# Amines and their Classification



# Naming Amines

Simple primary amines are named by adding *—amine* as suffix to the name of alkyl substituent; alternatively, suffix *—amine* can be used in place of the final *—e* in the name of the parent compound.



# Naming Amines (Cont'd) and their Properties

Symmetrical 2° and 3° amines are named by adding the prefix *di*- or *tri*- to the alkyl group; unsymmetrically subsituted 2° and 3° amines are name as *N*-substituted 1° amines with the largest alkyl group chosen as the parent name.



# **Physical Properties**



Amines form weaker hydrogen bonds than alcohols do

- Amines with <5 C atoms are generally water-soluble but solubility is less than corresponding alcohols; larger amines are insoluble in water;
- Boiling points of amines lie between those of the corresponding alkanes and alcohols.

TABLE 21-1 Physical Properties of Amines, Alcohols, and Alkanes						
Compound	Melting point (°C)	Boiling point (°C)	Compound	Melting point (°C)	Boiling point (°C)	
CH <sub>4</sub>	-182.5	-161.7	(CH <sub>3</sub> ) <sub>2</sub> NH	-93	7.4	
CH <sub>3</sub> NH <sub>2</sub>	-93.5	-6.3	$(CH_3)_3N$	-117.2	2.9	
CH <sub>3</sub> OH	-97.5	65.0				
			$(CH_3CH_2)_2NH$	-48	56.3	
CH <sub>3</sub> CH <sub>3</sub>	-183.3	-88.6	$(CH_3CH_2)_3N$	-114.7	89.3	
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	-81	16.6				
CH <sub>3</sub> CH <sub>2</sub> OH	-114.1	78.5	$(CH_3CH_2CH_2)_2NH$	-40	110	
			$(CH_3CH_2CH_2)_3N$	-94	155	
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-187.7	-42.1				
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	-83	47.8	NH <sub>3</sub>	-77.7	-33.4	
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	-126.2	97.4	H <sub>2</sub> O	0	100	

### **Spectroscopic Features of Amines**

Primary Amines give two strong peaks between 3250 and 3500 cm<sup>-1</sup>, 2° amines give only weak signal in this region, and 3° amines do not have N-H stretching absorption.



The <sup>1</sup>H NMR spectra of amines give broadened peaks of NH, similar to the OH signal in alcohols; the chemical shifts depend upon the exchange rate and the amount of hydrogen bonding of protons, but usually in the upper field and less broadened compared to the signals of OHs.



## **Basicity of Amines**

Amines are much stronger bases than alcohols and ethers.





Amides are **nonbasic**: usually not protonated by aqueous acids, and are poor nucleophiles



### **Basicity and Acidity of Amines**















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### **Reactions of Amines**

#### Hofmann elimination



# **Hofmann Elimination**



- NR<sub>3</sub> is a not as good a LG as Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>, so H leaves slightly prior to NR<sub>3</sub> (OH<sup>-</sup> is a relatively strong base);
- The conjugated base (carbanion) is not stable enough for E1cb to take place.

Hofmann elimination is thus an E1cb-like reaction — the double bond is hardly developed in the TS $\neq$  (a carbanion-like TS $\neq$ ), so the relative stability of the corresponding anion determines the major product.

Kinetic-controlled reaction: Base attacks the less hindered, more acidic protons that are present in a larger number.

- Hofmann product

Hofmann product increases as the proton acidity increases; the LG and the basicity and bulkiness of the base also influence the percentage of the Hofmann product.

	Hofmann	Product (%)	
L	CH₃O <sup>-</sup>	<i>t</i> -BuO⁻	
Ι	19.3	69.0	
Br	27.6	80.0	
CI	33.3	87.6	
F	69.9	97.4	
NMe <sub>3</sub> +	96.2	98	

BuCHCH<sub>3</sub>

#### Exceptions to Hofmann's Rule and Hofmann Degradation



#### Amine Oxide and Cope Elimination

1° and 2° amines are oxidized into hydroxyamines, nitroso compounds, etc., but usually in low yields, so the reactions are not synthetically useful.



- Amine oxidation and Cope rearrangement can be accomplished in one pot;
- When more than one  $\beta$ -hydrogen can be eliminated, reactions usually afford a mixture, with Hofmann product as the major one and the *E* configuration favored;
- Rearrangement does not take place.

# Nitrosation of Amines

Nitrosyl Cation from Nitrous Acid



# **Nitrosation of Amines**

#### **Demjanov rearrangement:**



n = 0-2

#### **Tiffeneau-Demjanov rearrangement:**





mechanism?



# Nitrosation of Amines



#### **Reactions of Diazomethane**



#### Reactions of Diazomethane and Diazotization of Aryl Amines



Diazonium salts of 1° alkyl amines are unstable, but the diazonium salts of aromatic amines are stable enough to undergo reactions with control (but usually generated in situ and applied to subsequent reactions without isolation).



# **Reactions of Arenediazonium Salts**



# **Decomposition of Arenediazonium Salts**

Mechanism involving copper (II) and radical intermediates:



# **Decomposition of Arenediazonium Salts**



# **Coupling Reactions of Arenediazonium Salts**



# **Coupling Reactions of Arenediazonium Salts**

Reaction with 3° arylamine is performed under slightly acidic conditions to increase solubility of amine in aqueous solution, but strongly acidic conditions will inhibit the reaction by completely protonating the amine.



Reaction with 1° and 2° arylamines







reacting in a similar fashion:



#### **Electrophilic Aromatic Substitution of Aryl Amines**



Similarly for **nitration** reactions, 1° and 2° amino groups need to be protected with acyl groups prior to being exposed to nitric acid, to avoid oxidation of amine. But 3° arylamine can be directly nitrated.

NH<sub>2</sub>, NHR, and NR<sub>2</sub> are *o*-, *p*- directing, strong activating groups; NH<sub>3</sub><sup>+</sup>, NRH<sub>2</sub><sup>+</sup>, NR<sub>2</sub>H<sup>+</sup> are *m*- directing strong deactivating group; NHCOR is *o*-, *p*- directing, medium activating group.

#### **Electrophilic Aromatic Substitution of Aryl Amines**



#### **Oxidation of Aryl Amines**

1° and 2° arylamines are easily oxidized, 3° amines and 4° ammonium ions relatively are inert to oxidations.



# **Nitroaromatics**

Many nitroaromatic compounds are high explosives:



Nitroaromatics are usually made by direct nitration of aromatic compounds :



# Nitroaromatics and Benzyne



# **Reactions of Benzyne**

