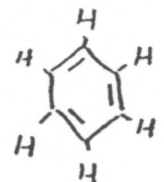


CHAPTER 9 LECTURE NOTES FOR ORGANIC CHEMISTRY © 2011 MM

AROMATIC COMPOUNDS

WHEN A NEW COMPOUND, C_6H_6 WAS DISCOVERED IN ≈ 1830 NO ONE COULD IMAGINE A STRUCTURE. MANY WERE PROPOSED, AND A GENERATION OF DEBATE FOLLOWED. IN 1858 CARBON CHAINS WERE PROPOSED IN ≈ 1860 , AUGUST KEKULE' HAD THE REVOLUTIONARY INSIGHT - A RING

KEKULE' STRUCTURE  WAS CONSIDERED QUITE BIZARRE

SINCE BENZENE FORMS ONLY 1 1,2-DICHLORO PRODUCT, KEKULE PROPOSED THIS FAST INTERCONVERSION



WHICH IS THE FORE RUNNER OF OUR CURRENT RESONANCE STRUCTURE



THESE ARE ONLY CONVENIENT CONSTRUCTS, A BETTER PICTURE IS

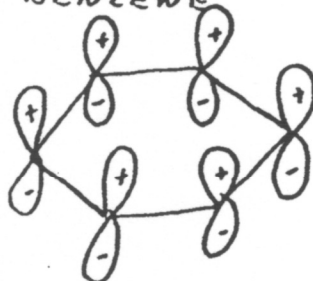


WE FIND BY HYDROGENATION THAT BENZENE HAS 36 KCAL/MOL RESONANCE STABILIZATION

THIS STABILITY MEANS THAT BENZENE DOES NOT UNDERGO ALKENE REACTION

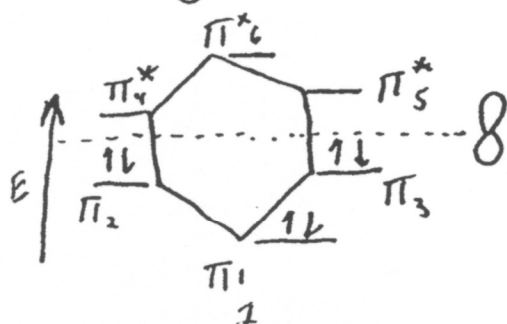


THE MOLECULAR ORBITALS OF BENZENE



THIS IS THE LOWEST OF 6 MO's ALL BONDING

THE ENERGY DIAGRAM OF BENZENE MO's

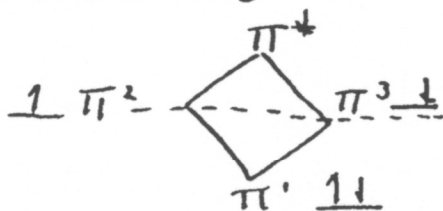


ALL 6 πe^- IN BONDING MO's VERY STABLE



IN CONTRAST TO BENZENE, THE 4 π OF CYCLOBUTADIENE OCCUPY LESS FAVORABLE MO₂

(2)



THE COMPOUND HAS 2 UNPAIRED ELECTRONS IN ORBITALS OF BOND ORDER ZERO

SO, YOU CAN DRAW 2 RESONANCE STRUCTURES FOR CYCLOBUTADIENE



BUT THE MO PICTURE SAYS NO RESONANCE STABILIZATION

AROMATIC, ANTIAROMATIC, NONAROMATIC

WE COMPARE MANY CYCLIC, CONJUGATED SYSTEMS

TO BE AROMATIC

- 1) CYCLIC, WITH CONJUGATED π BONDS
- 2) EACH RING ATOM MUST HAVE A P ORBITAL
- 3) THESE P ORBITALS MUST OVERLAP CONTINUOUSLY (USUALLY PLANAR)
- 4) DELOCALIZATION OF THE π ELECTRONS MUST RESULT IN LOWER ENERGY

AN ANTIAROMATIC COMPOUND MEETS CRITERIA 1-3 BUT π DELOCALIZATION INCREASES ENERGY



VIOLATING CRITERIA 1-3 MEANS \rightarrow NONAROMATIC



TO CRITERIA 1-4 WE ADD HÜCKEL'S RULE

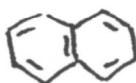
AROMATIC IF # π ELECTRONS = $4N + 2$ WHERE N IS AN INTEGER

- $N = 1 \rightarrow 6 \pi$ ELECTRONS
- $N = 0 \rightarrow 2 \pi$ ELECTRONS
- $N = 2 \rightarrow 10 \pi$ ELECTRONS

MOST LARGE RING SYSTEMS ARE NON PLANAR, THEREFORE NONAROMATIC
SOME LARGE $4N + 2$ ANNULENES ARE AROMATIC



FUSED RING SYSTEMS CAN BE PLANAR



NAPHTHALENE AROMATIC

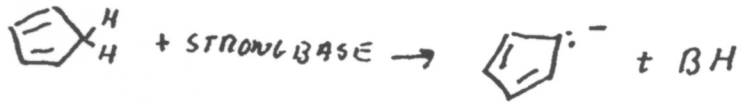
THE MO DERIVATION OF HÜCKEL'S RULE

MOs IN THESE SYSTEMS HAVE 1 LOWEST FILLED MO → THE "2"
AND PAIRS OF HIGHER LEVEL MOs FILLED WITH 4 ELECTRONS → THE "4N"
IF THERE ARE ONLY 2 ELECTRONS FOR THESE 2 MOs THE SHELL IS HALF FILLED, ANTI AROMATIC, LIKE CYCLOBUTADIENE

