

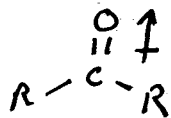
CHAPTER 18 LECTURE NOTES FOR ORGANIC CHEMISTRY © MM 2007

ALDEHYDES AND KETONES - CARBONYL COMPOUNDS

2 ALKYL GROUPS, → KETONE

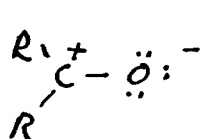
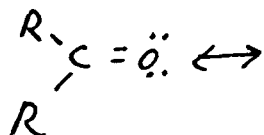
1 ALKYL GROUP, ONE H → ALDEHYDE

THE CHEMISTRY OF BOTH IS VERY SIMILAR, EXCEPT FOR OXIDATIONS



TRIGONAL, PLANAR
120° BOND ANGLES
HIGHLY POLAR

A RESONANCE PICTURE



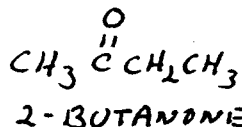
THIS IS A MINOR CONTRIBUTOR, BUT CLEARLY INDICATES THE BOND POLARITY

THE CARBONYL CARBON HAS A PARTIAL PLUS CHARGE SO IT IS ELECTROPHILIC (LEWIS ACID)

THE CARBONYL OXYGEN HAS A PARTIAL MINUS CHARGE SO IT IS NUCLEOPHILIC (LEWIS BASE)

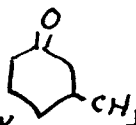
NOMENCLATURE

DROP THE "E" FROM THE ALKANE NAME, ADD "ONE" FOR KETONES NUMBER



NUMBER THE CARBONYL-CONTAINING CHAIN FROM THE C=O END

IN CYCLIC KETONES THE C=O IS #1

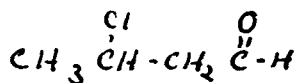


3-METHYLCYCLOHEXANONE

ALDEHYDES ARE AT THE END OF THE CHAIN

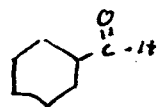
SO THE C=O IS ALWAYS #1

DROP THE "E", ADD -AL



3-CHLOROBUTANAL

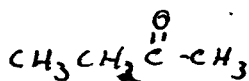
IF THE CHO UNIT IS ATTACHED TO A LARGE SUBSTITUENT OR RING, IT MAY BE NAMED "CARBALDEHYDE" (=CHO)



CYCLOHEXANE CARBALDEHYDE

COMMON NAMES

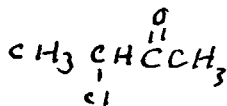
KETONES THE 2 R-GROUPS ARE NAMED



METHYL ETHYL KETONE
MEK

SUBSTITUENTS ON THE ALKYL GROUPS

ARE INDICATED USING GREEK LETTERS α, β, γ... ETC

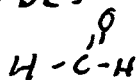


α-CHLOROETHYL METHYL KETONE

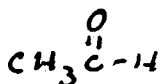
TWO MORE COMMON NAMES $\text{CH}_3\overset{\text{O}}{\parallel}\text{C}\text{CH}_3$ ACETONE

PHENYL KETONES ARE NAMED "PHENONE" $\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-\phi$ ACETOPHENONE

