Aromatic Hydrocarbons
(Also called Arenes)

- They possess an 'Aroma' or fragrance
- They possess a ringed structure that resemble that of benzene.

Benzene, C_6H_6

⇒ It is made up of 92.3% of Carbon by mass
7.7% of Hydrogen

Ratio of C : H = $\frac{92.3}{12\text{(Molar mass of C)}} : \frac{7.7}{1\text{(Molar mass of H)}}$

= 7.7 : 7.7

= 1 : 1

∴ Empirical formular = CH

Molecular formula = $(CH)_n$

Relative Molecular mass = $(12+1)_n = 13n$

Experimental mol. mass = 78

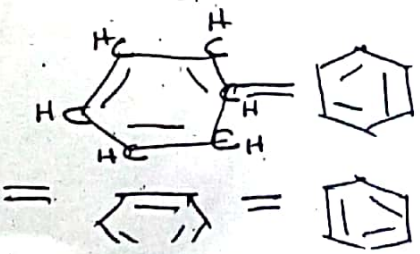
∴ $13n = 78$

∴ $n = 78/13 = 6$

∴ Molecular formula of benzene = C_6H_6

Indicating:

- A high degree of unsaturation (greater than that of alkenes & alkynes)
- A high carbon content

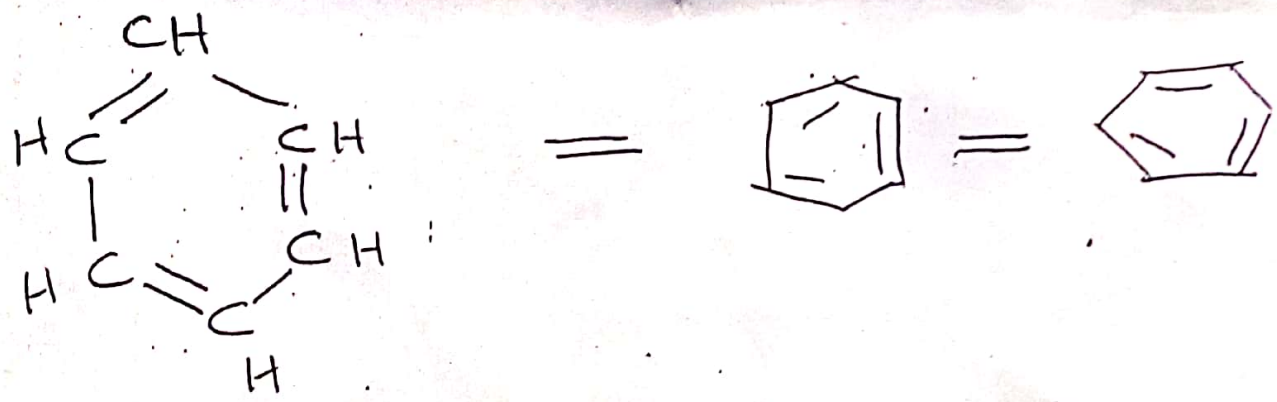


⇒ Kekulé formula for Benzene

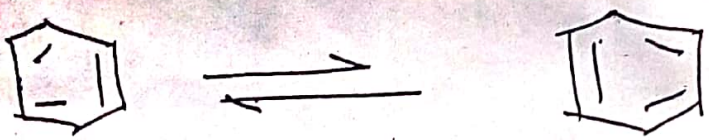
He 1st suggested that C_6H_6 should be an aromatic ring

Each C atom is joined to two other C atoms and to one H atom by covalent bonds

It is a cycloalkene with three alternating double bonds.



He later proposed that benzene alternated between two structures.



Indicating: (π but not σ)

- Double bonds are mobile (labile) ie can be moved from one position to another benzene is an equilibrium mixture.

Resonance Theory

A phenomenon whereby a molecule can be represented by 2 or more structures which have the same arrangement of their atoms but different arrangement of their electrons (eg: π electrons and not σ electrons).