AROMATIC IONS



ITS UNUSUALLY ACIDIC
pKa = 16 vs 46 FOR C1=CC=C1



4N+2 AROMATIC



THE CYCLOPENTADIENYL CATION HAS 4N ELECTRONS → ANTI AROMATIC

THE

CYCLOHEPTATRIENYL CATION IS ALSO 4N+2 AROMATIC

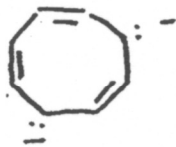


COMMON NAME TROPYLIUM ION

THE ANION IS ANTI AROMATIC

REPRESENTS THE MOST STABLE CARBOCATION WE'VE SEEN

VERY UNUSUAL DIANION OF CYCLOOCTATETRAENE CAN BE MADE



PLANAR
4N+2 AROMATIC

NON AROMATIC
NON PLANAR

NEXT PAGE SUMMARIZES AROMATIC, ANTI AROMATIC RINGS

ETEROCYCLIC AROMATIC COMPOUNDS

HETEROCYCLIC COMPOUNDS CONTAIN HETEROATOMS N, S, O

PYRIDINE IS THE AROMATIC ANALOG OF BENZENE WITH N IN THE RING

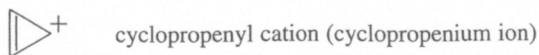


IT IS BASIC, LIKE AMMONIA →

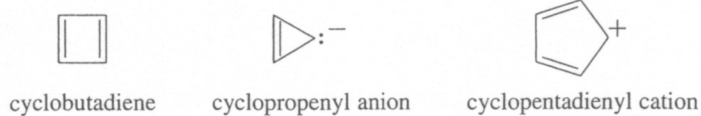


PYRIDINIUM ION

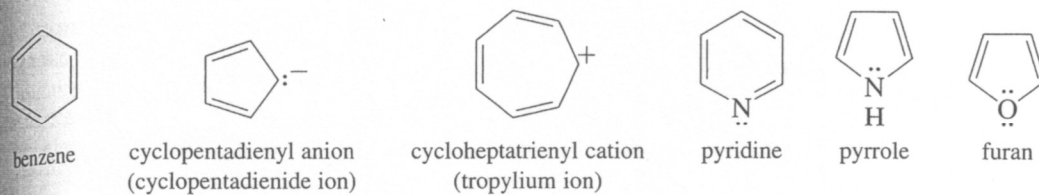
Two π -electron systems (aromatic)



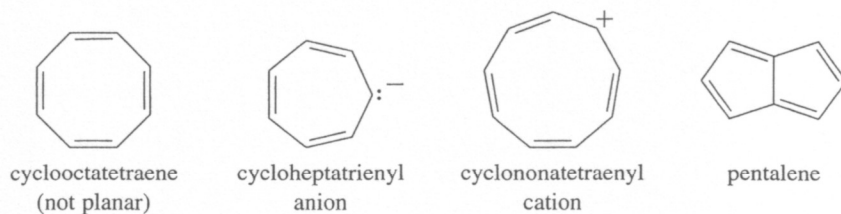
Four π -electron systems (antiaromatic)



Six π -electron systems (aromatic)



Eight π -electron systems (antiaromatic if planar)

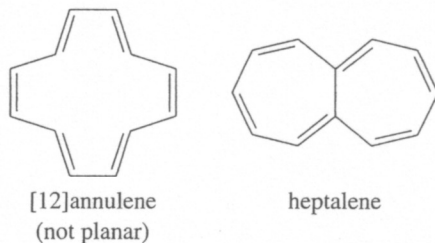


Ten π -electron systems (aromatic)



(Naphthalene can also be considered as two fused benzenes.)

Twelve π -electron systems (antiaromatic if planar)

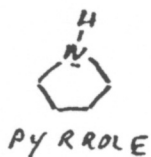


The criteria for Hückel's rule require a ring of atoms, all with unhybridized p orbitals overlapping in a continuous ring. In discussing aromaticity, we have considered only compounds composed of rings of sp^2 hybrid carbon atoms. **Heterocyclic compounds**, with rings containing sp^2 hybridized atoms of other elements, can also be aromatic. Nitrogen, oxygen, and sulfur are the most common heteroatoms in heterocyclic aromatic compounds.

16-9 Heterocyclic Aromatic Compounds

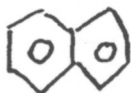
HETEROCYCLIC AROMATICS

(4)



ANISOELECTRONIC
SERIES WITH
6 π ELECTRONS

OLYNUCLEAR AROMATIC HYDROCARBONS (PAH) FUSED RING SYSTEMS



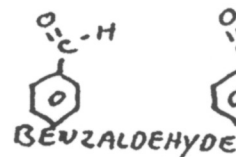
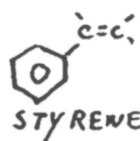
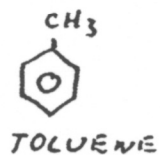
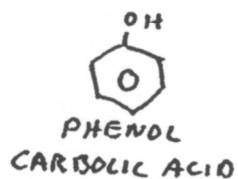
THE HIGHER PAH ARE CARCINOGENIC