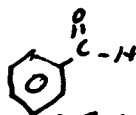
ALDEHYDES



FORMALDEHYDE

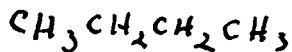


ACETALDEHYDE



BENZALDEHYDE

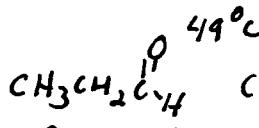
PHYSICAL



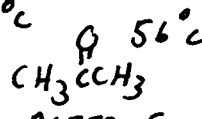
BUTANE 0°C



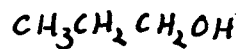
METHYLETHYLETHER 8°C



PROPANAL 49°C



ACETONE 56°C



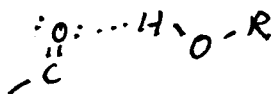
PROPANOL 97°C

THIS SERIES OF BOILING POINTS REFLECTS

POLARITY AND, FOR PROPANOL, HYDROGEN BONDING

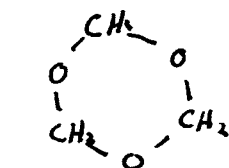
CARBONYL COMPOUNDS ARE HYDROGEN BOND ACCEPTORS, THUS

GOOD SOLVENTS FOR HYDROXYLIC COMPOUNDS

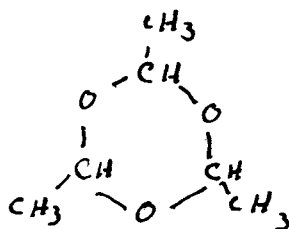


THE SMALLEST ALDEHYDES, FORMALDEHYDE AND ACETALDEHYDE

BOTH FORM SOLID, CYCLIC TRIMERS



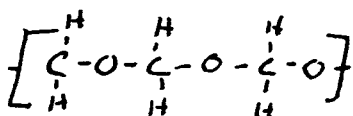
TRIOXANE



PARALDEHYDE

HEATING CONVERTS THESE TO THE MONOMERS

FORMALDEHYDE ALSO FORMS A LINEAR POLYMER, PARAFORMALDEHYDE



HEATING REGENERATES THE MONOMER

SPECTROSCOPY

IR $\text{C}=\text{O}$ STRETCH, ≈ 1710 , CONJUGATION LOWER TO ≈ 1680

ALDEHYDES FEATURE $\overset{\text{H}}{\text{C}}-\text{H}$ $\text{C}-\text{H}$ STRETCH $2710 + 2810$

RING STRAIN RAISES $\text{C}=\text{O}$ TO 1750 RANGE

NMR PROTONS α TO $\text{C}=\text{O}$ $2.1 \rightarrow 2.4$ ppm

ALDEHYDE H $9-10$ ppm AND SHARP

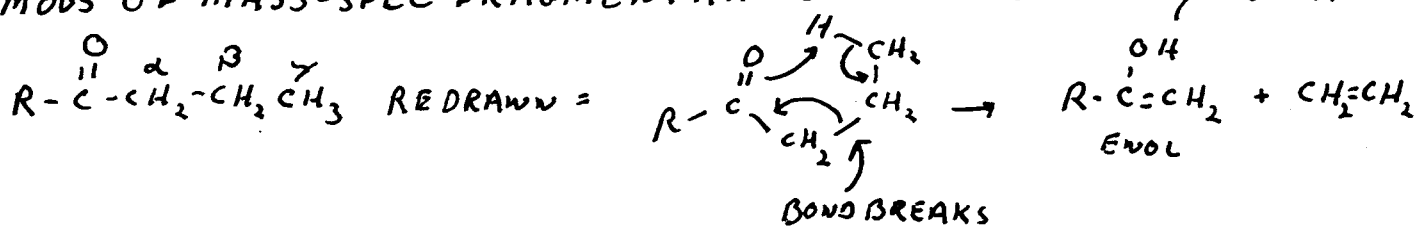
MASS SPECTRA

KETONES CLEAVE α TO $\overset{\text{O}}{\parallel}\text{C}$ TO GIVE ACyliUM $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{R}' \rightarrow \text{R}-\overset{\text{O}}{\parallel}\text{C}^+$

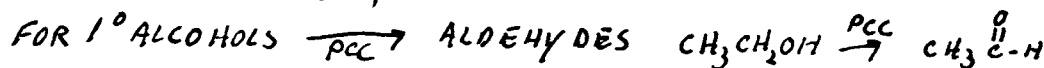
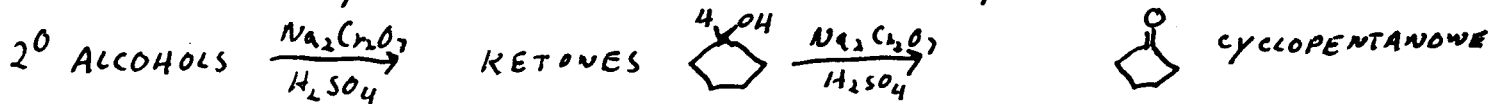
RECALL THE RESONANCE-STABILIZED ACyliUM FROM PG 758

AS THE ELECTROPHILE IN FRIEDEL-CRAFTS ACYLATION

ALDEHYDES AND KETONES WITH γ -HYDROGENS UNDERGO THE MOST FAMOUS OF MASS-SPEC FRAGMENTATIONS - THE MCCLAFFERTY REARRANGEMENT

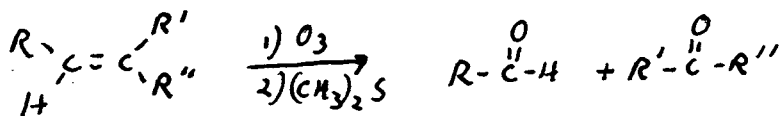


REVIEWING THE SYNTHESIS OF KETONES AND ALDEHYDES

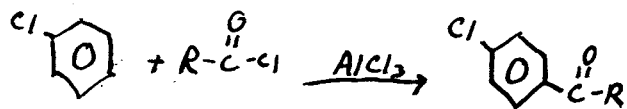


THE REVERSE REACTION IS REDUCTION WITH $LiAlH_4$, $NaBH_4$, OR H_2/CAT

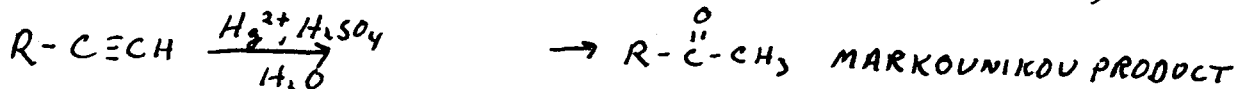
KETONES AND ALDEHYDES CAN BE MADE BY OZONOLYSIS OF ALKENES



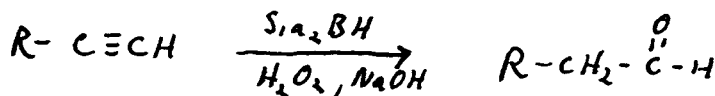
PHENYL KETONES CAN BE MADE FROM FRIEDEL-CRAFTS ACYLATION



ALKYNES CAN BE HYDRATED (HYDRATING ALKENES GIVES ALCOHOLS)

