

Carbenes and Nitrenes (Lecture 4)

1 Introduction

1.1 Review of Carbon Valencies and Hybridization



Methane
CH₄
*sp*³



Methyl anion
CH₃⁻
*sp*³



Methyl radical
CH₃[·]
*sp*²



Methyl cation
CH₃⁺
*sp*²

2 Carbenes

2.1 Definition

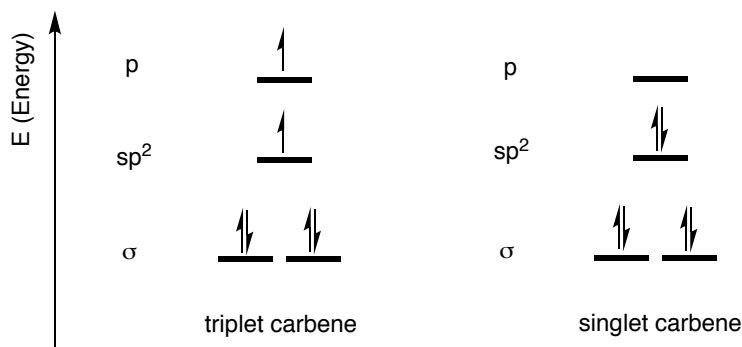
'Carbenes are neutral species containing a divalent carbon atom with an electron sextet'

Carbenes are classified as either singlet or triplet carbenes depending upon their electronic structure. Both types are very electron deficient (c.f. octet rule) and therefore highly reactive.

2.2 Comparison Between Singlet and Triplet Carbenes

2.2.1 Spin State

Singlet carbenes are closed-shell species, whereas triplet carbenes have two unpaired electrons. The total spin of a singlet carbene is 0, so it is diamagnetic. Conversely, triplet carbenes are paramagnetic, possessing a total spin of 1, and can be detected by electron paramagnetic resonance spectroscopy (EPR). Usually, triplet carbenes are lower in energy than singlet carbenes because of Hund's rules (reduced electronic repulsion).



2.2.2 Possible Hybridization and Geometry of Methyl Carbenes

From X-ray structures (see also subchapter 5.6.1) we know that both singlet and triplet states are bent.

Structure			
Hybridization	<i>sp</i> ²	<i>sp</i> ²	<i>sp</i>
Geometry	bent	bent	linear (not observed)
State	singlet	triplet	triplet





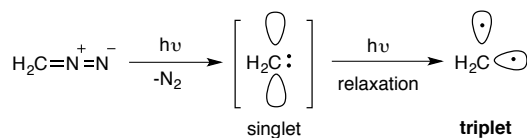
2.2.3 Bond Angles

The bond angles in triplet carbenes are larger than in singlet carbenes due to less electronic repulsion: triplet carbenes have only 1 electron in the sp^2 -orbital, while singlet carbenes have 2 electrons in the sp^2 -orbital.

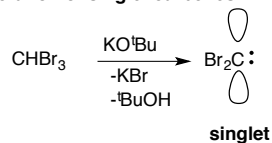
	Triplet carbene	Singlet carbene
Bond angle	130-150°	100-110°

2.2.4 Difference in Reactivity between Singlet and Triplet Carbenes

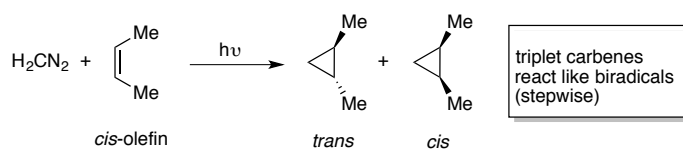
Generation of triplet carbenes



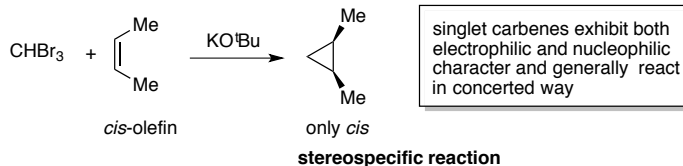
Generation of singlet carbenes



Different reactivities

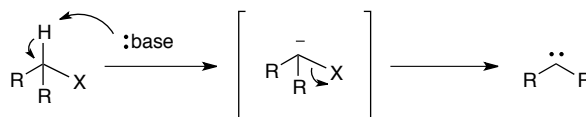


triplet carbenes react like biradicals (stepwise)

