

Reactions Of Enolizable Compounds With C-Electrophiles

from chapter(s) _____ in the recommended text

A. Introduction

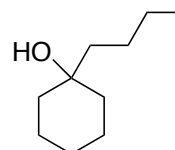
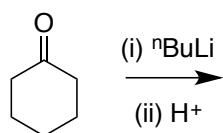
B. α -Alkylation Of Carbonyl Compounds Under Strongly Basic Conditions

C-Alkylation Of Ketones

nucleophilic

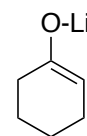
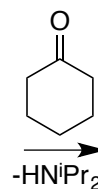
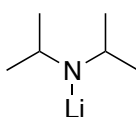
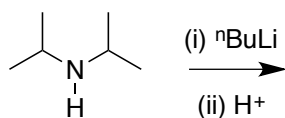
strong and *non-nucleophilic*.

hindered alkali



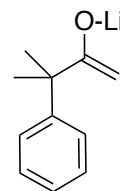
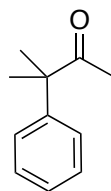
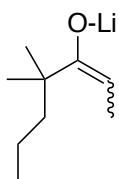
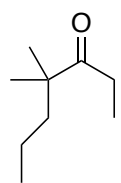
mostly

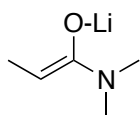
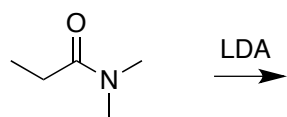
tertiary alcohol



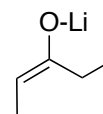
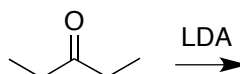
lithium diisopropylamide LDA
pKa 35

enolate

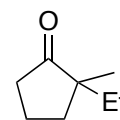
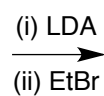
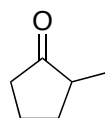
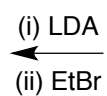
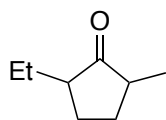




Z-enolate



draw E-enolate

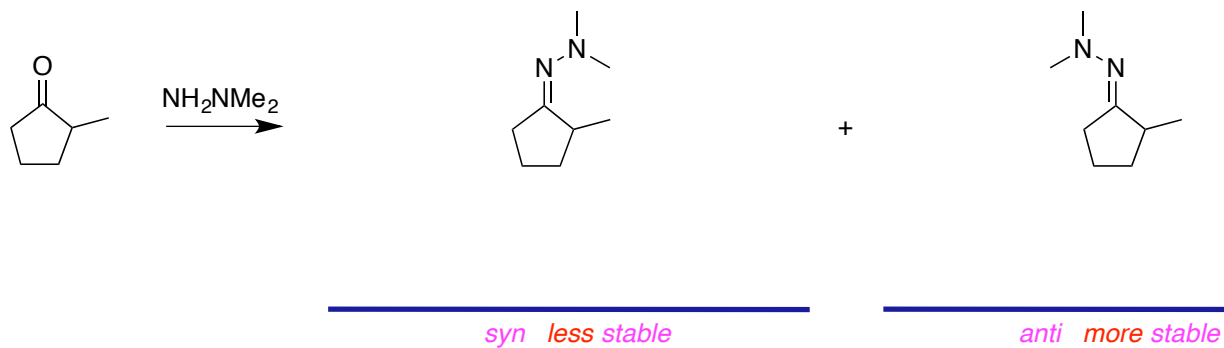
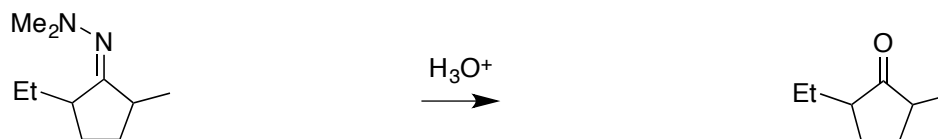
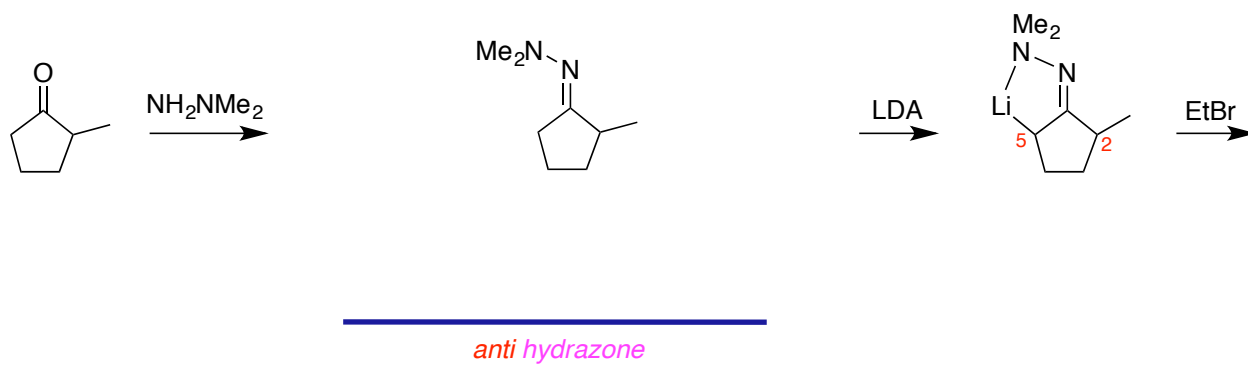