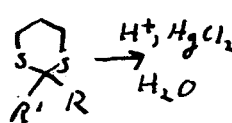
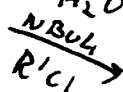
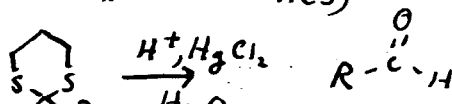
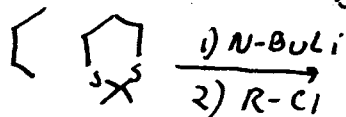
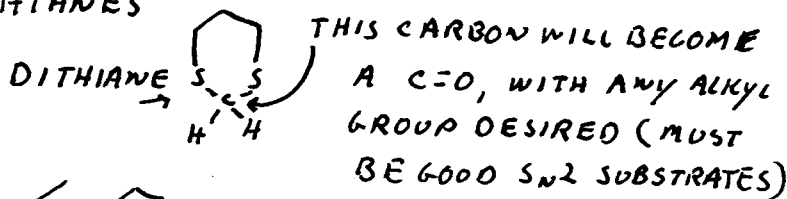


ANTI-MARKOVNIKOV HYDRATION OF ALKYNES \rightarrow HYDROBORATION/OXIDATION



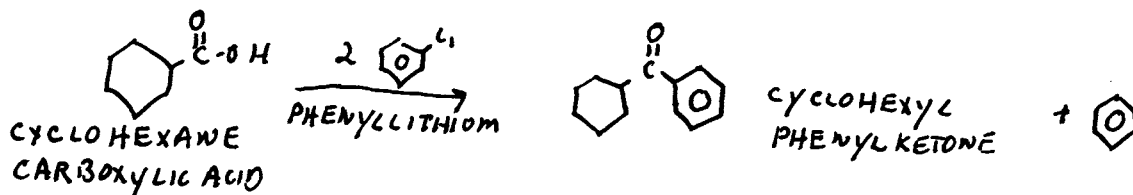
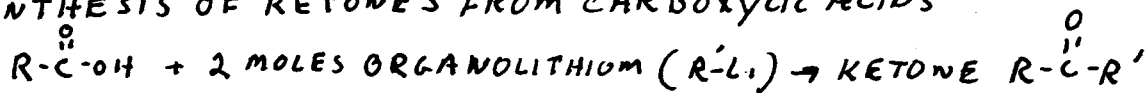
INTRODUCING NEW METHODS FOR SYNTHESIZING ALDEHYDES AND KETONES

DITHIANES

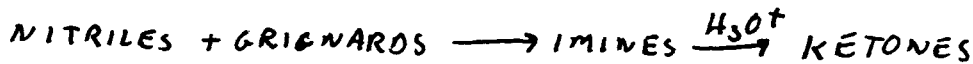


ALKYLATE ONCE FOR ALDEHYDES, TWICE FOR KETONES

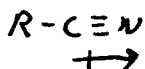
SYNTHESIS OF KETONES FROM CARBOXYLIC ACIDS



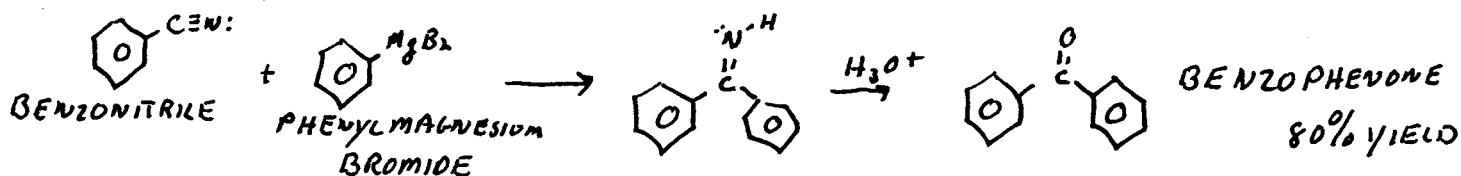
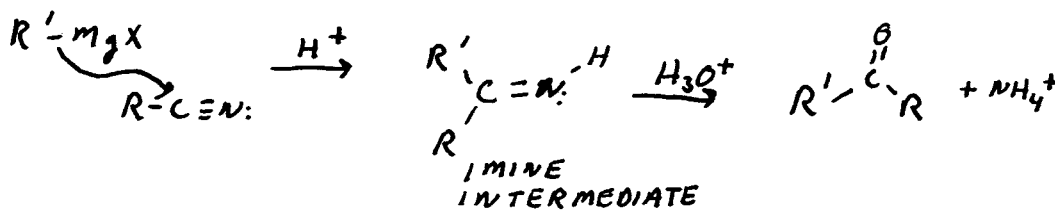
SYNTHESIS OF KETONES FROM NITRILES



