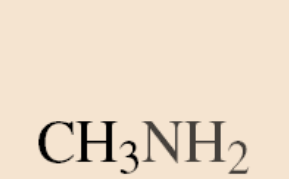
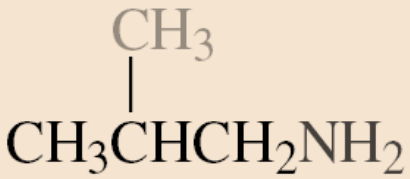
CHM-134 ORGANIC CHEMISTRY
CHAPTER-11: AMINES

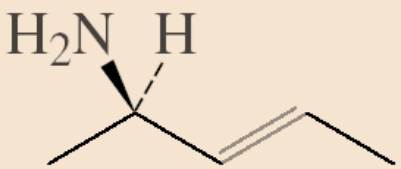
Primary amines



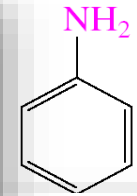
Methanamine



2-Methyl-1-propanamine

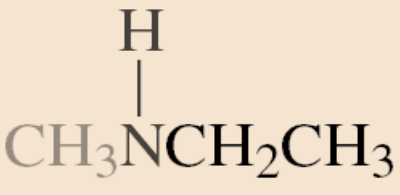


(*R*)-*trans*-3-Penten-2-amine



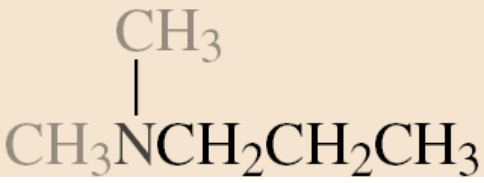
Benzenamine (Aniline)

Secondary amines



***N*-Methylethanamine**

Tertiary amines



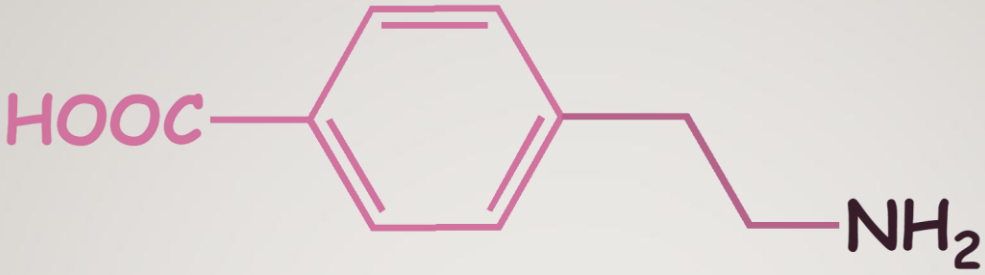
***N*,*N*-Dimethyl-1-propanamine**

Asst. Prof. Gülbin KURTAY

For more details please study: Organic Chemistry: Structure and Function Eighth Edition
K. Peter C. Vollhardt (Author), Neil E. Schore (Author) **ISBN-10:** 1319079458