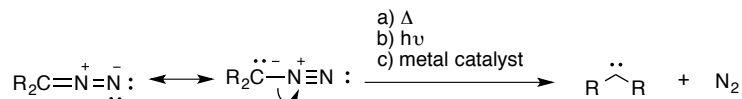


singlet carbenes exhibit both electrophilic and nucleophilic character and generally react in concerted way

3 Generation of Carbenes

3.1 By α -Elimination

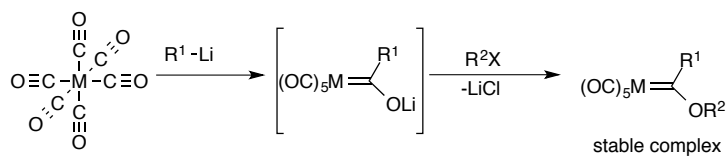
3.2 From Diazo Compounds



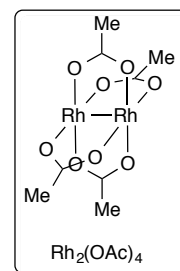
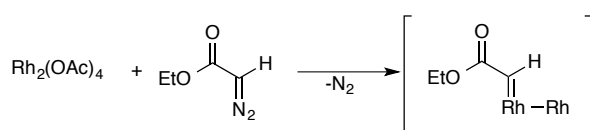
4 Carbenoids (Metal Stabilized Carbenes)

4.1 Generation

Fischer Route



From Diazo Compounds

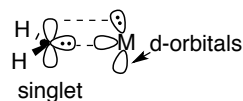


4.2 Properties

Improved thermodynamic and kinetic stability with respect to the non-stabilized carbenes.

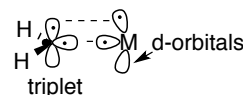
Fischer Carbenes

- low oxidation state metals
- middle and late transition metals Fe(0), Mo(0), Cr(0), W(0)
- π -acceptor metal ligands
- π -donor substituents on methylene group (-OR or -NR₂)

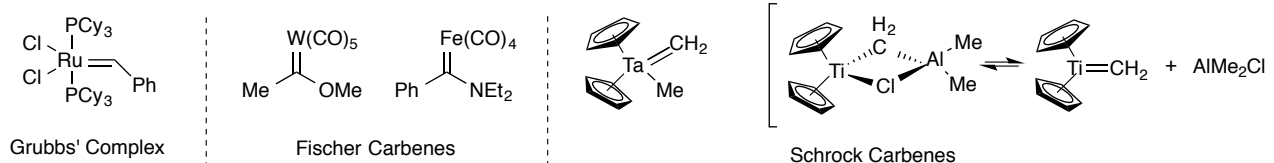


Schrock Carbenes

- high oxidation states metals
- early transition metals Ti(IV), Ta(V)
- non π -acceptor ligands non π -donor substituents

