

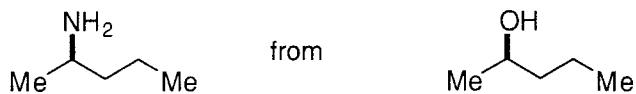
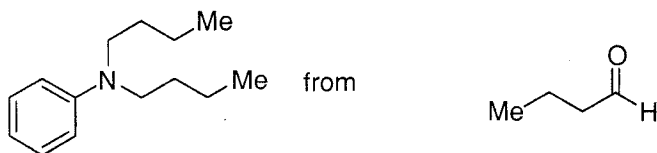
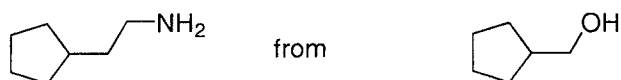
Massachusetts Institute of Technology

5.13: Organic Chemistry II

Spring 2003

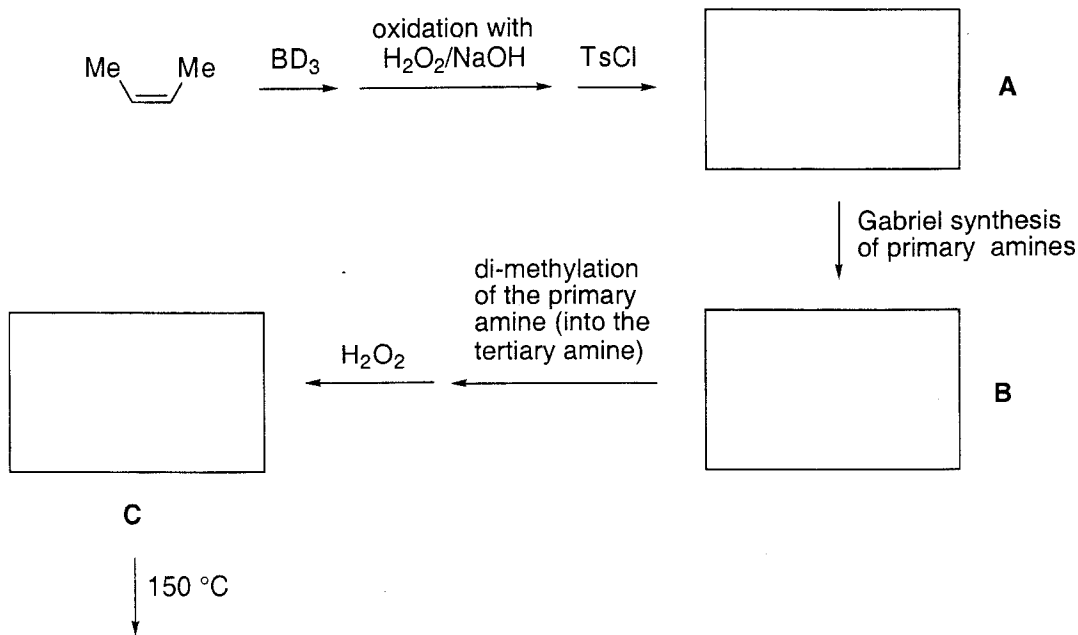
Problem Set 6: Amines
Due: Wednesday, April 9, by noon

- (1) Provide syntheses for the illustrated molecules (multiple steps may be required). Your solution must avoid the "over-alkylation" problem.



- (2) *ortho*-Methyl-*N,N*-dimethylaniline (pK_a of the conjugate acid = 6.1) is a much stronger base than *N,N*-dimethylaniline (pK_a of the conjugate acid = 5.1). Provide the best explanation for this observation.
- (3) Provide the best rationalization for the observation that $\text{PhN}(\text{CH}_2\text{CH}_2\text{Cl})_2$ reacts much more slowly with hydroxide ion than does $\text{MeN}(\text{CH}_2\text{CH}_2\text{Cl})_2$, which is converted to $\text{MeN}(\text{CH}_2\text{CH}_2\text{OH})_2$ within minutes.

(4) (a) Identify **A**, **B**, and **C**, including stereochemistry.



1-butene + *cis*-2-butene + *trans*-2-butene

(b) Two of the butene isomers that are produced in the pyrolysis contain one atom of deuterium per molecule, and the other isomer contains only hydrogens. Which isomer contains no deuterium? Explain.

(5) Consider the following data for the inversion of cyclic amines:

1	2	3	4
ΔG^\ddagger for inversion (kcal/mol) 7.0	20.5	17.1	11.7

- Draw the transition state structure for the inversion of **2**. Explain why this structure is higher in energy than the ground state structure.
- Explain why the activation energy for inversion of **2** is greater than the activation energy for inversion of **1**.
- Explain why the activation energy for inversion of **3** is less than the activation energy for inversion of **2**.
- Explain why the activation energy for inversion of **4** is less than the activation energy for inversion of **2**.