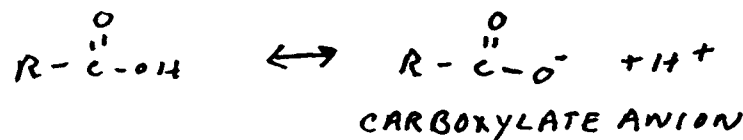
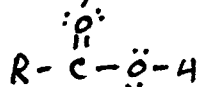


CHAPTER 19 CARBOXYLIC ACIDS

THE CARBOXYLIC ACID FUNCTIONAL GROUP IS $\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-OH}$
 THE PROTON IS IONIZABLE, WITH K_a IN THE 10^{-5} RANGE



CARBOXYLATE ANION



NOMENCLATURE

$\text{H}-\text{COOH}$ FORMIC
 CH_3COOH ACETIC
 $\text{CH}_3\text{CH}_2\text{COOH}$ PROPIONIC

ALIPHATIC ACIDS



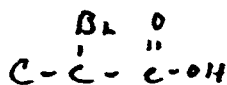
BENZOIC

AROMATIC ACIDS

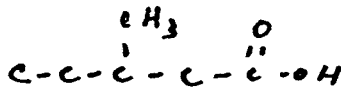
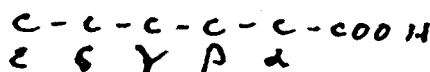


P-TOLUIC

COMMON NAMES DENOTE SUBSTITUENT CARBONS WITH GREEK LETTERS

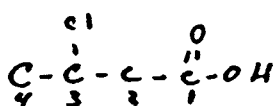


α -BROMOPROPIONIC



β -METHYLPENTANOIC

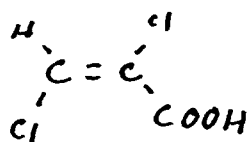
FOR IUPAC NAMES, DROP THE E FROM THE ALKANE NAME
 AND ADD -OIC



3-CHLOROBUTANOIC

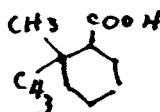
SUBSTITUENTS ARE NUMBERED FROM THE COOH CARBON #1

FOR UNSATURATED ACIDS, DROP THE E FROM THE ALKENE NAME
 ADD -OIC



(E)-2,3-DICHLOROPROPENOIC

CYCLIC ACIDS ARE NAMED AFTER THE CYCLOALKANE



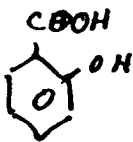
2,2-DIMETHYLCYCLOHEXANECARBOXYLIC ACID

NOMENCLATURE

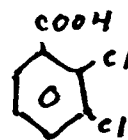
AROMATIC ACIDS ARE NAMED AS DERIVATIVES OF BENZOIC ACID



BENZOIC



O-HYDROXY BENZOIC
SALICYLIC ACID



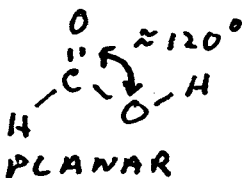
2,3-DICHLOROBENZOIC

THE SIMPLE DIACIDS RETAIN THEIR TRADITIONAL COMMON NAMES

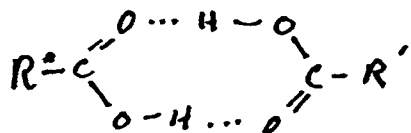
		IUPAC
$\text{HOOC}-\text{COOH}$	OXALIC	
$\text{HOOC}-\text{CH}_2-\text{COOH}$	MALONIC	PROPANE DIOIC
$\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$	SUCCINIC	
$\text{HOOC}-(\text{CH}_2)_3-\text{COOH}$	GLUTARIC	
$\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	ADIPIC	
$\text{HOOC}-(\text{CH}_2)_5-\text{COOH}$	HELMIC	HEPTANE DIOIC