SUCH AS PYRENE AND BaP

FOUND IN COMBUSTION PRODUCTS - FOREST FIRES, ENGINE EXHAUST, CIGARETTES

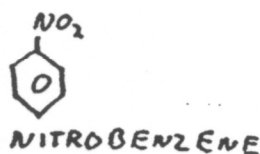
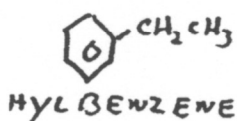
NOMENCLATURE OF BENZENE DERIVATIVES

MANY COMMON NAMES



COMPOUNDS MAY BE NAMED AS DERIVATIVES OF BENZENE

ALKYL BENZENES



BENZENE AS A SUBSTITUENT IS CALLED PHENYL (MAY BE ABBREVIATED AS

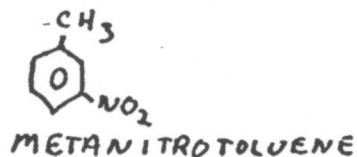
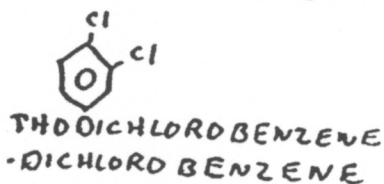
PH OR ϕ)

IN CONDENSED STRUCTURES)

ETHYLETHYL ETHER

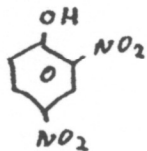
TRIPHENYL METHANE

SUBSTITUTED BENZENES ARE CALLED ORTHO (1,2), META (1,3), PARA (1,4)

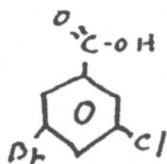


BENZENES WITH 3 OR MORE SUBSTITUENTS ARE NUMBERED

1 IS ASSIGNED TO THE CARBON BEARING THE FUNCTIONAL GROUP THAT DEFINES THE BASE NAME

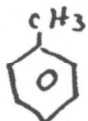


2,4-DINITROPHENOL

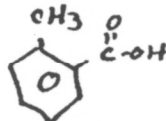


3-BROMO-5-CHLORO BENZOIC ACID

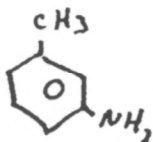
OME MORE COMMON NAMES



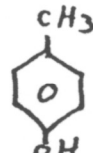
TOLUENE



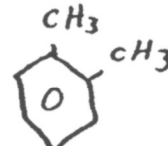
O-TOLUIC ACID



M-TOLUIDINE

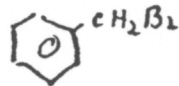
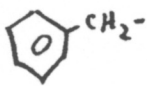


P-CRESOL

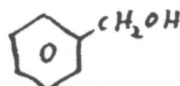


O-XYLENE

THE 7 CARBON UNIT IS CALLED BENZYL



BENZYL BROMIDE



BENZYL ALCOHOL

FINALLY, AROMATIC COMPOUNDS ARE SOMETIMES CALLED ARENES

AR- FOR SHORT

AR-O-R

AR-NH₂

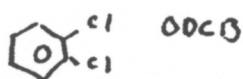
ARYL AS SUBSTITUENT

ARYL ALKYL ETHER

ARYL AMINE

PHYSICAL PROPERTIES

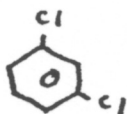
HIGH SYMMETRY MEANS LOW POLARITY IN THIS SERIES



OOCB

BP 181°C

MP -17°C



MOCB

BP 173°C

MP -25°C



POCB

BP 170°C

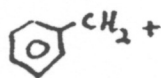
MP 54°C

HIGH SYMMETRY GIVES GOOD CRYSTAL PACKING

SPECTROSCOPY OF AROMATIC COMPOUNDS

IR C=C STRETCH 1600 LOWEST OF THE C=C STRETCHES

MASS BENZYLIC COMPOUNDS CLEAVE TO STABLE BENZYLIC CATIONS



$$C_7H_7 = 91$$

MR AR-H 6.5-8.2 PPM HIGHER SHIFTS FROM δ⁻ WITHDRAWING SUBSTITUENTS, -C≡N, -C=O, -NO₂

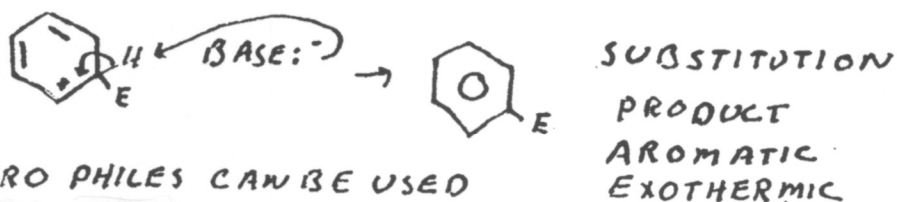
LOWER SHIFTS FROM δ⁻ DONATING -OH, -OR, -NH₂

LECTURE NOTES FOR ORGANIC CHEMISTRY © MM 2011

ELECTROPHILIC AROMATIC SUBSTITUTION

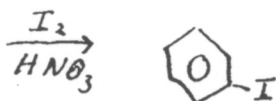
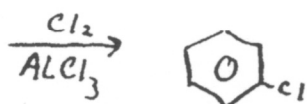
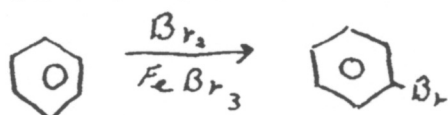