Benzene can be represented by various alternate structures in which the true structure (called 'Resonance Hybrid') lies somewhere between the alternative structures (I and II)

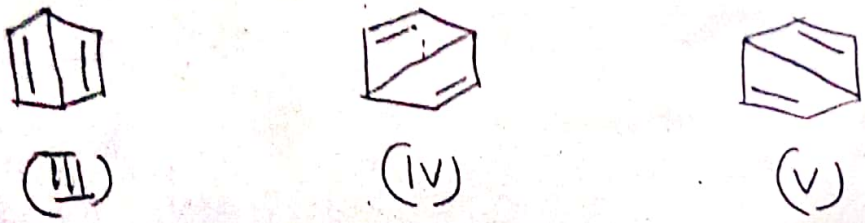
i.e. True structure = Resonance Hybrid (most stable)
other alternative structures = Canonical forms.

The relative contribution of each canonical forms to the resonance hybrid depends upon its energy content (the lesser the energy, the greater the stability, $E \propto \frac{1}{\text{stability}}$)

(I) True struct. of benzene lies here (II)
Represents a resonance hybrid between the 2 structures (≈ 80% contributi

Both (I) and (II) have equal energy content
Both I and II are Kekulé's structures/ Kekulé's canonical forms.

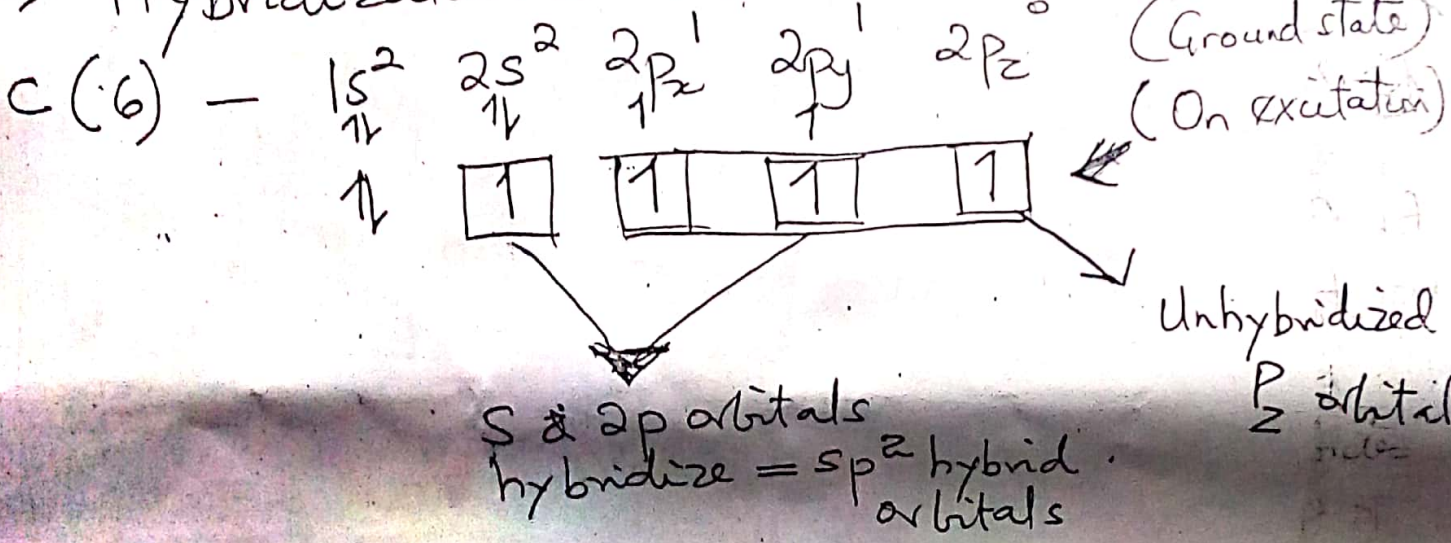
Other Canonical forms:



(III) (IV) (V)

(III – V) are Dewar's structures (contributes 20%).