STRUCTURE AND PHYSICAL PROPERTIES OF THE CARBOXYL GROUP

THE CARBONYL CARBON IS sp^2 HYBRIDIZED, TRIGONAL PLANAR



CARBOXYLIC ACIDS FORM STRONG HYDROGEN BONDS, LEADING TO DIMERIZATION IN SOLUTION



THIS LEADS TO CONSIDERABLY HIGHER BOILING POINTS AND MELTING POINTS THAN NON-HYDROGEN BONDING SPECIES

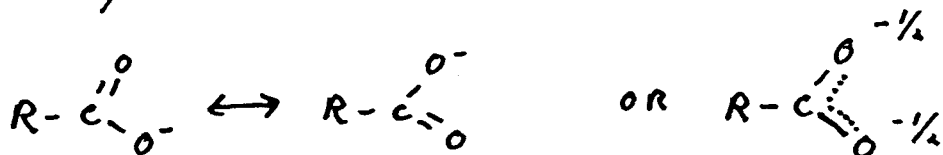
SMALLER CARBOXYLIC ACIDS ARE WATER SOLUBLE
LARGER CARBOXYLIC ACIDS MAKE SOAPS

THESE LARGER FATTY ACIDS $\text{C}_6 - \text{C}_{18}$ ARE
PLENTIFUL IN FATS, BOTH ANIMAL AND VEGETABLE

ACIDITY OF CARBOXYLIC ACIDS

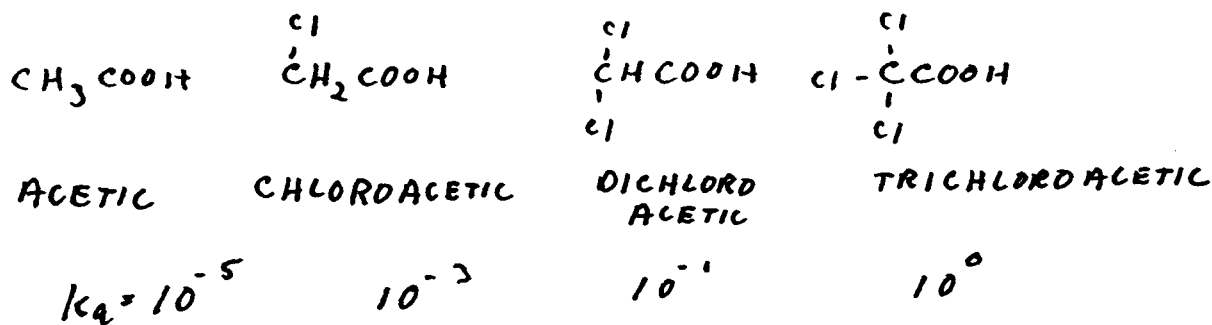
UNLESS ENHANCED BY ELECTRONEGATIVE SUBSTITUENTS,
CARBOXYLIC ACIDS ARE WEAK, $K_a \approx 10^{-5}$

THE CARBOXYLATE ANION IS RESONANCE STABILIZED

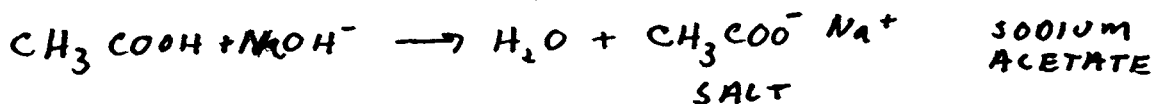


EACH C-O BOND HAS BOND
ORDER = $\frac{3}{2}$

ELECTRONEGATIVE SUBSTITUENTS ENHANCE IONIZATION AND ACID
STRENGTH BY STABILIZING THE ANION



SALTS OF CARBOXYLIC ACIDS



SALTS ARE NAMED BY REPLACING THE -IC ENDING WITH -ATE

SPECTROSCOPY

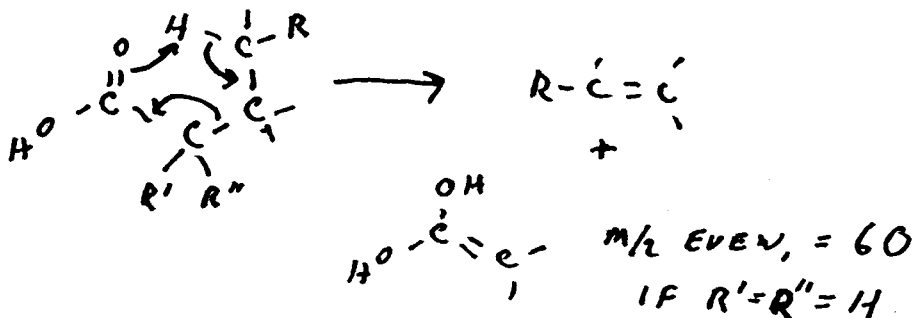
IR SPECTRA FEATURE A BROAD OH STRETCH FROM 2500 TO 3500
THIS ABSORPTION IS LOWER THAN THE ALCOHOL OH, WHICH IS
CENTERED AT 3300 cm^{-1}

THE OH STRETCH OF ACIDS IS RIGHT ON TOP OF THE C-H STRETCH
SO IT LOOKS LIKE A BROAD BAND WITH SHARPER SPIRES ON IT
A STRONG C=O STRETCH APPEARS AT 1710 cm^{-1} , SLIGHTLY LOWER
FREQUENCY IF CONJUGATED