ABSTRACTION OF H⁺



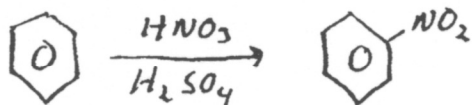
MANY DIFFERENT ELECTROPHILES CAN BE USED
SUMMARY PG 356

HALOGENATION



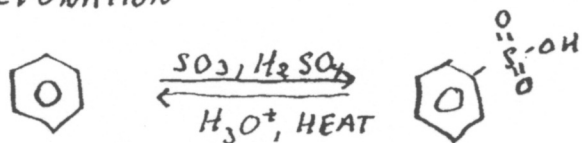
PG 326
FOR MECHANISM

NITRATION



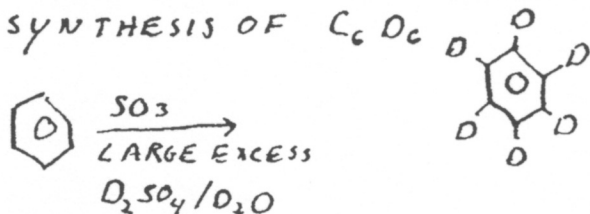
HNO₃ + H₂SO₄ PRODUCE THE NITRONIUM ION
+ NO₂ $\text{:}\ddot{\text{O}}=\text{N}^+=\text{O}\text{:}$
WHICH IS THE ELECTROPHILE

SULFONATION



SO₃ IS THE ELECTROPHILE
SULFONATION IS REVERSIBLE

SINCE DESULFONATION SUBSTITUTES A H ON THE RING, IT PROVIDES
A SYNTHESIS OF C₆D₆



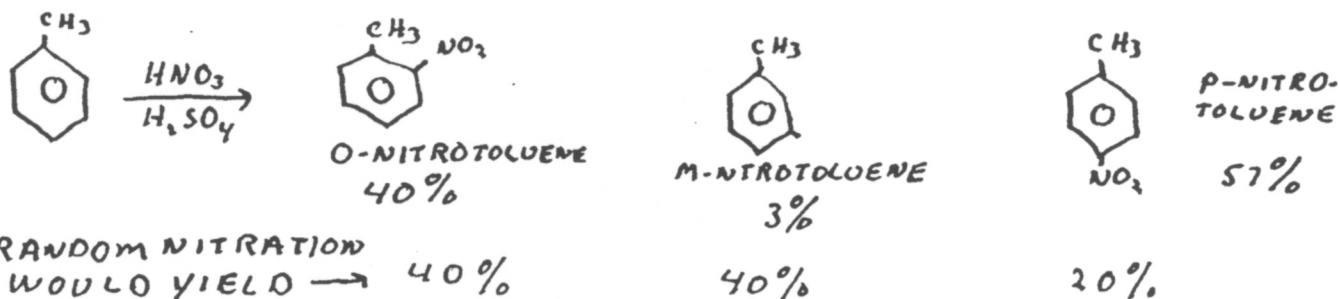
ACTIONS OF SUBSTITUTED BENZENES

ACTIVATION, DEACTIVATION, DIRECTING GROUPS

NITRATION OF TOLUENE

TOLUENE REACTS 25X FASTER THAN BENZENE

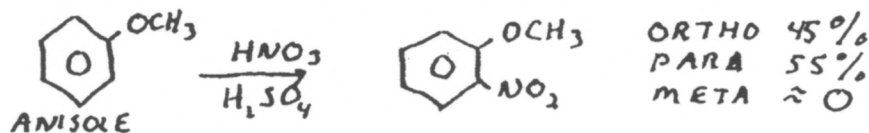
TOLUENE IS "ACTIVATED" AND THE METHYL IS THE ACTIVATOR
ACTIVATED RINGS ARE SUBSTITUTED MOSTLY AT O, P POSITIONS



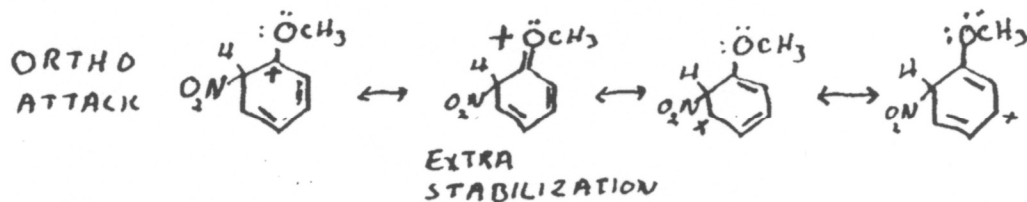
THE STRUCTURE OF THE SIGMA COMPLEX REVEALS O, P SUBSTITUTION IS
TABILIZED BY A 3° CATION, WHILE META IS NOT PG 675

THE STABILIZING EFFECT OF ANY ELECTRON DONATING GROUP HAS THIS SAME
POSITIONAL PREFERENCE AND REACTION RATE ENHANCEMENT
TREMELY STRONG ACTIVATION COMES FROM SUBSTITUENTS WITH
NONBONDING ELECTRONS