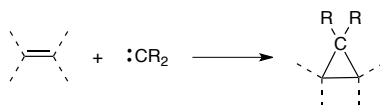


4.3 Examples

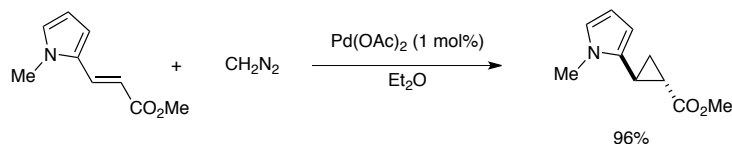


5 Reactions of Carbenes and Carbenoids

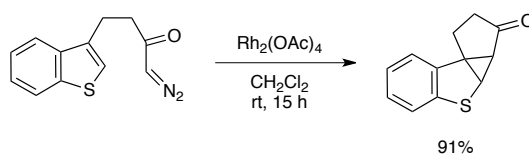
5.1 Cyclopropanation



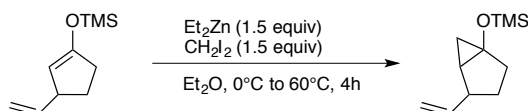
5.1.1 Intermolecular Reaction



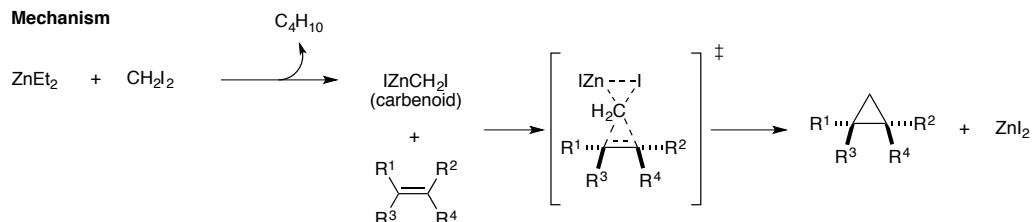
5.1.2 Intramolecular Reaction



5.1.3 Simmons-Smith



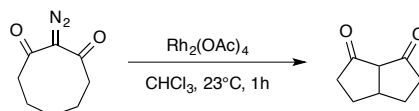
Mechanism



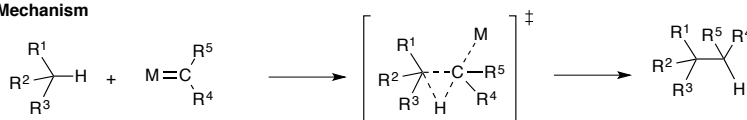


A directing effect can be observed with functional groups that contain heteroatoms (strong for e.g. OH, OMe, OBn, NHR; weaker for OAc, NHAc, NHBoc). If there are multiple double bonds present in the molecule, the reaction takes place at the double bond closest to the heteroatom. Electron rich double bonds react faster than electron deficient double bonds.

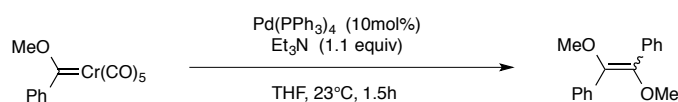
5.2 C–H Insertion Reaction



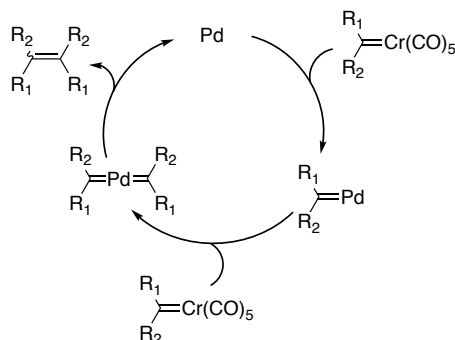
Mechanism



5.3 Dimerization Reaction

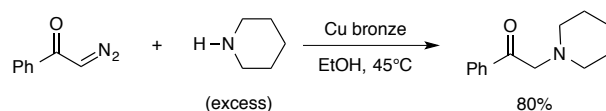


Mechanism

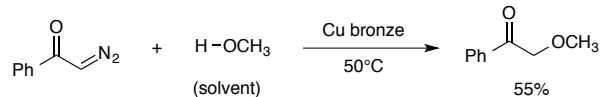


5.4 O–H and N–H Insertion

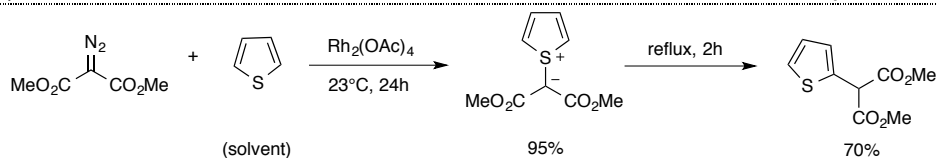
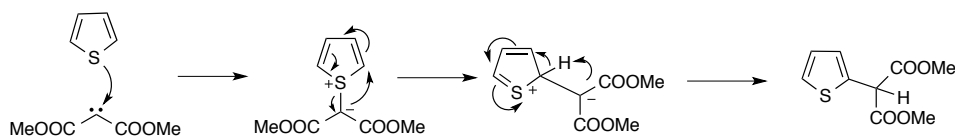
N–H Insertion



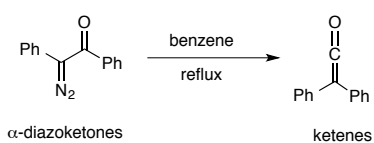
O–H Insertion



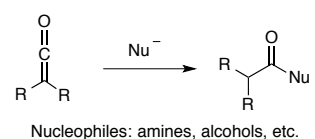
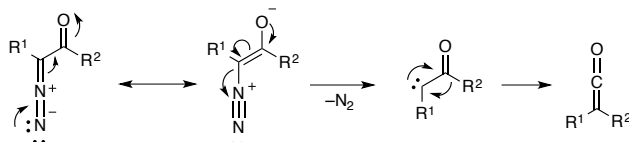
5.5 Ylide Formation

