



Advanced Organic Chemistry/ Organic Synthesis – CH 621

Organometallics

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Organometallics – General Principles



Metal – Carbon bond

- Polarization
- C-C bond forming reactions
- Sensitive reactions and reagents

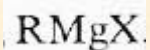
Grignard reagents and electrophiles

Other organometallics and electrophiles

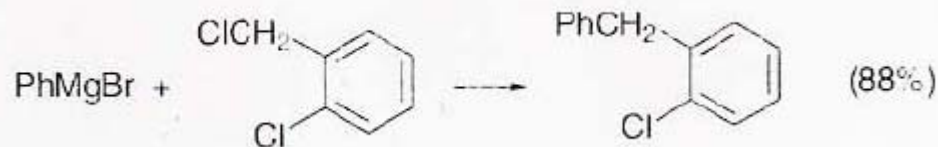
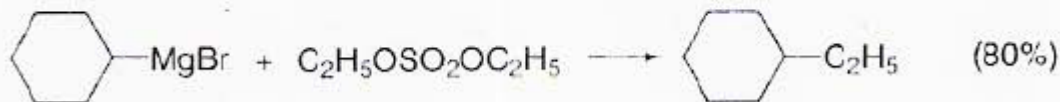
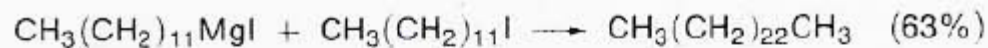
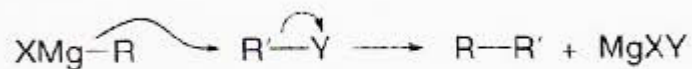
Reactions of nucleophiles derived from alk-1-yne

Organometallics – Grignard reagent

Grignard reagents

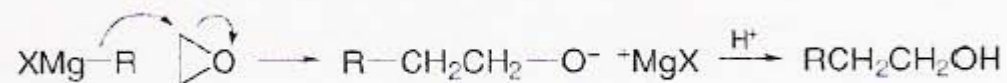


Alkylation



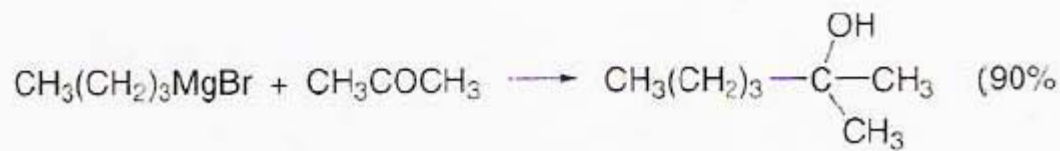
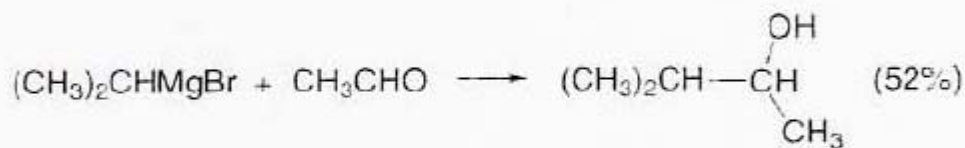
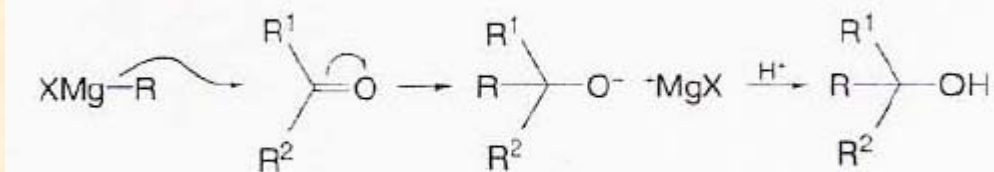
Organometallics – Grignard reagent

Alkylation



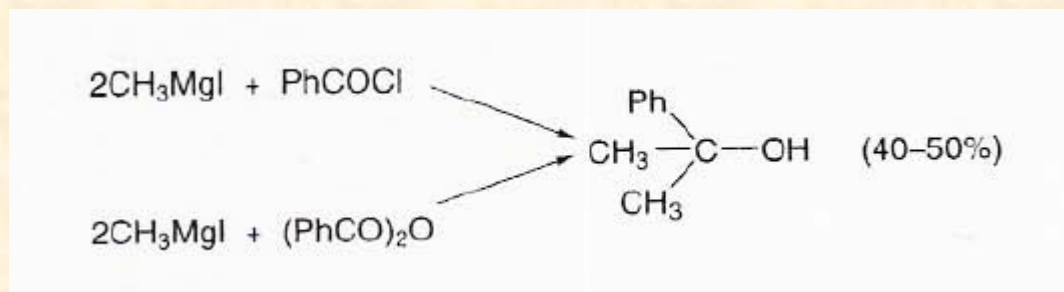
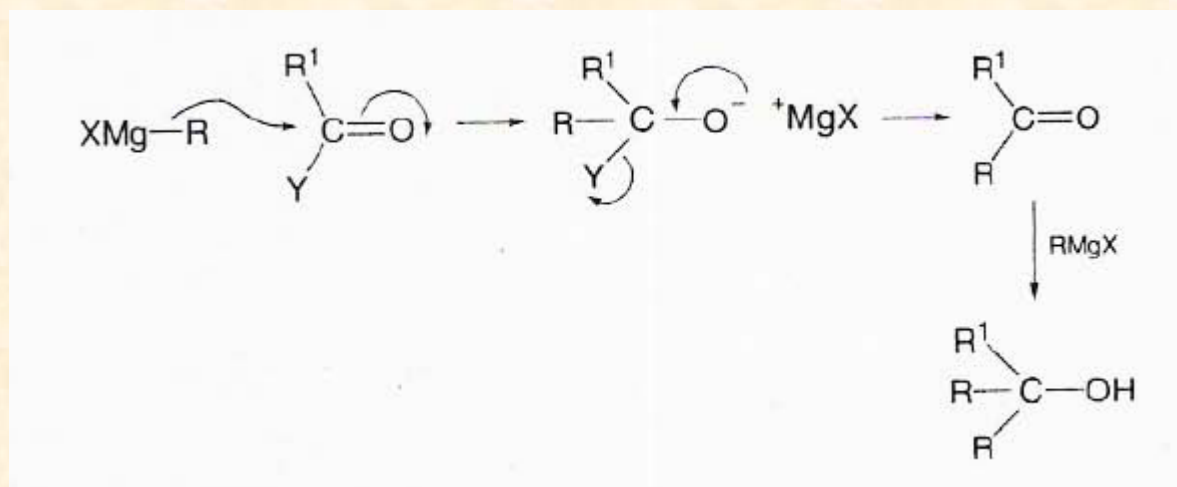
Organometallics – Grignard reagent