THE NITRILE FUNCTIONAL GROUP IS POLAR, THE CARBON IS ELECTROPHILIC

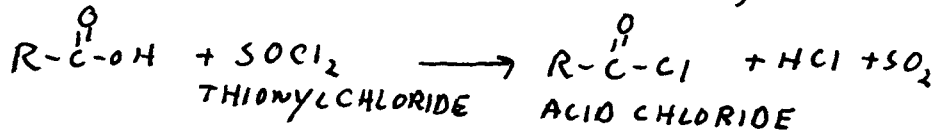


NUCLEOPHILES, SUCH AS GRIGNARDS OR ORGANOLITHIUMS ATTACK NITRILE CARBONS



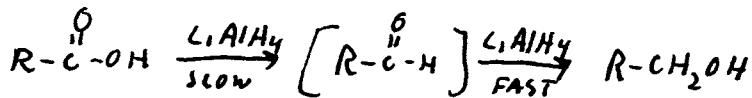
SYNTHESIS OF ALDEHYDES AND KETONES FROM ACID CHLORIDES

ACIDS CAN BE CONVERTED TO THE VERSATILE, REACTIVE ACID CHLORIDES

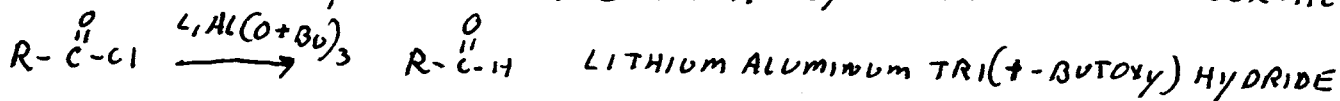


ACIDS THEMSELVES CANNOT BE REDUCED TO ALDEHYDES

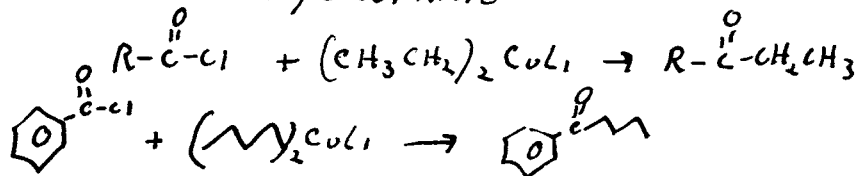
ANY REDUCING AGENT STRONG ENOUGH TO REDUCE AN ACID QUICKLY REDUCES ALDEHYDE



BUT ACID CHLORIDES, MORE REACTIVE THAN ACIDS, CAN BE REDUCED UNDER MILD CONDITIONS

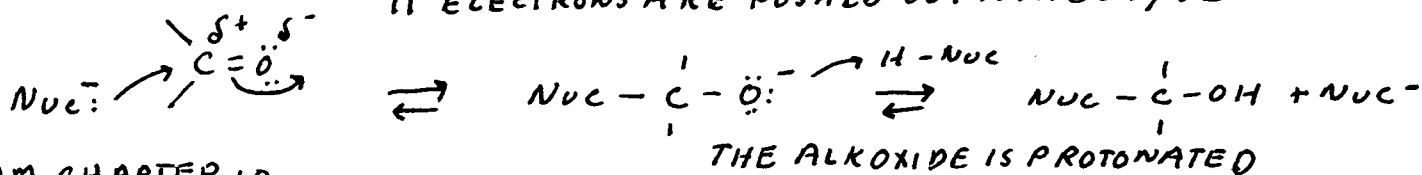


KETONES ARE MADE FROM ACID CHLORIDES BY REACTION WITH LITHIUM DIALKYL CUPRATE



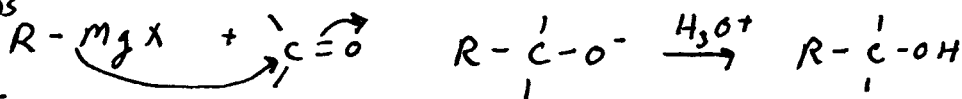
NUCLEOPHILIC ADDITION TO CARBONYLS

THE MAIN REACTION OF CARBONYL COMPOUNDS IS NUCLEOPHILIC ADDITION
 A NUCLEOPHILE ATTACKS THE PARTIALLY POSITIVE CARBONYL CARBON
 π ELECTRONS ARE PUSHED OUT TO THE OXYGEN