ANISOLE REACTS 10,000 TIMES FASTER THAN BENZENE

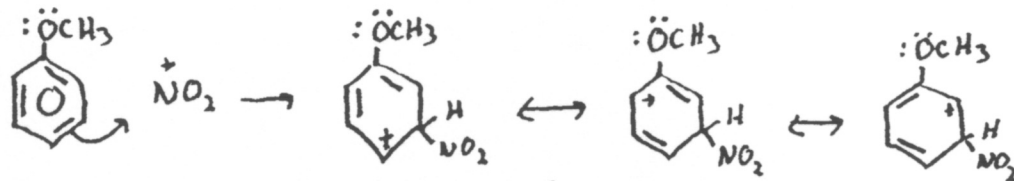


RESONANCE STRUCTURES OF THE SIGMA COMPLEX



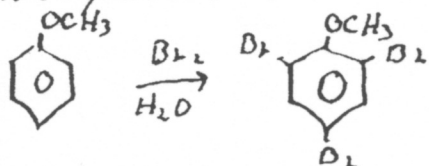
YOU SHOULD BE
ABLE TO DRAW
RESONANCE
STRUCTURES
FOR PARA
ATTACK

BUT THERE IS NO EXTRA STABILIZATION FOR META ATTACK



THE + CHARGE IS NEVER ON THE
RIGHT CARBON (THE -OCH₃ CARBON)

THE METHOXY GROUP IS SO STRONGLY ACTIVATING THAT NO F₂ B₂ IS NEEDED



AMINO (-NH₂) GROUPS LIKEWISE ACTIVATE SEE SUMMARY OF
ACTIVATING, O, P DIRECTORS PG

DEACTIVATING SUBSTITUENTS (META DIRECTORS)

NITROBENZENE REACTS 10^5 X SLOWER THAN BENZENE

O, P POSITIONS ARE MOST STRONGLY DEACTIVATED, LEAVING META POSITIONS MOST REACTIVE (LEAST DEACTIVATED)

IN NITROBENZENE, THE NITROGEN CARRIES A FORMAL + CHARGE

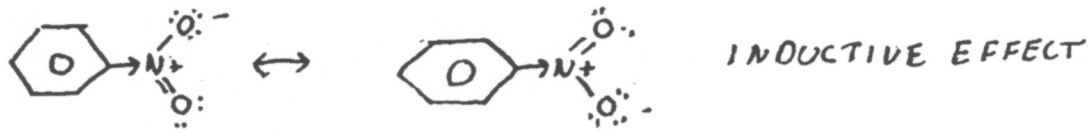
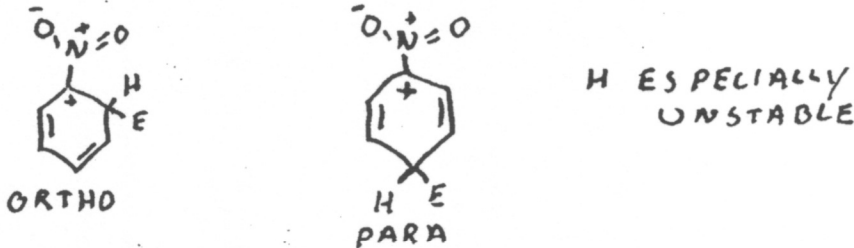


FIGURE 17-4 SHOWS THE RCD FOR NITROBENZENE REACTIONS
O AND P SIGMA COMPLEXES ARE HIGHLY DESTABILIZED IN RESONANCE FORMS WHERE THE + CHARGE IS ON THE CARBON BEARING THE NITROGEN



MOST DEACTIVATING GROUPS ARE O, P META DIRECTORS

ANY SUBSTITUENT WITH A FORMAL + CHARGE OR PARTIAL + CHARGE DEACTIVATES AND META DIRECTS

FOR EXAMPLE, THE CARBONYL GROUP



DEACTIVATING META DIRECTORS ARE SUMMARIZED ON PG 747-680

NALLY, HALOGENS

THE HALOGENS ARE BOTH INDUCTIVELY WITHDRAWING AND RESONANCE DONATING
THIS COMBINATION MAKES HALOGENS DEACTIVATING, BUT O, P DIRECTING

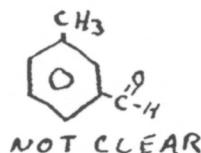
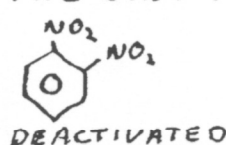
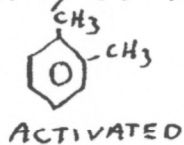
SEE FIGURE 17-5

ALL DIRECTING EFFECTS ARE SUMMARIZED ON PG 337

EFFECTS OF MULTIPLE SUBSTITUENTS

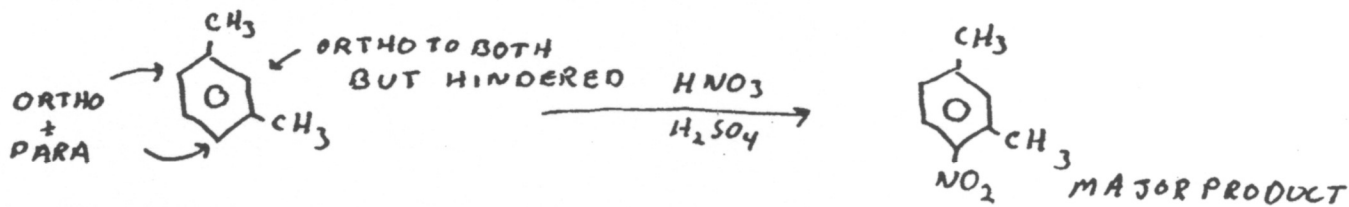
IMPLY SUM UP THE DIRECTING EFFECTS. OFTEN THE RESULT IS CLEAR