Reactions with carbonyl compounds



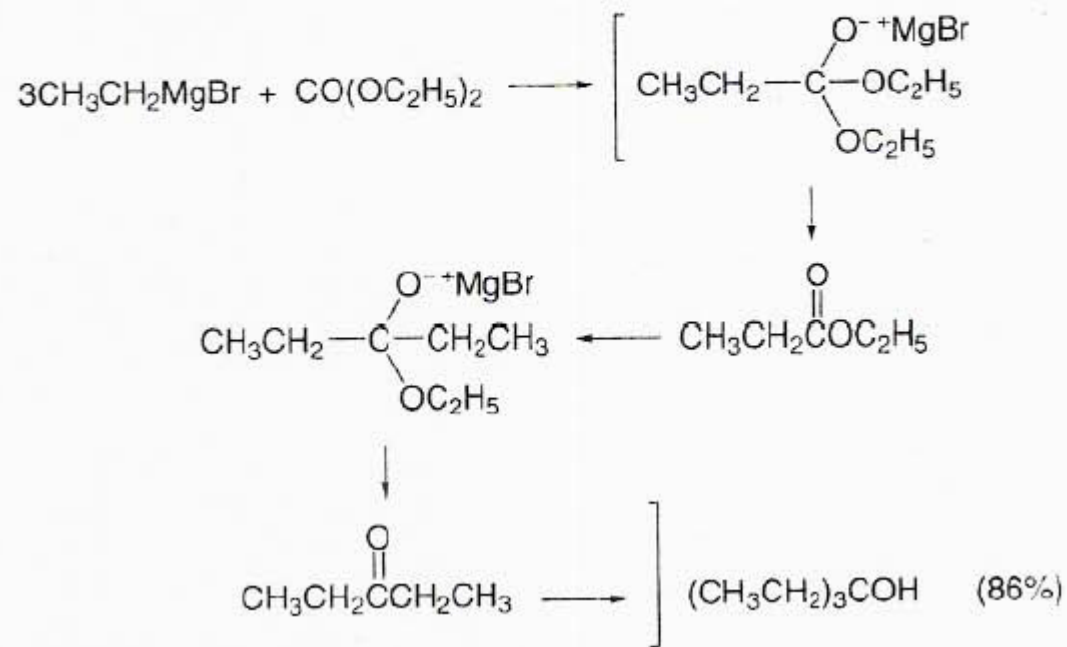
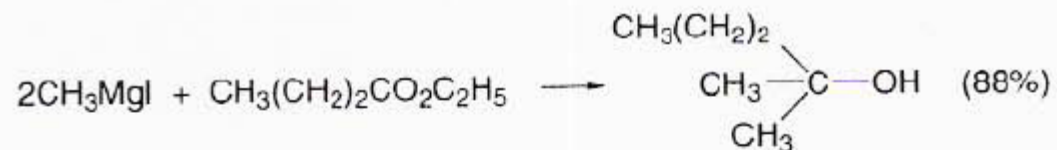
Organometallics – Grignard reagent

Reaction with carboxylic acid derivatives



Organometallics – Grignard reagent

Reaction with carboxylic acid derivatives

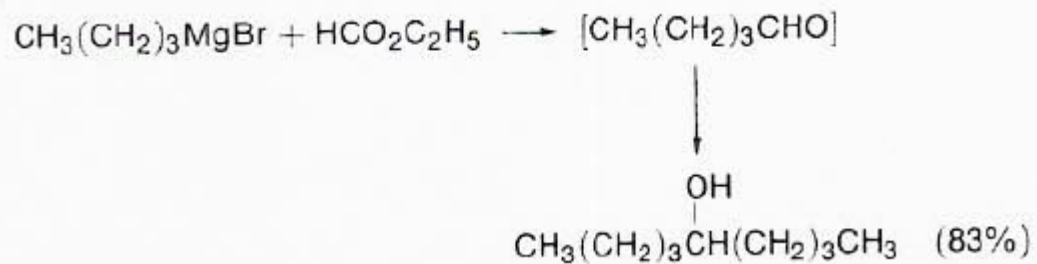


Organometallics – Grignard reagent

Reaction with carboxylic acid derivatives

Formate esters

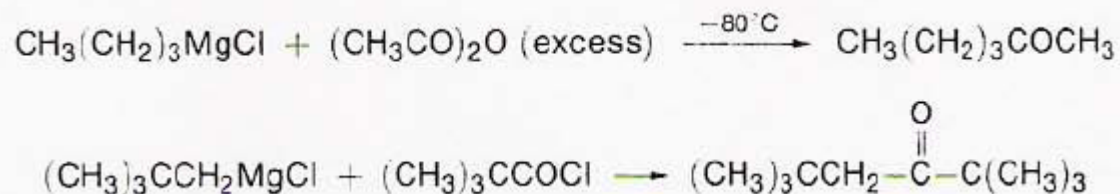
secondary alcohols



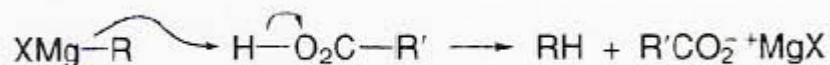
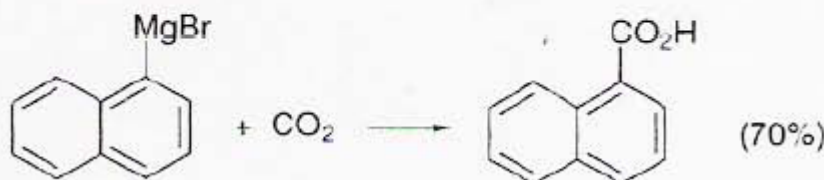
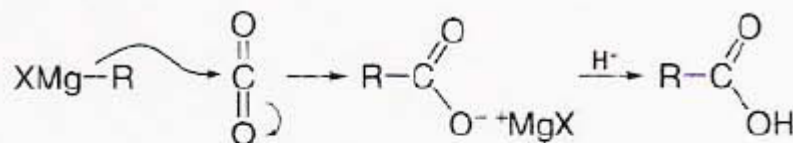
Organometallics – Grignard reagent

