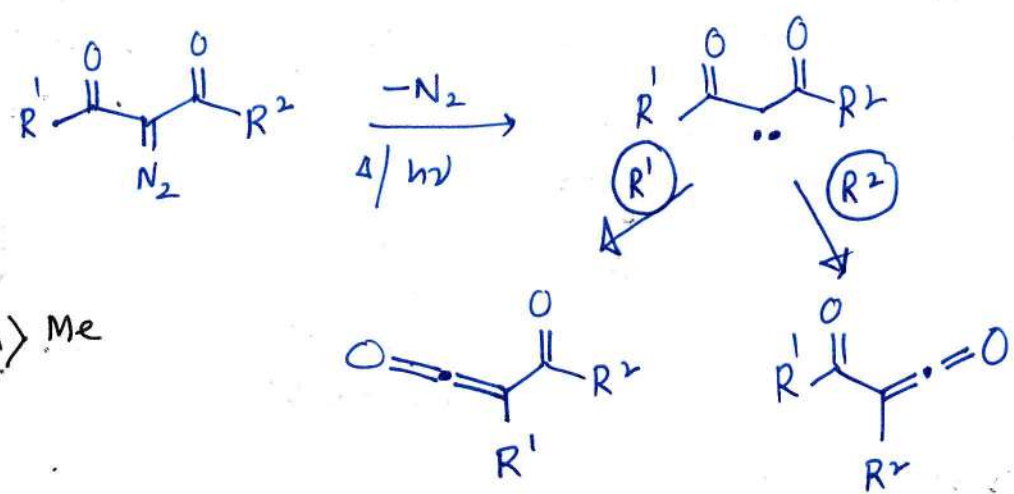
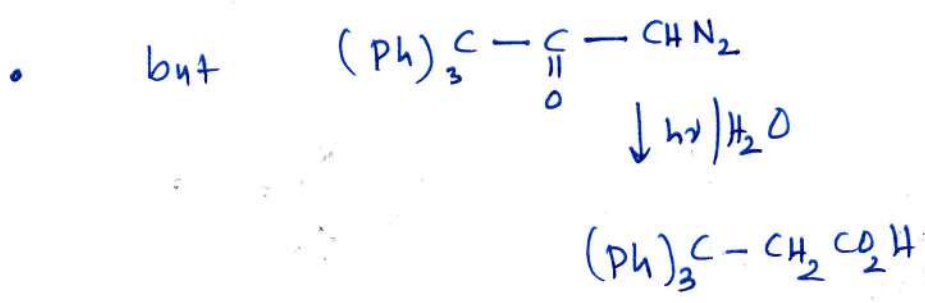
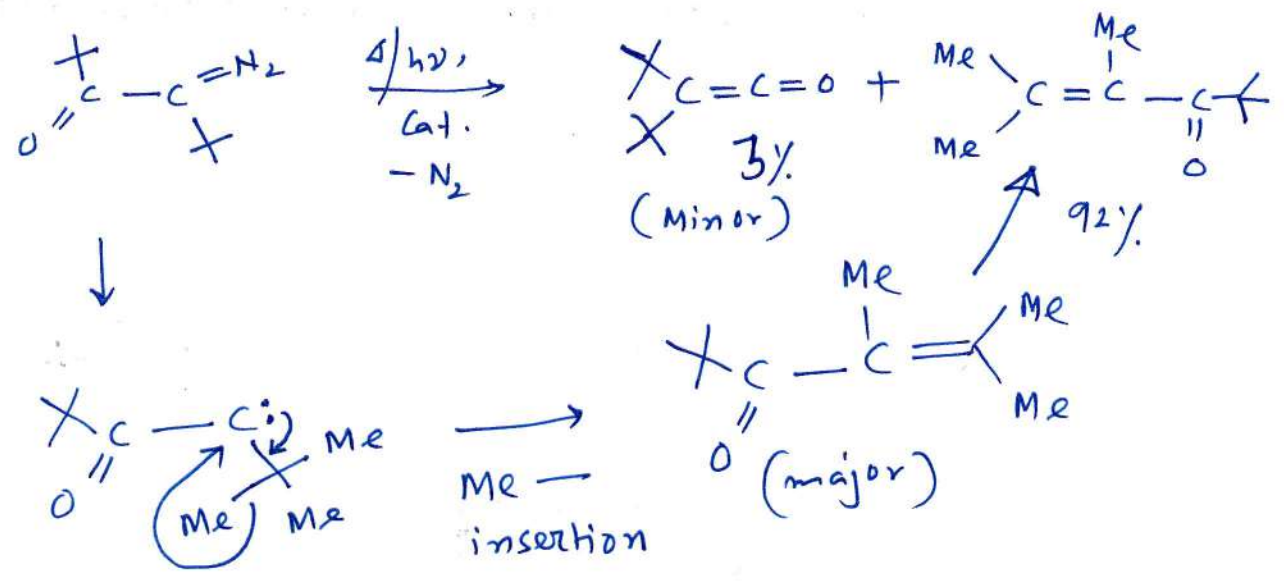
Thermolysis :



Photolysis :



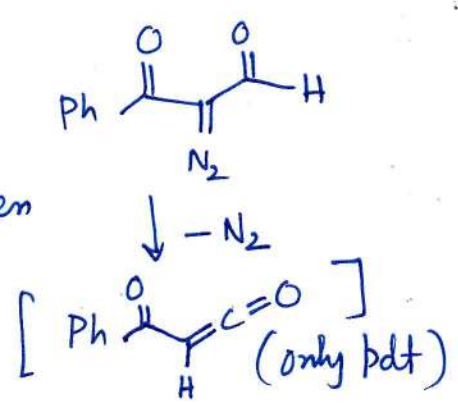
open-chain α -diazo ketone

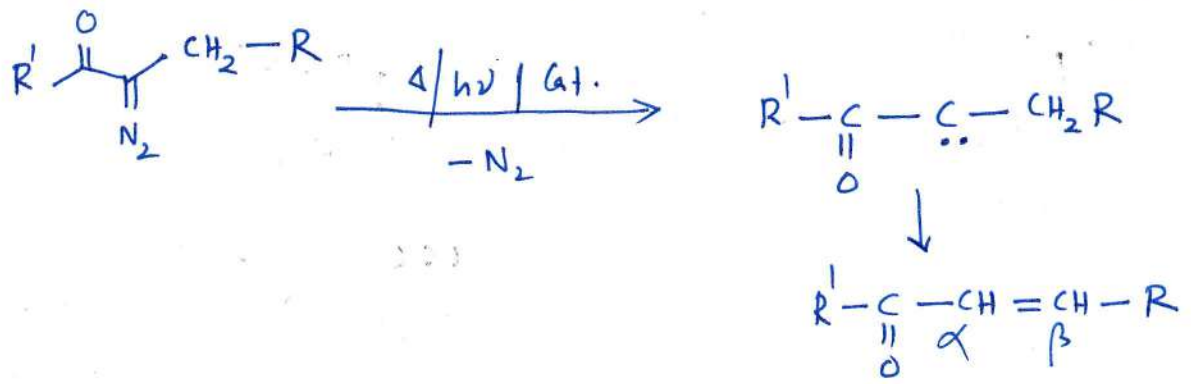


H > Ph > Me

if $\text{R}^1 = \text{Ph}, \text{R}^2 = \text{H}$
 Condition: $\Delta/h\nu / \text{Ag}^+ \text{Cat.}$

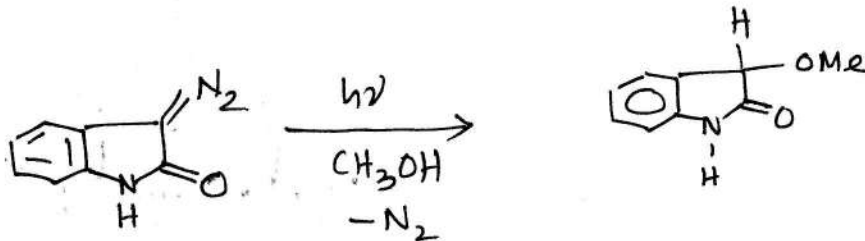
[1.2]-hydrogen shift.