BUT NOT ALWAYS

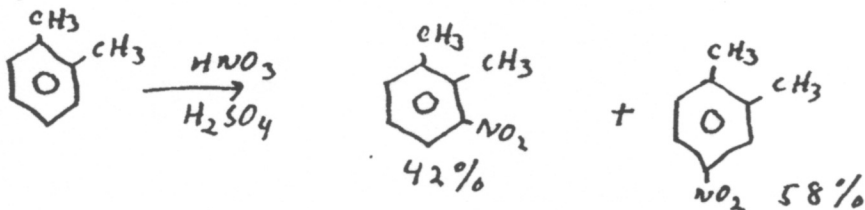


**ACTIVATORS
WIN**

THE ORIENTATION OF SUBSTITUTION IS ALSO OFTEN CLEAR



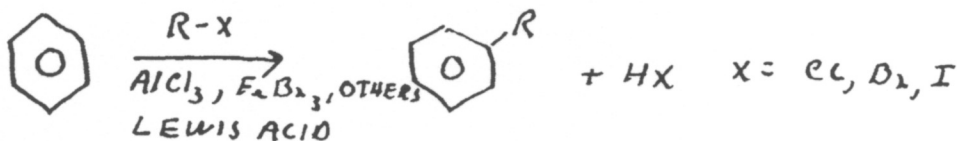
HOWEVER, MIXTURES ARE POSSIBLE



ACTIVATING GROUPS ARE USUALLY STRONGER THAN DEACTIVATING GROUPS
 STRONG ACTIVATORS THAT STABILIZE VIA RESONANCE RANK HIGHEST
 OH, -OR, -NR₂

MODERATE O, P DIRECTORS -R, -X ARE NEXT
 META DIRECTORS LAST SEE SOLVED PROBLEM 1

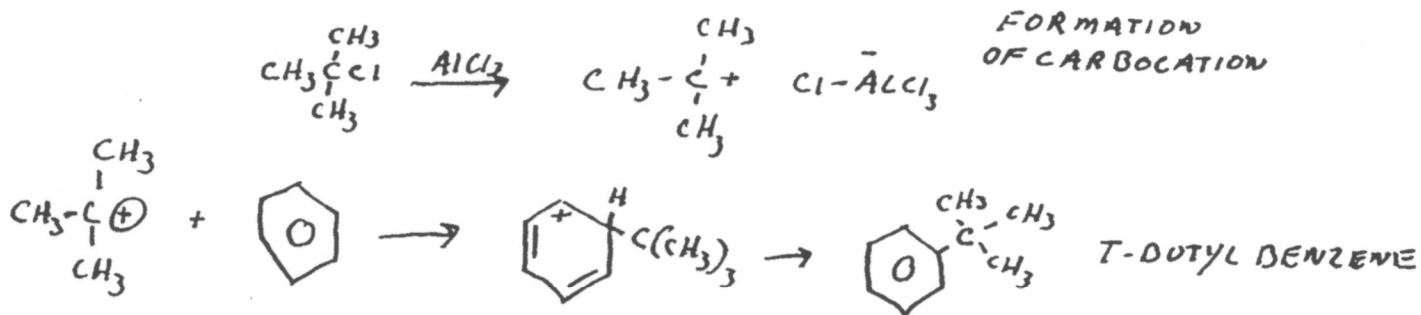
FEED-CRAFTS ALKYLATION



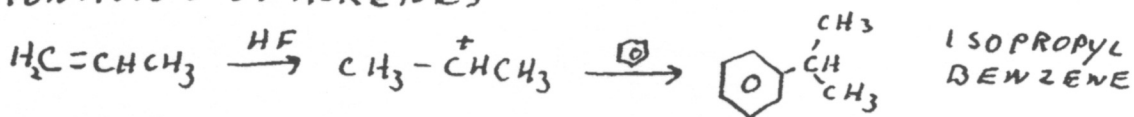
ALKYL HALIDES

ALKYLATE THE RING IN THE PRESENCE OF LEWIS ACIDS

IT'S A TYPICAL ELECTROPHILIC AROMATIC SUBSTITUTION
 CARBOCATION IS THE ELECTROPHILE



ALTERNATIVE CARBOCATION SOURCES MAY ALSO BE USED, SUCH AS
 PROTONATION OF ALKENES



THE F⁻ ANION IS A POOR

NUCLEOPHILE, NOT TOO REACTIVE TOWARDS THE CATION

IMITATIONS OF FRIEDEL-CRAFTS ALKYLATION

- 1) WORKS ONLY WITH ACTIVATED RINGS
- 2) CARBOCATION REARRANGEMENTS
- 3) AFTER ALKYLATION, RING IS MORE ACTIVATED, GIVING POLY ALKYLATION PRODUCTS

OF THESE 3 LIMITATIONS ARE OVERCOME BY FRIEDEL CRAFTS ACYLATION

ITS VERY SIMILAR, BUT THE ELECTROPHILE IS THE ACYLIUM ION
 IN ACYL GROUP IS $R-\overset{\overset{O}{\parallel}}{C}-$ NAMED BY DROPPING THE E FROM THE ALKANE NAME AND ADD -OYL

