Amines

Part B

B. Pharm. Semester-1

Course Code: 0510210; Session: 2022-2023

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Learning Outcomes

At the end of this lesson, students will be able to describe

Amines

- **Preparations of Amines**
- **Reactions of Amines**
- **Spectroscopy of Amines**

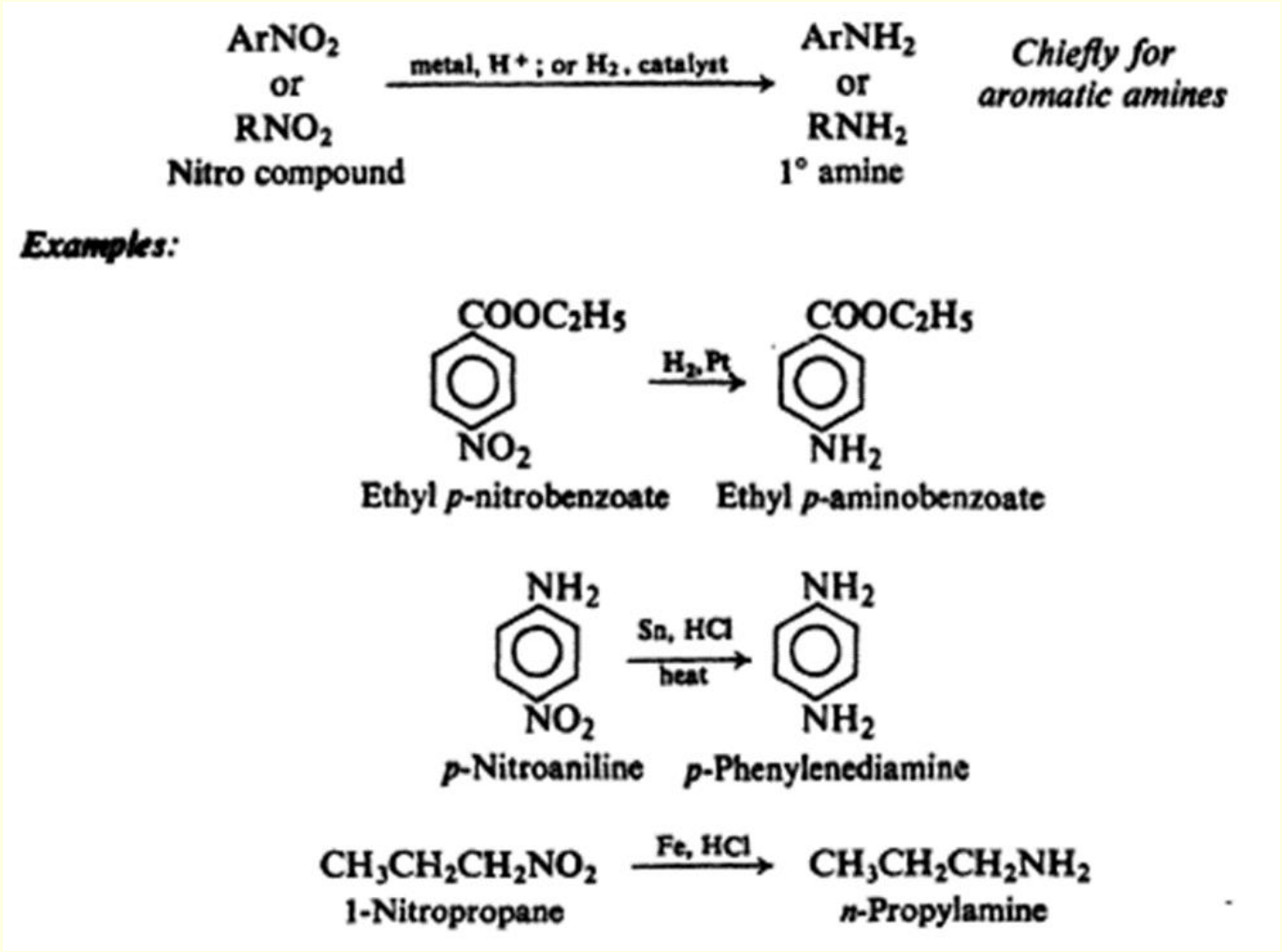
Objective

The objective of this course is to give to the students of pharmacy the basic knowledge about the organic chemistry.