NMR

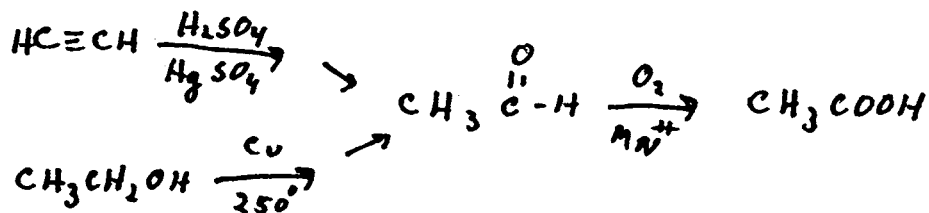
ACIDIC PROTONS ARE VERY DESHIELDED, 10 to 13 ppm (EXCHANGEABLE PROTONS α TO THE CARBONYL 2.1 ppm, LIKE ACETONE)
 THE C=O CARBON IS ABOUT 180 ppm
 α C ABOUT 30-40 ppm

UV SPECTROSCOPY ONLY STRONG WITH CONJUGATED ACIDS
 MASS SPECTRUM GIVES A SMALL MOLECULAR ION, OFTEN A McLAFFERTY REARRANGEMENT PEAK

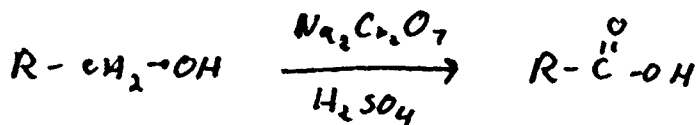


SYNTHESIS OF CARBOXYLIC ACIDS

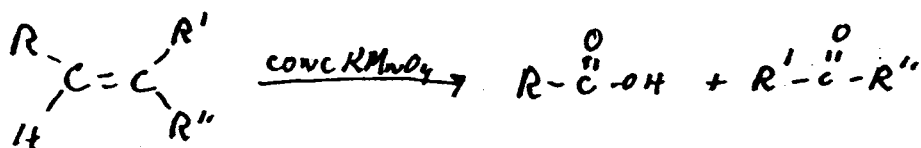
THE LARGEST VOLUME SYNTHESIS IS FOR ACETIC, FROM ETHANOL OR ACETYLENE VIA ACETALDEHYDE



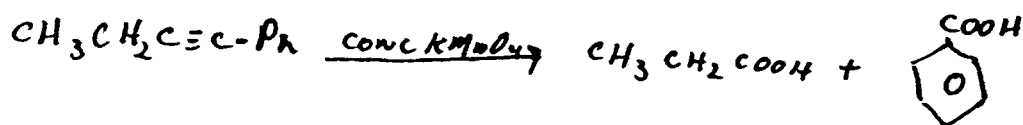
ACIDS CAN BE MADE BY OXIDATION OF PRIMARY ALCOHOLS AND ALDEHYDES



ALKENES ARE OXIDIZED BY CONC. KMnO_4 TO KETONES AND ACIDS

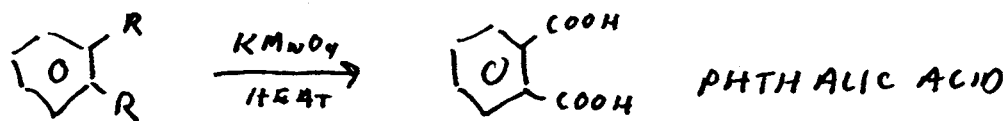


ALKYNES REACT SIMILARLY

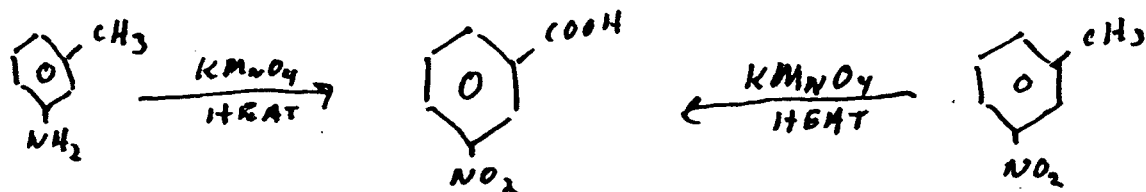


ACID SYNTHESIS CONTINUED

SIDE CHAINS OF ALKYL BENZENES ARE OXIDIZED TO COOH

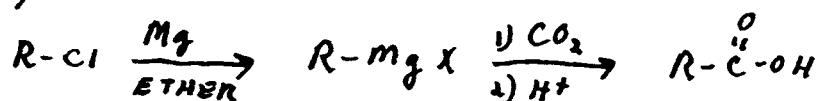


DUE TO THE VERY VIGOROUS OXIDATION CONDITIONS, ONLY OXIDATION RESISTANT FUNCTIONAL GROUPS WILL REMAIN UNCHANGED ON THE RING - Cl, NO₂, SO₃H AND COOH