10.1 NOMENCLATURE RULES

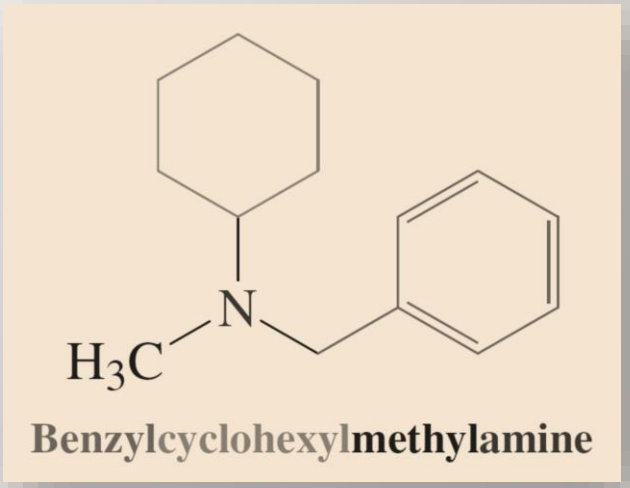
Substituent name: Amino-



4-(2-Aminoethyl)benzoic acid

Common names: Alkylamine

CH_3NH_2 **Methylamine**	$(CH_3)_3N$ **Trimethylamine**



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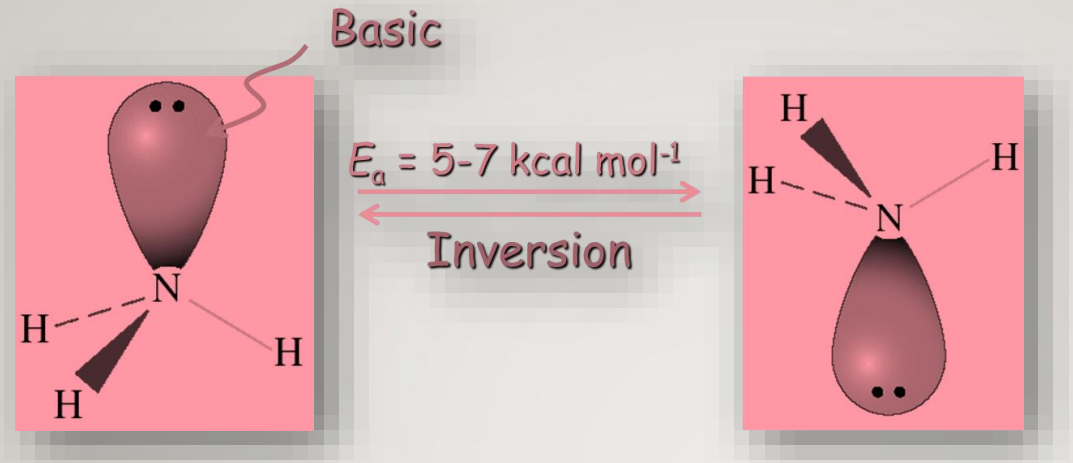
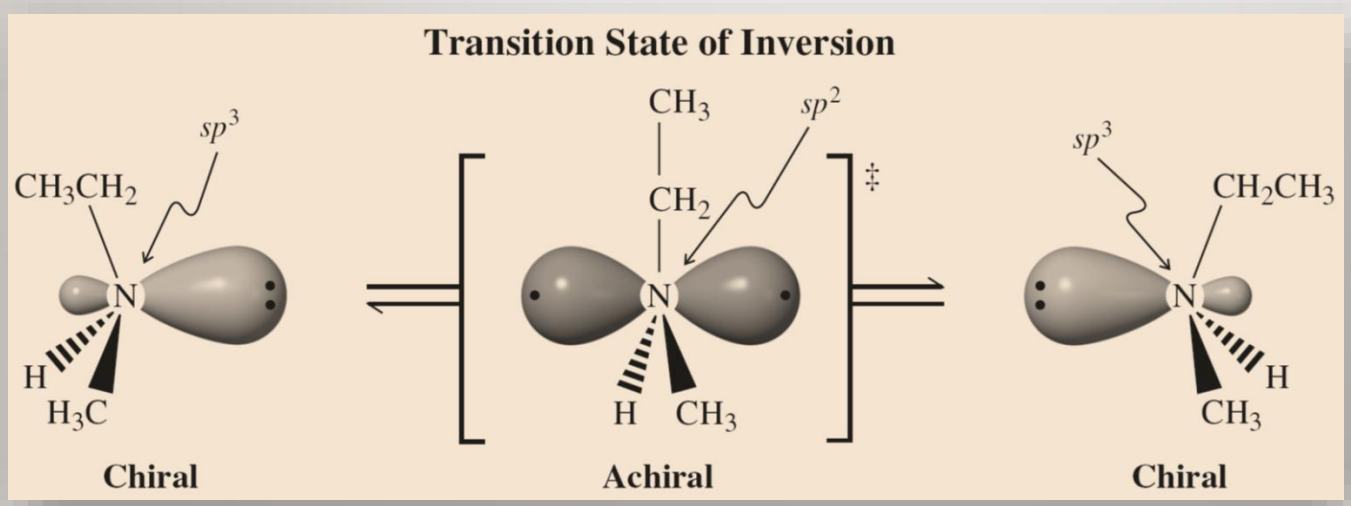
10.2 PHYSICAL PROPERTIES