Reaction with carboxylic acid derivatives

when the acyl compound is used in excess

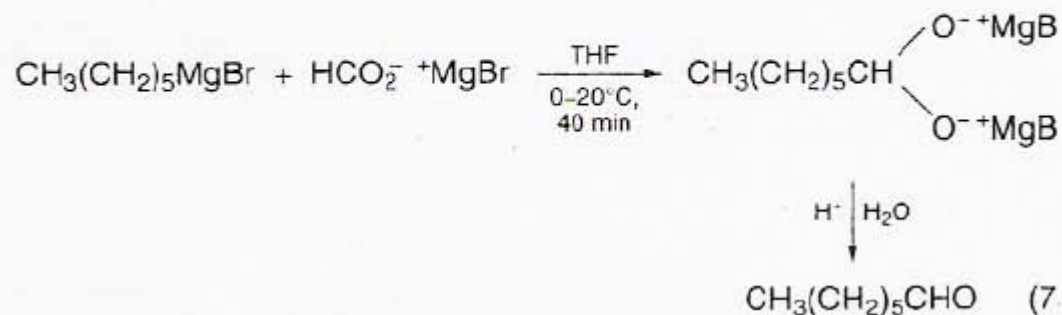


carbon dioxide

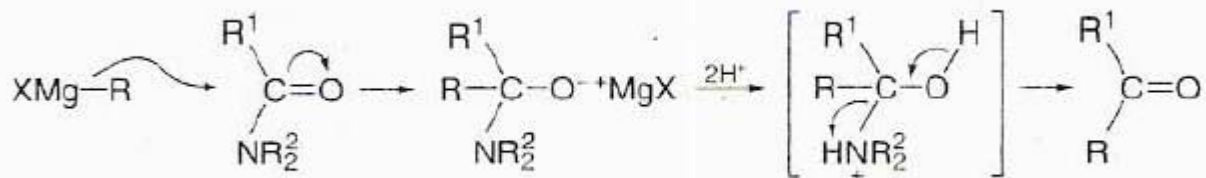


Organometallics – Grignard reagent

Reaction with carboxylic acid derivatives

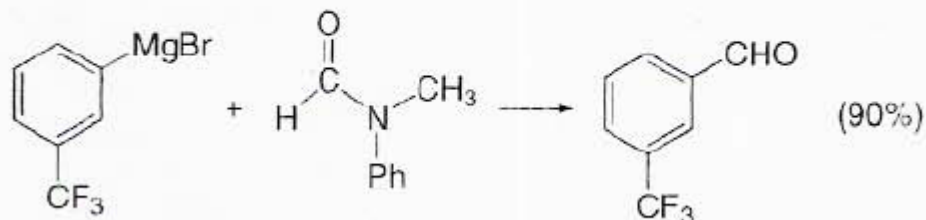
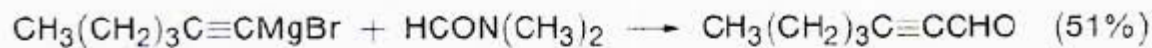