2,5-dialkyl product

2,2-dialkyl product

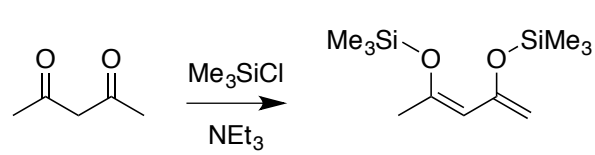
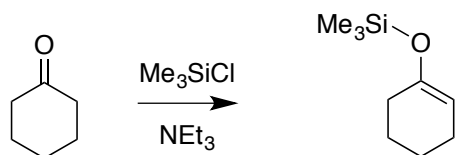
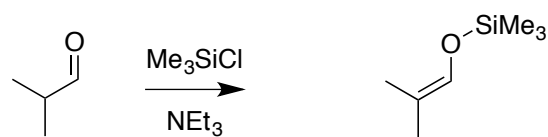
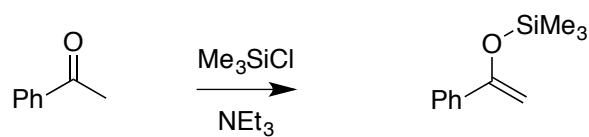
It is *difficult* to

Alkylation Of Hydrazones

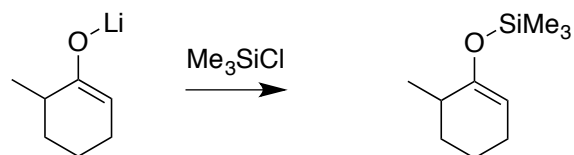
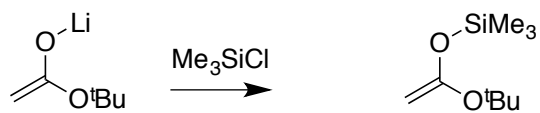
*thermodynamic**alkylation at least hindered carbon**2,5-dialkylation product*

Silylation and α -Silylation Of Aldehydes And Ketones

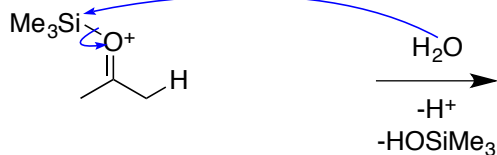
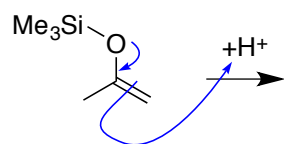
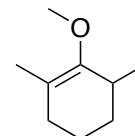
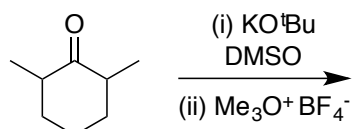
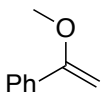
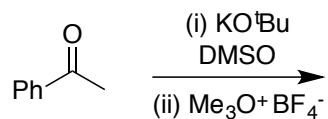
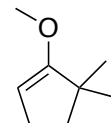
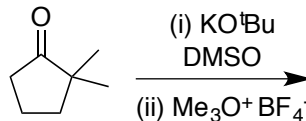
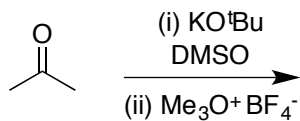
strong
O-atoms



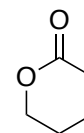
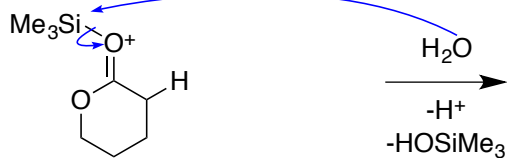
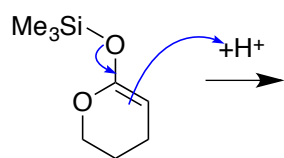
disilyl enol ether



carbon.
polar aprotic
O-alkylation
hard electrophiles
concentrated positive

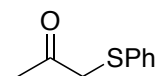
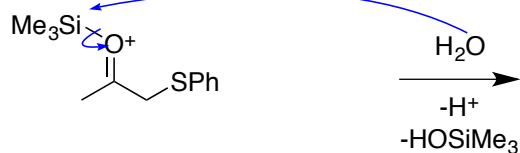
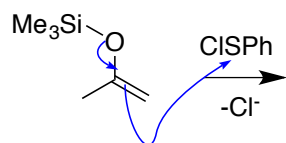


