B.Sc. Semester-VI GroupA / DSE-4 Organic Synthesis



# II. Pericyclic Reactions7. 1,3-Dipolar Cycloaddition Reaction



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#### 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:

$$: \stackrel{\cdot}{N} = \stackrel{\cdot}{N} - \stackrel{\cdot}{C}R_2 \longrightarrow : \stackrel{\cdot}{N} = \stackrel{\cdot}{N} - \stackrel{\cdot}{C}R_2 \qquad Diazoalkane$$

$$: \stackrel{\cdot}{N} = \stackrel{\cdot}{N} - \stackrel{\cdot}{N}R \longrightarrow : \stackrel{\cdot}{N} = \stackrel{\cdot}{N} - \stackrel{\cdot}{N}R \qquad Azide$$

$$R\stackrel{\cdot}{C} = \stackrel{\cdot}{N} - \stackrel{\cdot}{C}R_2 \longrightarrow RC = \stackrel{\cdot}{N} - \stackrel{\cdot}{C}R_2 \qquad Nitrile ylide$$

$$R\stackrel{\cdot}{C} = \stackrel{\cdot}{N} - \stackrel{\cdot}{N}R \longrightarrow RC = \stackrel{\cdot}{N} - \stackrel{\cdot}{N}R \qquad Nitrile imine$$

$$R\stackrel{\cdot}{C} = \stackrel{\cdot}{N} - \stackrel{\cdot}{O}: \longrightarrow RC = \stackrel{\cdot}{N} - \stackrel{\cdot}{O}: \qquad Nitrile oxide$$

$$R_2\stackrel{\cdot}{C} - \stackrel{\cdot}{N} - \stackrel{\cdot}{C}R_2 \longrightarrow R_2C = \stackrel{\cdot}{N} - \stackrel{\cdot}{C}R_2 \qquad Azomethine ylide$$

$$R_2\stackrel{\cdot}{C} - \stackrel{\cdot}{N} - \stackrel{\cdot}{O}: \longrightarrow R_2C = \stackrel{\cdot}{N} - \stackrel{\cdot}{O}: \qquad Nitrone$$

$$R_2\stackrel{\cdot}{C} - \stackrel{\cdot}{O} - \stackrel{\cdot}{O}: \longrightarrow R_2C = \stackrel{\cdot}{O} - \stackrel{\cdot}{O}: \qquad Carbonyl oxide$$

## 1,3-Dipolar Cycloaddition Reaction (Intermolecular)

#### A. Intermolecular cycloaddition

$$O_2N$$
 $N=\tilde{N}=\tilde{N}+$ 
 $N=\tilde{N}$ 
 $N=\tilde{N}$ 

$$CH_2N_2 + H_2C = CH \longrightarrow O \longrightarrow N$$

PhCH=
$$\stackrel{\uparrow}{N}$$
CH<sub>3</sub> + H<sub>2</sub>C=CHC=N  $\stackrel{CH_3}{\longrightarrow}$   $\stackrel{CH_3}{\longrightarrow}$   $\stackrel{CH_3}{\longrightarrow}$   $\stackrel{O}{\longrightarrow}$   $\stackrel$ 

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

### 1,3-Dipolar Cycloaddition Reaction (Intramolecular)

#### B. Intramolecular cycloaddition

7g (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH=O 
$$\frac{\text{CH}_{3}\text{NHOH-HCl}}{\text{NaOCH}_{3} \text{ toluene.}}$$
 O CH<sub>3</sub> CH<sub>3</sub> 64-67% CH<sub>3</sub>

8h O-
N CH<sub>2</sub>CH=CH<sub>2</sub> toluene
$$\Delta$$
 N O
 $\Delta$  1) H<sub>2</sub>, Pd/C
 $\Delta$  CH<sub>3</sub>N OH

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### Thank You



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