tertiary amides



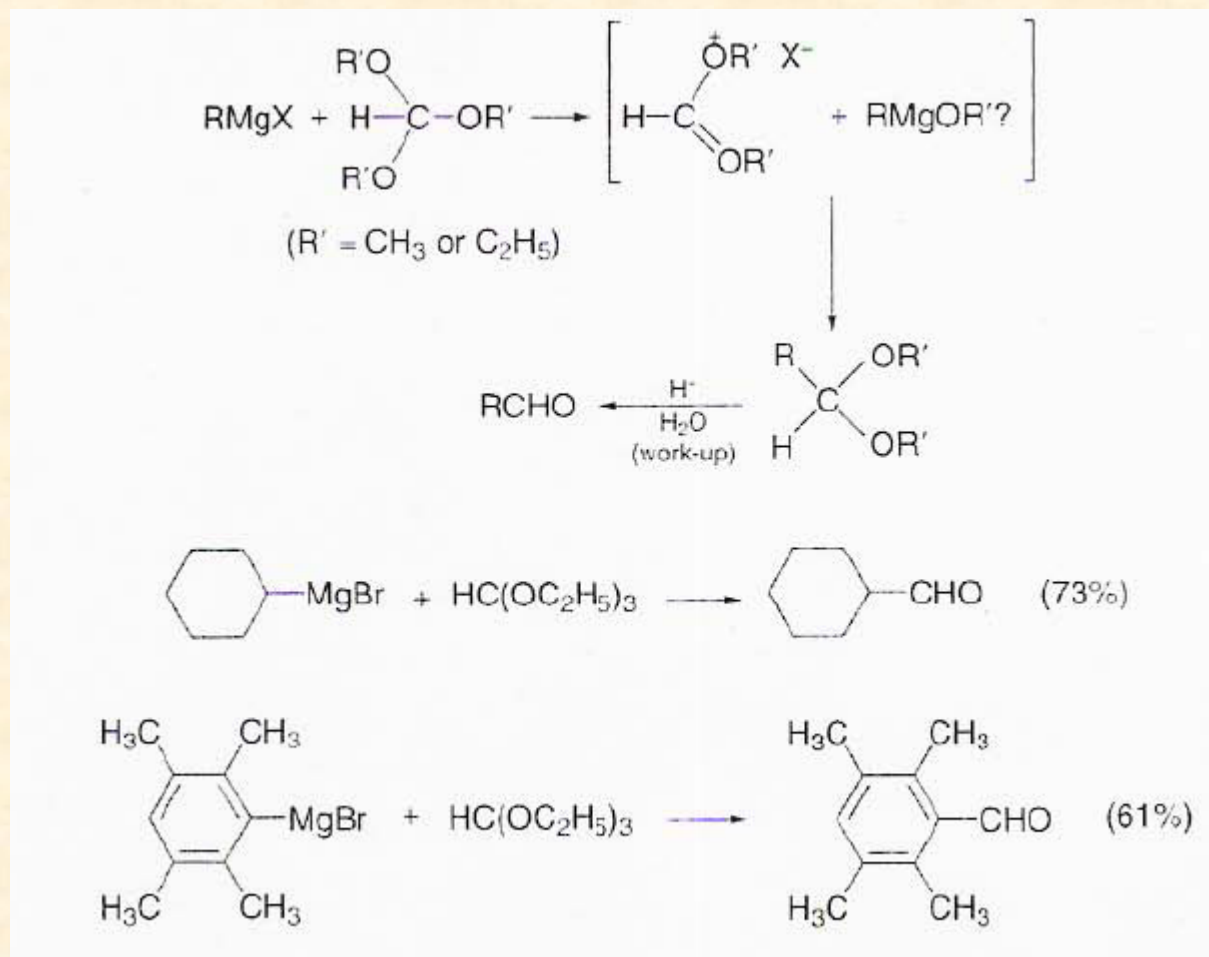
Organometallics – Grignard reagent

Reaction with carboxylic acid derivatives



Organometallics – Grignard reagent

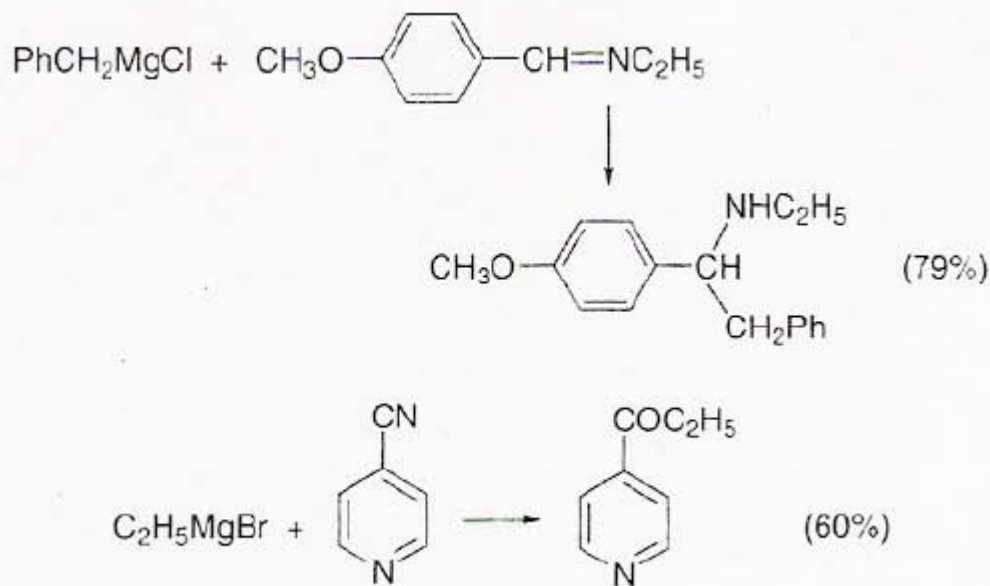
Reaction with carboxylic acid derivatives



orthoformate esters

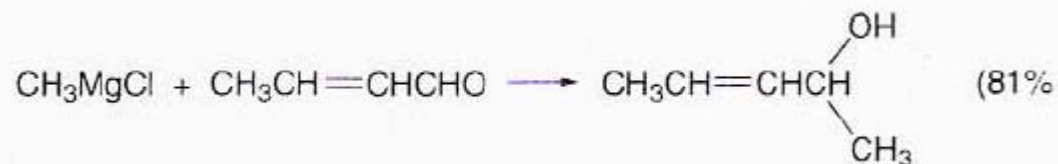
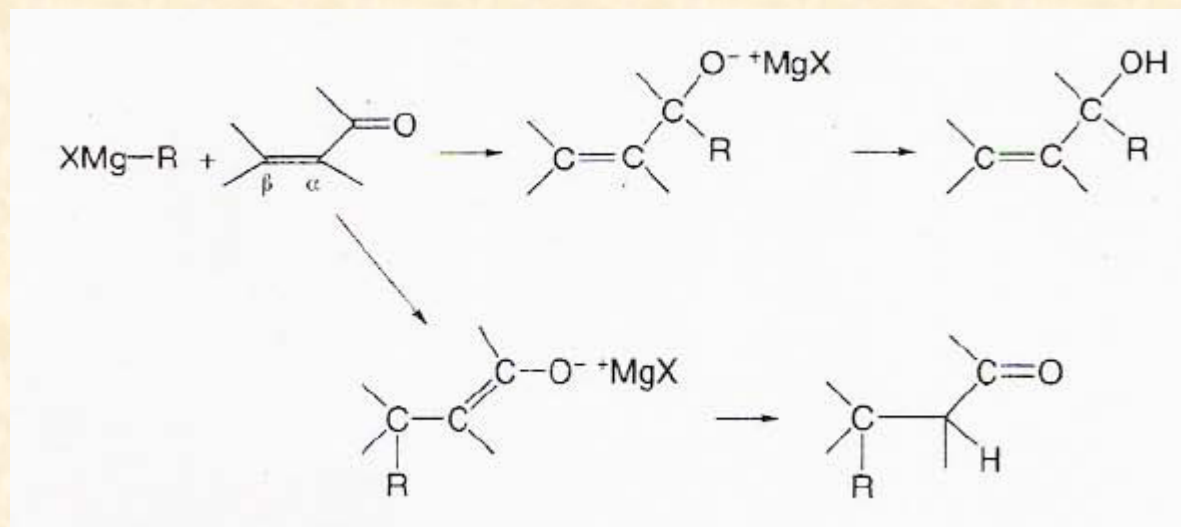
Organometallics – Grignard reagent

Reactions with compounds containing $>C=N-$ and $-C\equiv N$.



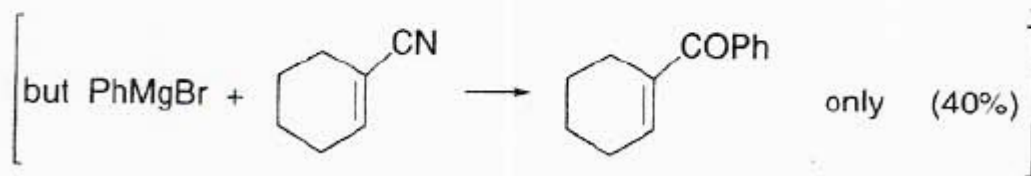
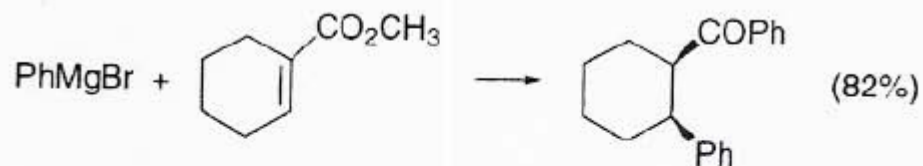
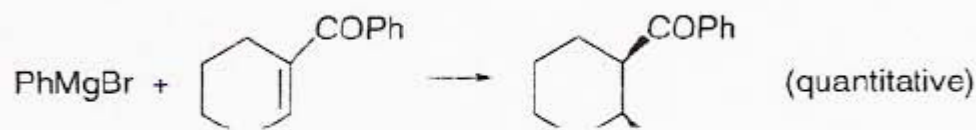
Organometallics – Grignard reagent

Reactions with $\text{>C}=\overset{\text{C}}{\overset{|}{\text{C}}}-\overset{\text{C}}{\overset{|}{\text{C}}}=\text{O}$ and related systems