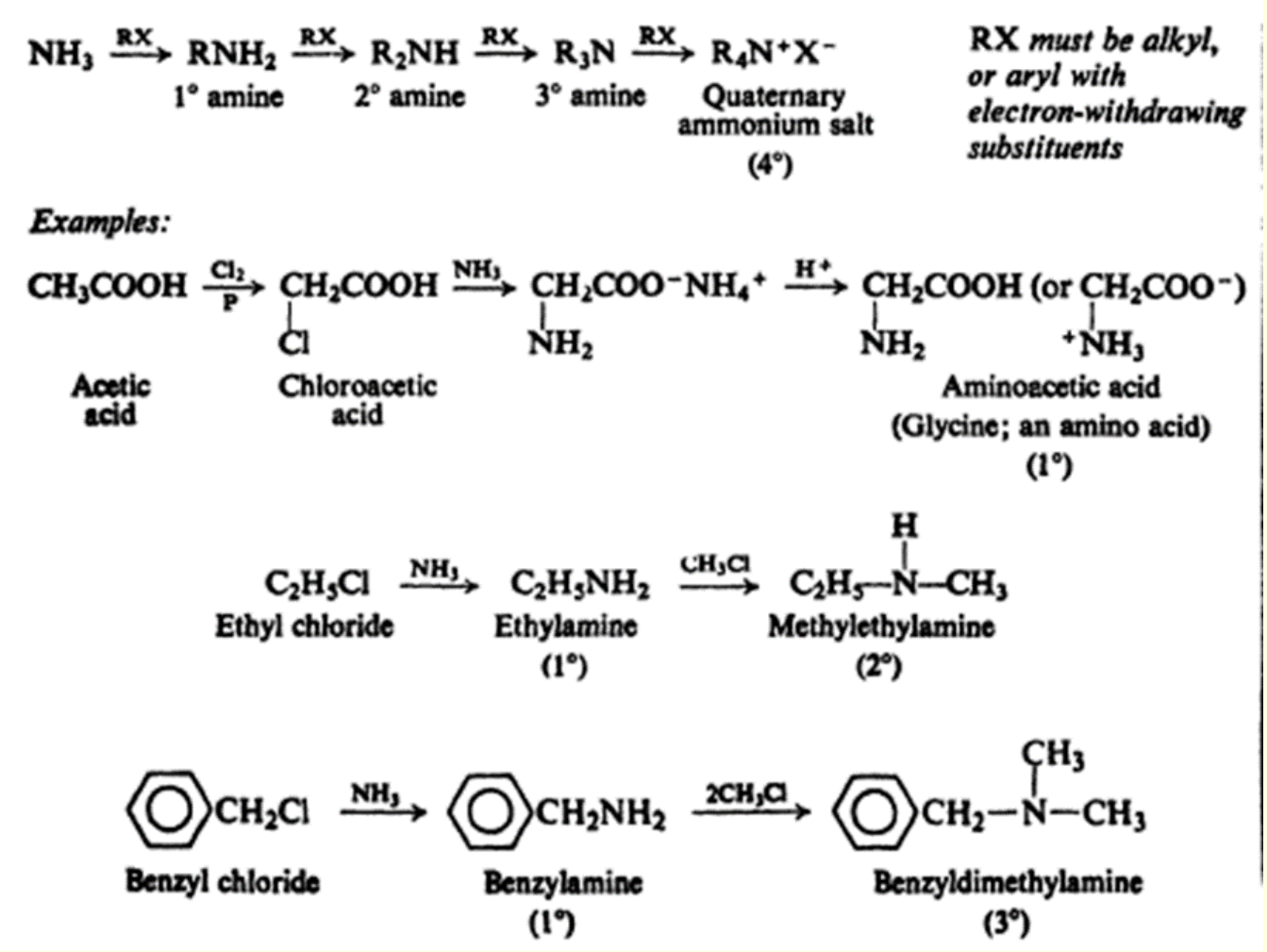
Preparation of Amines

1. **Reduction of nitro compounds**
2. **Reduction of halides with Ammonia or amines**
3. **Reductive amination**
4. **Reduction of nitriles**
5. **Hoffmann degradation of amides**