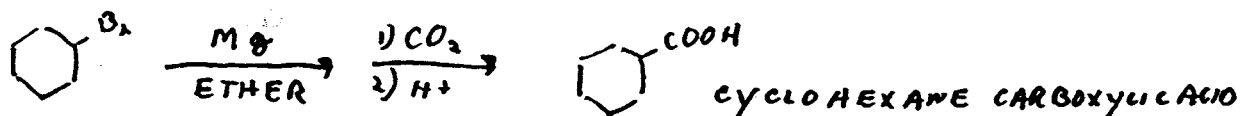


CARBOXYLATION OF GRIGNARD REAGENTS

GRIGNARD REAGENTS PROVIDE A CONVENIENT WAY TO MAKE ACIDS FROM ALKYL HALIDES

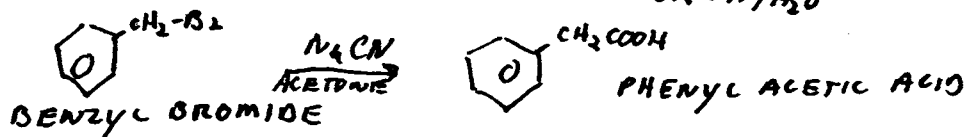
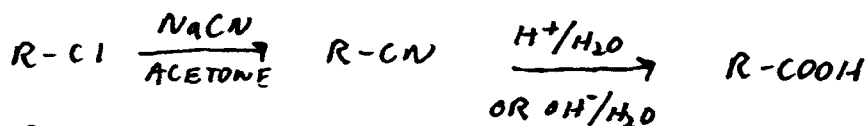


THE RESULTING ACID HAS ONE MORE CARBON THAN THE HALIDE



FORMATION AND HYDROLYSIS OF NITRILES

ALKYL HALIDES MAY BE MADE INTO ACIDS BY MAKING A NITRILE AND HYDROLYSING IT



A SUMMARY DO PROBLEM 20-10

ACIDS WITH FEWER CARBON ATOMS → OXIDATIVE CLEAVAGE OF ALKENES AND ALKYNES (NONCYCLIC)

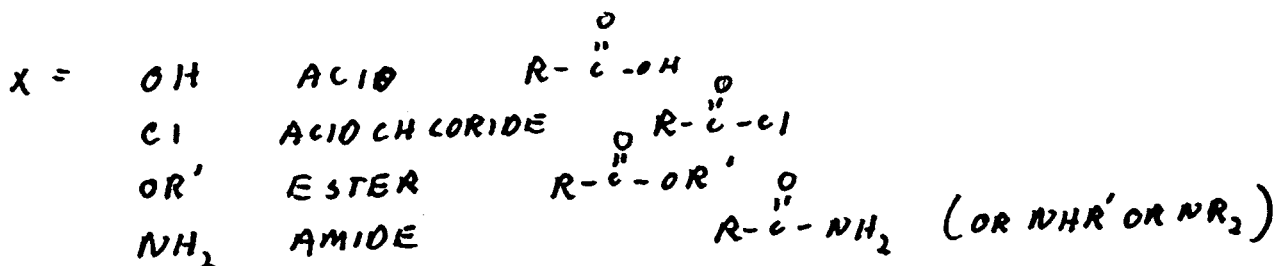
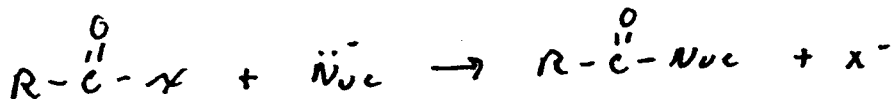
ACIDS WITH THE SAME # CARBONS → OXIDATION OF ALCOHOLS