1. Tetrahedral structure



2. Chiral amines racemize



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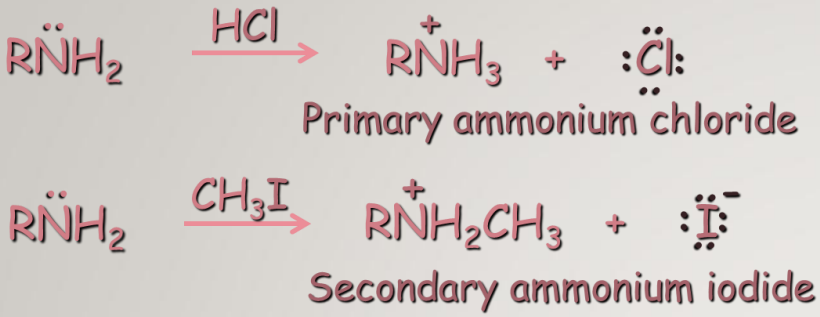
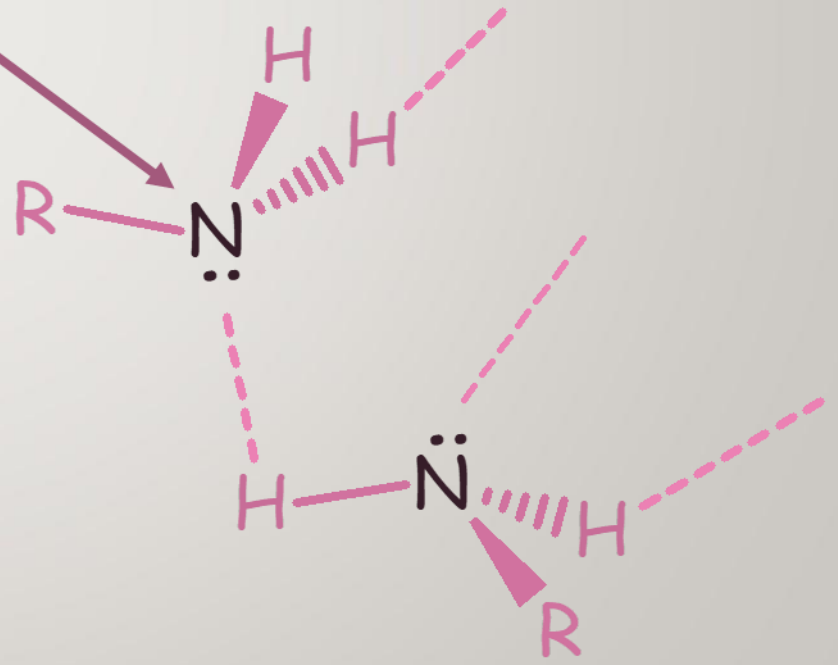
10.2 PHYSICAL PROPERTIES

3. Basicity-Nucleophilicity



Less electronegative than oxygen

4. Weaker hydrogen bonds than OH



NH_3 b.p. –33.4 °C

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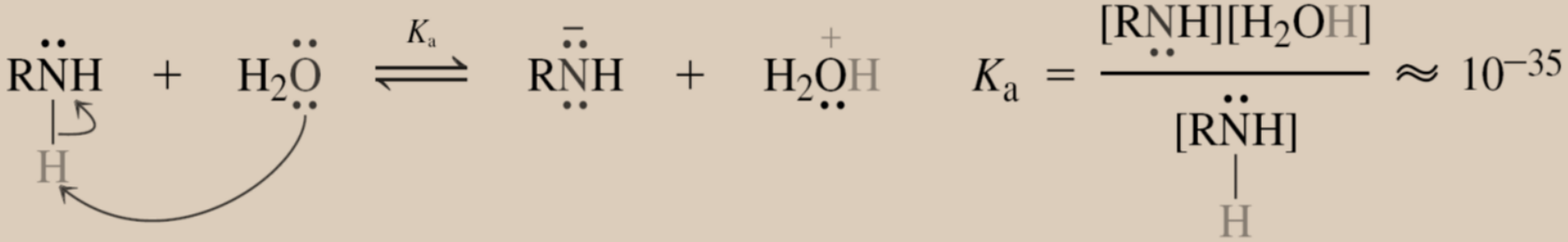
10.3 ACIDITY

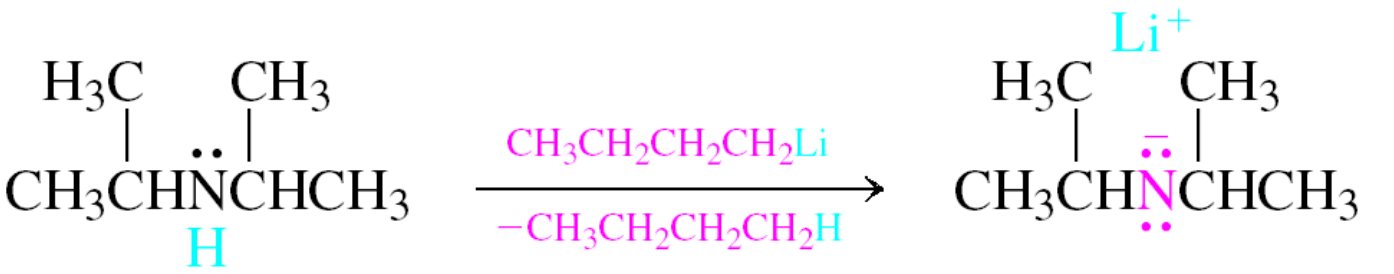
Acidity of Amines



Amine (Weak acid)

Amide ion (Strong base)