⇒ Hybridization & Molecular Orbital Image



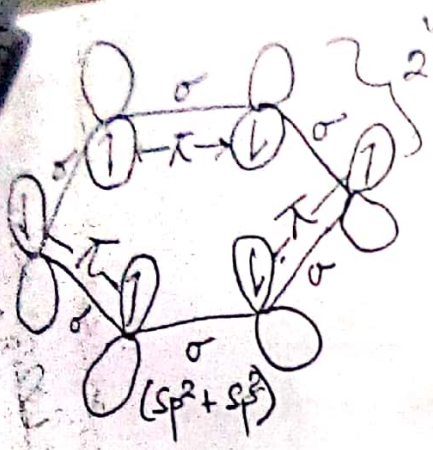
- Sp^2 hybrid orbitals will combine with 1s of H=σ

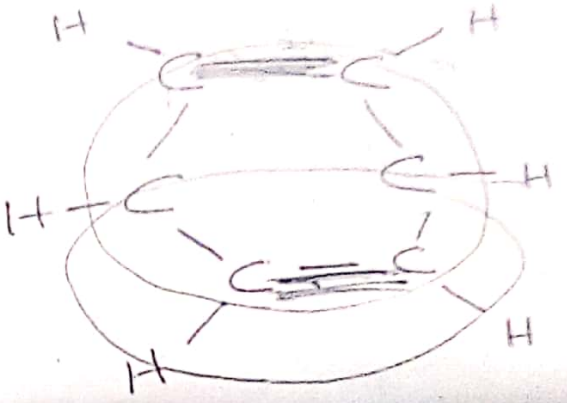
Since there are 6 C atoms;

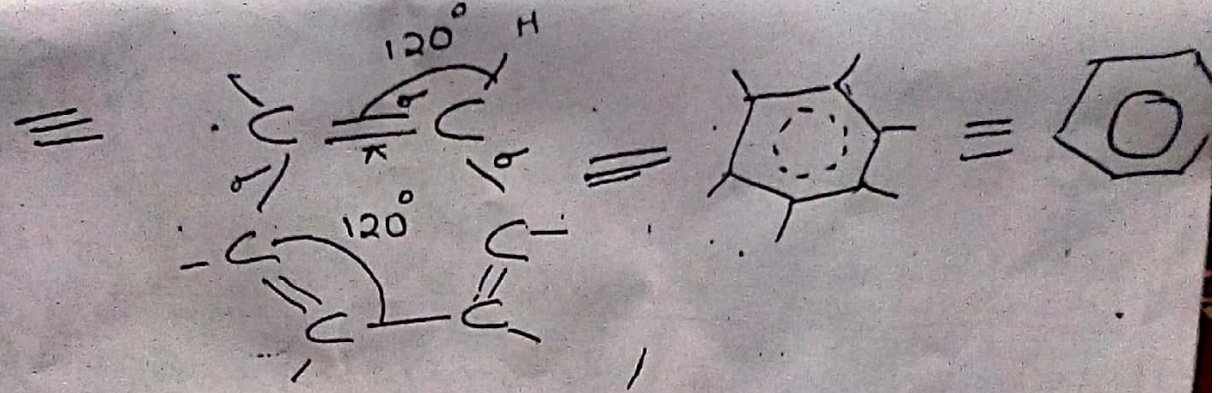
6 C atoms ~~having~~ (sp^2 hybrid orbitals) will combine with 6 1s H = 6σ bonds. All atoms in one plane.

The unhybridized Pz orbitals of 6C atoms overlap sideways @ right angle to the plane to form π bonds.