ACIDS WITH 1 MORE CARBON → GRIGNARDS + CO₂ OR HYDROLYSIS OF NITRILES

REACTIONS OF CARBOXYLIC ACIDS

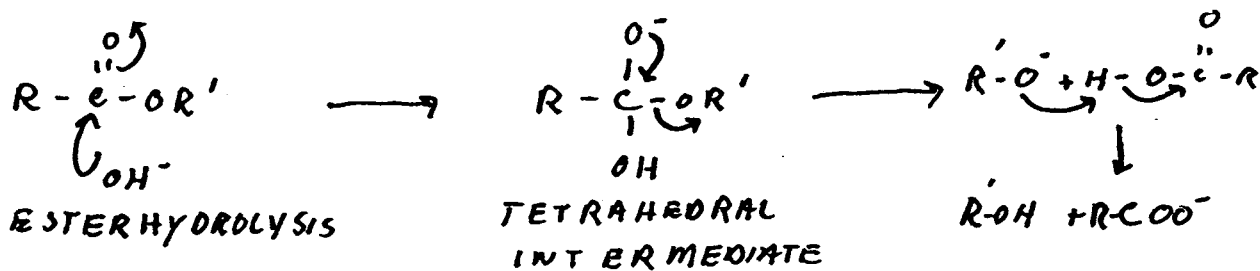
NUCLEOPHILIC ACYL SUBSTITUTION

IN NUCLEOPHILIC ACYL SUBSTITUTION, ONE NUCLEOPHILE REPLACES ANOTHER ON THE ACYL CARBON C=O

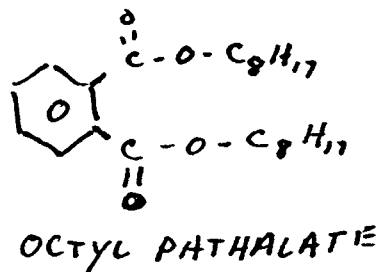
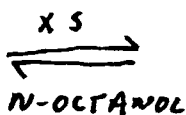
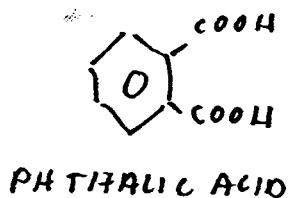
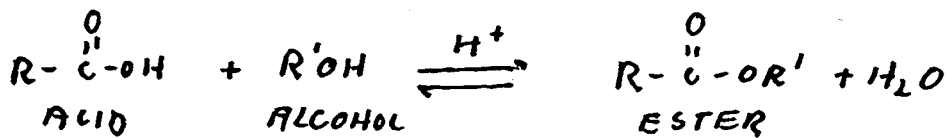


THERE WILL BE 2 IMPORTANT MECHANISMS FOR ACYL SUBSTITUTION

- 1) UNDER BASIC CONDITIONS A STRONG NUCLEOPHILE CAN ADD TO THE CARBONYL GROUP TO FORM A TETRAHEDRAL INTERMEDIATE WHICH THEN EXPELS A LEAVING GROUP



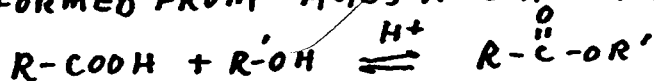
- 2) UNDER ACIDIC CONDITIONS, THE CARBONYL OXYGEN IS PROTONATED ACTIVATING IT TOWARD NUCLEOPHILIC ACYL SUBSTITUTION NOW A WEAKER NUCLEOPHILE CAN ATTACK, FORM A TETRAHEDRAL INTERMEDIATE, AND EXPEL A LEAVING GROUP. THE LEAVING GROUP IS OFTEN PROTONATED AND LEAVES AS A NEUTRAL MOLECULE AS IN THE FISCHER ESTERIFICATION



THIS IS AN EXTREMELY COMMON PLASTICIZER IT IS UBIQUITOUS

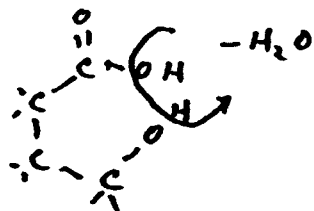
CARBOXYLIC ACID DERIVATIVES

ESTERS ARE FORMED FROM ACIDS AND ALCOHOLS

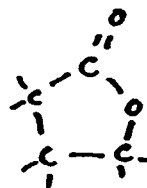


CYCLIC ESTERS ARE CALLED LACTONES

A γ -HYDROXY OR δ -HYDROXY ACID CAN FORM LACTONES



4-HYDROXY BUTANOIC ACID
 γ -HYDROXY BUTYRIC ACID



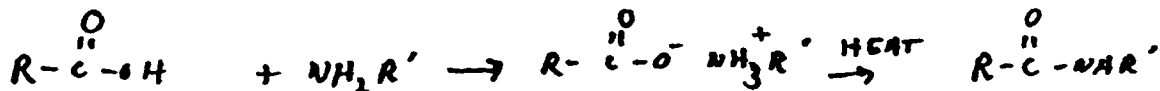
4-HYDROXY BUTANOIC ACID LACTONE
 γ -BUTYROLACTONE