$pK_a \approx 35$



***N*-(1-Methylethyl)-2-propanamine (Diisopropylamine)**

Needs strong base

Lithium diisopropylamide, LDA

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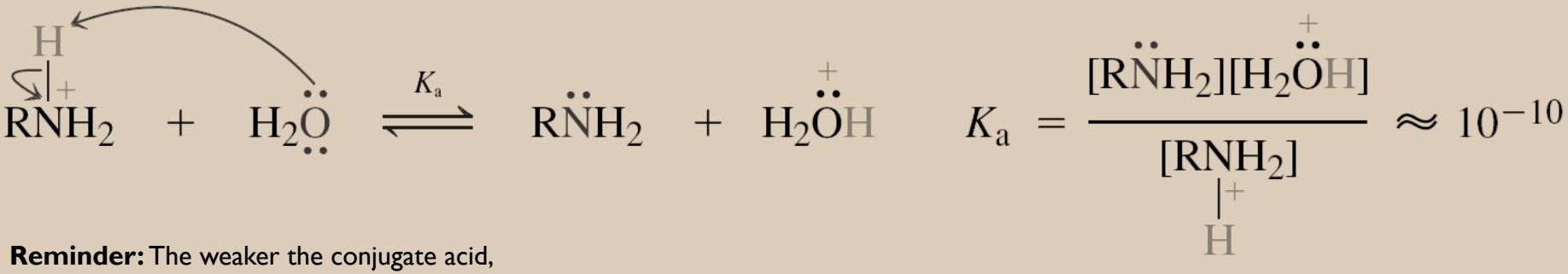
10.4 BASICITY

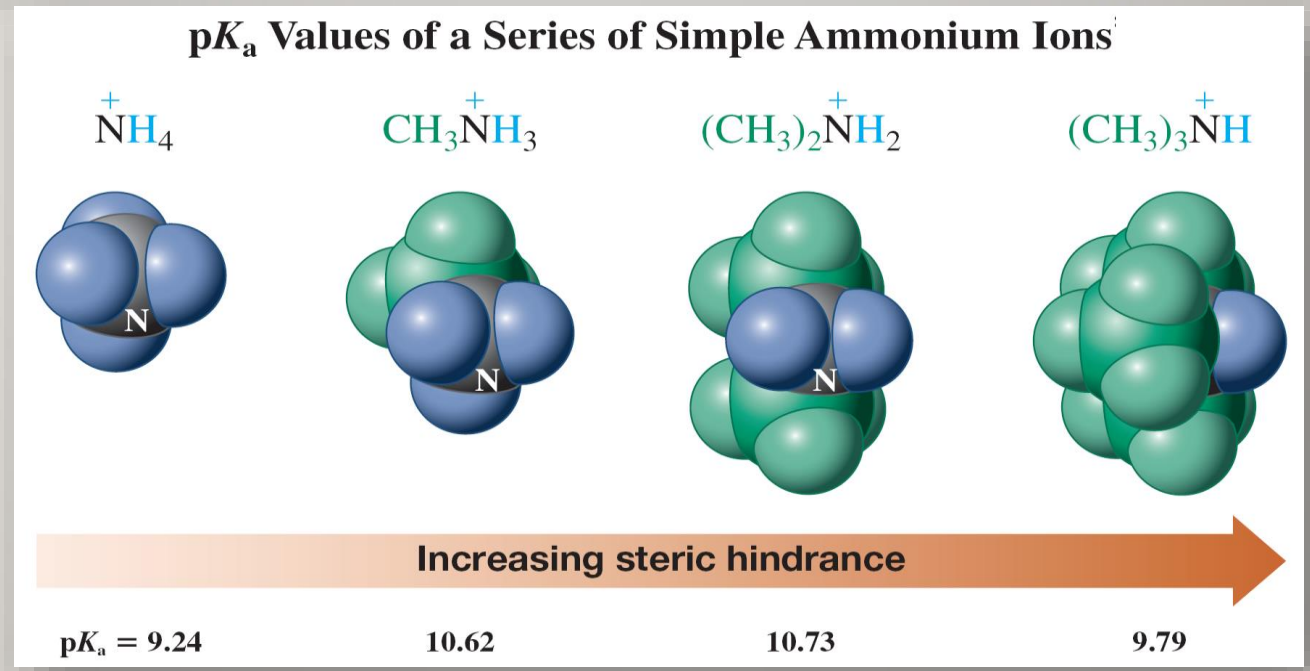
Acidity of Ammonium Ions



Reminder: The weaker the conjugate acid, the higher its pK_a and the stronger the corresponding base