Electron cloud is above and below the plane of the ring, forming a delocalized π orbitals around the







Benzene is therefore
C_6H_6 (all Hydrogen are equivalent)
cyclic & planar, bond angle 120°
Unsaturated $(4n+2)\pi$ electrons (Huckel's rule)
Each C atom is sp^2 hybridized (σ) and p_z
There is conjugation (= — = — = —)
The π electrons are labile and could be found in any part of the electron cloud
electrons do not maintain a permanent position (only σ electrons does)
= delocalization of electrons
Delocalization of electrons in an aromatic ring confers a great stability on benzene (Compound that show Huckel's rule have special stability)

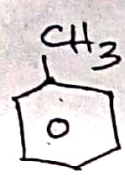
⇒ Nomenclature

Its derivatives are named as derivatives of benzene.

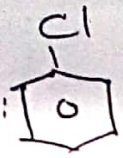
Monosubstituted benzene derivatives:

replacing 1 H atom on C_6H_6 with another atom/group.

=gs



methylbenzene (Toluene)



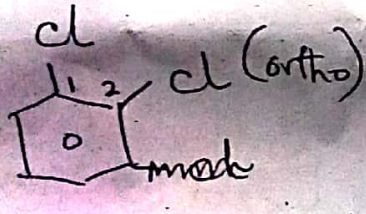
chlorobenzene (halobenzene)

Nitrobenzene

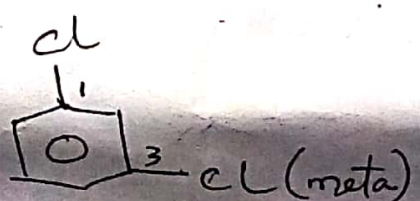
Disubstituted benzene derivatives:

replacement of 2H atoms with another atoms/group

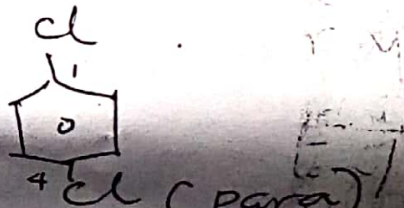
=gs



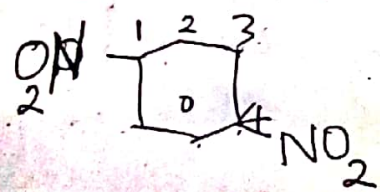
1, 2-dichloro benzene (o-Dichloro benzene)



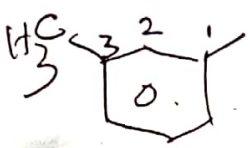
1, 3-dichloro benzene (m-Dichloro benzene)



1, 4-dichloro benzene (p-Dichloro benzene)

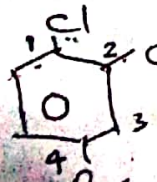


1, 4-dinitrobenzene

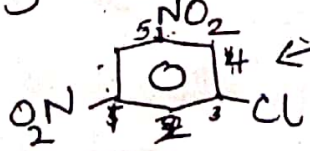


1-Bromo-3-methylbenzene

Trisubstituted benzene derivatives (o, m & p not applicable here)



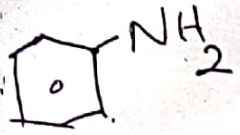
1-Bromo-1-chloro-3-methylbenzene



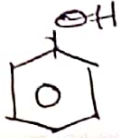
3-chloro-1,5-dinitro benzene

Generally, C_6H_5 ($C_6H_6 - 1H$) = Phenyl

Phenyl chloride (chlorobenzene)



Phenylamine (aminobenzene)/Anilin



Phenyalcohol (Phenol)

(Phenylmethoxide/methoxyben
Anisole

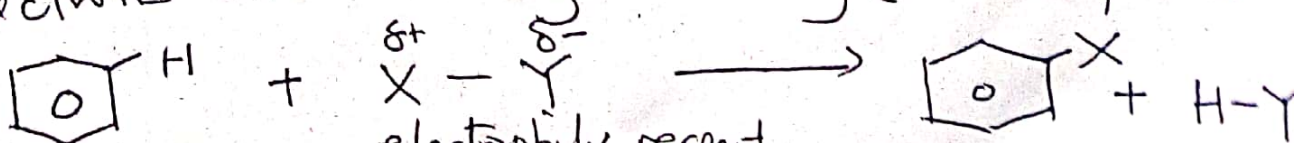
⇒ Physical Properties of Benzene.