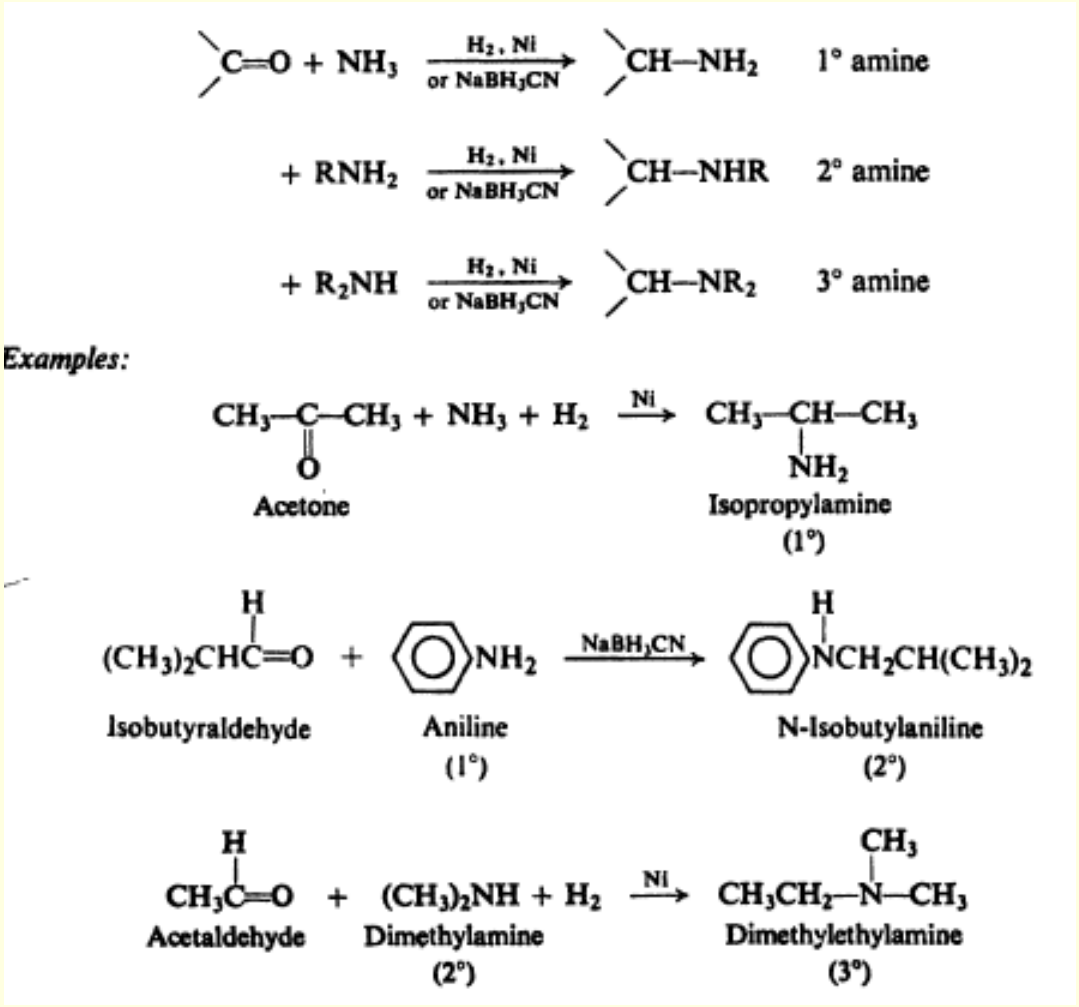
1. Reduction of nitro compounds



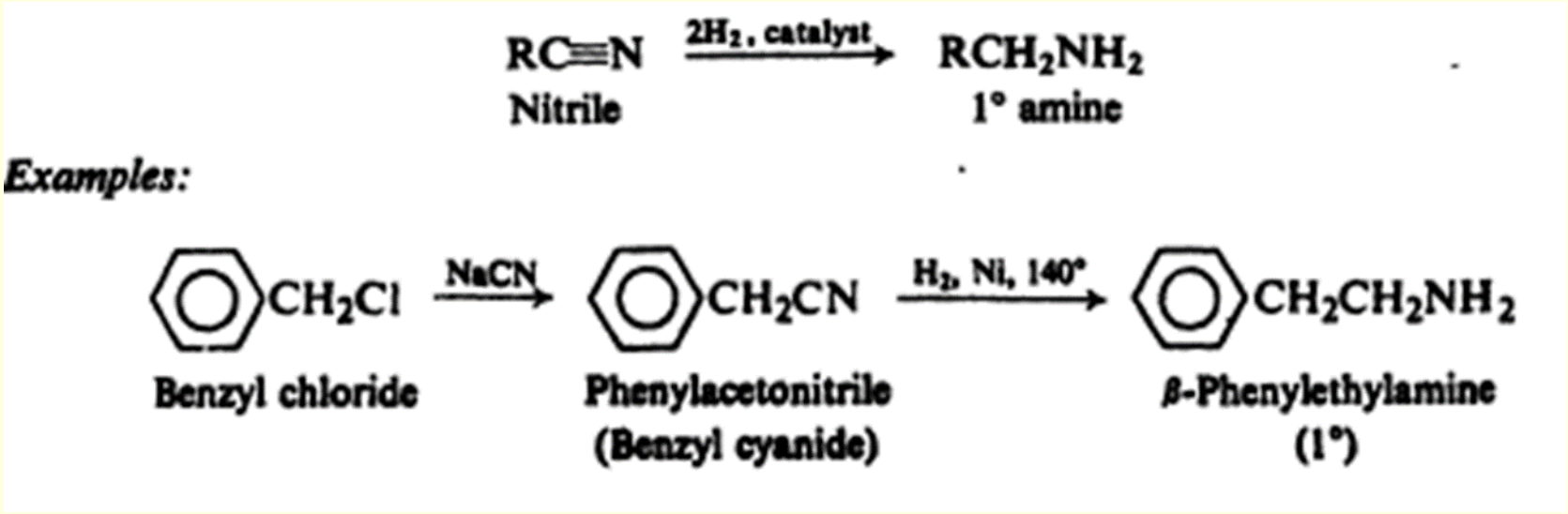
2. Reduction of halides with ammonia or amines



3. Reductive amination

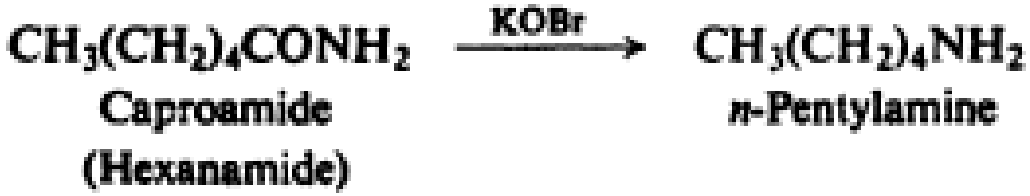


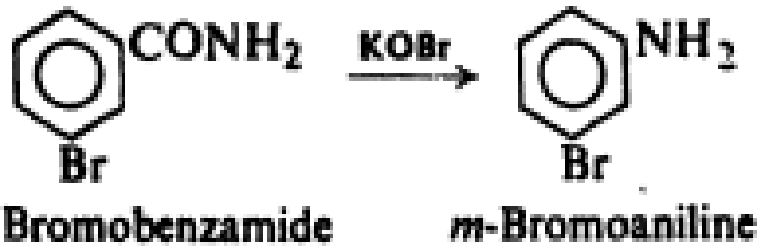
4. Reduction of nitriles



5. Hofmann degradation of amides

Examples:

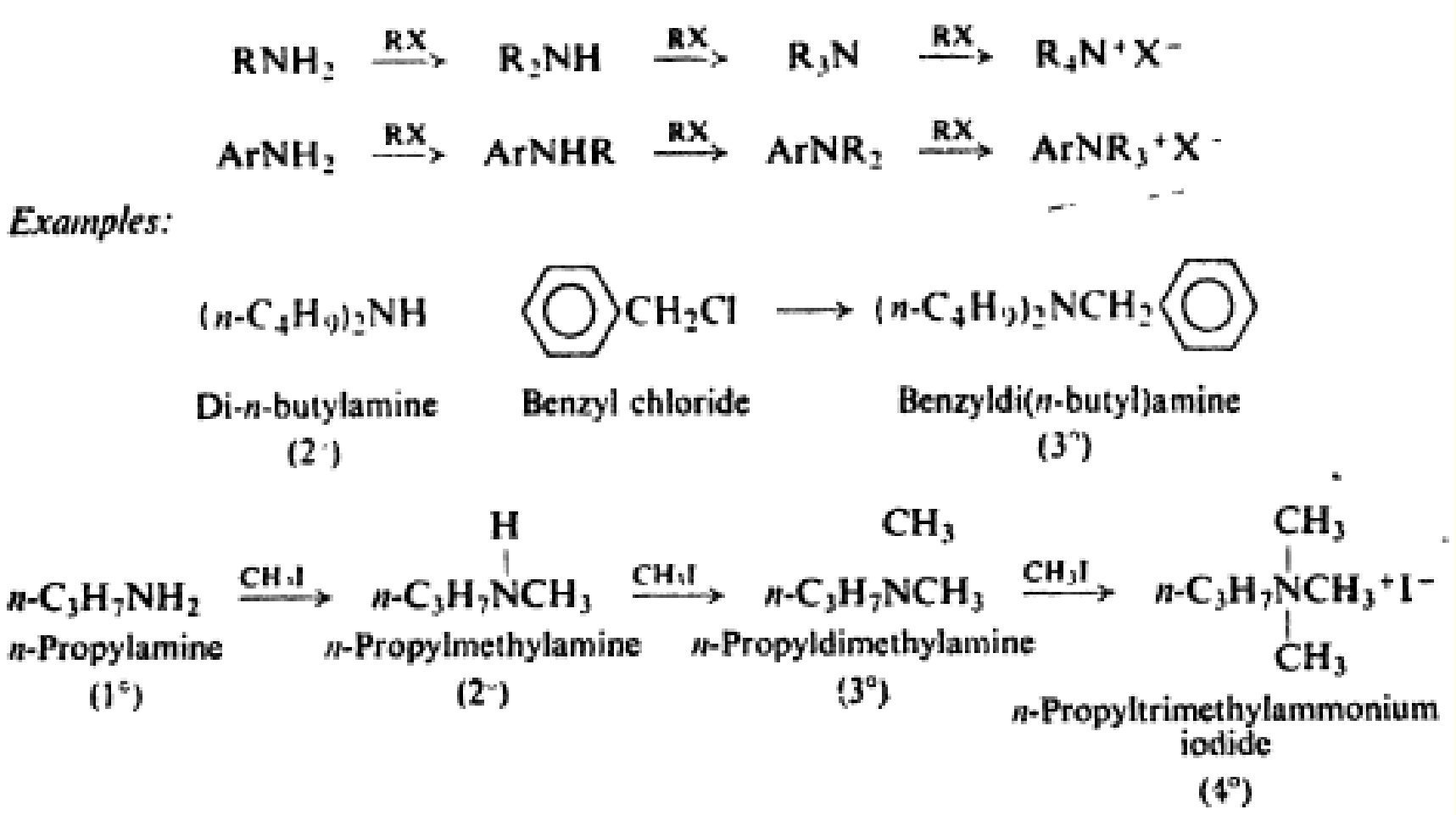




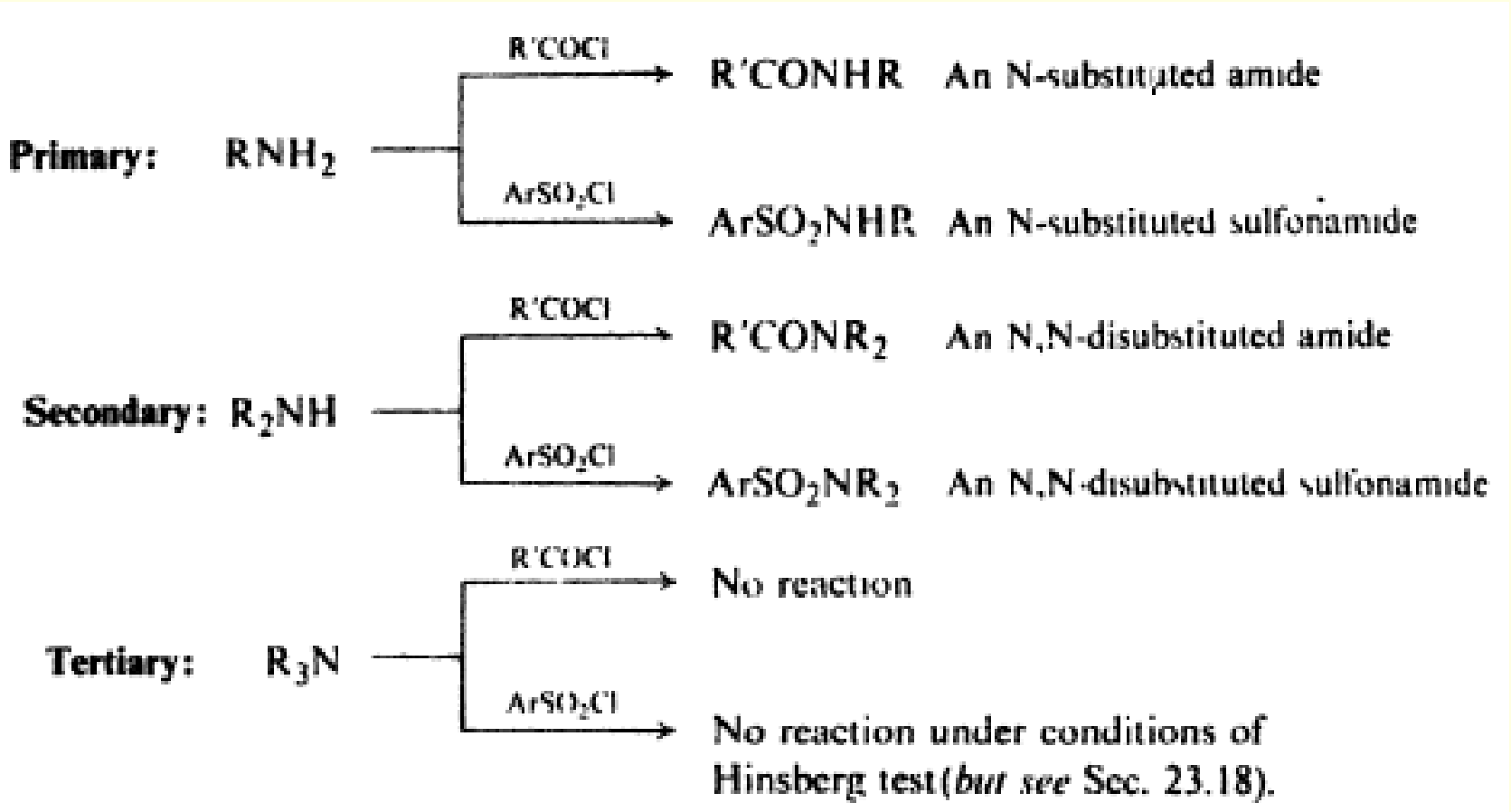
Reactions of Amines

1. **Alkylation of amines**
2. **Conversion into amides**
3. **Ring substitution in aromatic amines**
4. **Hoffmann elimination from quaternary ammonium salts**
5. **Reactions with nitrous acid**