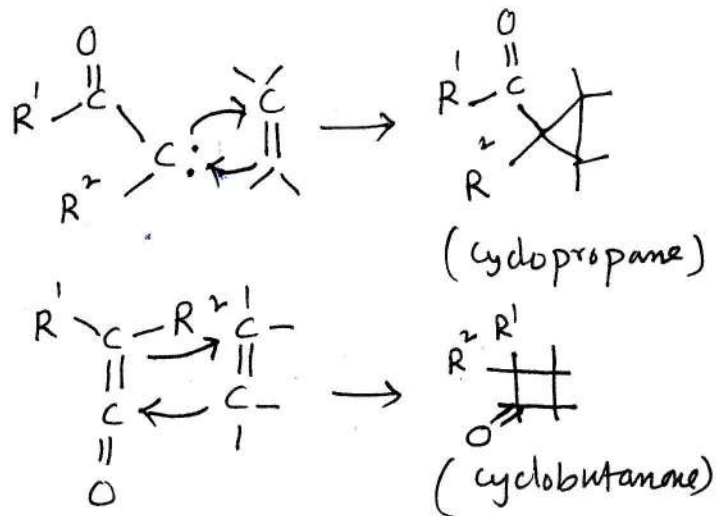
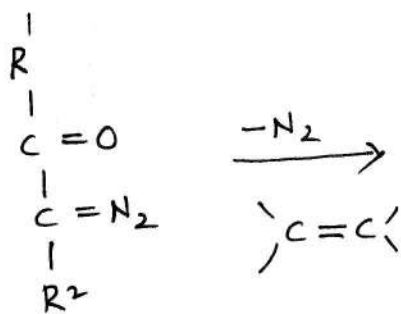


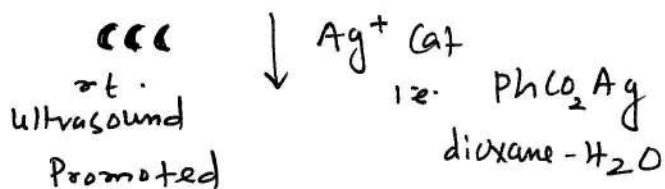
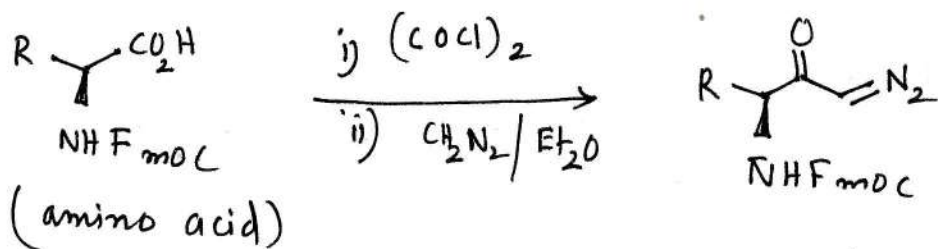
(α, β -unsaturated ketone)

- α -oxo carbenes as intermediates derived from Wolff-rearrangement reaction frequently insert into C-H, C-C, C-O, C-S, C-N, C-Hal, N-H, S-H bonds.

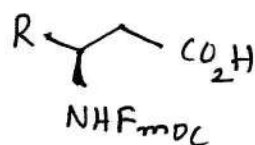


(α -diazoketone)

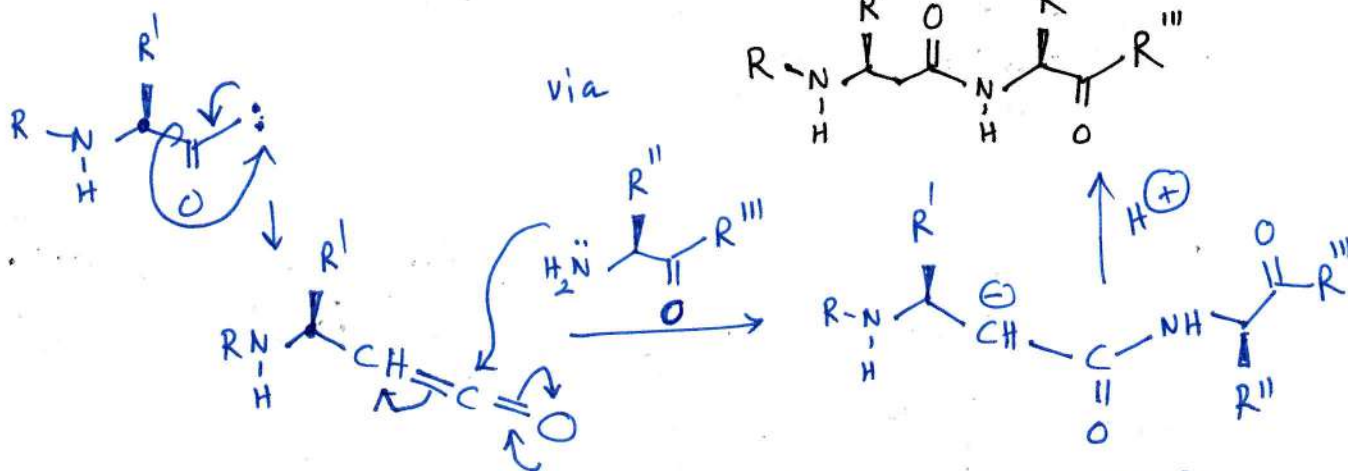
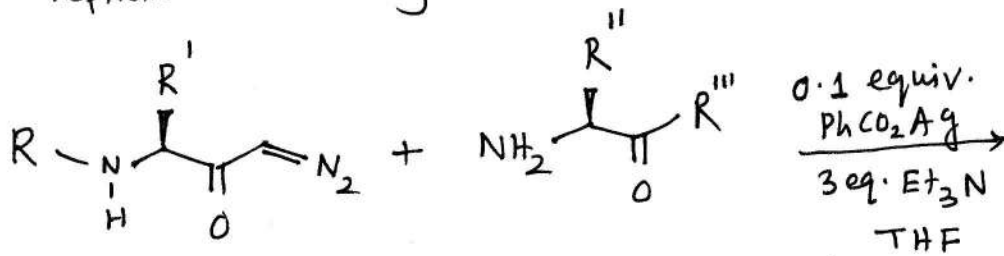




(Synthesis 1998, 837-841)

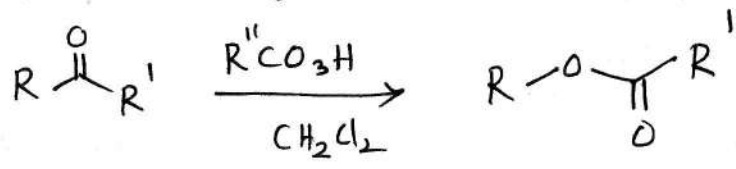


"Peptide chemistry"