**Mechanism**

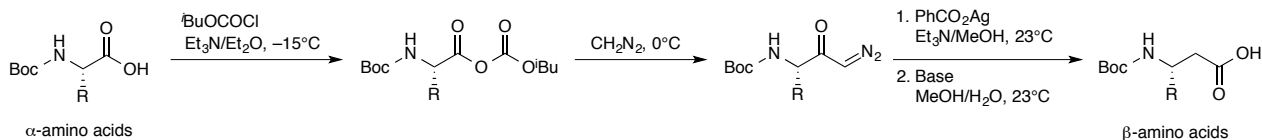
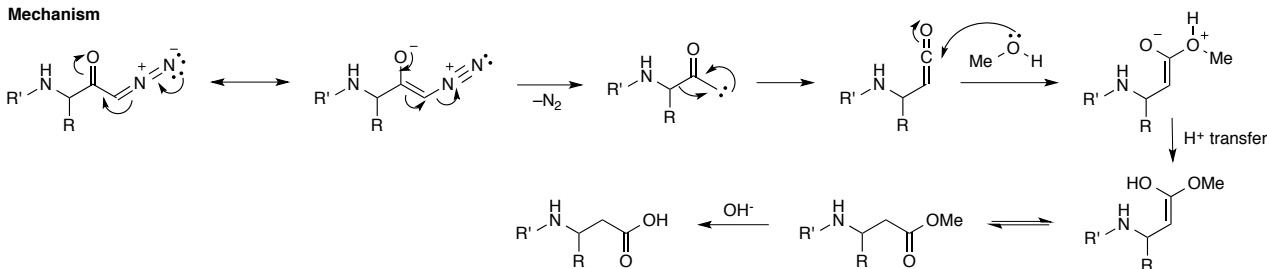
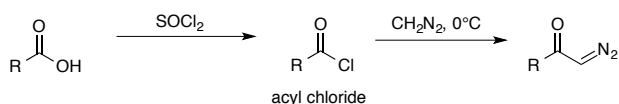
5.6 Wolff Rearrangement



Reminder:

**Mechanism**

5.6.1 Arndt-Eistert Homologation

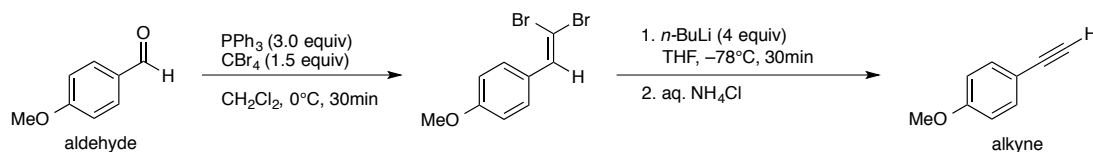
**Mechanism****Other Variant for the Synthesis of the Diazo Intermediate - Using SOCl₂**

In the first step, the carboxylic acid needs to be activated i.e. by conversion to the acid chloride (using SOCl₂). However, in the case of α -amino acid homologation the conversion to an acyl chloride would lead to undesired epimerization. To prevent this, an acyl carbonate can be used as activated intermediate.