Organometallics – Grignard reagent

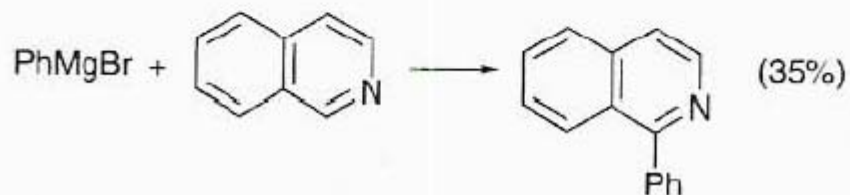
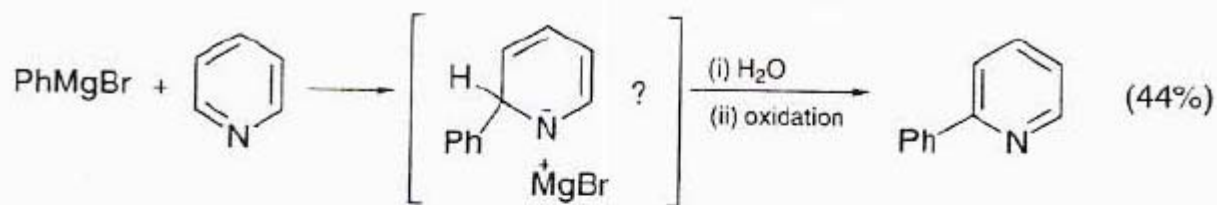
Reactions with $\text{>C}=\overset{|}{\text{C}}-\overset{|}{\text{C}}=\text{O}$ and related systems



Organometallics – Grignard reagent

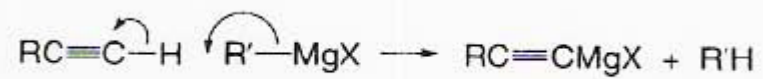
Reactions with >C=C-C=O and related systems

' π -deficient' heterocycles



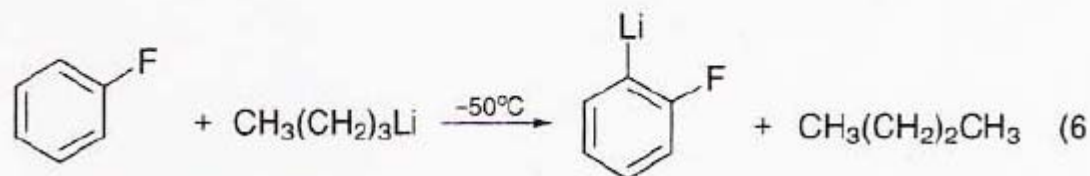
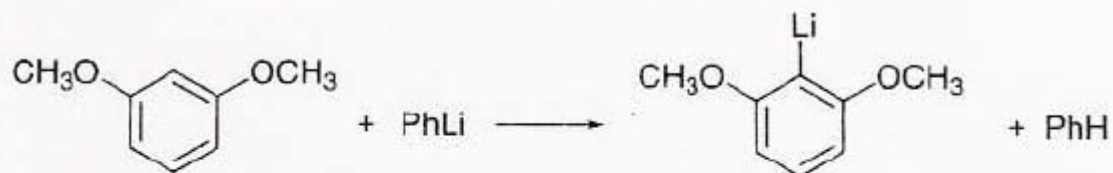
Organometallics – Grignard reagent

Alkenyl and alkynyl Grignard reagents



Organometallics – Other reagents

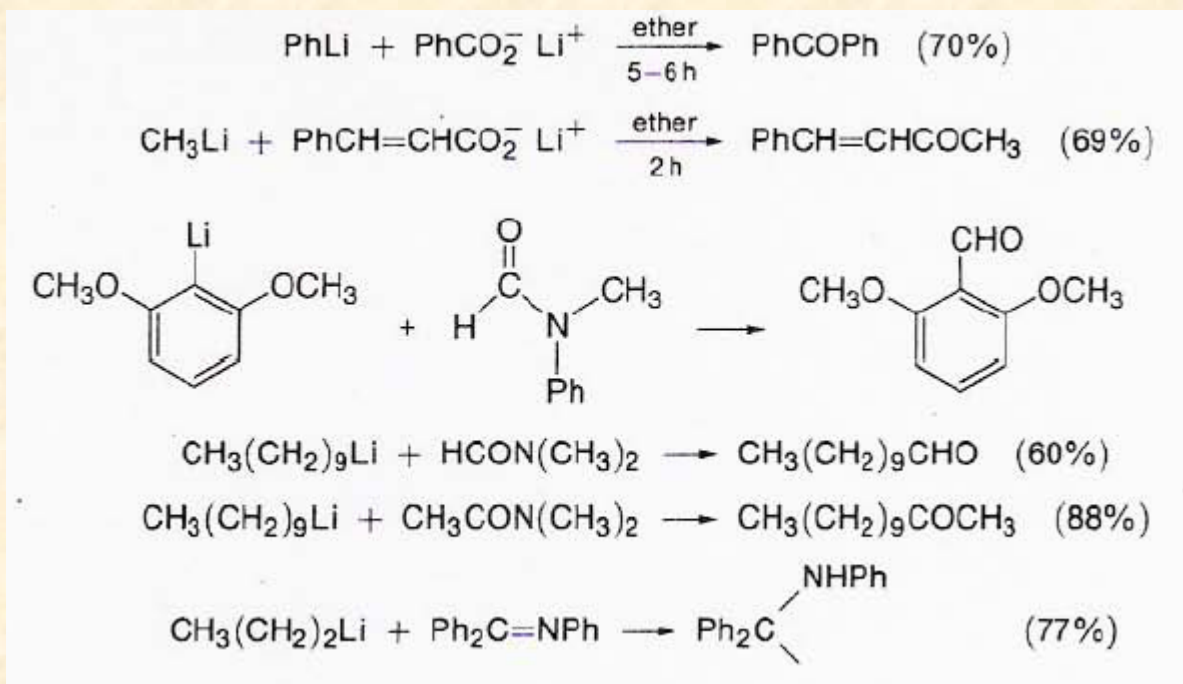
Organolithium reagents



Organometallics – Other reagents

Organolithium reagents

More nucleophilic than Grignard reagents!