p$K_a \approx 10$

pK_a Values of a Series of Simple Ammonium Ions



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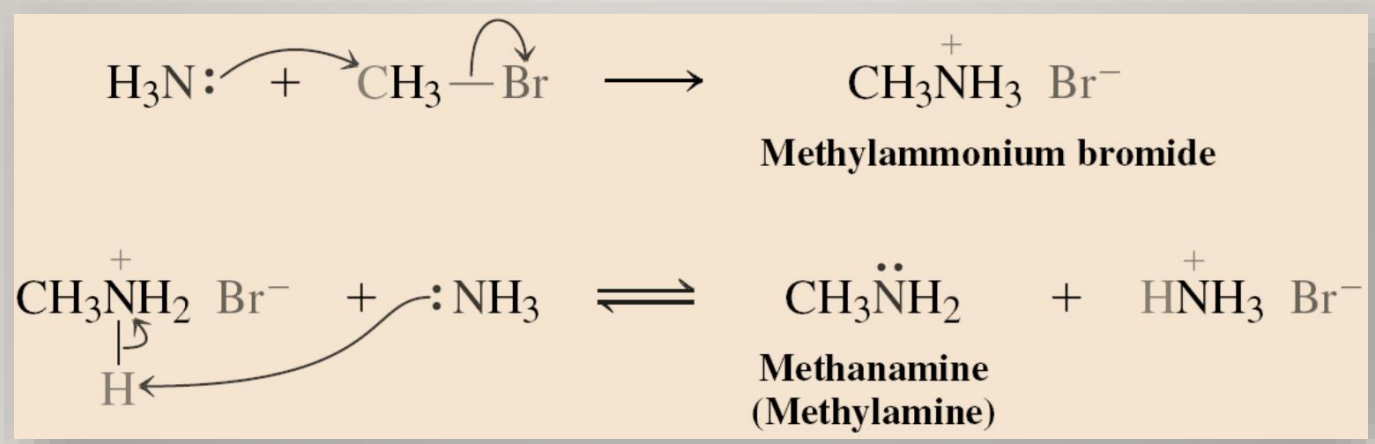
10.5 SYNTHESIS OF AMINES

1. Alkylation of NH_3, primary, and secondary amines



Overalkylation: Even though amine gets more hindered, it also gets more nucleophilic.

One solution is to have excess of RNH_2 and use RX as limiting reagents.

2. Via nitriles

Conversion of a Haloalkane into the Homologous Amine by Cyanide Displacement–Reduction

$$RX + {}^{-}CN \longrightarrow RC{\equiv}N + X^{-}$$

$$RC{\equiv}N \xrightarrow{LiAlH_4 \text{ or } H_2, \text{ metal catalyst}} RCH_2NH_2$$

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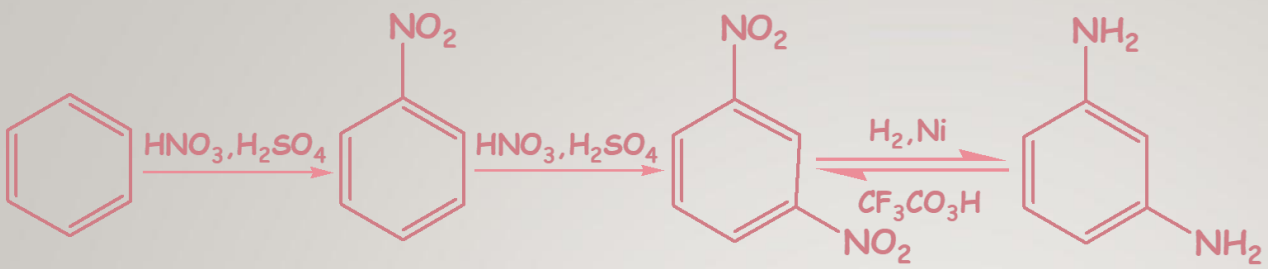
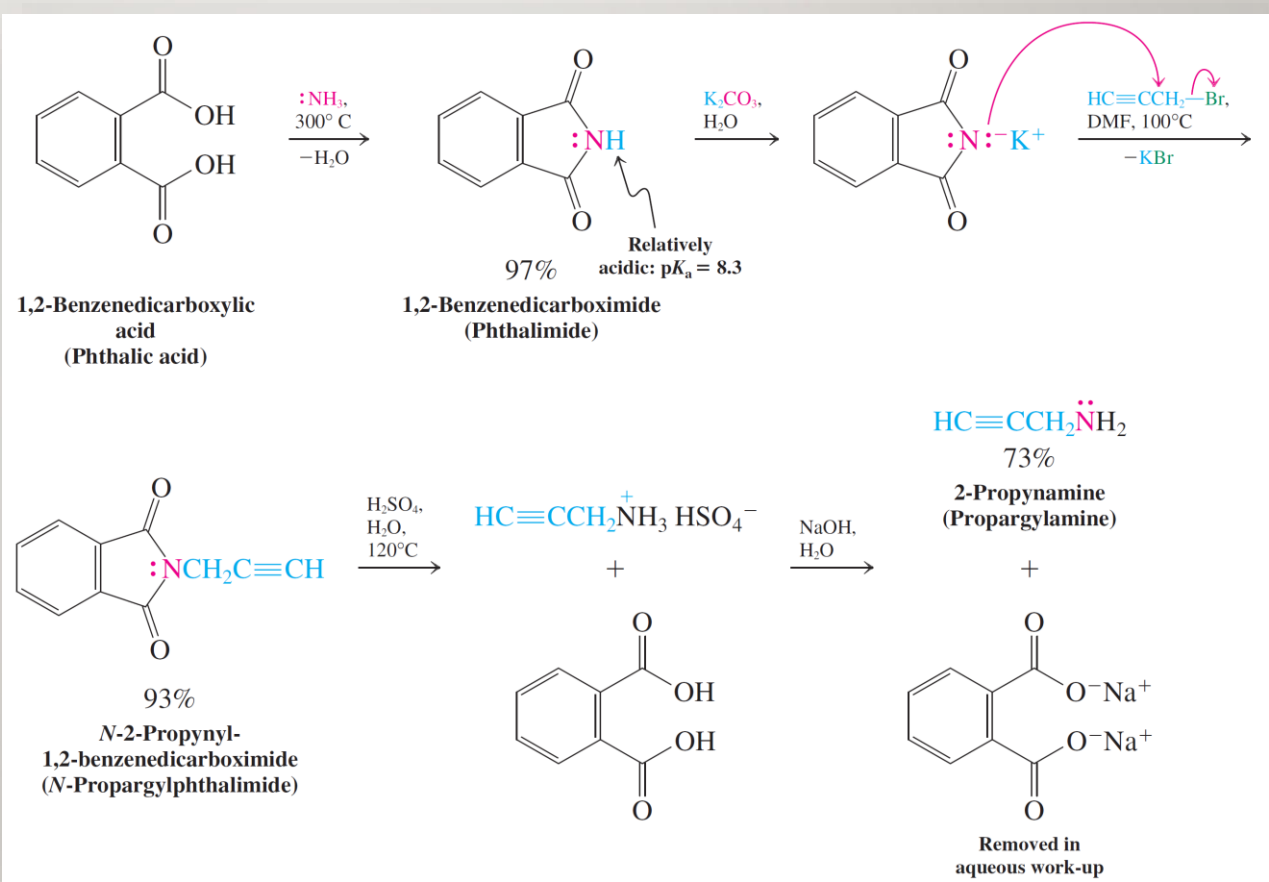
10.5 SYNTHESIS OF AMINES