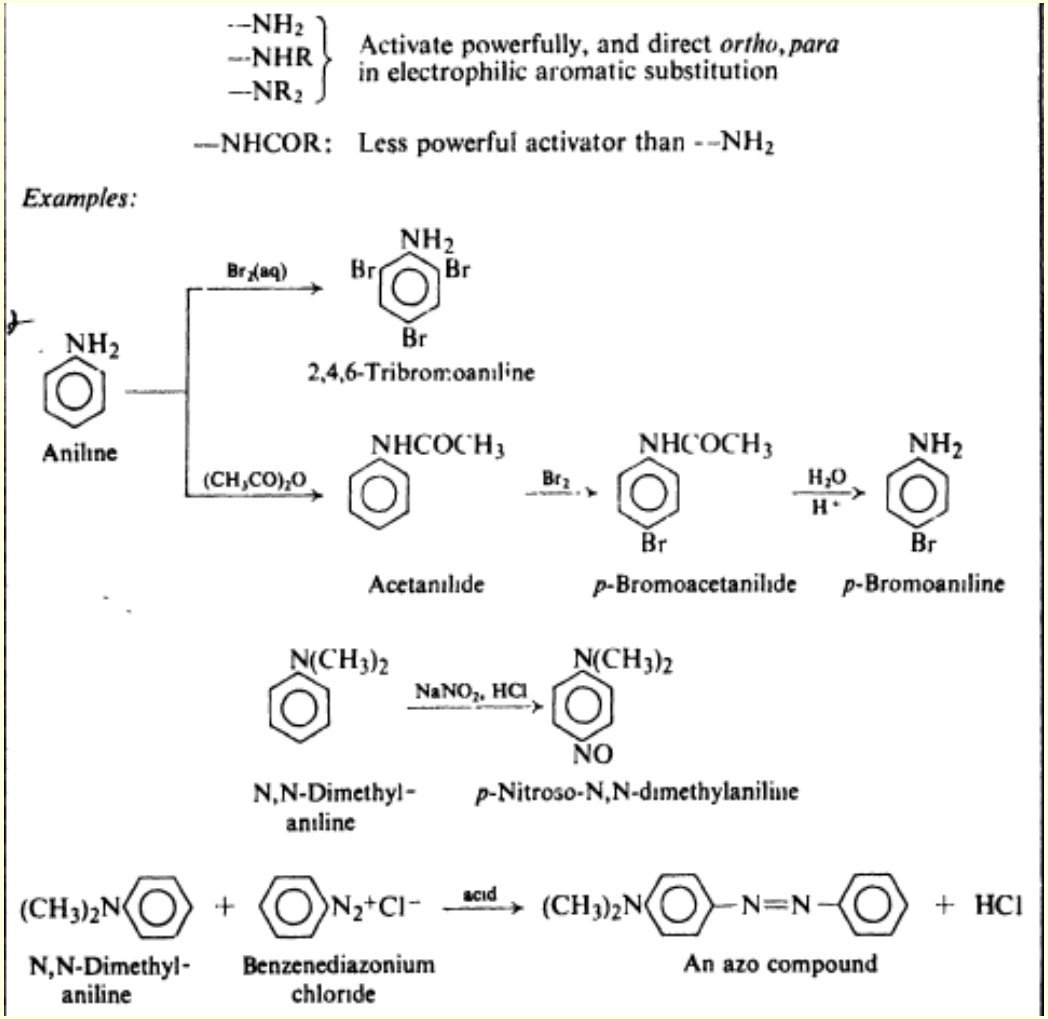
1. Alkylation of amines



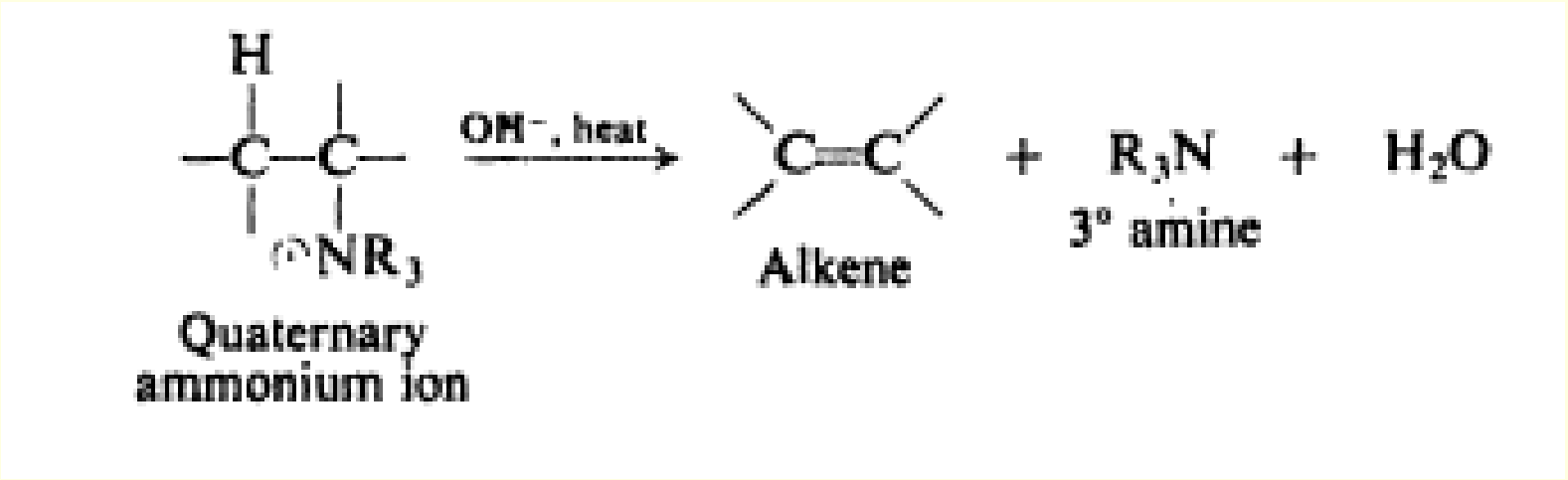
2. Conversion into amides



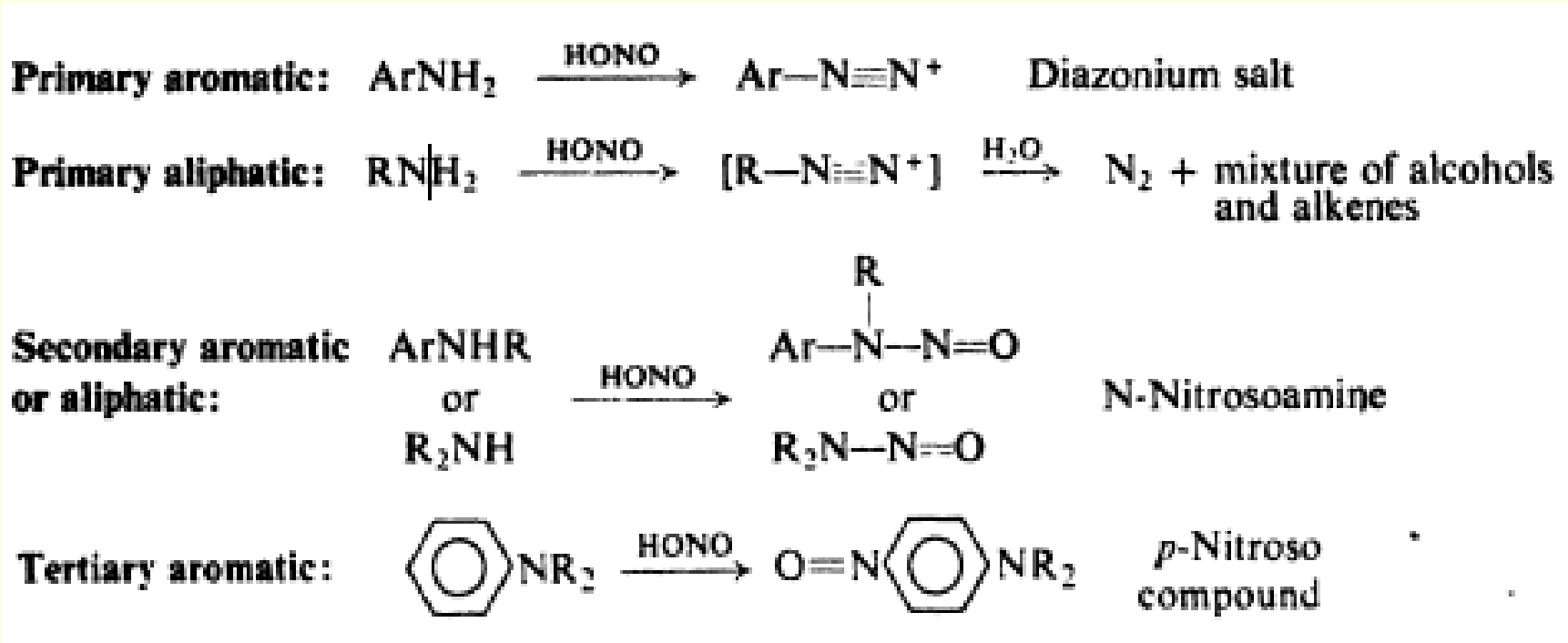
3. Ring substitution in aromatic amines



4. Hoffmann elimination



5. Reactions with nitrous acid

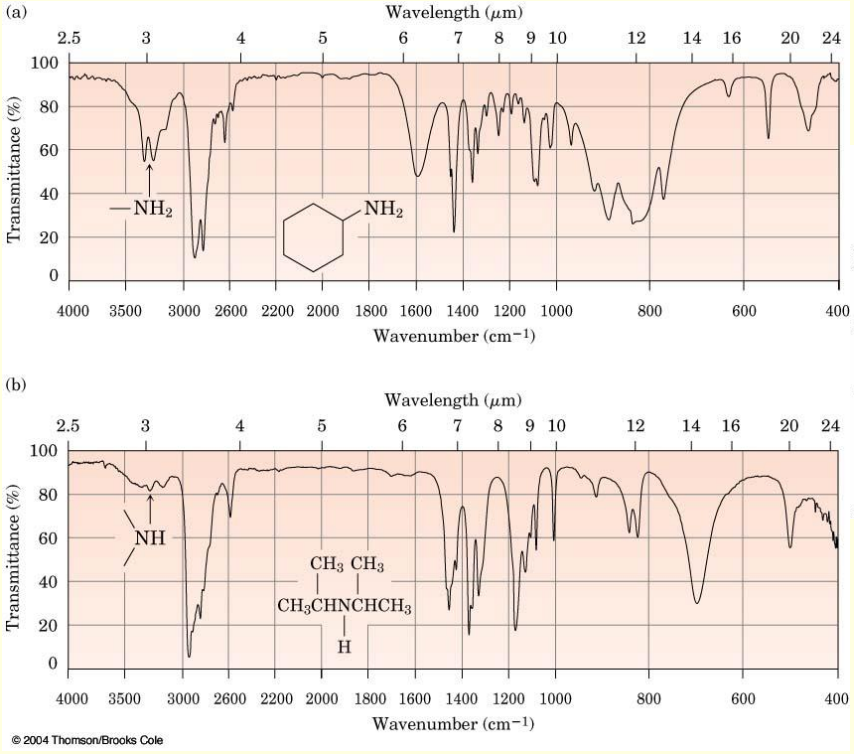


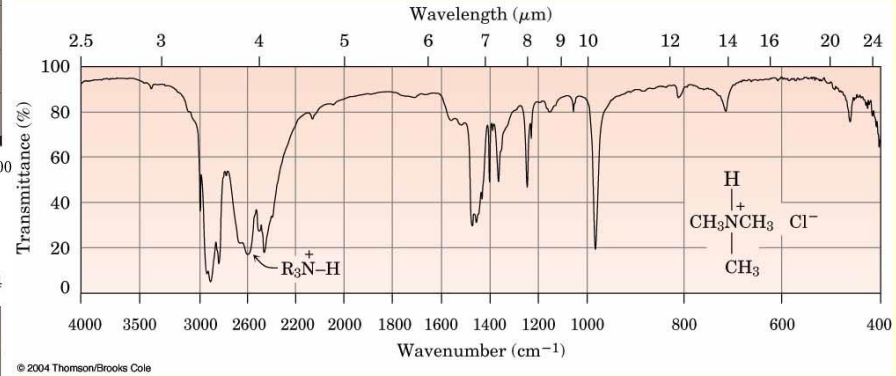