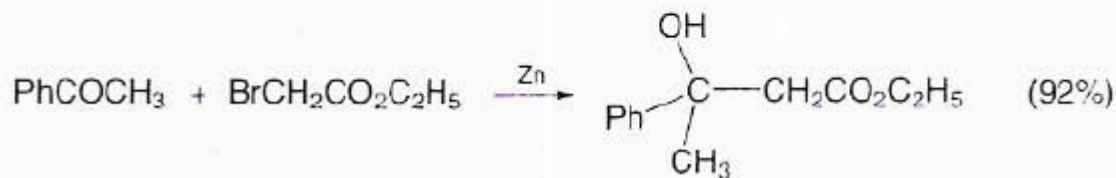
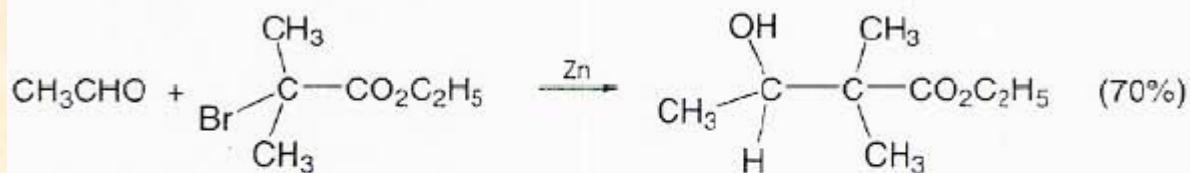
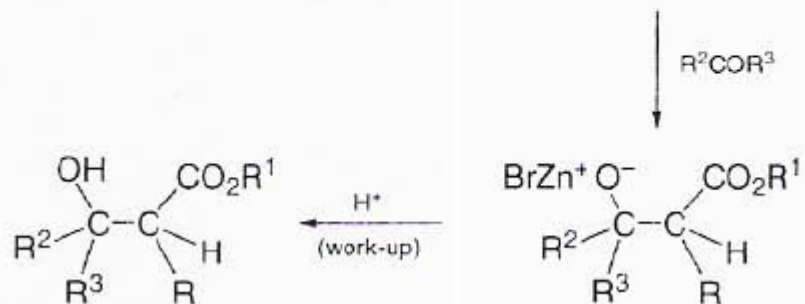
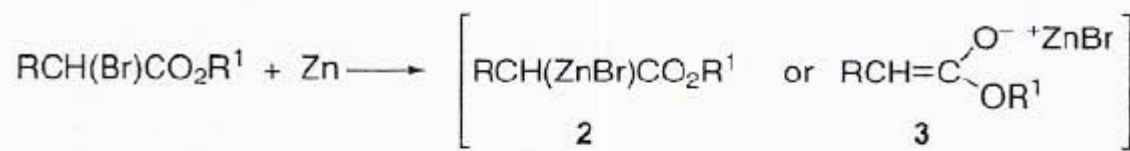


Organometallics – Other reagents

Organozinc and organocadmium reagents

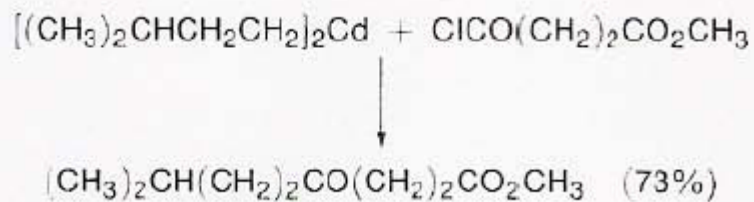
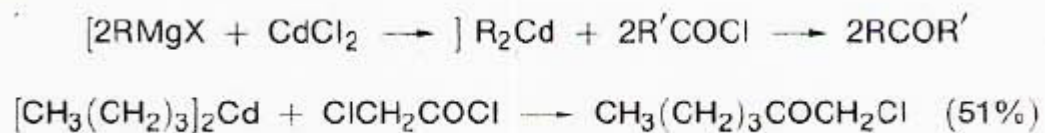
Less nucleophilic than Grignard reagents!

Reformatsky reaction



Organometallics – Other reagents

Organozinc and organocadmium reagents



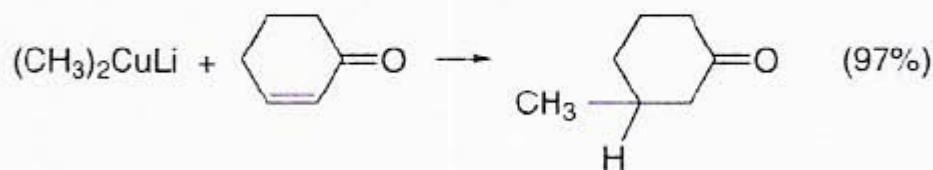
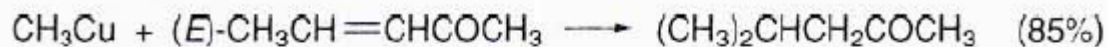
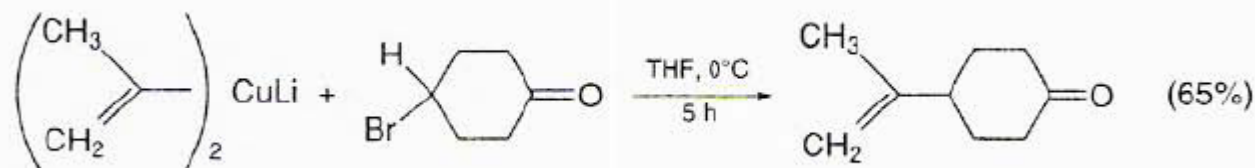
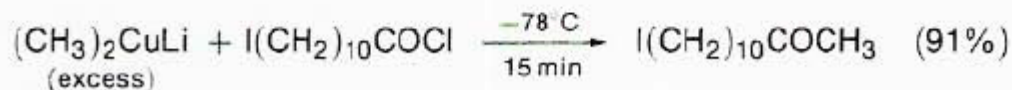
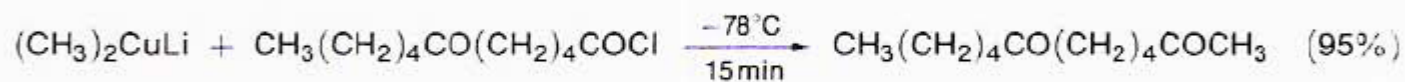
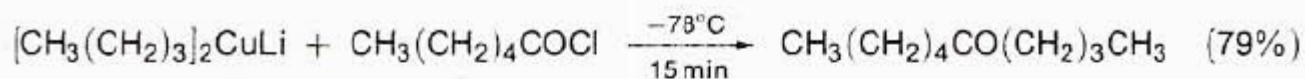
Organometallics – Other reagents