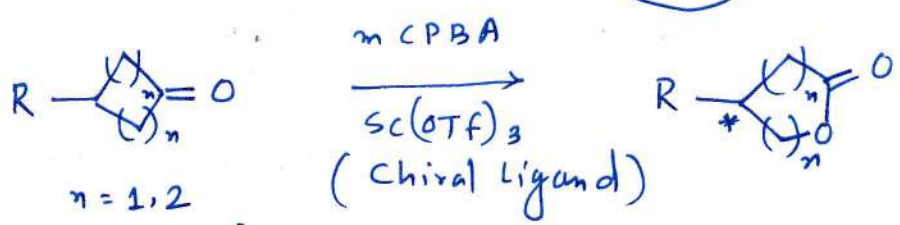
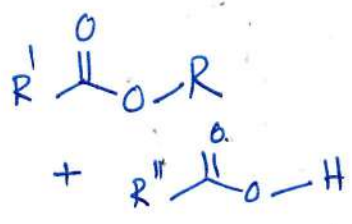
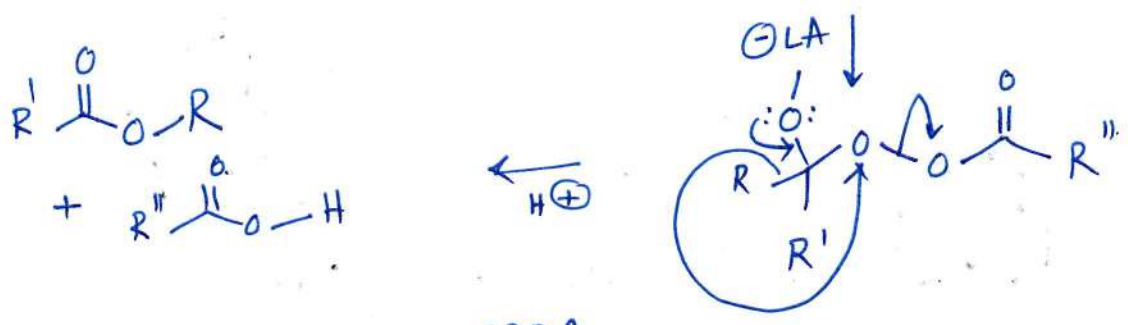
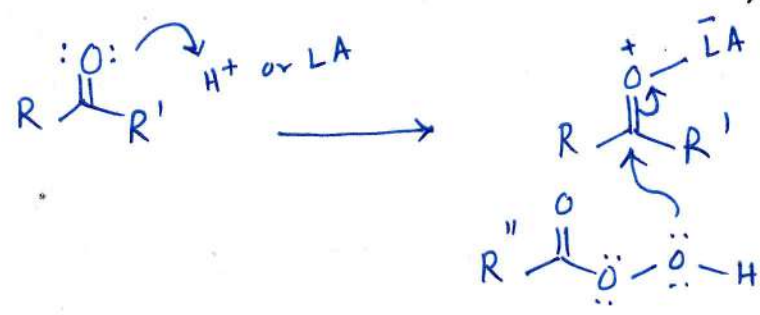
(Angew.chem. Int. Ed. 1995, 34, 471-472)

Baeyer-Villiger Oxidation :



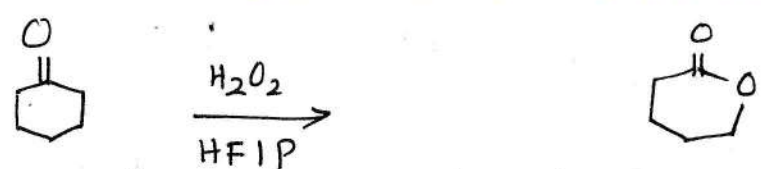
oxidation of ketone — in the presence of peracid (mCPBA, RCO₃H) / H₂O₂-BF₃ in Et₂O.

Mech:

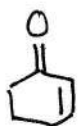


Desymmetrization of Meso - Cyclic ketone

JACS 2012, 134, 17023

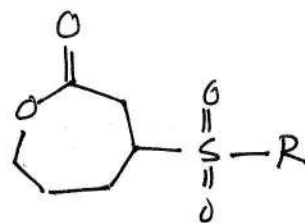


(Hexafluoroisopropanol) Solvent org. Lett. 2000, 2, 2861

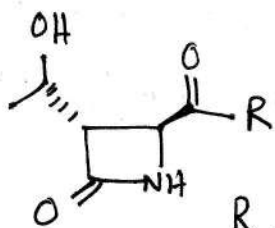


1. Thia-Michael Addition

2. Baeyer-Villiger oxidation

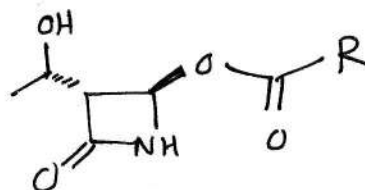


Macromolecules 2014, 47, 9, 2842



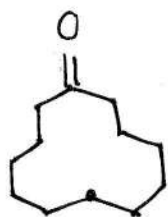
R = cyclopropyl

B.V. oxidation

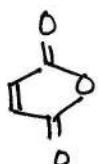


(Carbapenem)

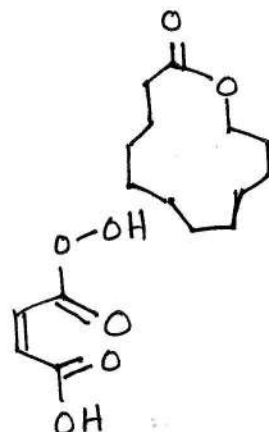
J. Org. Chem. 2004, 69, 3194-3197



Permaleic Acid

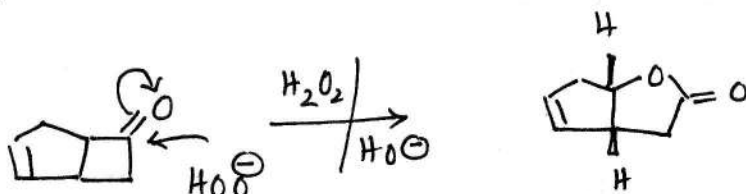


30% H₂O₂
Ac₂O

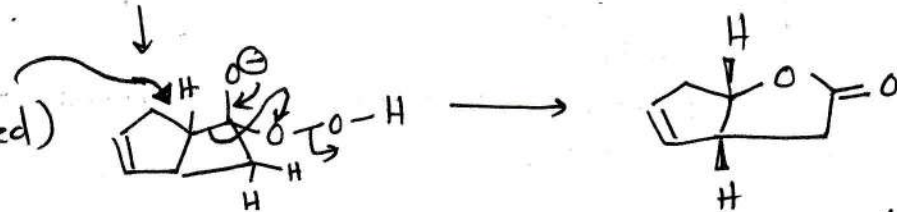


(Permaleic acid)

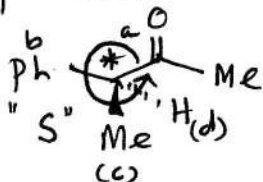
J. Chem. Educ. 2013, 90, 8, 1103-1104



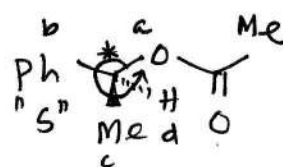
(More substituted)



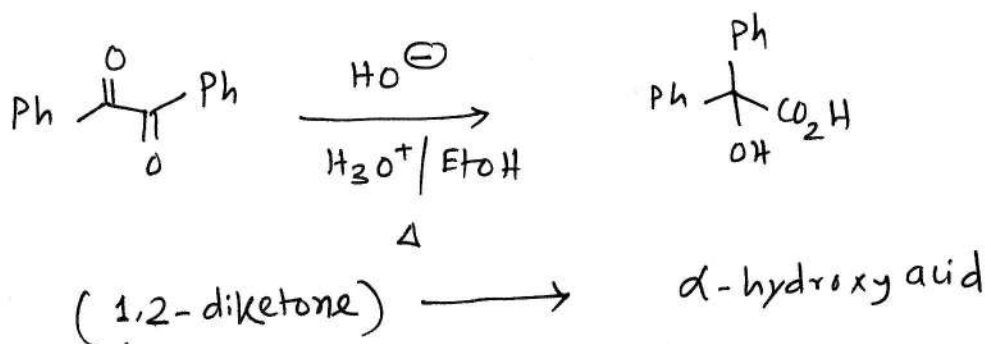
Starting material stereochemistry is retained in the ppt.