Spectroscopy of Amines

IR Spectroscopy

- Characteristic N–H stretching absorptions appear at 3300 to 3500 cm^{-1}
- Amine absorption bands are sharper and less intense than hydroxyl bands.
- Protonated amines show an ammonium band in the range 2200 to 3000 cm^{-1}

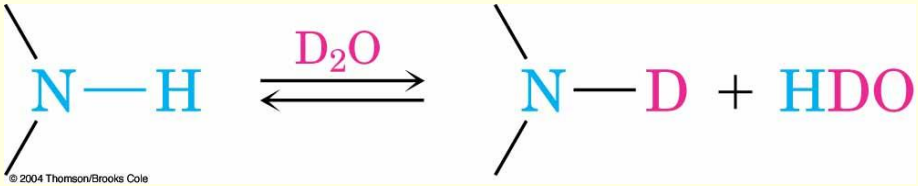
IR Spectroscopy of Amines: Examples





^{1}H-NMR Spectroscopy of Amines

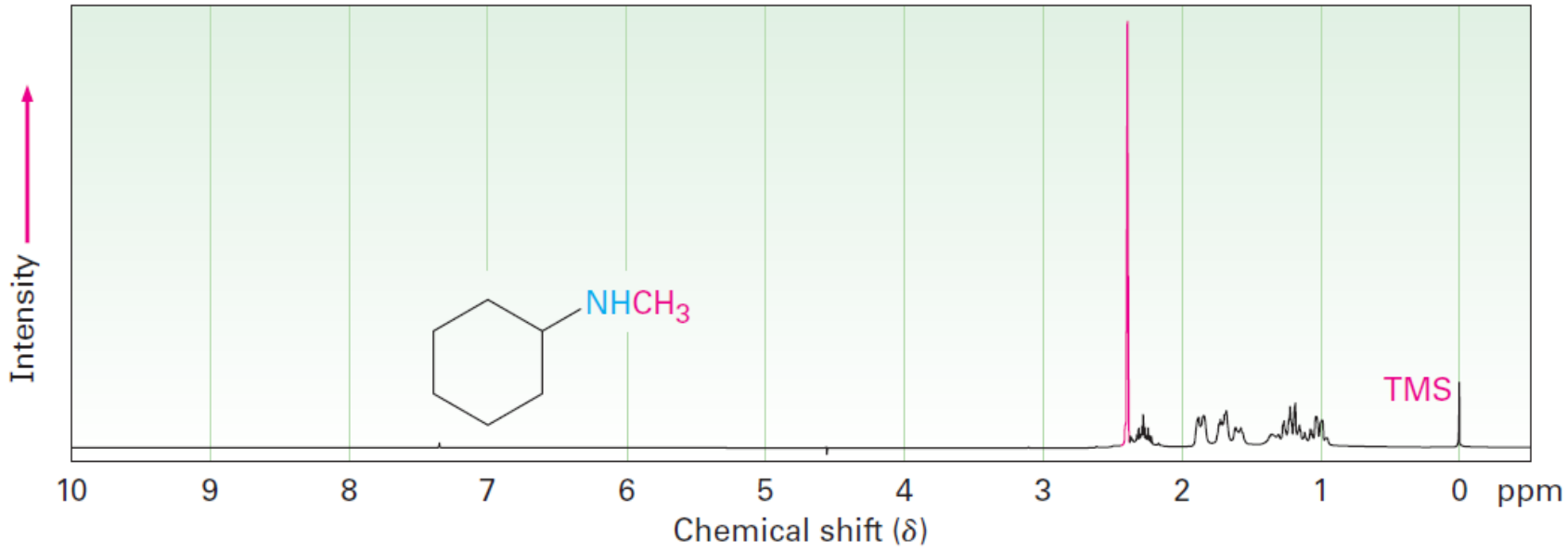
- N–H hydrogens appear as broad signals without coupling to neighboring C–H hydrogens.
- In D_2O exchange of N–D for N–H occurs, and the N–H signal disappears.



- Hydrogens on C next to N and absorb at lower field than alkane hydrogens
- N-CH_3 gives a sharp three-H singlet at δ 2.2 ppm to δ 2.6 ppm.