Organocopper(I) reagents



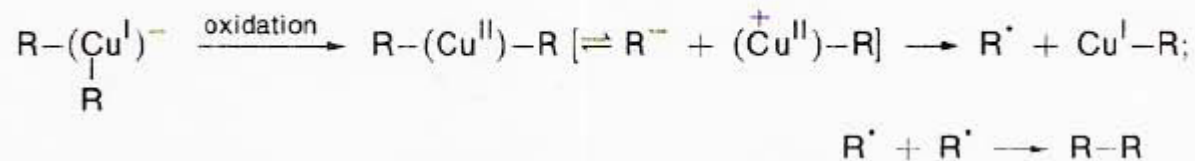
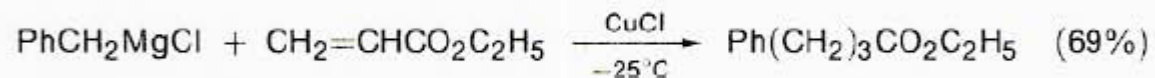
Organometallics – Other reagents

Organocopper(I) reagents



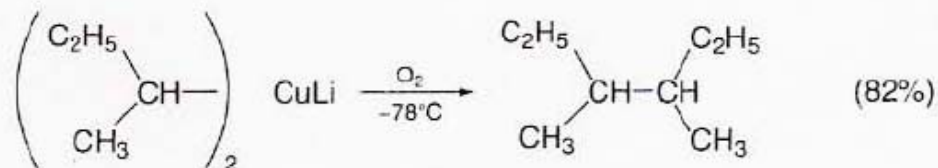
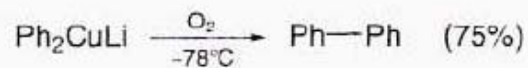
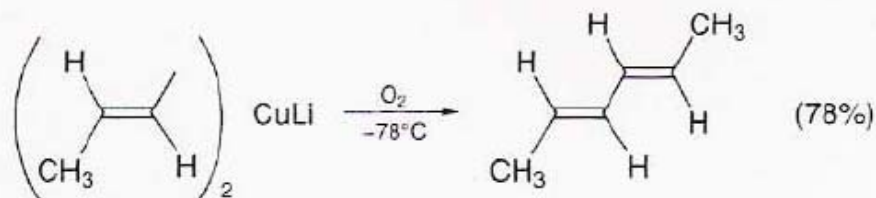
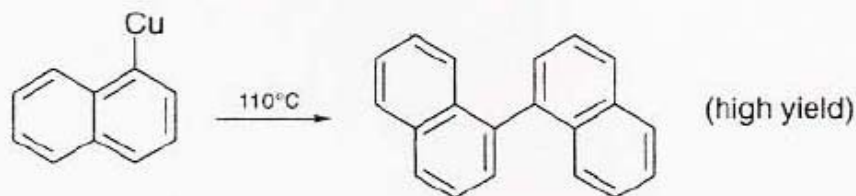
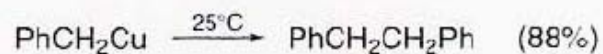
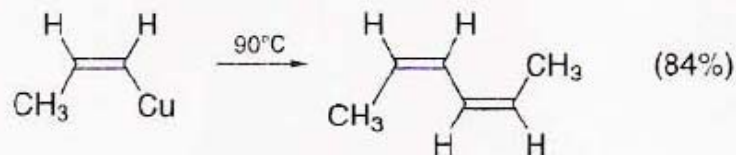
Organometallics – Other reagents

Organocopper(I) reagents



Organometallics – Other reagents

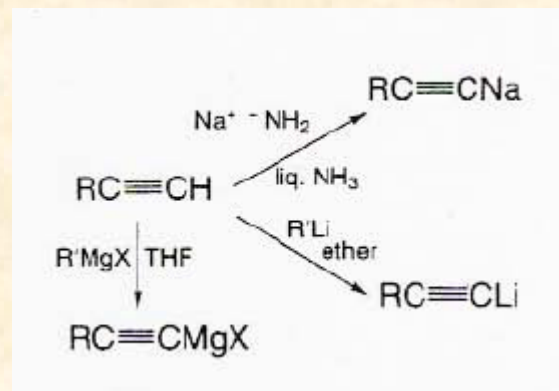
Organocopper(I) reagents



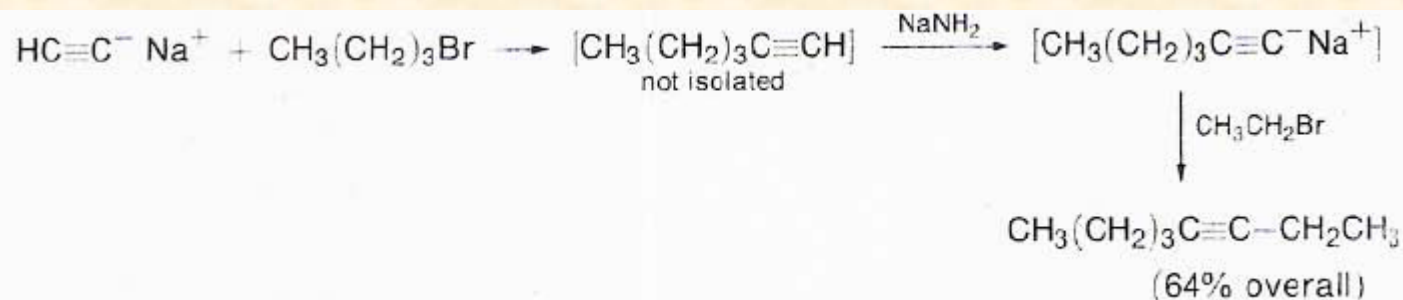
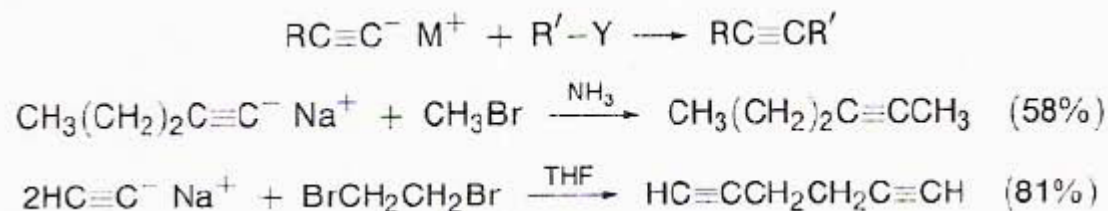
Organometallics – Nucleophiles from alk-1-ynes

Sodium, lithium and magnesium derivatives

Less powerful than
Grignard reagents!