3. Arenamine via nitroarene



4. Gabriel Synthesis



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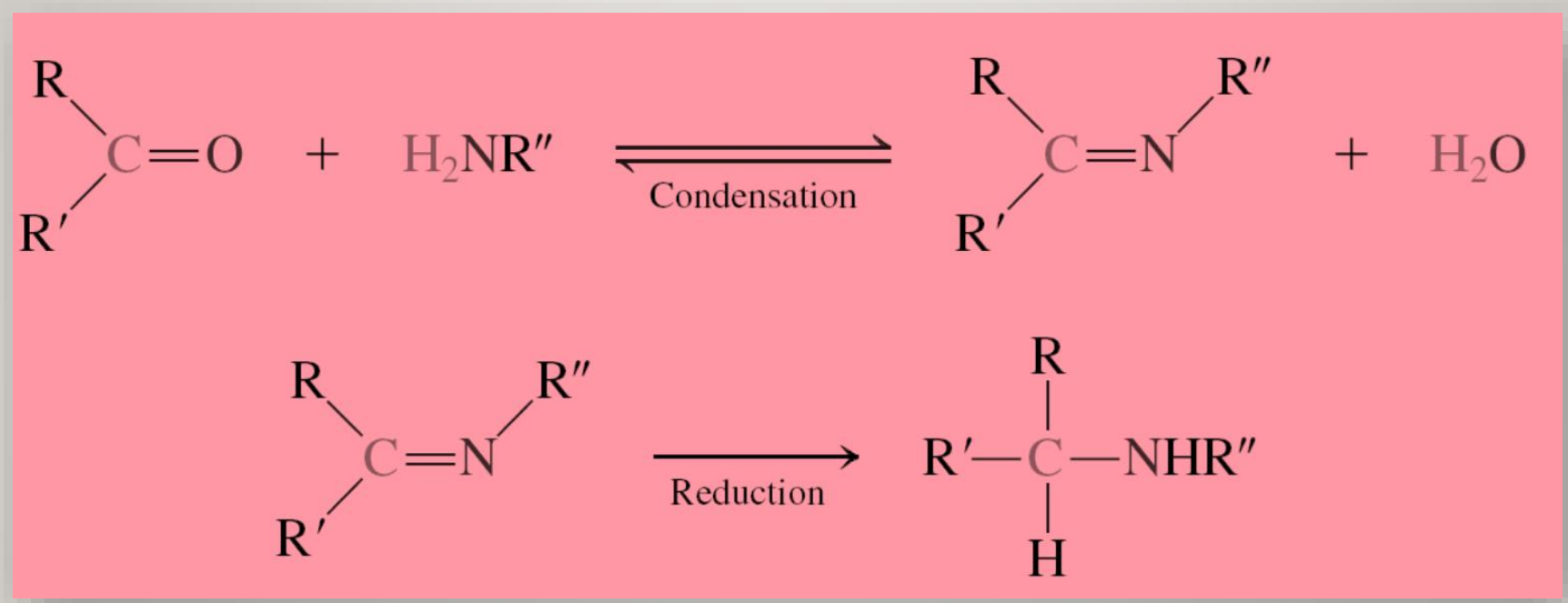
10.5 SYNTHESIS OF AMINES