- Colourless liquid (bpt 80°c, mpt 55°c)
- ⇒ Immiscible with water, soluble in non-polar solvents
- Volatile, non-polar, less dense than H_2O
- A useful organic solvent, though highly carcinogenic/highly toxic
- Like all aromatic compounds, it burns with a smoky luminous flame (as a result of high carbon content).

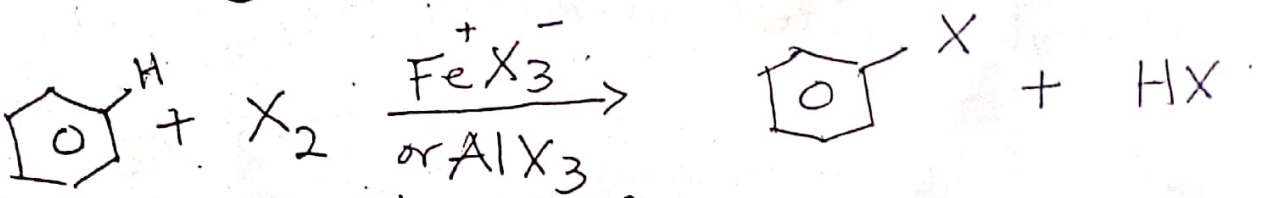
⇒ Reactions

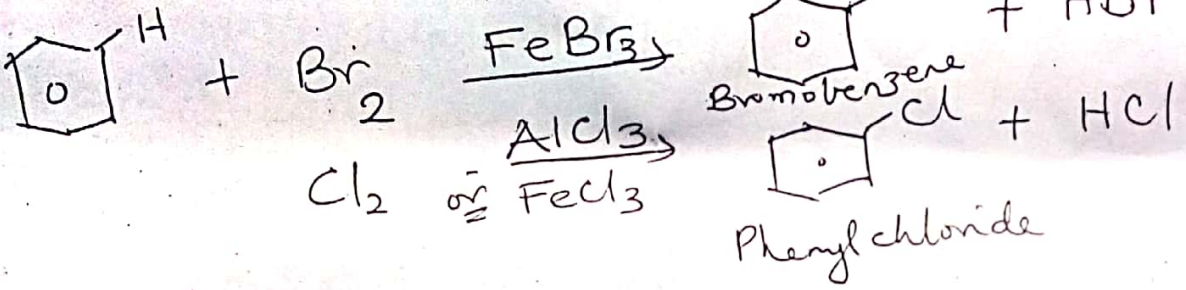
They undergo electrophilic aromatic substituti reactions (ie substitute H atom(s) with electrophiles).

Electrophiles are electron deficient species (positively charged) which have affinity for the π electrons in a benzene ring (nucleophile)