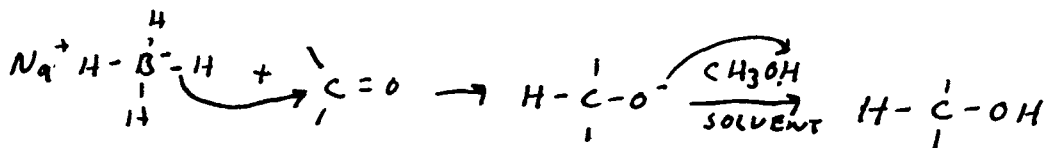


FROM CHAPTER 10

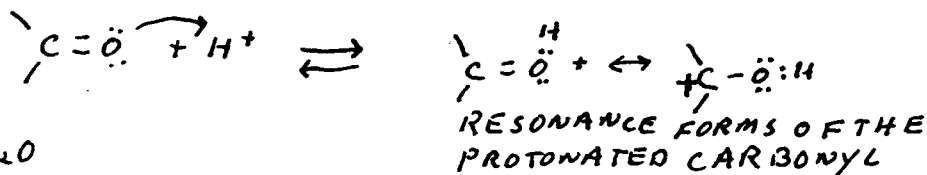
GRIGNARDS



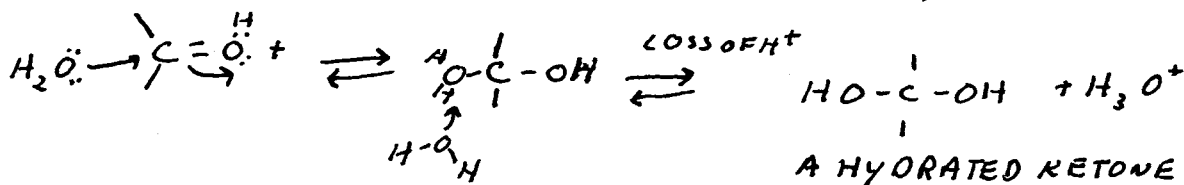
HYDRIDE
 REDUCTION



WEAKER NUCLEOPHILES SUCH AS H₂O AND R-OH CAN ALSO ADD TO C=O,
 AFTER THE C=O IS ACTIVATED BY PROTONATION



ATTACK BY H₂O

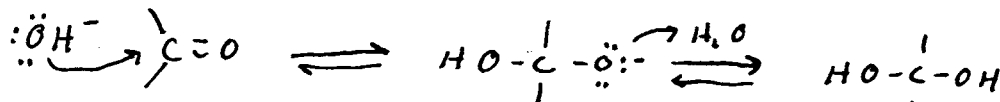


KETONES AND ALDEHYDES ARE

USUALLY IN EQUILIBRIUM WITH THEIR HYDRATES

ALDEHYDES ARE USUALLY MORE REACTIVE THAN KETONES DUE TO STERIC
 EFFECTS (LESS CROWDING) AND INDUCTIVE EFFECTS (ONE LESS ALKYL GROUP
 FOR ELECTRON DONATION)

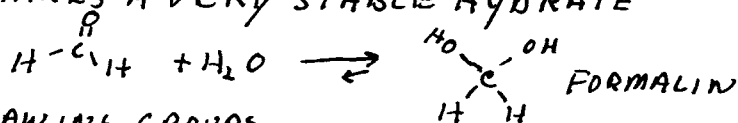
IN BASIC SOLUTION, ALDEHYDES AND KETONES ARE ALSO IN EQUILIBRIUM
 WITH THEIR HYDRATES. OH⁻ IS THE NUCLEOPHILE