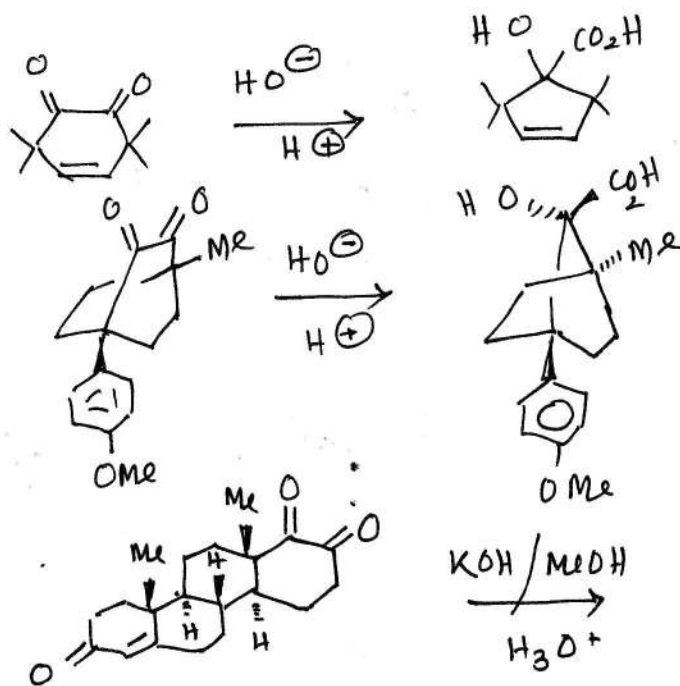
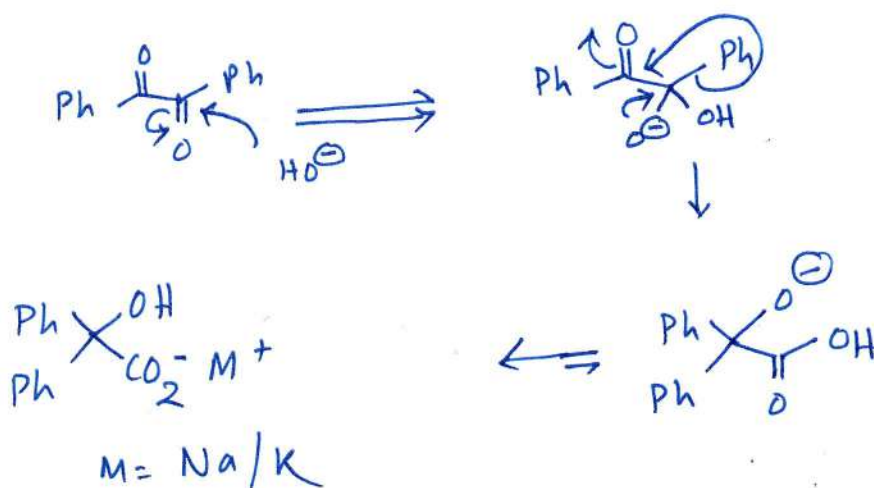
RCO₃H



Benzilic Acid Rearrangement :



Mech:

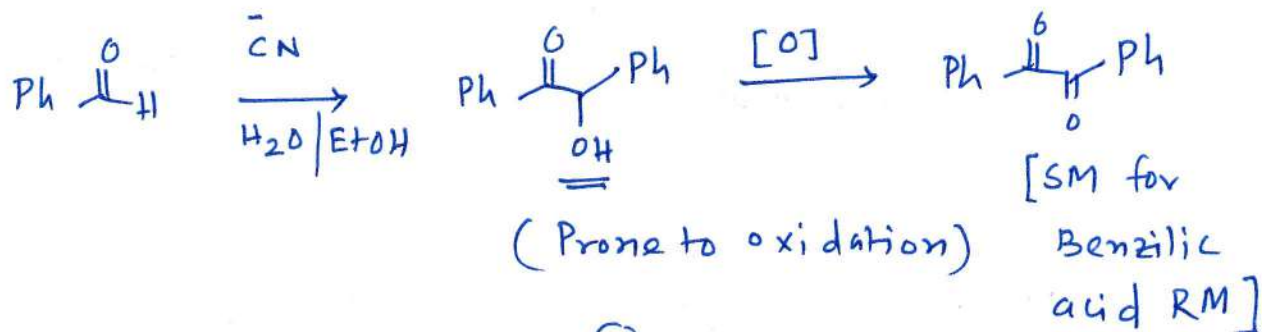


Helvetica Chimica Acta
1986, 69, 1666.

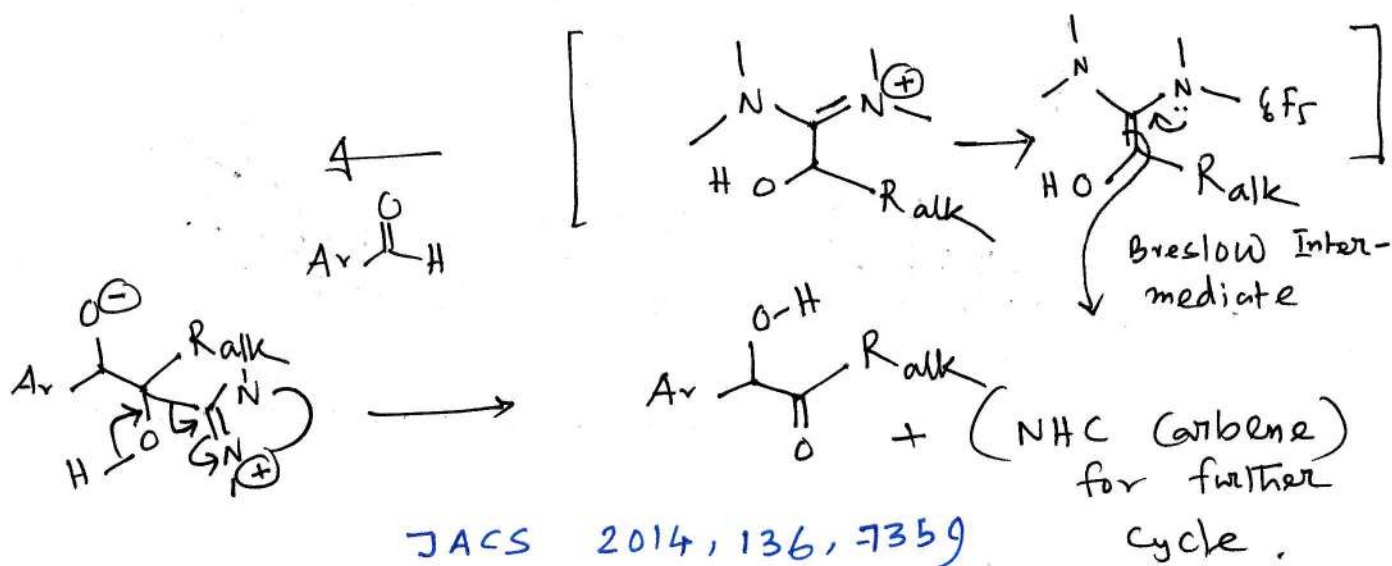
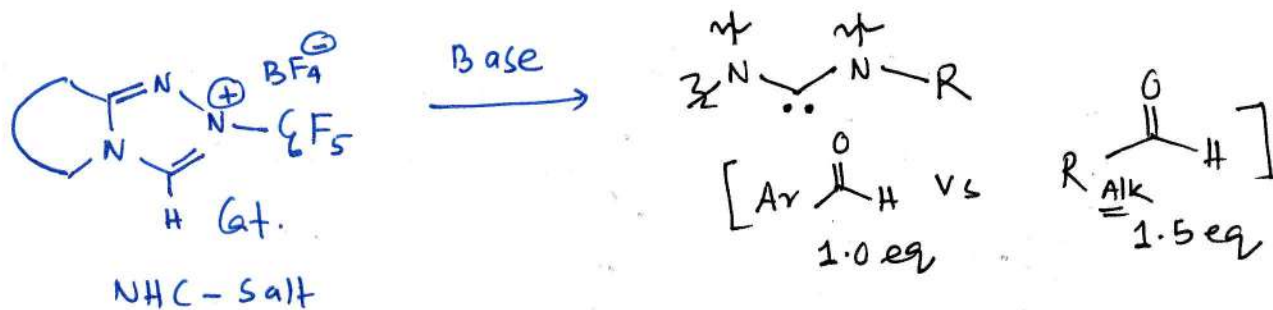
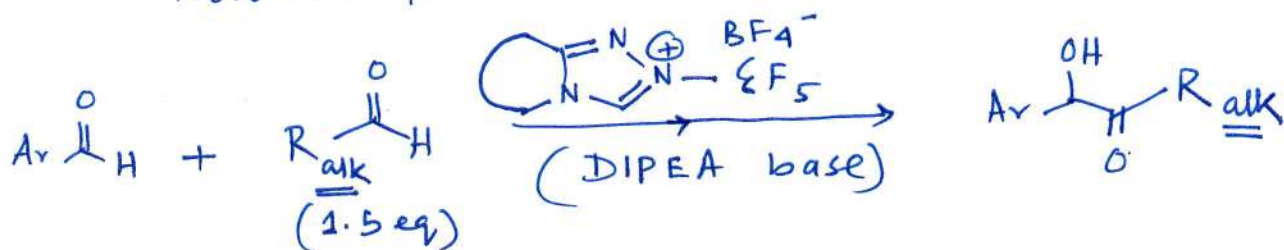
Synth. Commun. 1993,
23, 913