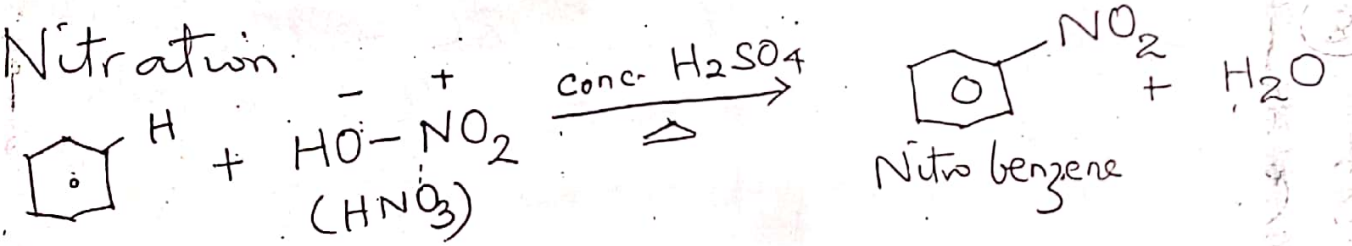


1) Halogenation

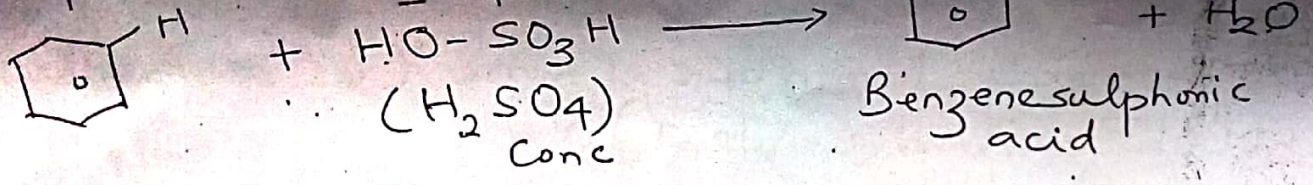


eg 

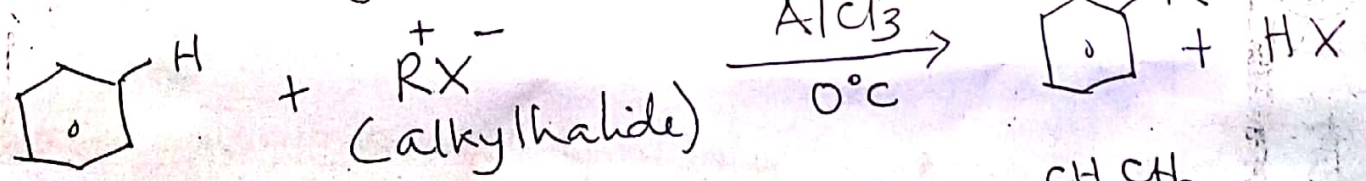
2) Nitration

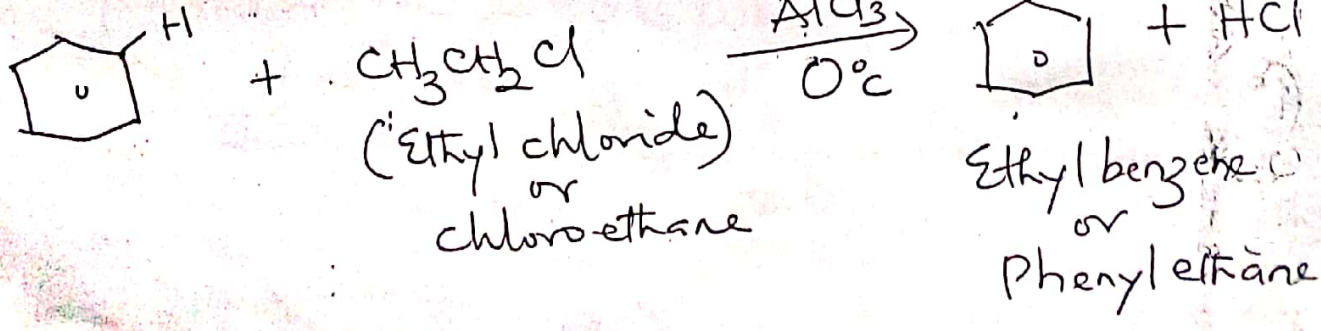


3) Sulphonation



4) Friedel Craft's alkylation



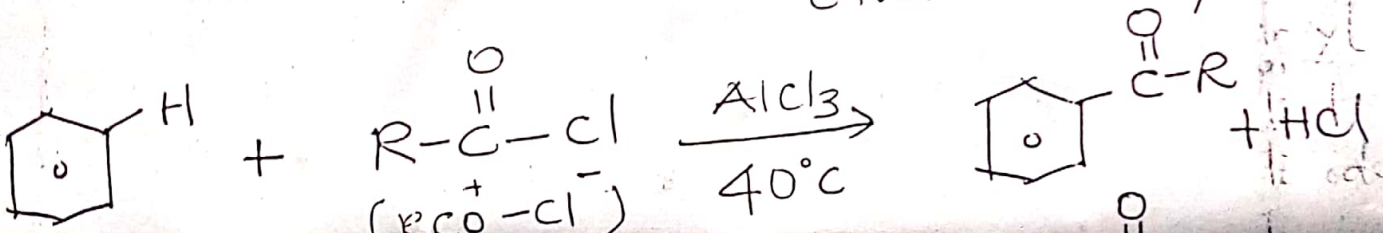
eg 

5) Friedel Crafts Acylation

Egs of acylating agents:

- $R-\overset{O}{\overset{\|}{C}}-Cl$ (Acid chloride) eg CH_3COCl = Acetyl chloride (Ethanoyl chloride)