BENZENE \rightarrow BENZOYL 

SMALL ACYL GROUPS GET COMMON NAMES

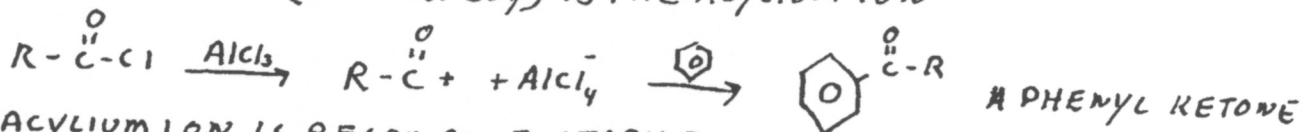
$H-\overset{\overset{O}{\parallel}}{C}-$
FORMYL

$CH_3-\overset{\overset{O}{\parallel}}{C}-$
ACETYL

$CH_3CH_2-\overset{\overset{O}{\parallel}}{C}-$
PROPIONYL

WHEN AN ACYL GROUP IS BONDED TO A CHLORINE, ITS CALLED AN ACID CHLORIDE

FRIEDEL-CRAFTS ACYLATION IS THE STANDARD ELECTROPHILIC SUBSTITUTION
 THE ELECTROPHILE (SIMPLISTICALLY) IS THE ACYLIUM ION

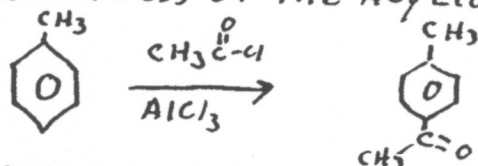


THE ACYLIUM ION IS RESONANCE-STABILIZED

SO NO REARRANGEMENTS

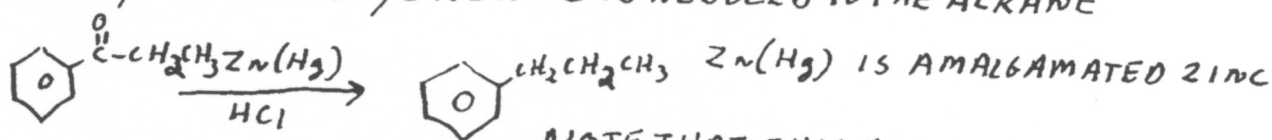


BUT THE ACYLATED PRODUCT IS DEACTIVATED TOWARD FURTHER SUBSTITUTION
 THE BULKINESS OF THE ACYLIUM COMPLEX OFTEN FAVORS PARA SUBSTITUTION



ACYLATION AND ALKYLATION ARE SUMMARIZED ON PG 759

FREQUENTLY THE PHENYL KETONE IS REDUCED TO THE ALKANE



THIS IS CALLED THE CLEMMENSEN REDUCTION

NOTE THAT THIS ALKYL BENZENE COULD NOT BE MADE BY ALKYLATION DUE TO REARRANGEMENT PROBLEMS

DIAZONIUM SALTS

ALKYLAMINES REACT WITH NITROUS ACID TO FORM DIAZONIUM SALT



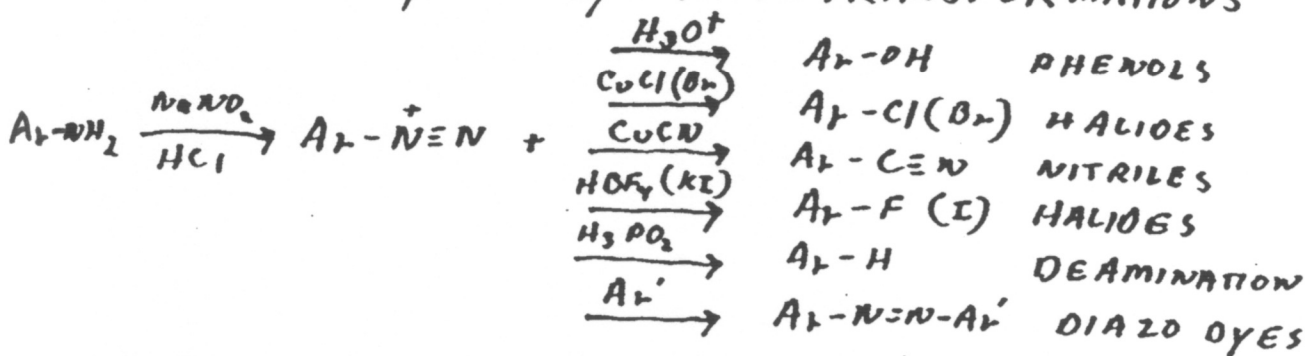
PRIMARY DIAZONIUM SALTS DECOMPOSE TO FORM CARBOCATIONS R^+ , WHICH THEN EITHER REARRANGE, ELIMINATE H TO FORM AN ALKENE OR UNDERGO NUCLEOPHILIC SUBSTITUTION