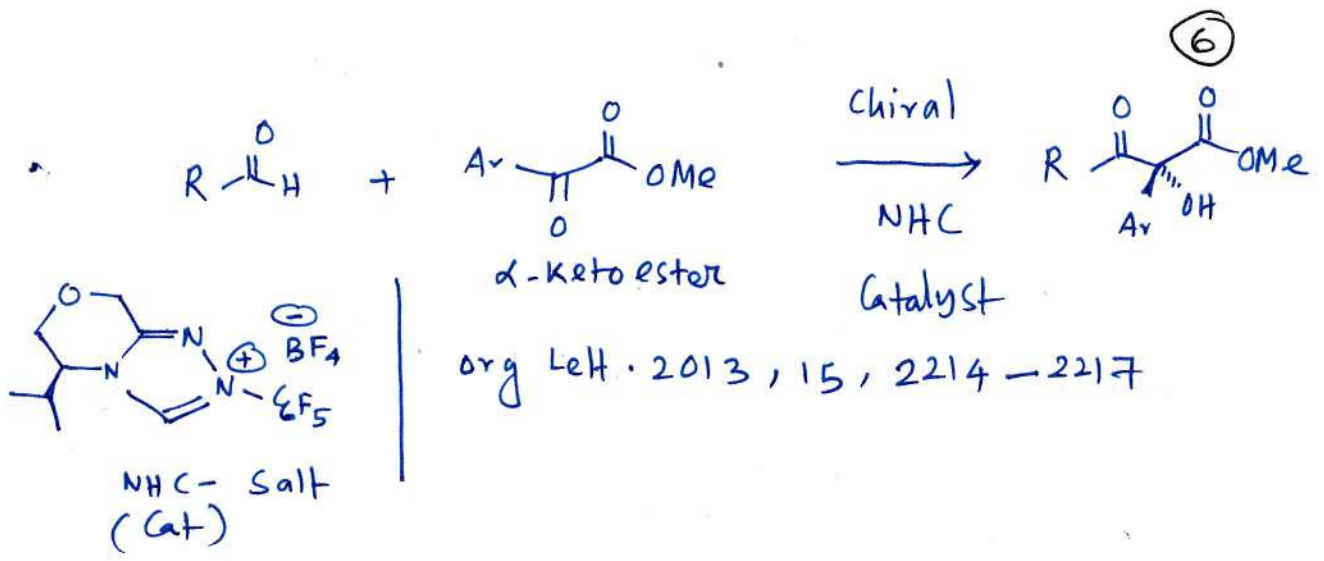
Tetrahedron 1963, 19, 1037.

- Benzoin Condensation: Coupling reaction between two aldehydes that allows the preparation of α -hydroxy ketone which can be readily oxidized to give 1,2-diketones.

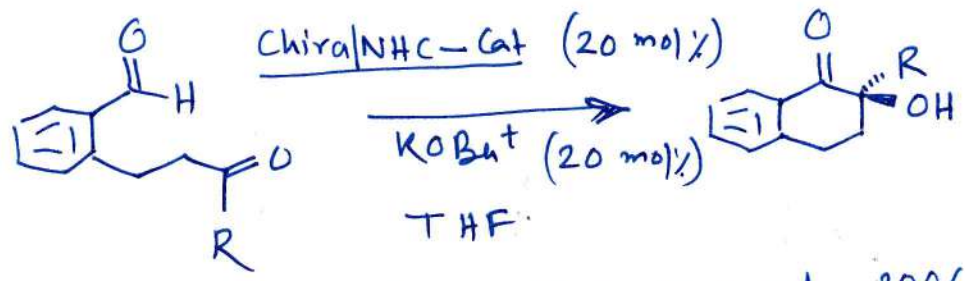


Previous method — CN^- Catalyzed
 Now-a-days — NHC "





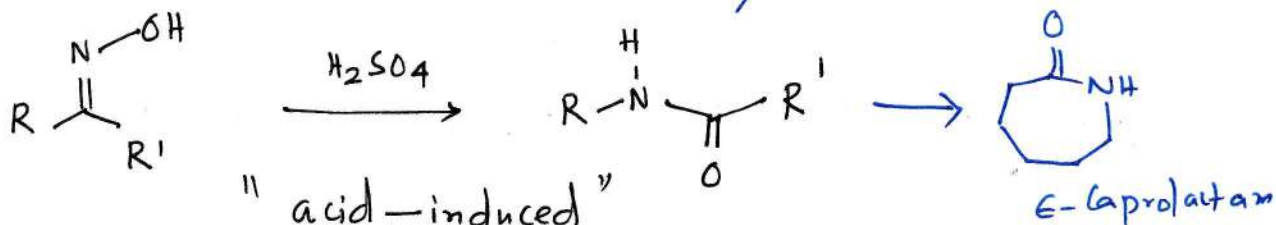
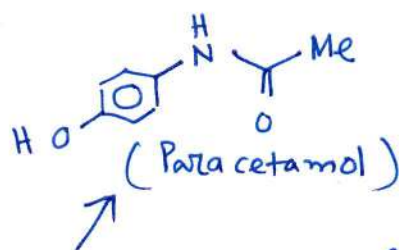
Intramolecular Benzoin Reaction:



Angew. Chem. Int. Ed. 2006, 45, 1463.