IN EITHER ACID OR BASE, ESTERS MAY UNDERGO TRANS ESTERIFICATION
TREATING THE ESTER WITH A DIFFERENT ALCOHOL RESULTS IN AN
EXCHANGE OF ALKOXY GROUPS

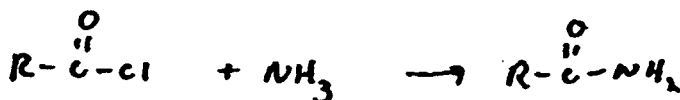


A LARGE EXCESS OF THE NEW ALCOHOL ENSURES GOOD YIELDS

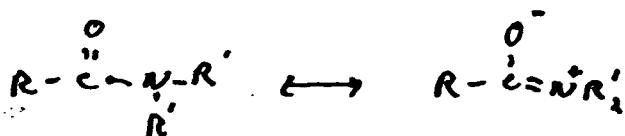
AMIDES ARE FORMED FROM ACIDS AND AMINES



THE REACTION IS OFTEN DONE WITH ACID CHLORIDES

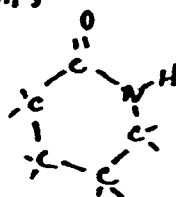
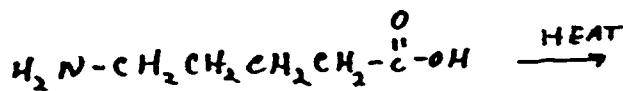


THE C-N BOND HAS PARTIAL DOUBLE BOND CHARACTER



AS A RESULT OF THIS STABILIZATION, AMIDES ARE VERY WEAK BASES

CYCLIC AMIDES ARE CALLED LACTAMS

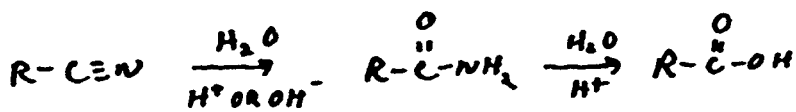


5-AMINO
PENTANOIC
ACID
LACTAM

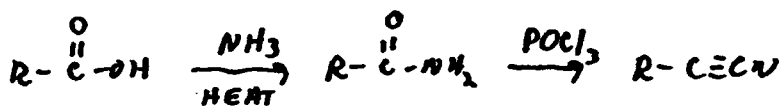
5-AMINOPENTANOIC ACID

NITRILES ARE CONSIDERED ACID DERIVATIVES

HYDROLYSIS



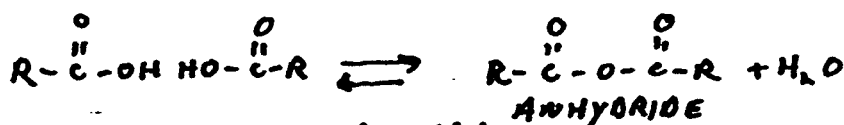
SYNTHESIS



THE NITRILE NITROGEN IS NOT BASIC BECAUSE ITS LONE PAIR IS TIGHTLY HELD IN A SP HYBRID ORBITAL

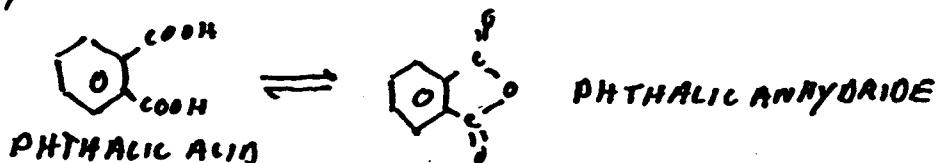
ANHYDRIDES

MADE FROM TWO MOLES OF ACID WITH LOSS OF WATER



DIACIDS MAY FORM CYCLIC ANHYDRIDES

ESPECIALLY IF A 5 OR 6 MEMBER RING RESULTS

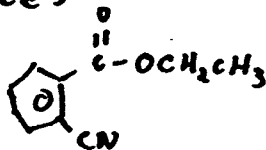


NOMENCLATURE OF MULTIFUNCTIONAL COMPOUNDS

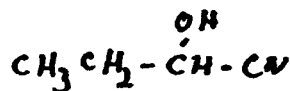
WHEN THERE IS MORE THAN ONE FUNCTIONAL GROUP IN A MOLECULE USE THE FOLLOWING PRIORITIES

ACID > ESTER > AMIDE > NITRILE > ALDEHYDE > KETONE > ALCOHOL > AMINE > ALKENE
 TABLE IS VERY USEFUL FOR REVIEWING THESE PRIORITIES AND NAMING CONVENTIONS. PROBLEM
 ALKYNE
 ETHERS
 HALIDES