THIS EQUILIBRIUM OFTEN LIES TO THE LEFT, FAVORING THE CARBONYL FORM

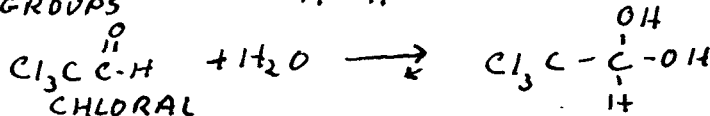
ALDEHYDES ARE MORE LIKELY THAN KETONES TO FORM STABLE HYDRATES

FORMALDEHYDE MAKES A VERY STABLE HYDRATE



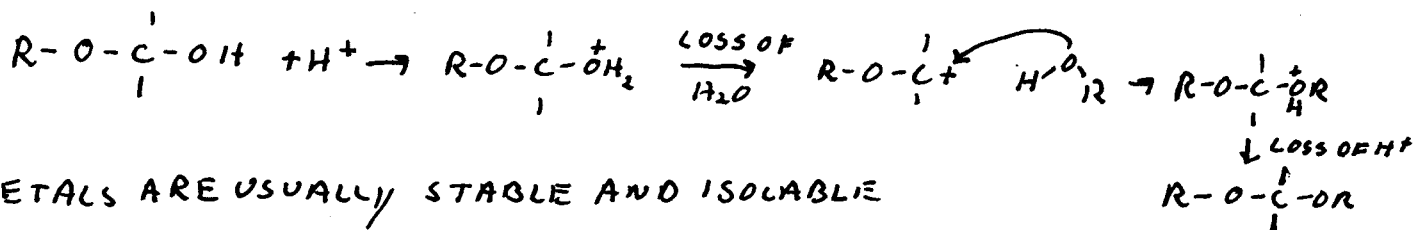
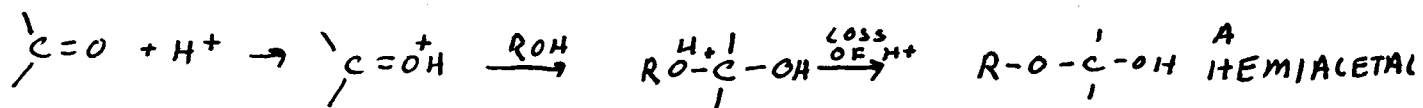
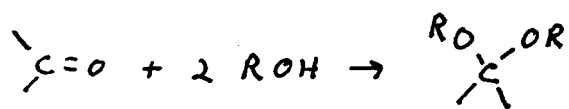
ELECTRON WITHDRAWING GROUPS

FAVOR THE HYDRATE

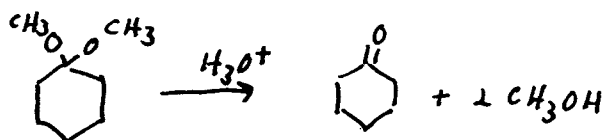


CHLORAL
 HYDRATE
 A SEOATIVE

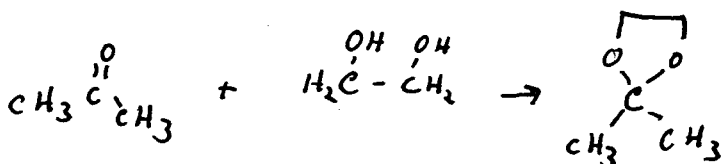
ALDEHYDES AND KETONES DO THE SAME REACTIONS WITH ALCOHOLS
 REACTION WITH THE WEAK NUCLEOPHILE R-OH REQUIRES ACID CATALYSIS
 THE PRODUCTS ARE CALLED ACETALS
 THE OVERALL REACTION



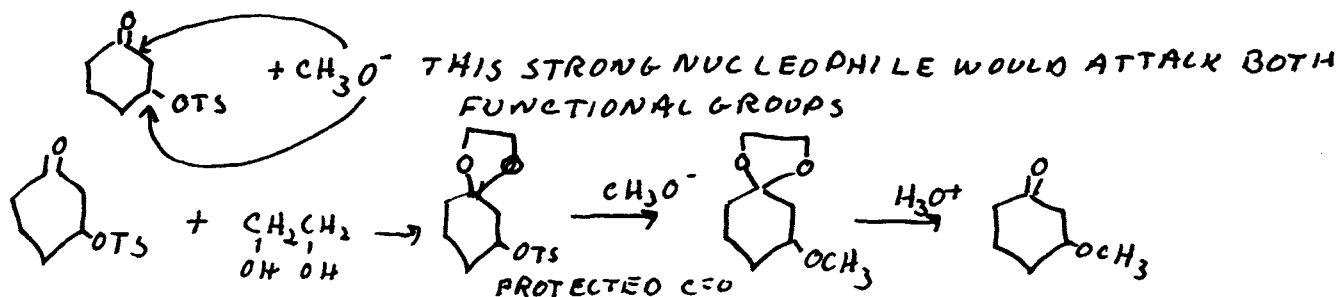
ACETALS ARE USUALLY STABLE AND ISOLUBLE
 BUT THE REACTION IS REVERSIBLE, AND ACETALS CAN BE
 HYDROLYSED WITH EXCESS H_3O^+



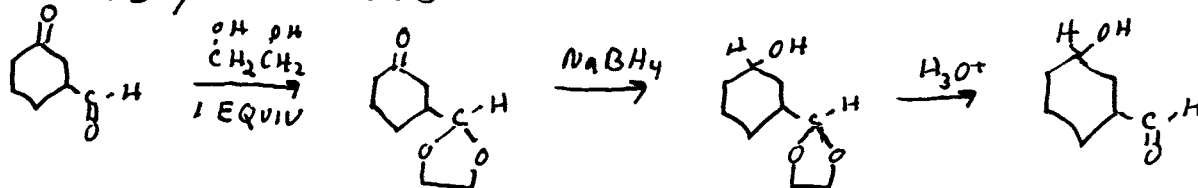
DIOLS ARE USED TO FORM CYCLIC ACETALS



ACETALS ARE EASILY HYDROLYSED, BUT STABLE TO STRONG BASES AND
 NUCLEOPHILES. SINCE STRONG BASES AND NUCLEOPHILES ATTACK CARBONYLS,
 ACETALS ARE USED TO "PROTECT" CARBONYLS DURING SYNTHESIS