Beckmann

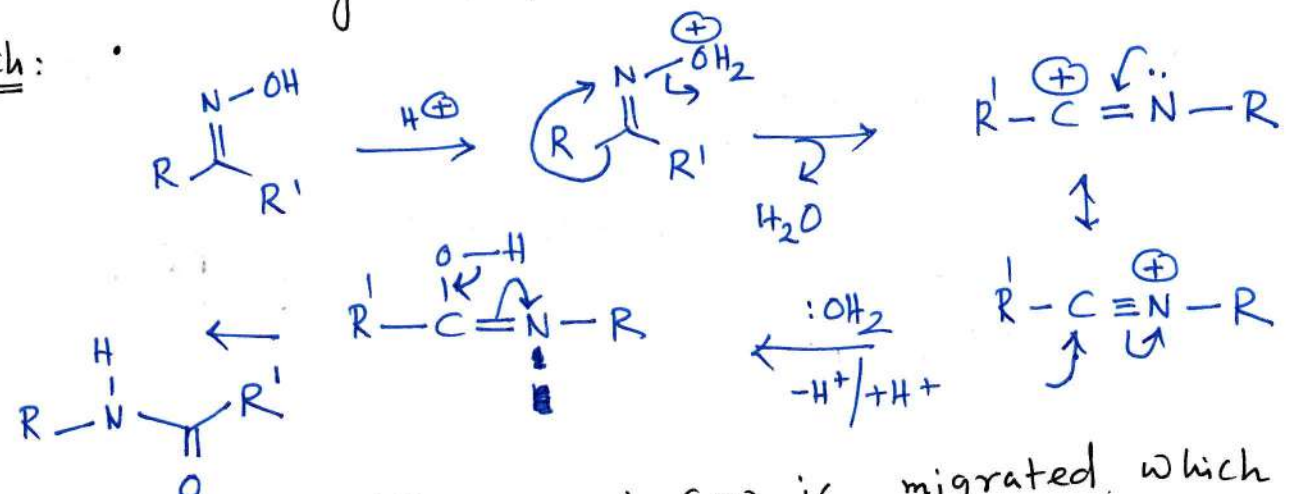
Rearrangement



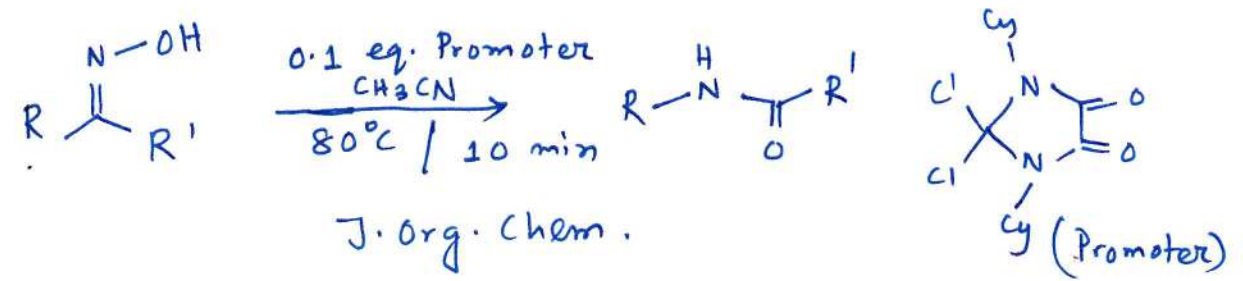
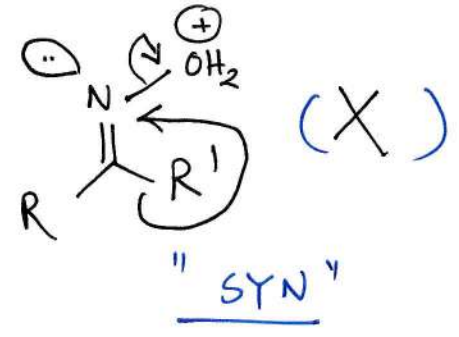
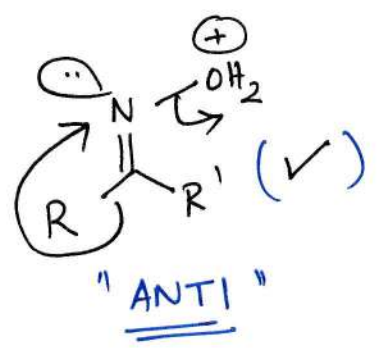
"acid-induced"

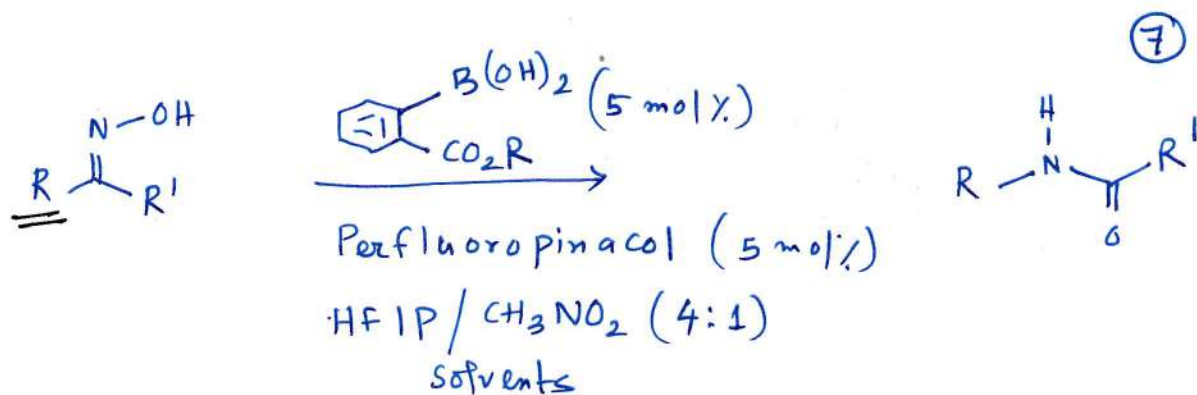
- rearrangement of oxime to amide

Mech:

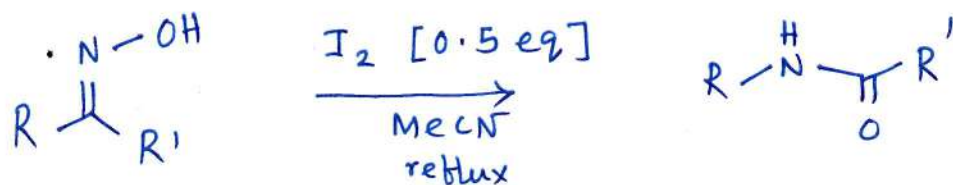


- The group (R) is migrated which is ANTI to the " $>N=OH$ "