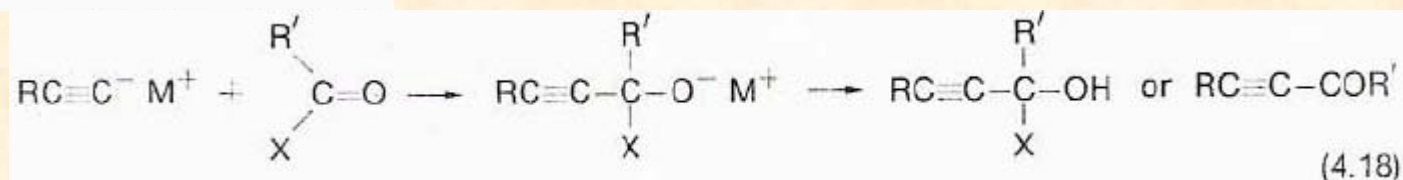


Alkylation:

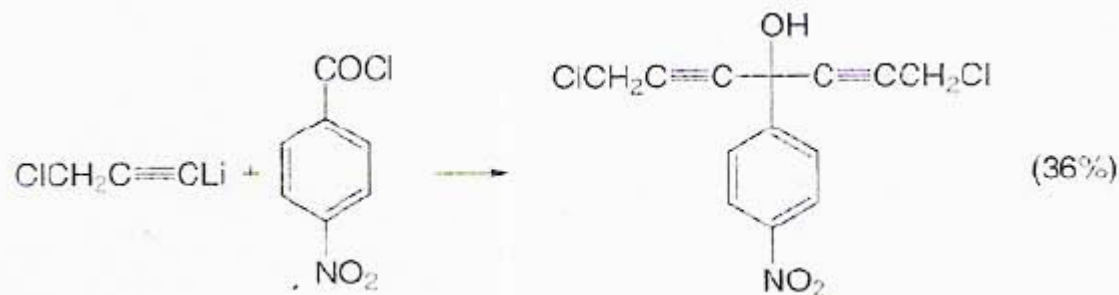
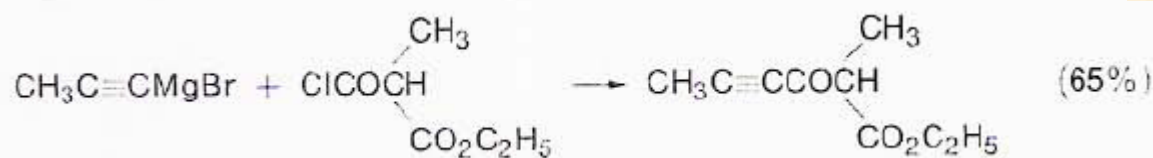
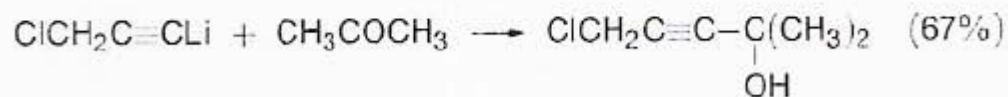


Organometallics – Nucleophiles from alk-1-ynes

Sodium, lithium and magnesium derivatives



Reactions with carbonyl compounds:

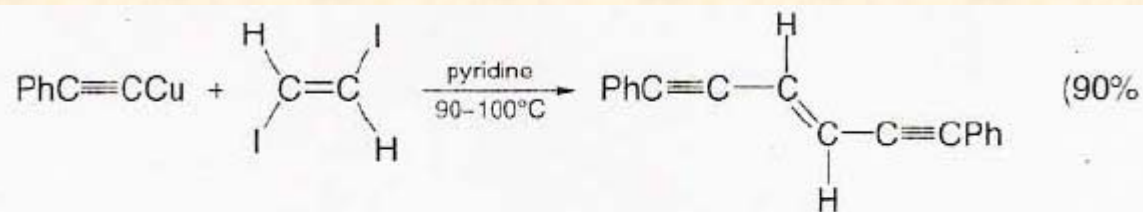


Organometallics – Nucleophiles from alk-1-ynes

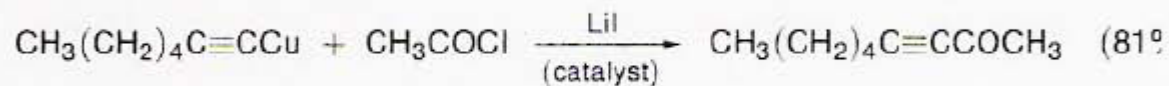
Alkynylcopper(I) compounds



Displacements of halogens
from 'unreactive' positions.



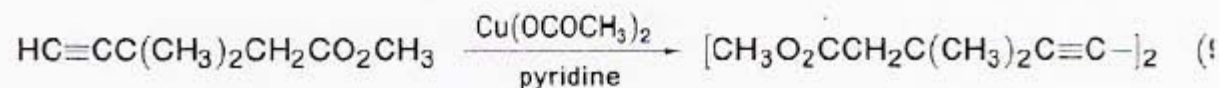
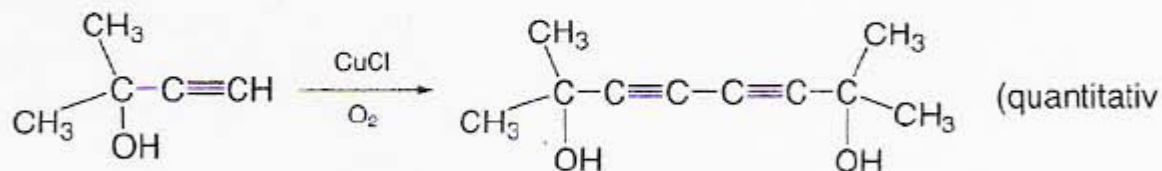
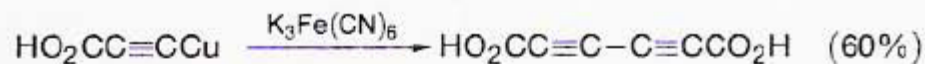
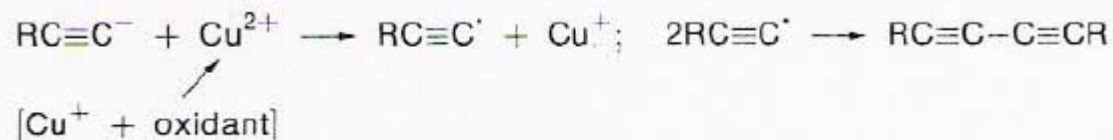
acyl chlorides



Organometallics – Nucleophiles from alk-1-ynes

Alkynylcopper(I) compounds

Coupling reactions



Organometallics – Nucleophiles from alk-1-ynes

Alkynylcopper(I) compounds

Coupling reactions

unsymmetrical diynes