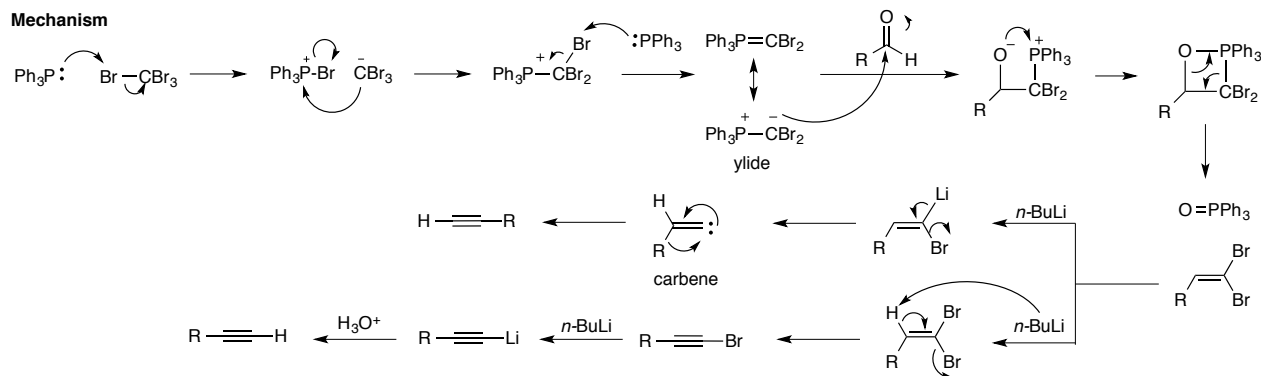
5.7 Alkyne Synthesis

5.7.1 Corey-Fuchs Reaction

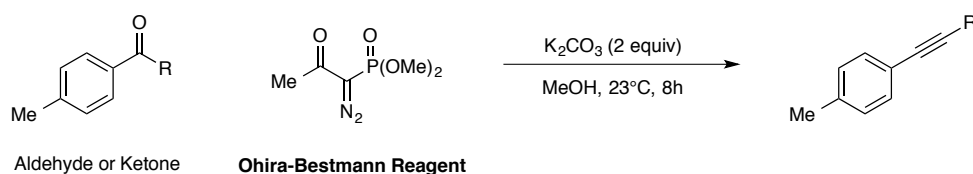
Little is known about the reaction mechanism from the conversion of the dibromo olefin to the alkyne. However, one of the accepted mechanisms proceeds via a carbene intermediate.



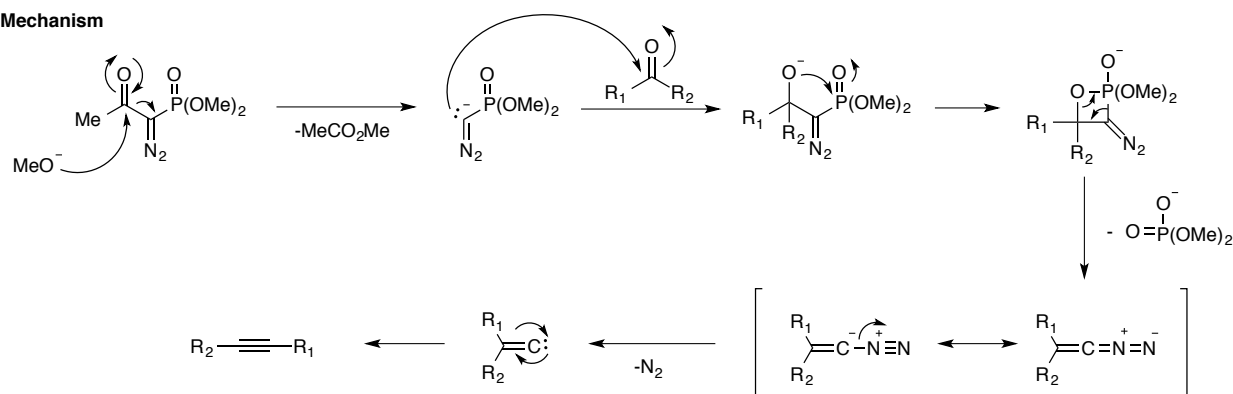
Mechanism



5.7.2 Seyferth-Gilbert Homologation



Mechanism



6 N-heterocyclic Carbenes (NHCs)

See lecture on Benzoin and related reactions.

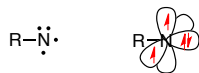




7 Nitrenes

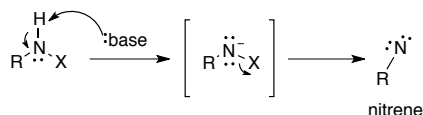
7.1 Structure and Hybridization

Nitrenes are monovalent nitrogen analogs of carbenes, in which the nitrogen atom possesses only six valence electrons. In nitrenes the triplet state is lower in energy than the singlet state.