EXAMPLES



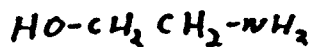
ETHYL O-CYANOBENZOATE



2-HYDROXYBUTANENITRILE



DICHLOROACETYL CHLORIDE



2-AMINOETHANOL

COMMON NAME

ETHANOL AMINE

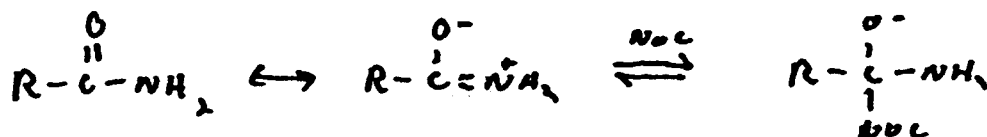
REACTIVITY OF ACID DERIVATIVES

THE REACTIVITY OF ACID DERIVATIVES TOWARD NUCLEOPHILIC ATTACK DEPENDS ON THEIR STRUCTURE AND ON THE BASICITY OF THE LEAVING GROUP

REACTIVITY	DERIVATIVE	LEAVING GROUP	BASICITY
MOST	ACID CHLORIDE $R-\overset{\overset{O}{\parallel}}{C}-Cl$	Cl^-	INCREASING BASICITY ↓
↑	ANHYDRIDE $R-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R$	$R-\overset{\overset{O}{\parallel}}{C}-O^-$	
↑	ESTER $R-\overset{\overset{O}{\parallel}}{C}-OR$	^-OR	
↑	AMIDE $R-\overset{\overset{O}{\parallel}}{C}-NH_2$	$^-NH_2$	
LEAST REACTIVE	ACID ANION $R-COO^-$		

RESONANCE STABILIZATION MAY ALSO AFFECT REACTIVITY

AMIDES LOSE RESONANCE STABILIZATION ON NUCLEOPHILIC ATTACK



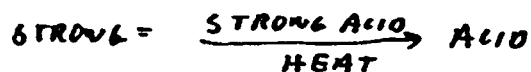
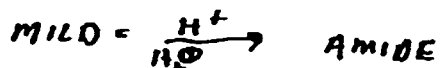
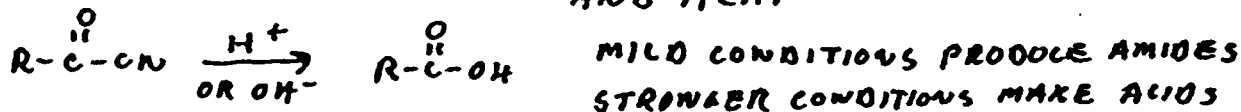
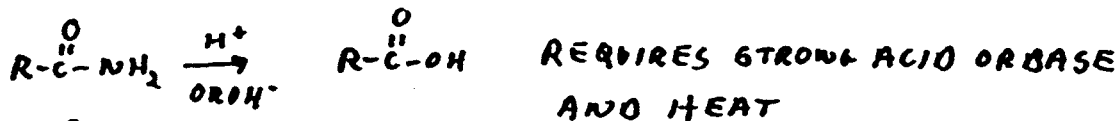
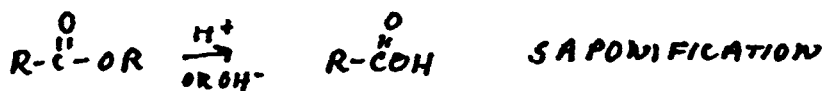
ESTERS AND ANHYDRIDES EXPERIENCE LESS RESONANCE STABILIZATION
ACID CHLORIDES VERY LITTLE

IN GENERAL REACTIONS ARE EASILY DONE THAT CONVERT MORE REACTIVE DERIVATIVES TO LESS REACTIVE ONES

THERE IS A NICE SUMMARY OF REACTIONS ON PAGES 966 AND 967

HYDROLYSIS OF CARBOXYLIC ACID DERIVATIVES

ALL DERIVATIVES HYDROLYSE TO THE ACID



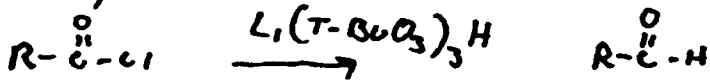
SUMMARY OF REDUCTIONS

TO ALCOHOLS

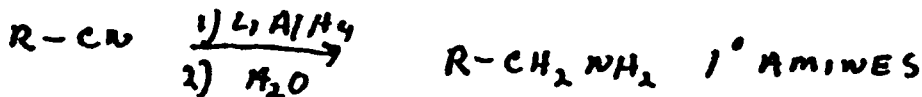
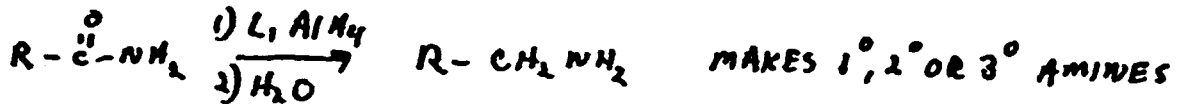