- RCOOH (Acid eg $CH_3C(=O)-OH$ = Ethanoic acid
- $R-C(=O)-O-C(=O)-R = (RCO)_2O$ = $CH_3-C(=O)-O-C(=O)-CH_3 = (CH_3CO)_2O$

= Acetic anhydride or Ethanoic anhydride



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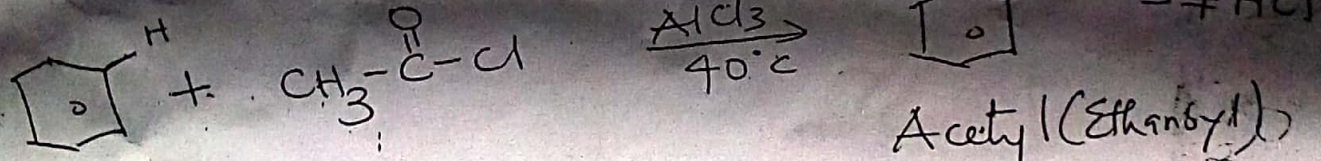
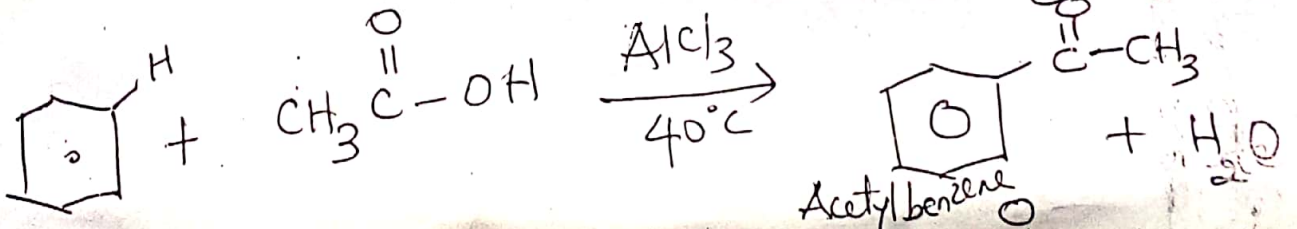
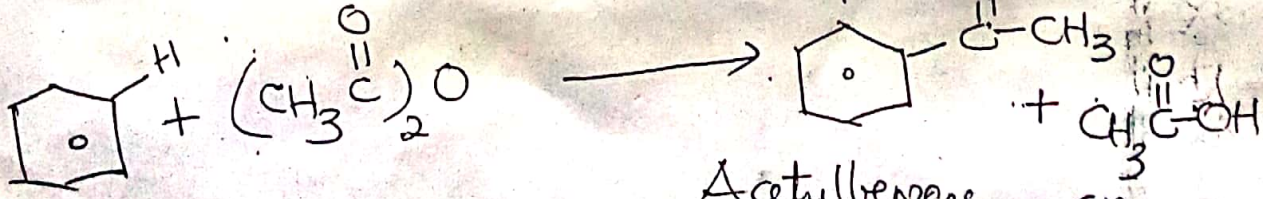


Acetyl (Ethanoyl) benzene



Acetylbenzene



Acetylbenzene

Ethanoic acid