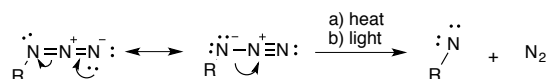


7.2 Generation

7.2.1 By α -Elimination

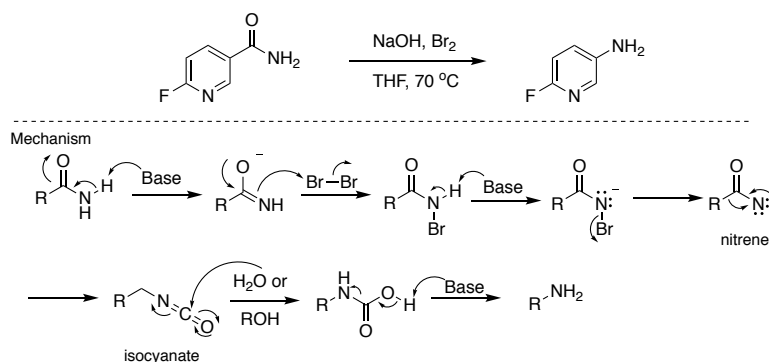


7.2.2 From Azides

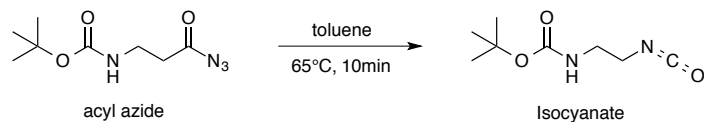


7.3 Hoffman-Type Rearrangements

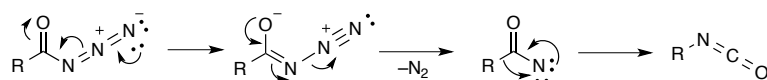
7.3.1 Hoffman Rearrangement



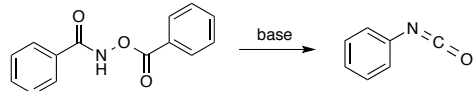
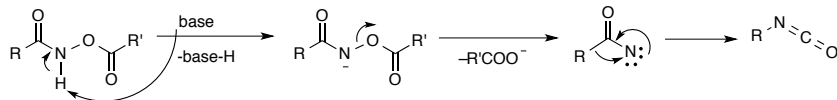
7.3.2 Curtius Rearrangement



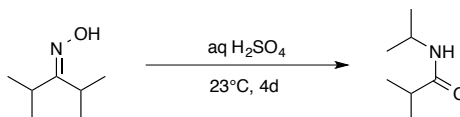
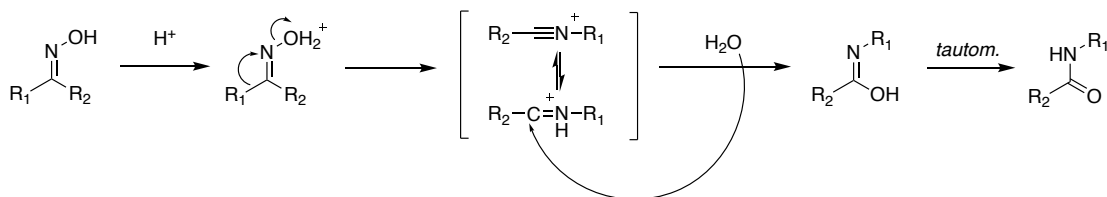
Mechanism



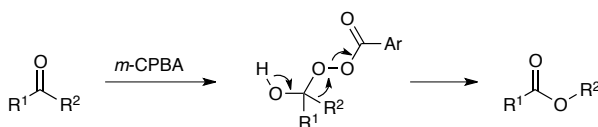
7.3.3 Lossen Rearrangement

**Mechanism**

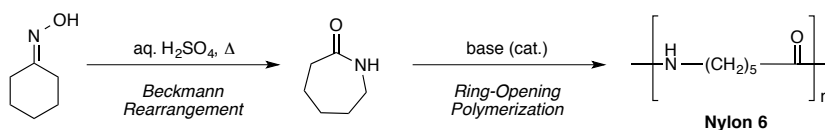
7.4 Beckmann Rearrangement

**Mechanism**

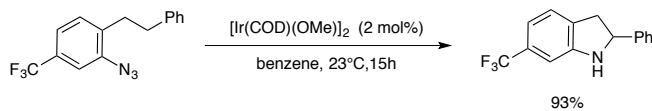
7.4.1 Mechanistic Analogy to Baeyer-Villiger Reaction



7.4.2 Industrial Nylon Synthesis



7.5 Metal-catalyzed C–H Insertion

**Mechanism**