ACIDS, ACIDCHLORIDES, ESTERS

TO ALDEHYDES

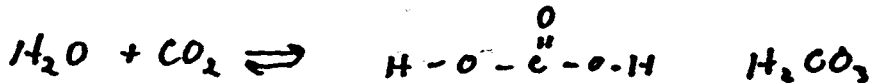


TO AMINES

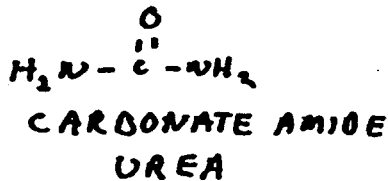
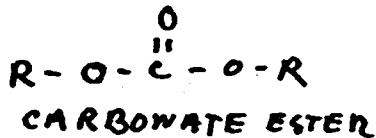


ESTERS AND AMIDES OF CARBONIC ACID

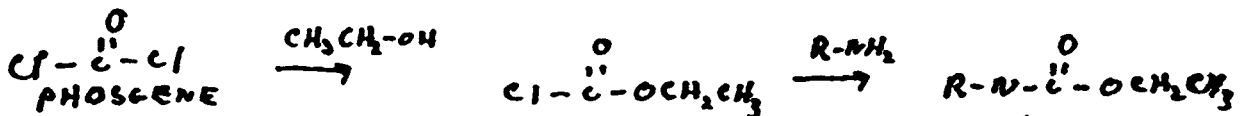
WHEN CO₂ DISSOLVES IN WATER → CARBONIC ACID



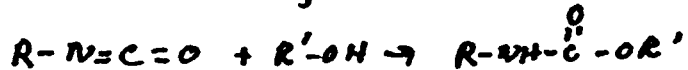
ALTHOUGH CARBONIC ACID IS NOT STABLE, ITS DERIVATIVES ARE



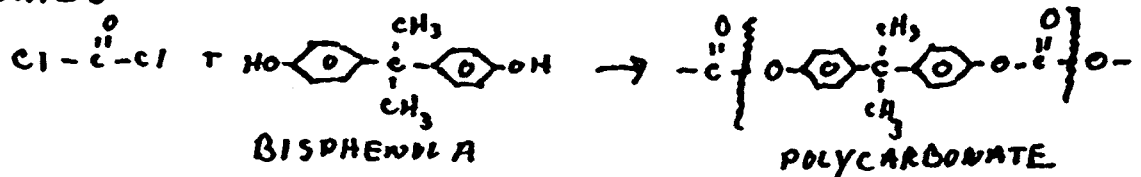
SYNTHESIS



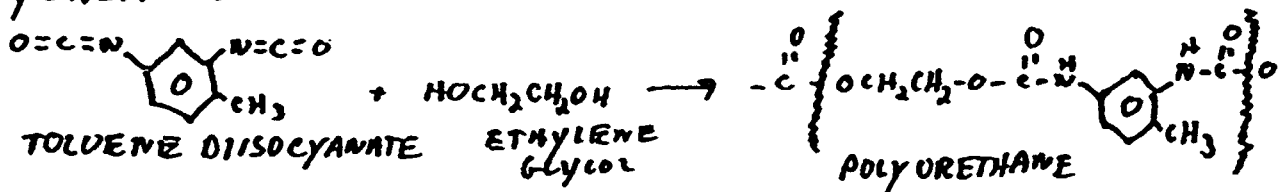
OR FROM ISOCYANATE



'IFE WOULDN'T BE THE SAME WITHOUT
POLYCARBONATES



OR POLYURETHANES



CHAPTER 19

SHOW THE PRODUCTS
OF ACYL DERIVATIVE
INTERCONVERSIONS

26-29 33-36

UNDERSTAND THE MECHANISM
OF THESE REACTIONS

44, 45, 50

UNDERSTAND REACTIVITY/STRUCTURE
RELATIONSHIPS OF CARBONYL CARBONS

30, 31

USE THESE REACTIONS IN SYNTHESIS

32, 38, 39

SS Ex 2 90