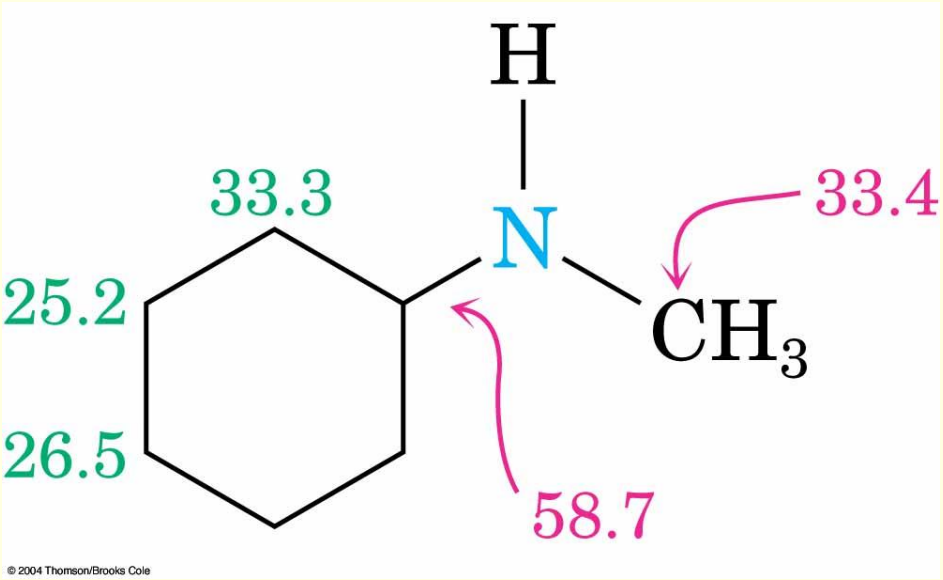
^{1}H-NMR Spectroscopy of Amines: Example

_N_-methyl cyclohexylamine



^{13}C-NMR Spectroscopy of Amines

Carbons next to amine N are slightly deshielded - about 20 ppm downfield from where they would absorb in an alkane.

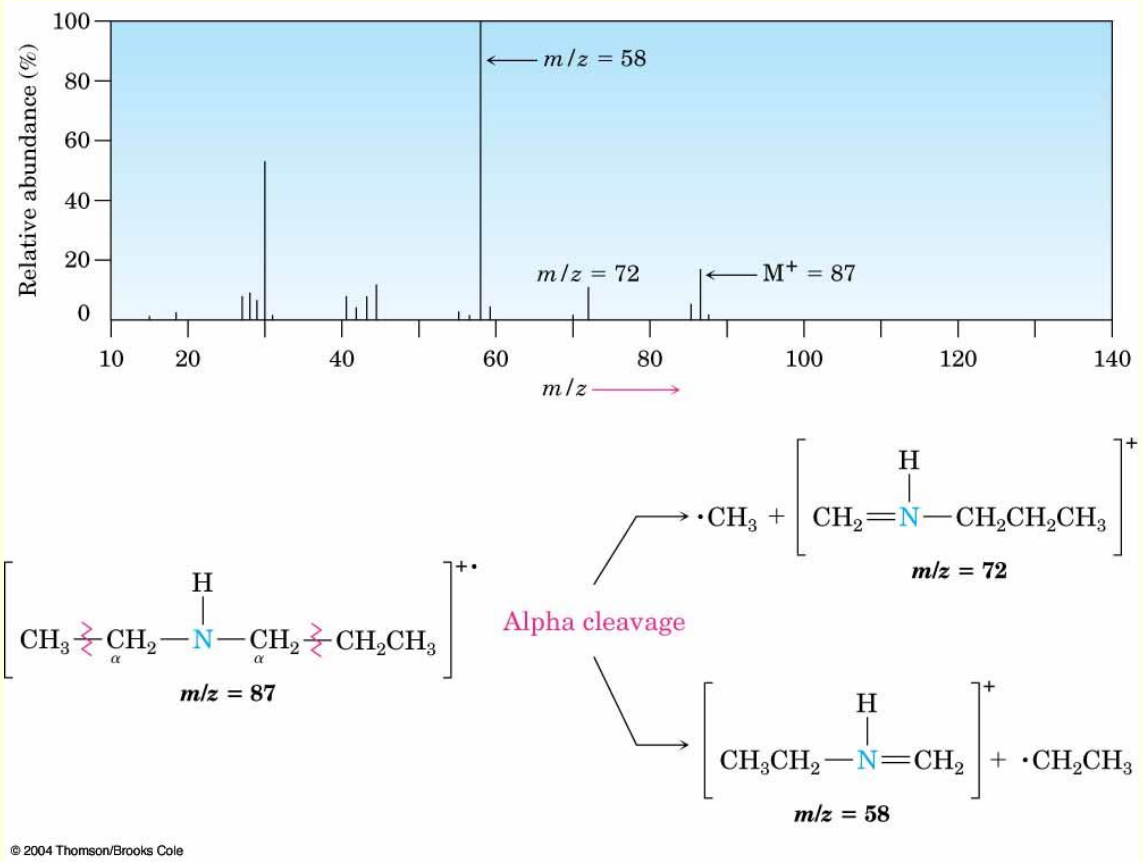


Mass Spectrometry of Amines

- ✓ The nitrogen rule of mass spectrometry says that a compound with an odd number of nitrogen atoms has an odd-numbered molecular weight.
- ✓ Thus, the presence of nitrogen in a molecule is detected simply by observing its mass spectrum.
- ✓ An odd-numbered molecular ion usually means that the unknown compound has one or three nitrogen atoms, and an even-numbered molecular ion usually means that a compound has either zero or two nitrogen atoms.
- ✓ The logic behind the rule derives from the fact that nitrogen is trivalent, thus requiring an odd number of hydrogen atoms.

Mass Spectrum of *N*-Ethyl propylamine

The two modes of a cleavage give fragment ions at m/z = 58 and m/z = 72.



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2. **Organic Chemistry, 7th Edition, 2010, Authors: Saibal Kanti Bhattacharjee, Robert Thornton Morrison, Robert Neilson Boyd, Publisher: Pearson India, ISBN: 978-0199270293.**
3. **Textbook of Organic Chemistry, 22nd Edition, 2022, Authors: Arun Bahl & B S Bahl, Publisher: S Chand, ISBN: 978-9352531967.**

Supplementary book:

Organic Chemistry, 11th Edition, 2015, Authors: Francis Carey Robert Giuliano Neil Allison Susan Bane, Publisher: McGraw Hill, ISBN: 978-1260148923.