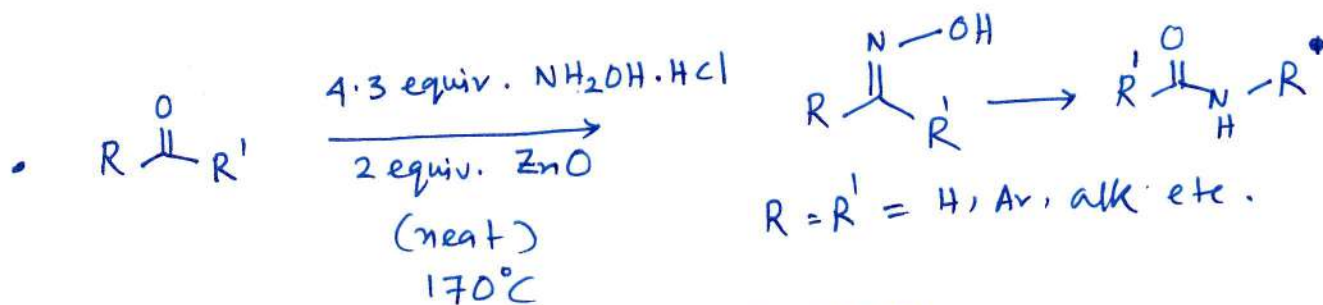




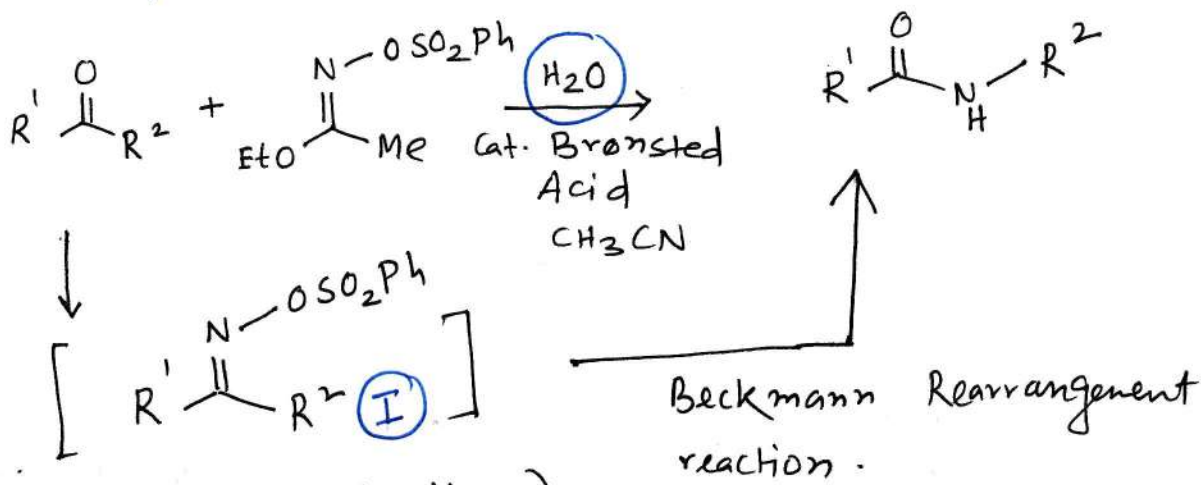
J. Am. Chem. Soc. 2018, 140, 5264



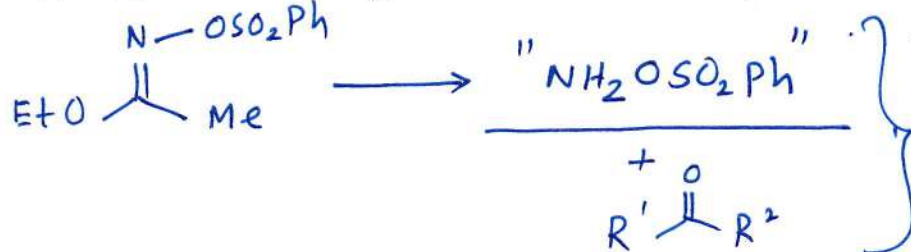
Synthesis 2010, 3705-3709

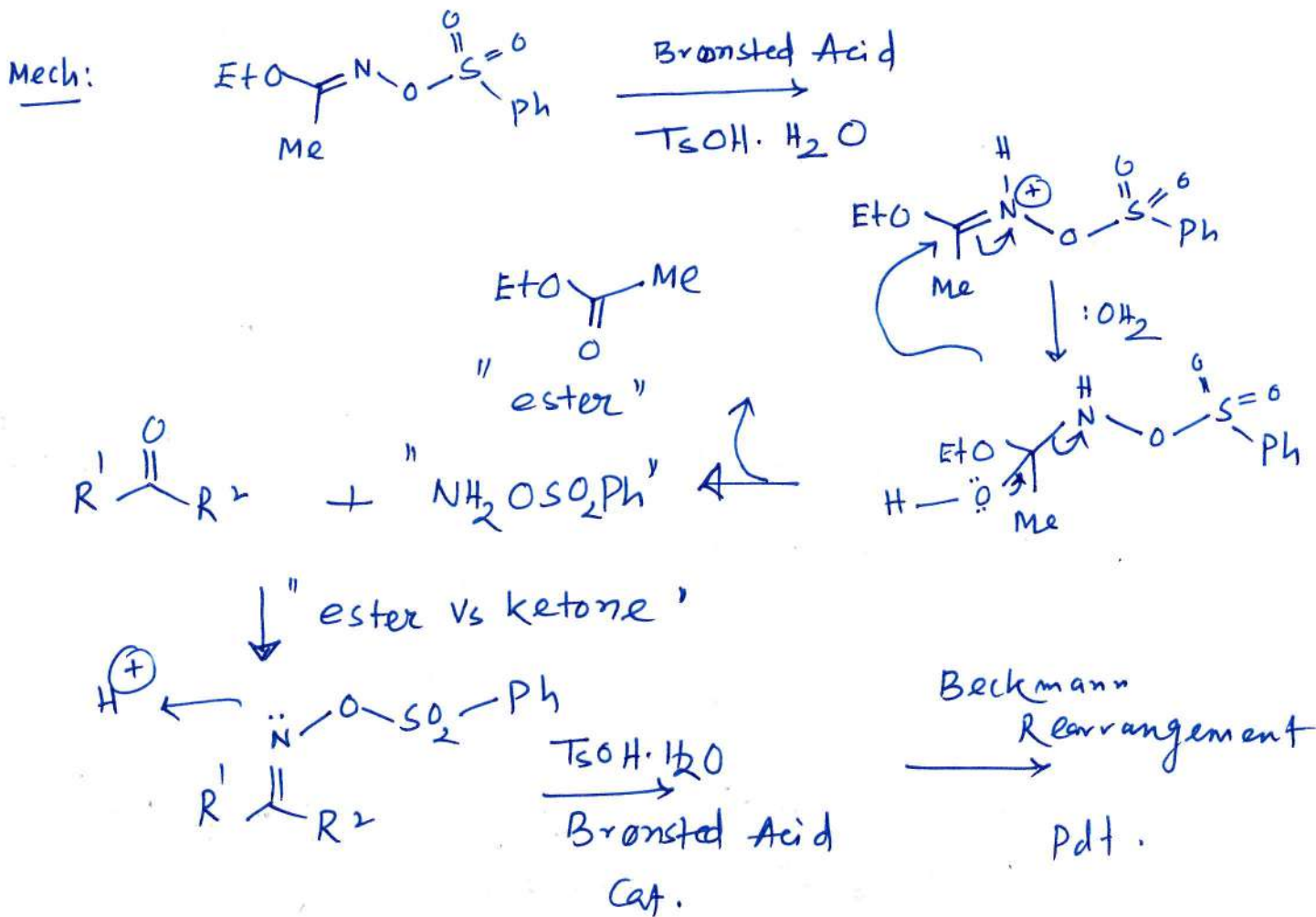
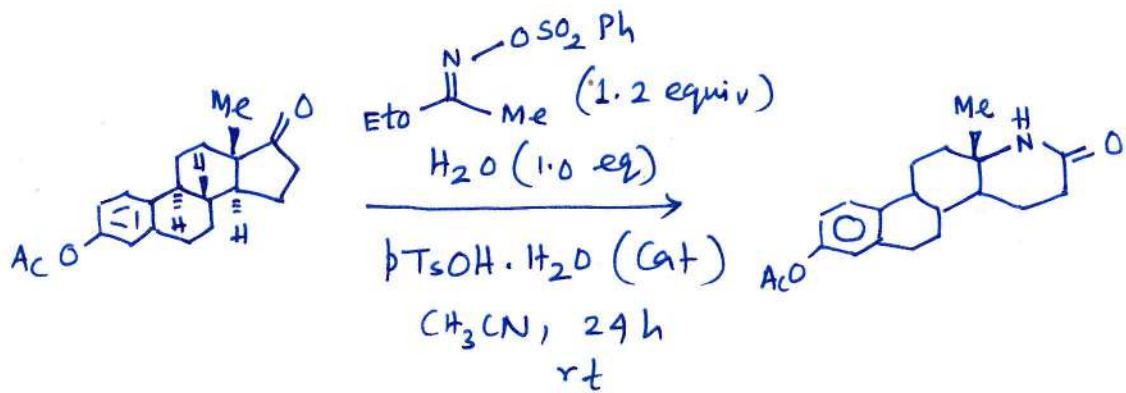


Synthesis 2002, 1057-1059

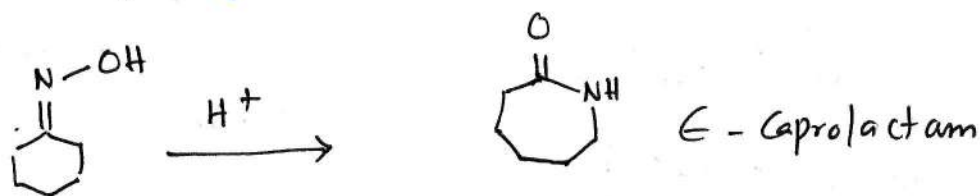


(Abbe's Transoximation)

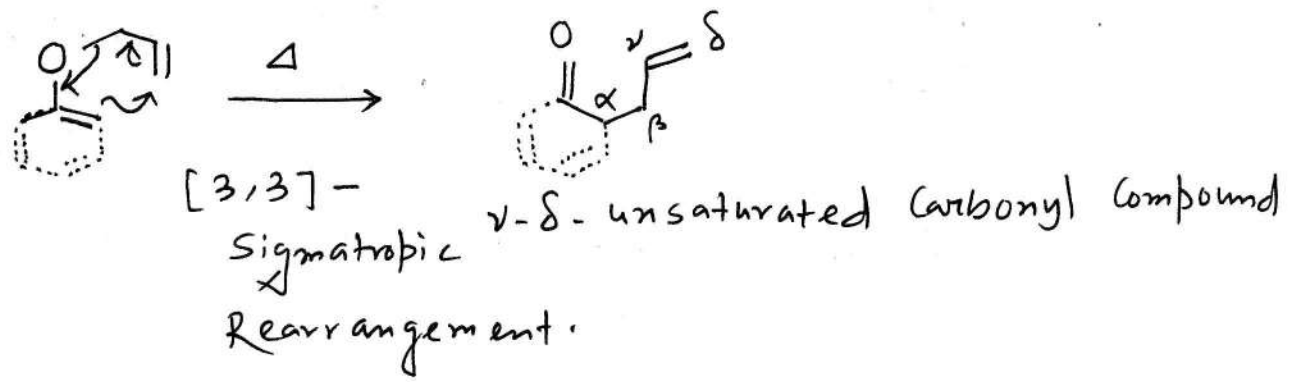




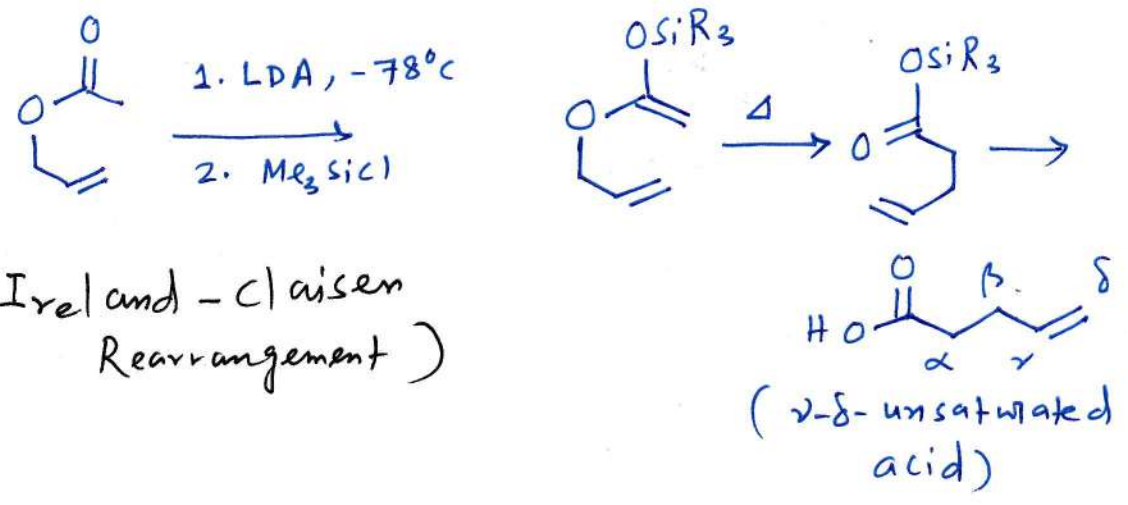
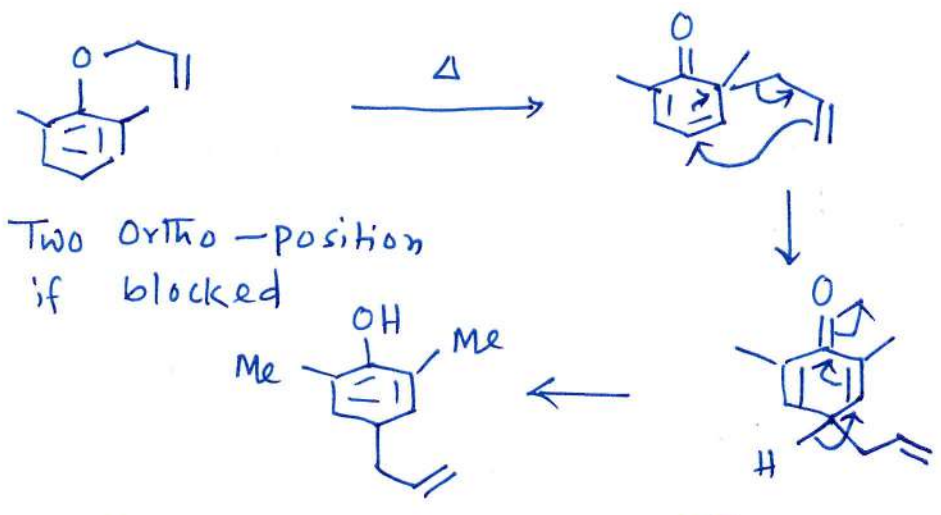
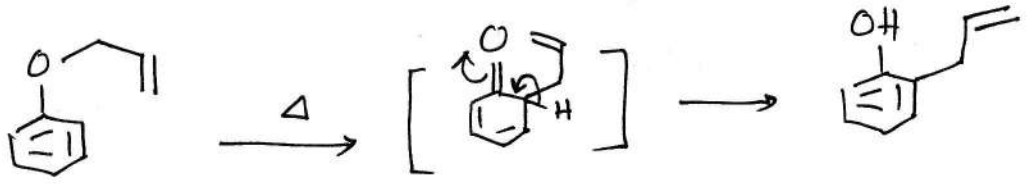
J. Org. Chem. 2018, 83, 13080-87.



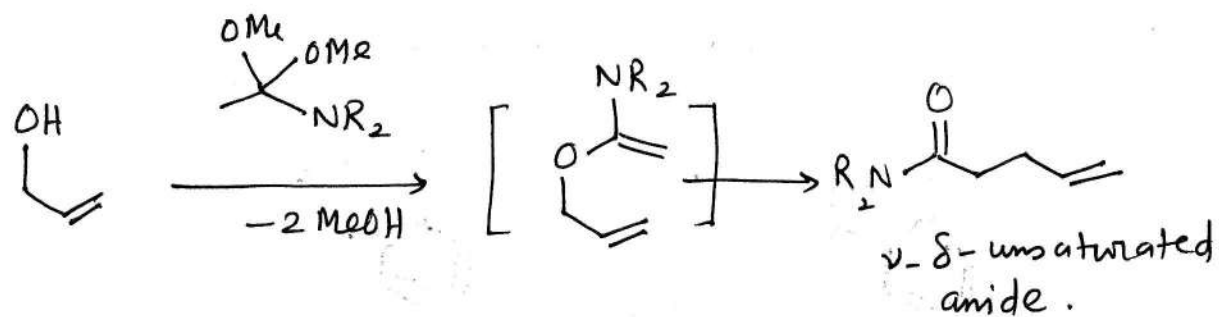
Claisen Rearrangement :



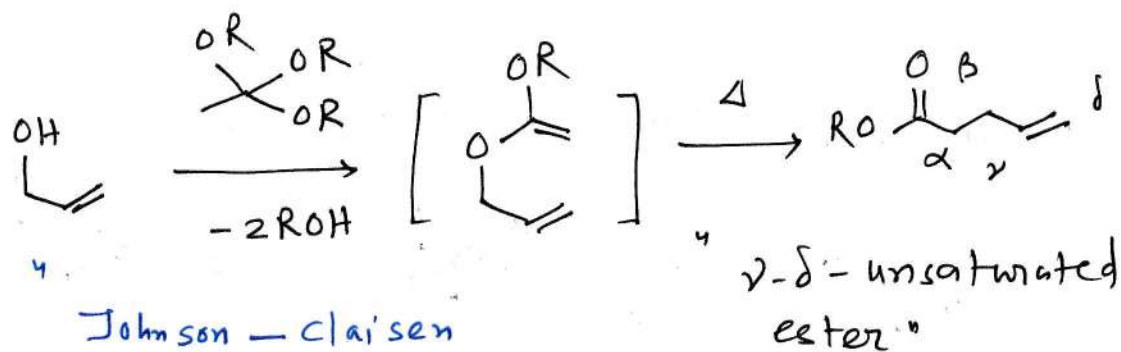
Aromatic Claisen Rearrangement :



(Ireland-Claisen Rearrangement)

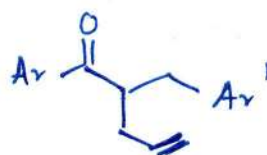
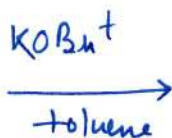
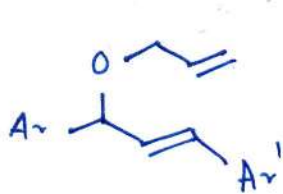


(Eschenmoser — Claisen Rearrangement Reaction)

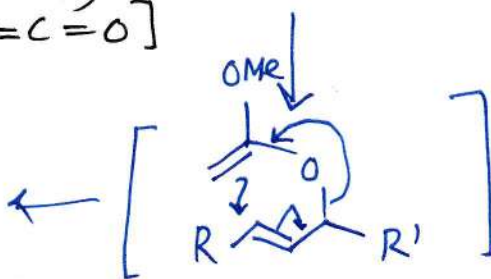
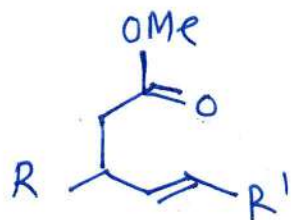
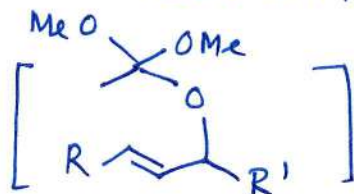
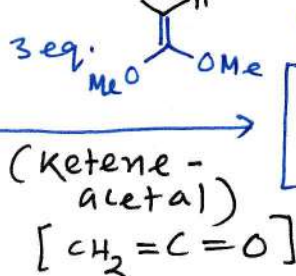
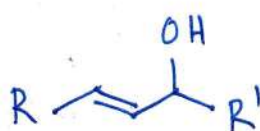


Johnson — Claisen

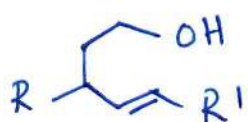
Rearrangement Reaction



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Synlett 2009, 1749, 1752.