SECONDARY DIAZONIUM SALTS FORM NITROSAMINES, ONE OF THE MOST POTENT CLASSES OF CARCINOGEN KNOWN



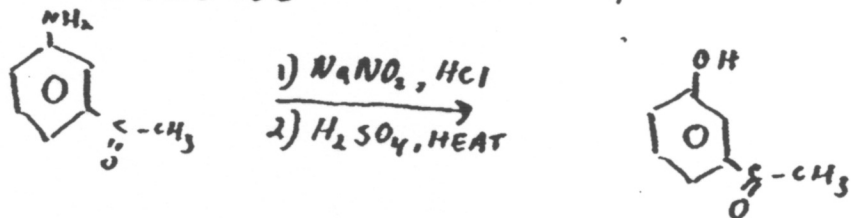
THE MAIN USEFULNESS OF DIAZONIUM SALTS IS WITH AROMATIC AMINES, WHICH MAY BE CONVERTED INTO A WIDE VARIETY OF FUNCTIONALITIES AFTER DIAZOTIZATION

A SUMMARY OF ARYL AMINE TRANSFORMATIONS

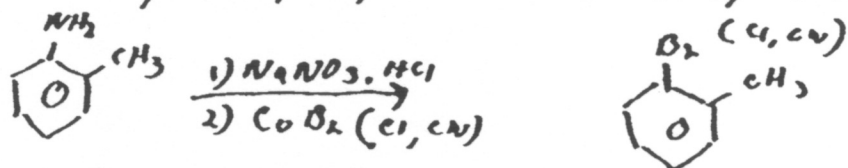


EXAMPLES

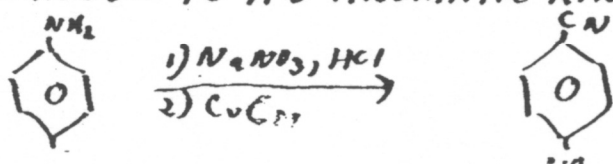
HYDROLIS TO THE PHENOL



REPLACEMENT BY Cl, Br, CN THE SANDMEYER REACTION

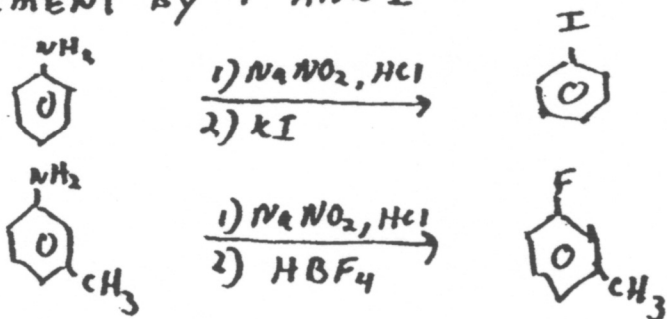


THIS IS A USEFUL WAY TO ATTACH A NEW CARBON TO AN AROMATIC RING



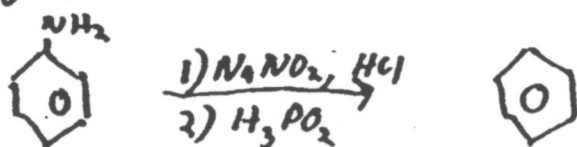
ONCE YOU HAVE THE NEW CARBON ON THE RING, YOU CAN GO ON TO MODIFY IT

10 MORE DIAZONIUM REACTIONS
REPLACEMENT BY F AND I

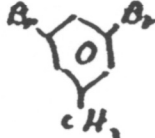


THIS IS THE BEST WAY TO GET F OR I ONTO AN AROMATIC RING

DEAMINATION

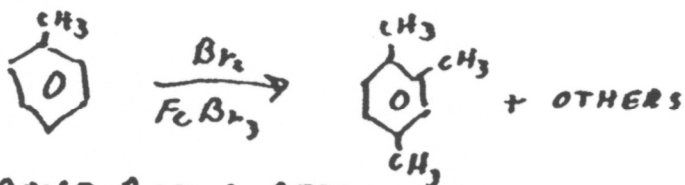


AN AMINO GROUP MAY BE ADDED TO A RING TO ACTIVATE IT AND DIRECT SUBSTITUTION

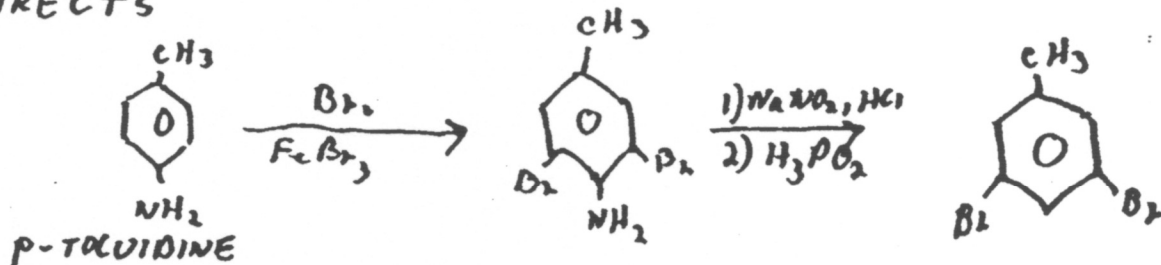
A GOOD EXAMPLE IS THE SYNTHESIS OF  FROM TOLUENE

DIRECT BROMINATION OF TOLUENE

GIVES A MIXTURE OF ORTHO AND PARA SUBSTITUTION



AN AMINO GROUP ACTIVATES AND DIRECTS



DIAZOCOUPLING PRODUCES AZO DYES



THESE HIGHLY CONJUGATED SYSTEMS ARE STRONGLY COLORED
USED IN TEXTILES