SINCE ALDEHYDES FORM ACETALS MORE READILY THAN KETONES, THEY CAN BE
 SELECTIVELY PROTECTED

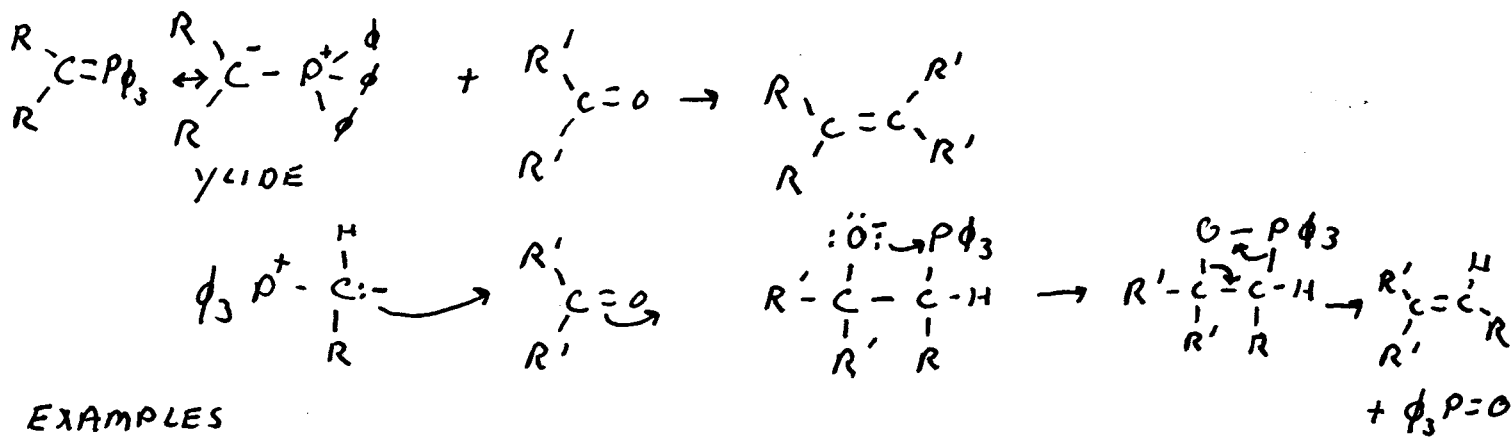


THE WITTIG REACTION

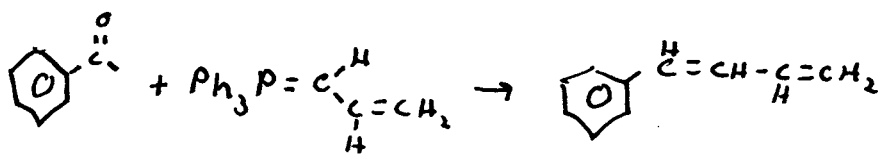
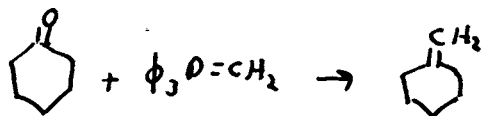
ANOTHER EXAMPLE OF NUCLEOPHILIC ADDITION

OVERALL $\text{>C=O} \rightarrow \text{C=C}$ THIS IS A USEFUL ALKENE SYNTHESIS

THE WITTIG REAGENT IS A PHOSPHOROUS-STABILIZED CARBANION



EXAMPLES



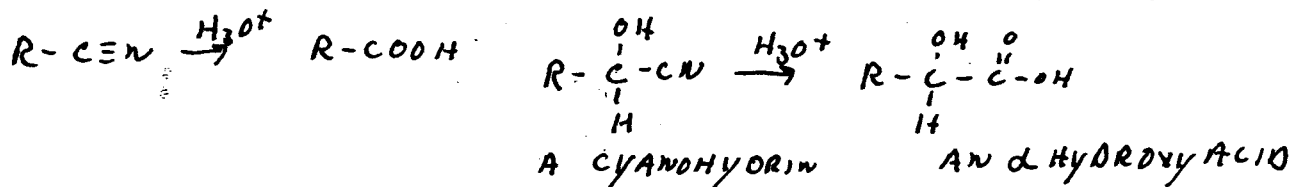
CYANOHYDRINS

$\text{C}\equiv\text{N}^-$ CYANIDE ION, AN EXCELLENT NUCLEOPHILE

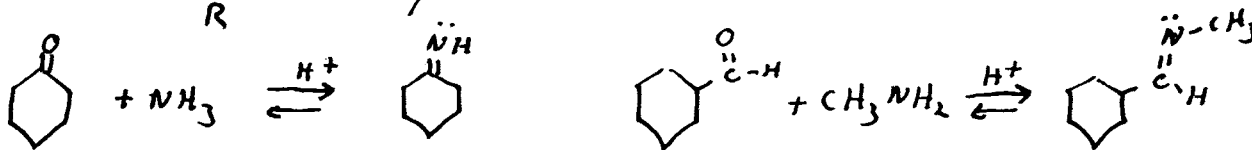
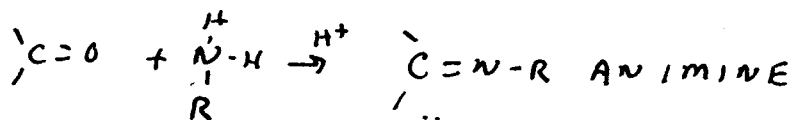