5. Reductive Amination



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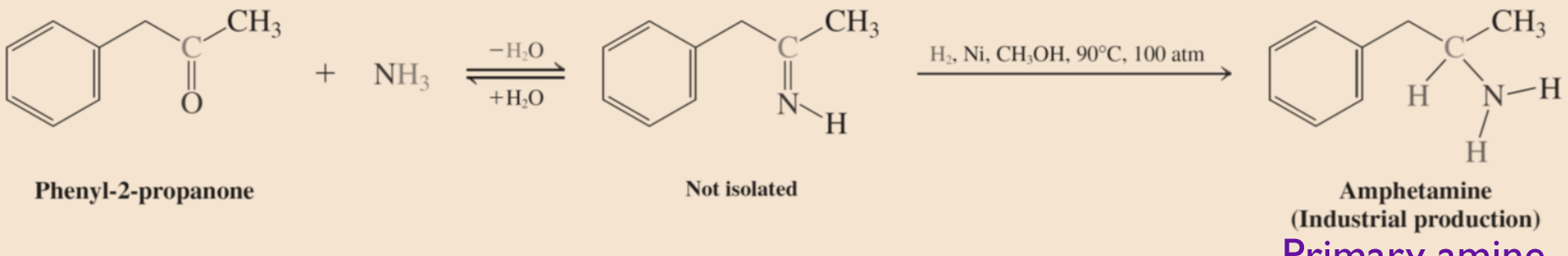
10.5 SYNTHESIS OF AMINES