C-protonated form



C-protonated form

addition of a PhS⁺ electrophile

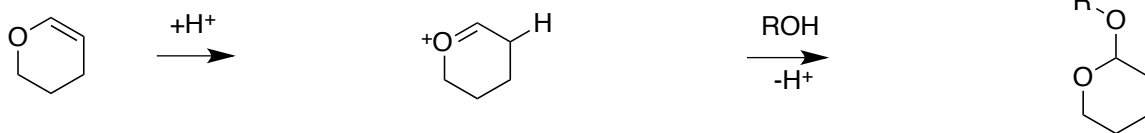


thioether silyloxonium ion

thioether

acetal; it is

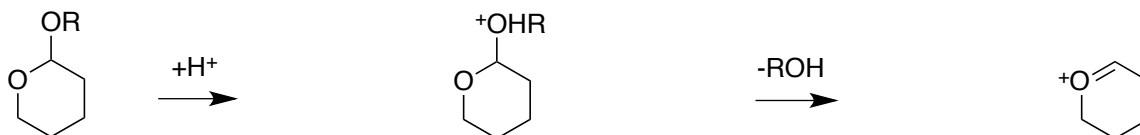
protonation then quench of the oxonium ion with an alcohol



dihydropyran

C-protonated form

THP-protected alcohol

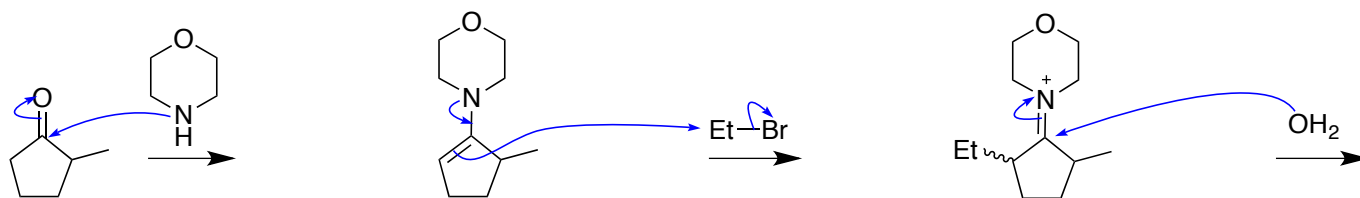


THP ether

C. α -Alkylation Of Carbonyl Compounds Under Near-neutral Conditions

Enamines From Ketones and Aldehydes

iminium ions



least hindered enamine

iminium



tetrahedral intermediate

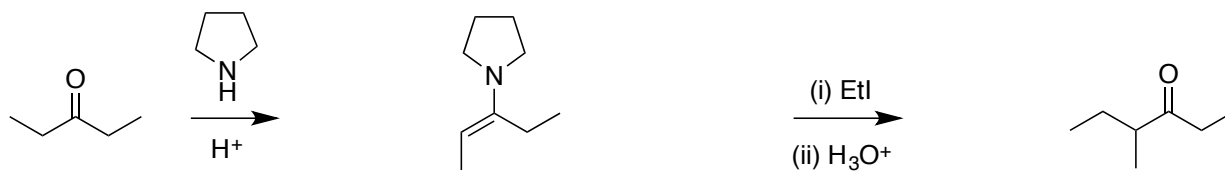
ammonium intermediate



protonated carbonyl

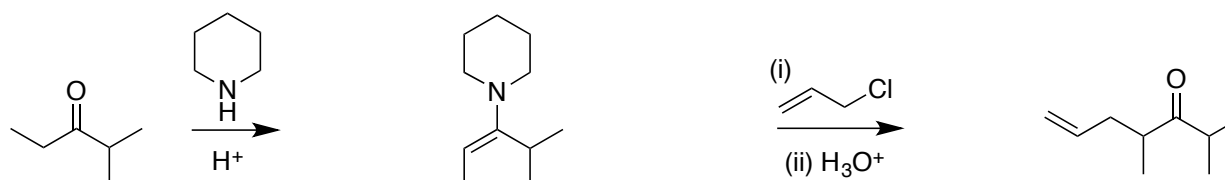
2

least substituted



enamine

4-methyl-3-hexanone



enamine