IN BULKY KETONES THE EQUILIBRIUM LIES TO THE LEFT

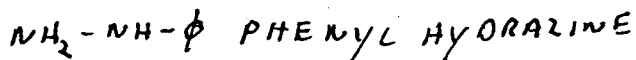
NITRILES ARE USEFUL SYNTHETIC INTERMEDIATES, HYDROLYSING TO ACIDS



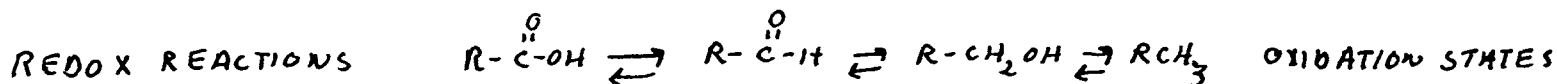
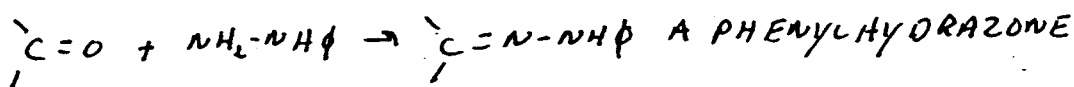
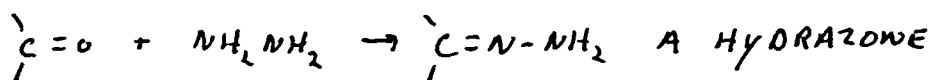
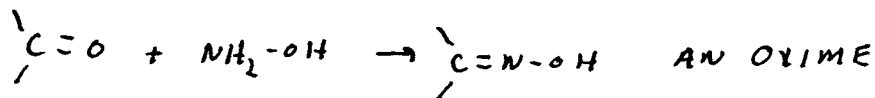
CONDENSATIONS WITH AMMONIA, AMINES \rightarrow FORMATION OF IMINES



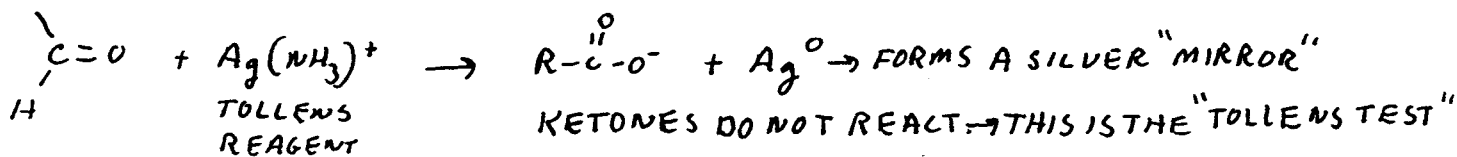
KETONES AND ALDEHYDES ALSO CONDENSE WITH AMMONIA DERIVATIVES



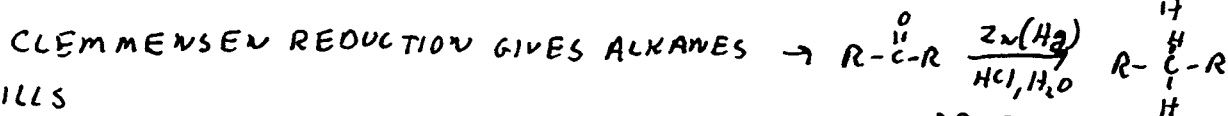
WE WILL USE THESE PRODUCTS IN CHAPT. 19 FOR SYNTHESIS. THEY ARE ALSO USED FOR QUALITATIVE IDENTIFICATION OF CARBONYL COMPOUNDS



ALDEHYDES ARE SO EASILY OXIDIZED THAT EVEN SILVER ION Ag^+ REDUCES



REDUCTIONS



SKILLS

PROBLEMS

SYNTHESIS

7A, 8, 9A, 10A, 11, 12

MECHANISM OF NUCLEOPHILIC ADDITION

17, 20B, 23

BE ABLE TO CREATE

MULTI STEP SYNTHESSES

S1, 6, S2, 16ABOE, 29AB

NOMENCLATURE AND STRUCTURES

33B, 35A, B

SPECTRA

1, 37A-C

MCLAFFERTY REARRANGEMENT

2, 39, 41

3, 4, 43