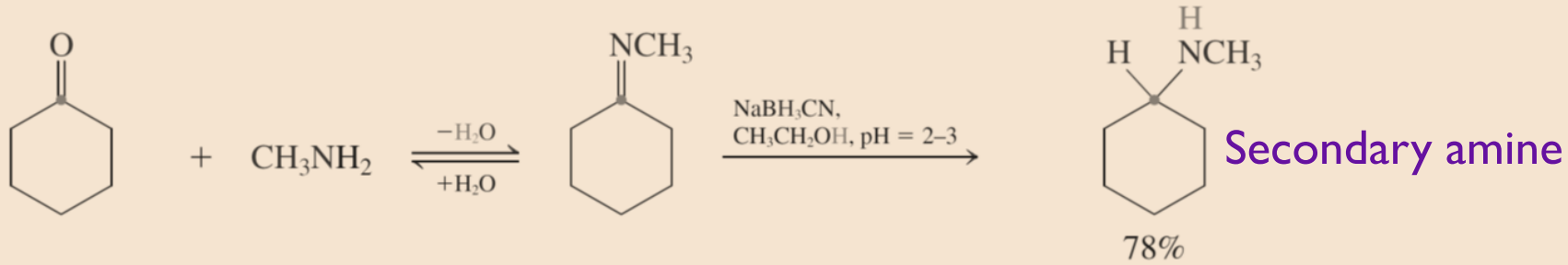
5. Reductive Amination

Amine Synthesis by Reductive Amination



Phenyl-2-propanone — **Not isolated** — **Amphetamine (Industrial production)**

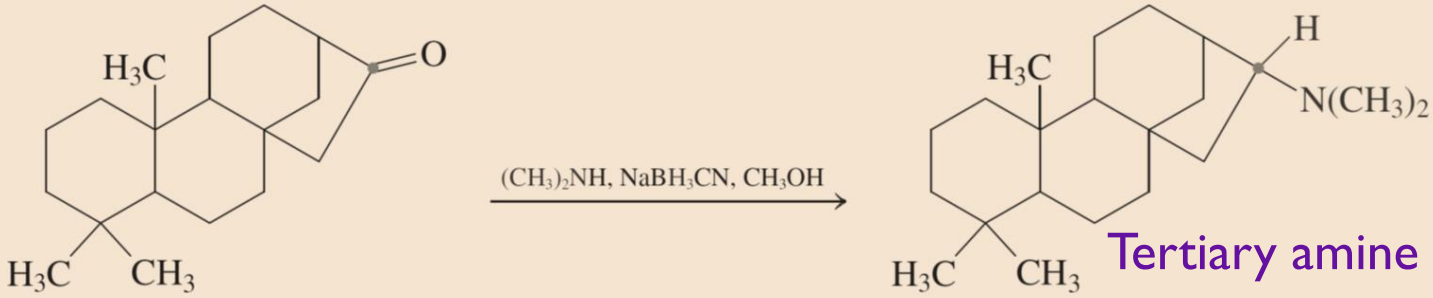
Primary amine



Cyclohexanone — **Not isolated** — ***N*-Methylcyclohexanamine**

Secondary amine

78%



Tertiary amine

89%

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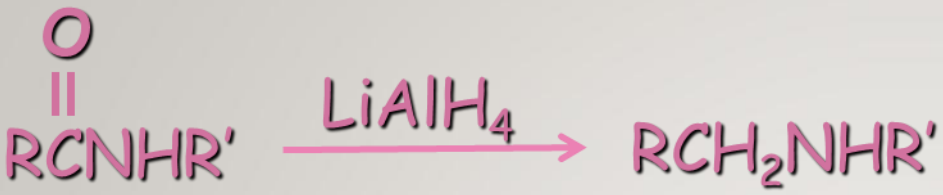
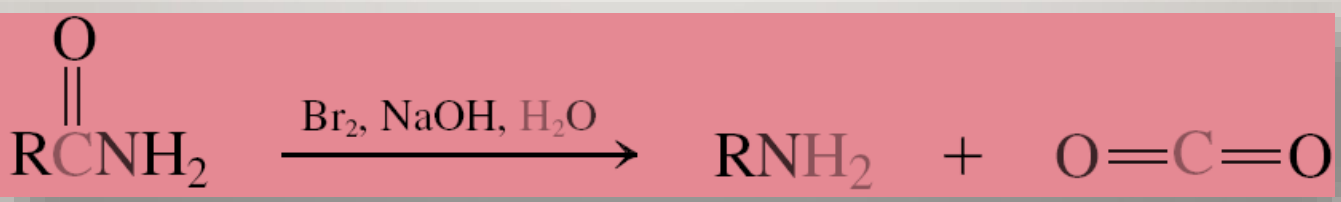
10.5 SYNTHESIS OF AMINES

6. Reduction of amides



Utility of Amides in Amine Synthesis

7. Hofmann Rearrangement



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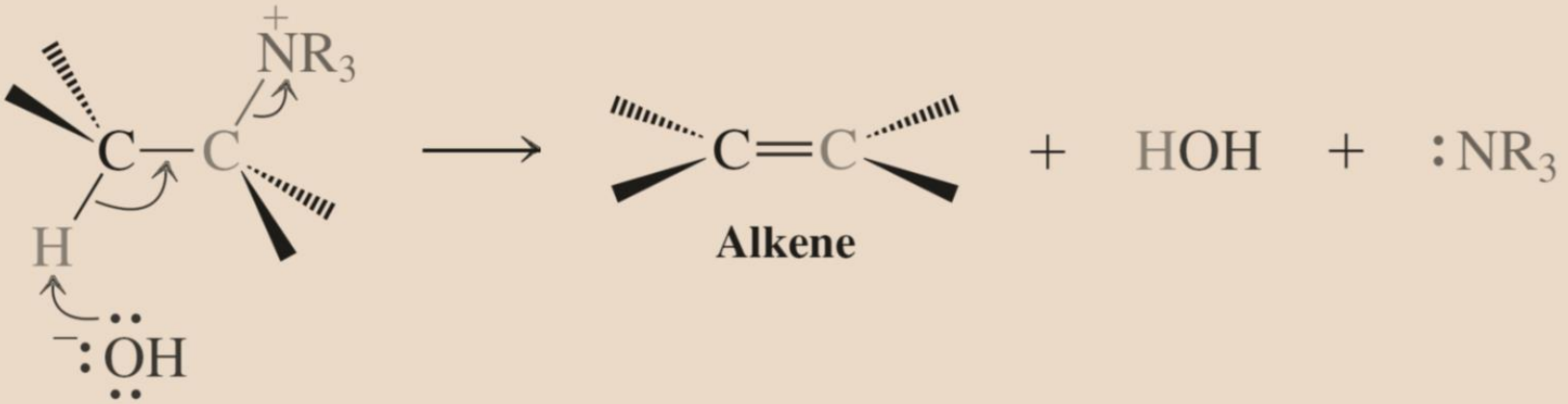
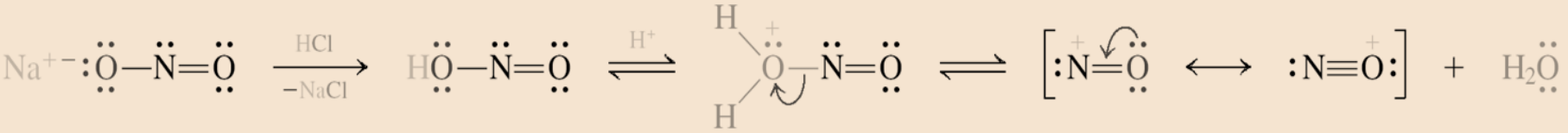
10.6 REACTIONS OF AMINES

Hofmann Elimination

Bimolecular Elimination of Quaternary Ammonium Ions



Reaction with Nitrous Acid (*see the experiment video*)



Sodium nitrite **Nitrous acid** **Nitrosyl cation**

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