M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry

II. Pericyclic Reactions

7. 1,3-Dipolar Cycloaddition Reaction

Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

II Pericyclic Reactions 20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

Electrocyclic reactions: Conrotatary and disrotatary motion, 4n and (4n+2) systems, Cycloaddition reaction: [2+2] and [4+2] cycloaddition reaction, Cycloaddition of ketones, Secondary effects in [4+2] cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

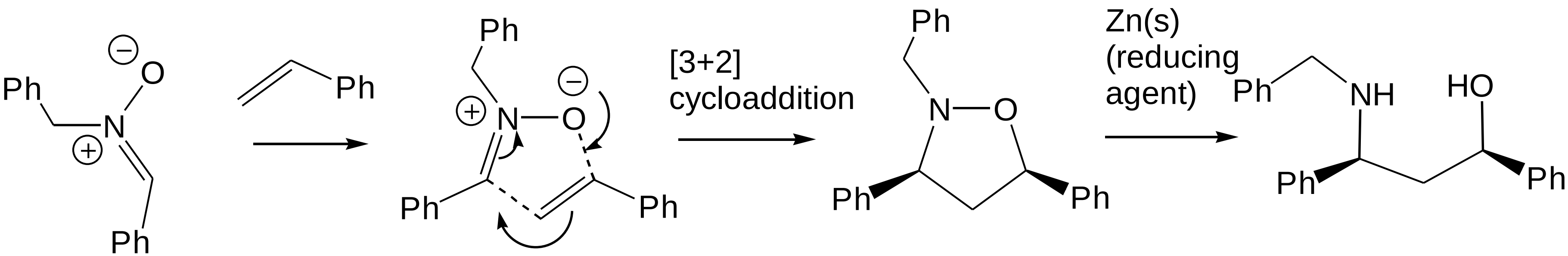
Sigmotropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration, [3,3]-, [1,5]-, [2,3]-, [4,5]-, [5,5]-, and [9,9]-Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

Coverage:

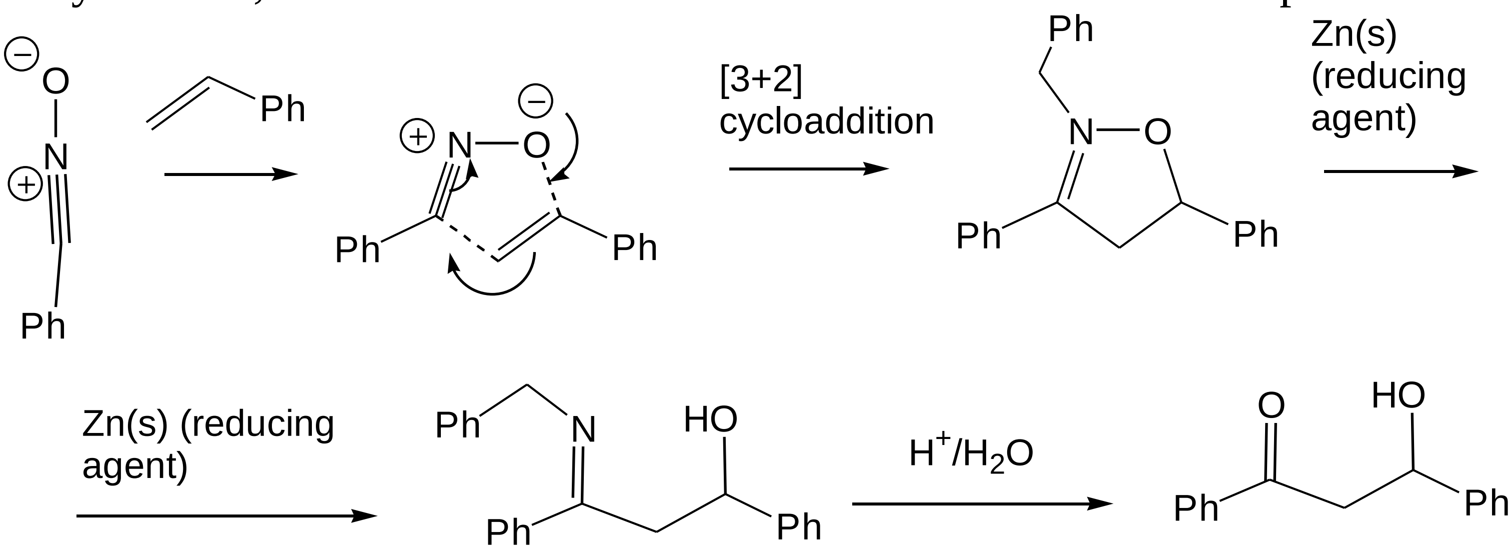
1. 1,3-Dipolar Cycloaddition Reaction

1,3-Dipolar Cycloaddition Reactions

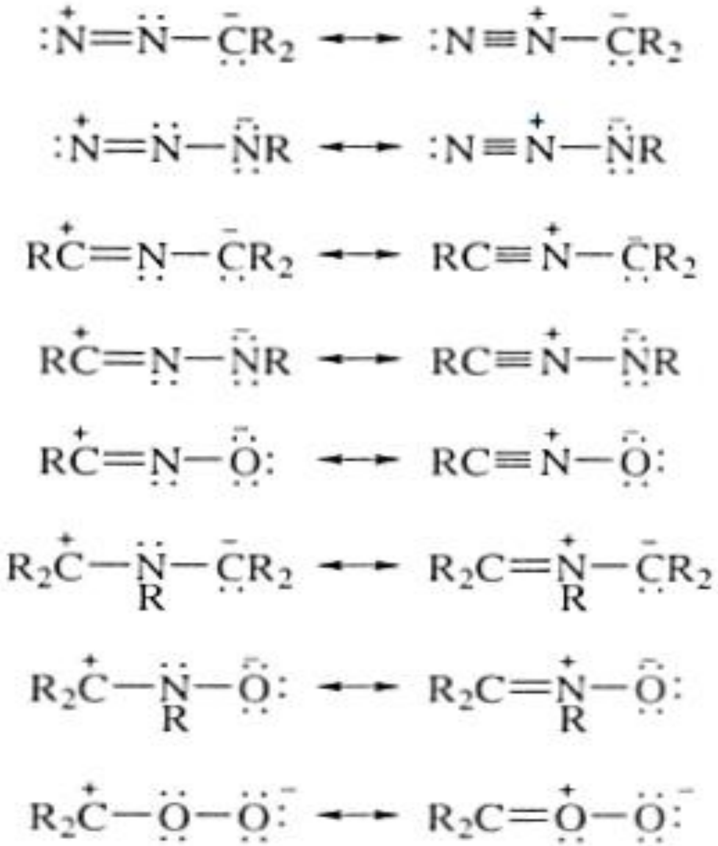
The cycloaddition of nitrones to alkenes (below) is a 6-electron process which proceeds in a suprafacial manner. The cycloaddition product can be reductively opened, thus providing a stereoselective method for the synthesis of 1,3-aminoalcohols.



A similar cycloaddition of nitrile oxides provides a method for the synthesis of 3-hydroxy ketones, all these reactions involve 4n+2 electrons and are suprafacial:



1,3- Dipolar Compounds:



Diazoalkane

Azide

Nitrile ylide

Nitrile imine

Nitrile oxide

Azomethine ylide

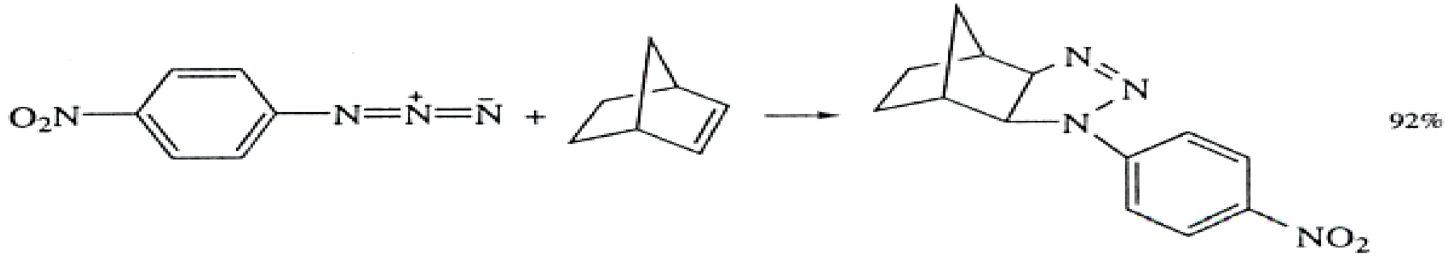
Nitrone

Carbonyl oxide

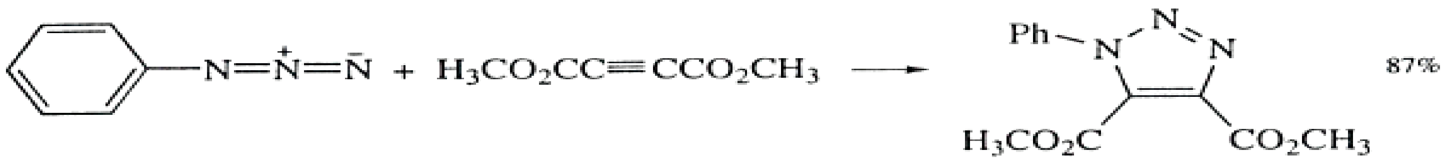
1,3-Dipolar Cycloaddition Reaction (Intermolecular)

A. Intermolecular cycloaddition

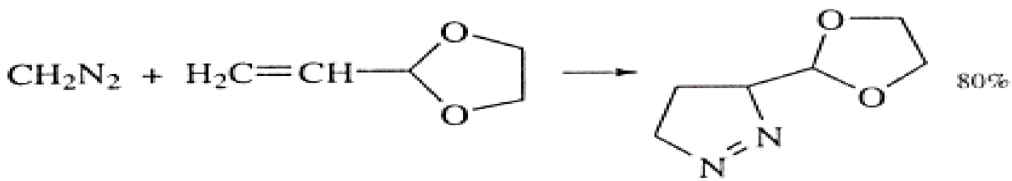
1[a]



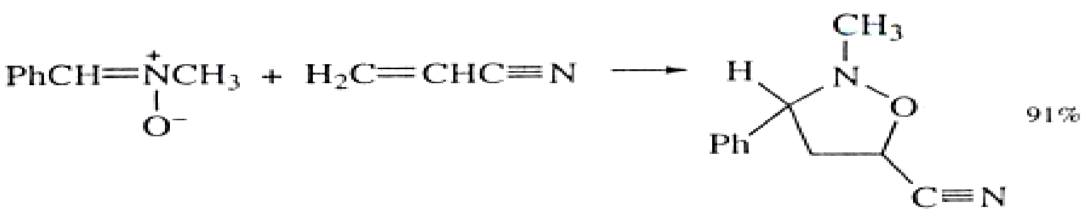
2[b]



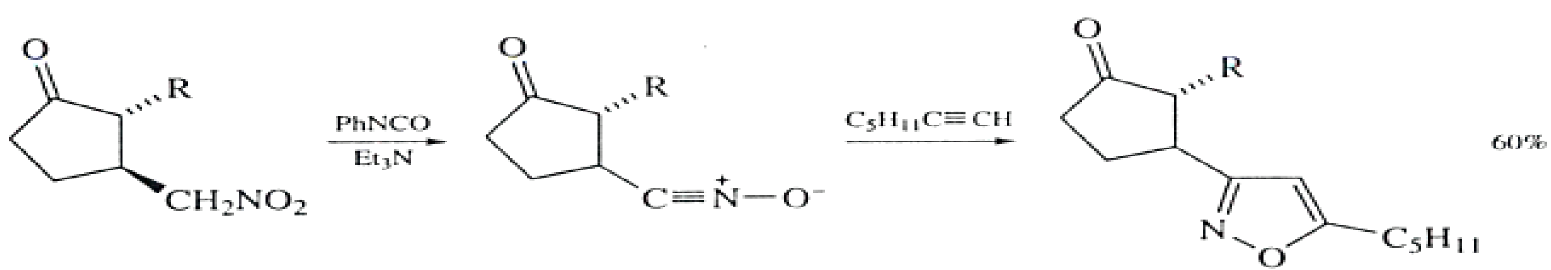
3[c]



4[d]



5[e]



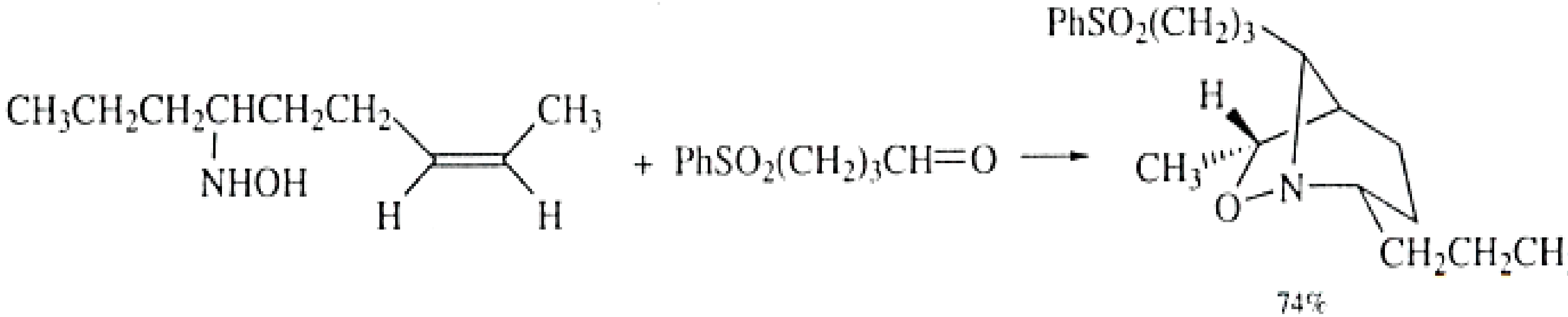
$R = -(CH_2)_6CO_2(CH_2)_3CH_3$

Dr. Rajeev Ranjan

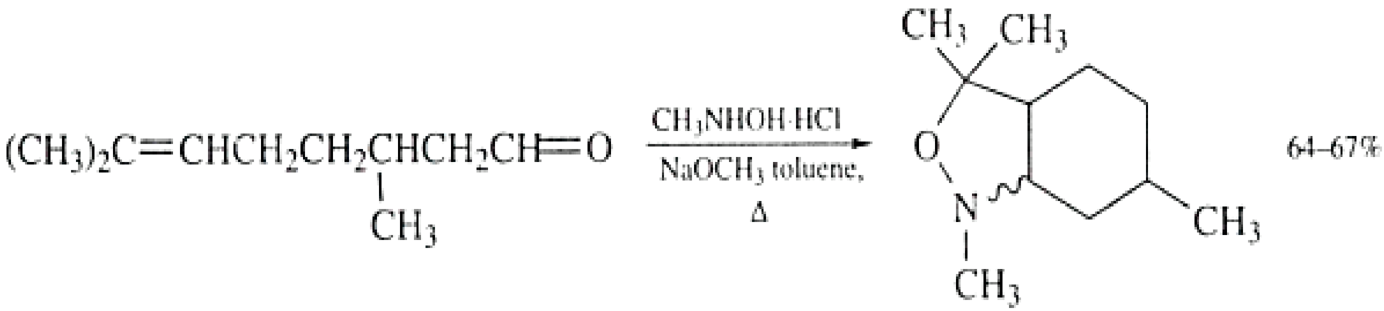
1,3-Dipolar Cycloaddition Reaction (Intramolecular)

B. Intramolecular cycloaddition

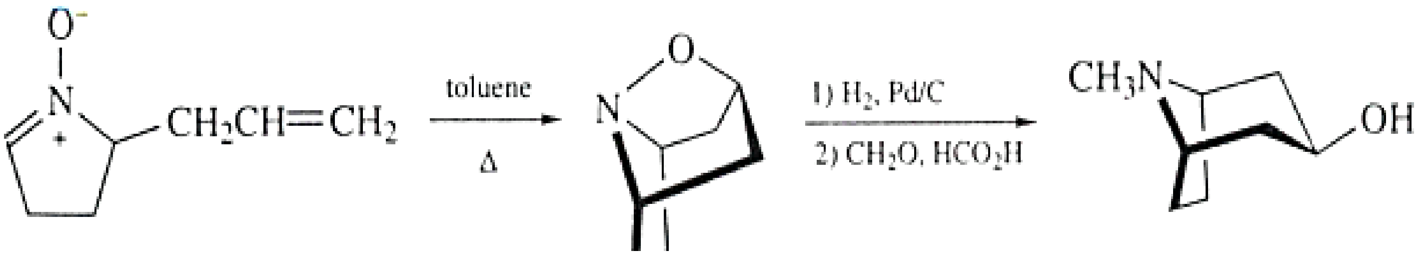
6[f]



7[g]



8[h]



Thank You

Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi