AROMATIC ELECTROPHILIC SUBSTITUTION REACTION

Friday 13

Aromatic compounds substitution takes place by electrophilic, nucleophilic and free radical mechanism. The π electron cloud above and below the aromatic ring are loosely held as compared to σ electron and are available to electrophile. Thus electrophilic substitution are characteristic reaction of aromatic compounds. On the

Saturday 14

other hand, the electron cloud above and below the plane of an aromatic ring shield of the ring carbon from the attack of a nucleophile.

Aronium ion Mechanism — Aromatic electrophilic

Sunday 15

Substitution is a bimolecular and involve arenium ion intermediate. It is called SE_2 mechanism as it is bimolecular.

16 Monday

~~ion intermediate~~ In this step electrophile attacks the substrate to give carbocation (known as arenium ion a σ complex a benzenonium ion a cyclohexadienyl cation in the case of benzenoid system). The leaving group (Electrofuge) depart the second ~~stage~~ step. This resembles with tetrahedral mechanism but the charges

17 Tuesday

are reversed. The first step is rate determing step and the reaction follow second order.

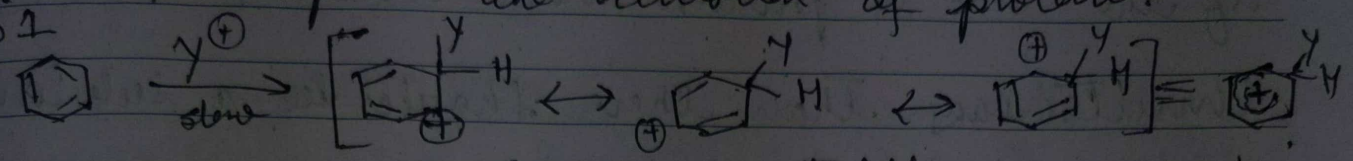
The attacking electrophile may be positive ion or a dipole. The arenium ion is stabilised by resonance but due to lose of aromaticity its R.E. is much less than that of the parent aromatic system. Thus the arenium ion loses a proton and revert to the more stable aromatic step.

A base present in the reaction

Wednesday 18

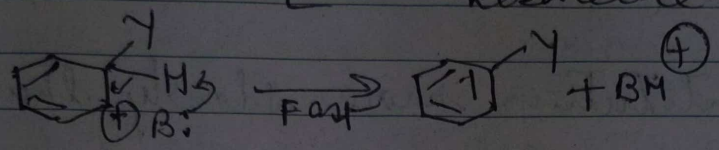
mixture help in the removal of proton.

Step I



[Resonance stabilized arenium ion Resonance]

Step II

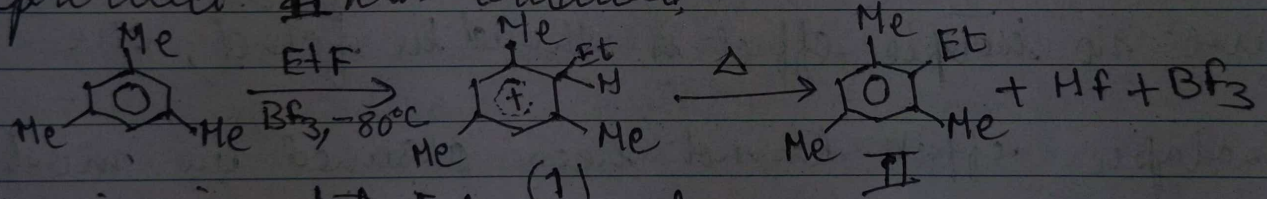


Evidence of the Arenium ion Mechanism →

(a) Isolation of Arenium ion intermediate —

Isolation of arenium ion intermediate in many cases. e.g. The arenium ion 1 was isolated in the following reaction and when it was heated the normal substitution product II was obtained

Thursday 19



(1) II

Arenium ion detected as such

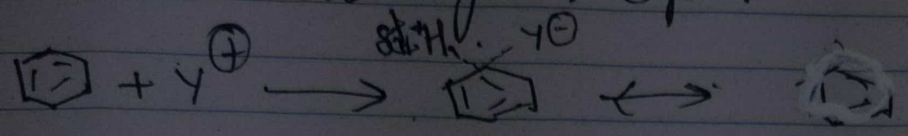
(2) Isotope effect — The difference in the rate of reaction due to difference in the isotope present in the reaction system is called isotope effect. (A) If the proton is lost before the original

20 Friday of the electrophile (SE, mechanism) or if the loss of proton and arrival of $\bar{e}$ are simultaneous than there should be a substantial isotope effect (i.e deuterium substrate should undergo substitution more slowly than undeuterated substance) because in each case the C-H bond is broken is the rate deteing step. In the

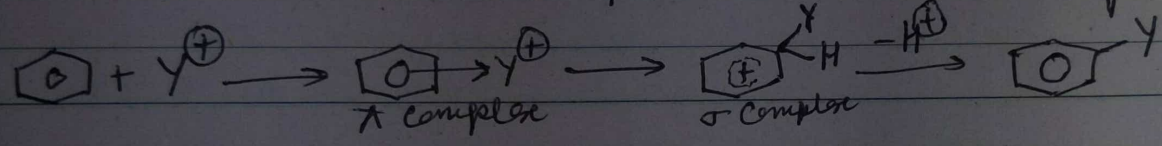
21 Saturday arenium ion mechanism the C-H bond is not broken in the rate deteing step, hence no isotopic effect is should be found, The isotopic effect has not been observed in most aromatic electrophilic substitution, e.g. Rate

22 Sunday of nitration of deuterium and nitrobenzene are the same as the rate of benzene. It clearly shows that aromatic aliphatic substitution involves two ~~of~~ steps and the loss of proton is not

the rate determing step.

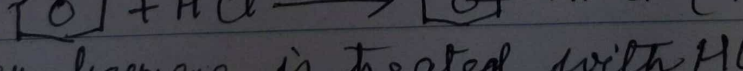


σ & π complex — Positive ion can form addition complex (π complexes) with π system i.e. aromatic aliphatic system π complex is formed first and then converted to arenium ion (σ complex. π complex do not involve actual chemical bonding but electrophile is held near the π e⁻ cloud of the aromatic ring. But σ complex there is actual chemical bonding between the electrophile and a carbon atom of the aromatic ring.

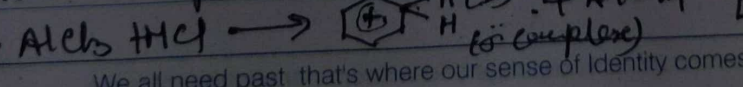


Evidence for the formation of σ and π complex

When benzene is treated with HCl alone a π complex is formed which is colourless & does not conduct electricity. Furthermore when DCl is used for π complex no deuterium exchange takes place because there is no covalent bond between the electrophile and the ring.



But when benzene is treated with HCl in presence of $AlCl_3$, solution of arenium ion (σ complex) is obtained, which is coloured and conduct electricity (showing the presence of positive & negative ion.)



[If DCl & $AlCl_3$ are used for σ complex D-exchange takes place]

Wednesday, January 17

$LiAlH_4$ (Lithium Aluminium Hydride)

It is prepared by the gradual addition of the limited quantity of anhydrous $AlCl_3$ to a thin film of lithium hydride in ether.

$$4\,LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$$

[In presence of excess of $AlCl_3$, Al-hydride is alkanid ~~as~~ ~~the~~ the main product.]

$$[6\,LiH + 2AlCl_3 \rightarrow Al_2H_6 + 6LiCl]$$

The precipitate of lithium chloride is removed by filtration and the filtrate is evaporated in absence of air and CO_2 to get the solid reagent. It is gray white solid, which is rapidly hydrolysed by water with the evolution of H_2. It is spontaneously inflammable powder which reacts violently with water. It is extremely valuable reagent for the wide range of functional groups (e.g. $>C=O$, & $-COOH$ & derivatives) nitrile, nitro azide, alkyl halide, epoxide, ozonide, sulphonid ester. Excess of reagent destroyed by adding ethyl acetate.

$$4\,CH_3COOC_2H_5 + LiAlH_4 \rightarrow LiOC_2H_5 + Al(OC_2H_5)_3 + 4C_2H_5OH$$

The reduction by $LiAlH_4$ proceed under mild conditions or at room temperature, though some case heat required. "$LiAlH_4$ not attacking the double bond, hence unsaturated aldehyde or ketone can be reduced to unsaturated alcohol." $LiAlH_4$ has low mol wt. and mol reduces four moles

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of carbonyl compounds, 2 moles of ester, it is very favourable ratio of reducing capacity of mass.

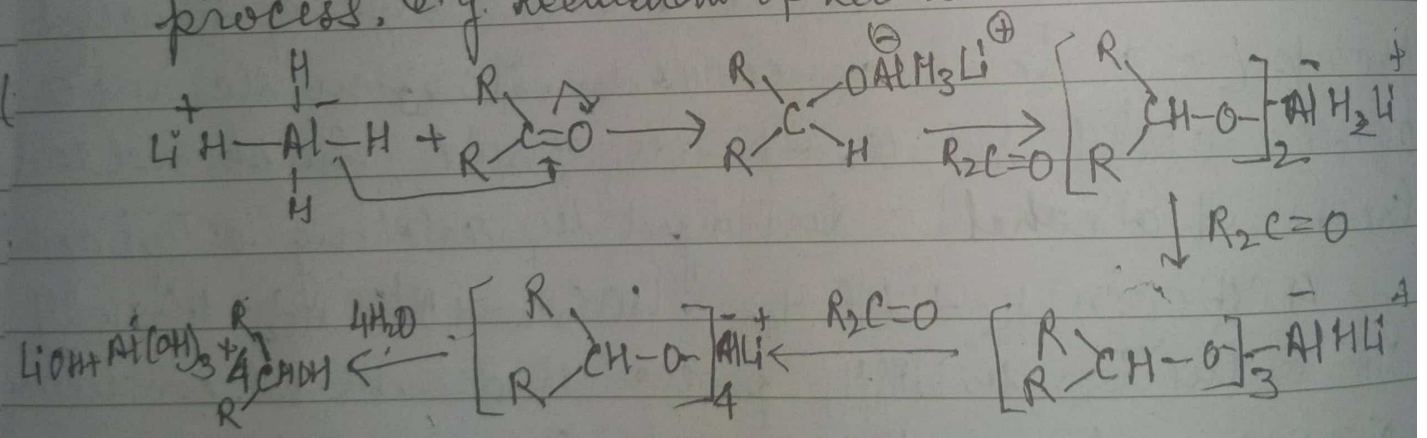
1. Reduction of carbonyl compounds :-

$$4\,RCOR + LiAlH_4 \longrightarrow [(R_2CHO)_4Al^-]Li^+ \xrightarrow[H^+]{4H_2O} 4\,R_2CHOH$$

$$4\,R_2CHOH + LiOH + Al(OH)_3$$

It is clear from the equation that one mole of $LiAlH_4$ reduces 4 moles of carbonyl compounds.

<u>Mechanism</u> :- Lithium aluminium hydride is nucleophilic reagent, attack polarised multiple bond such as C=O, C≡N, by transfer of hydride ion to the more positive atom. All the four hydride ion may be used for reduction, the hydride ions are transferred in a step wise process, e.g. Reduction of ketone



The reduction of $LiAlH_4$, each successive transfer of hydride ion takes place more slowly than before because the e⁻ withdrawing inductive effect of the alkoxy group opposes lab of the hydride ion.

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a. $CH_3(CH_2)_5-CHO \xrightarrow{LiAlH_4} CH_3(CH_2)_5-CH_2OH$

b. $C_6H_5-CH=CHCH_2OH \xrightarrow{LiAlH_4} C_6H_5-CH_2-CH_2OH$

In (b) double bond is also reduced as α, β unsaturated compound contains phenyl group in β position. This is the selective reduction of the carbonyl group

2. <u>Reduction of acid</u> → Reduced to alcohol.

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$$

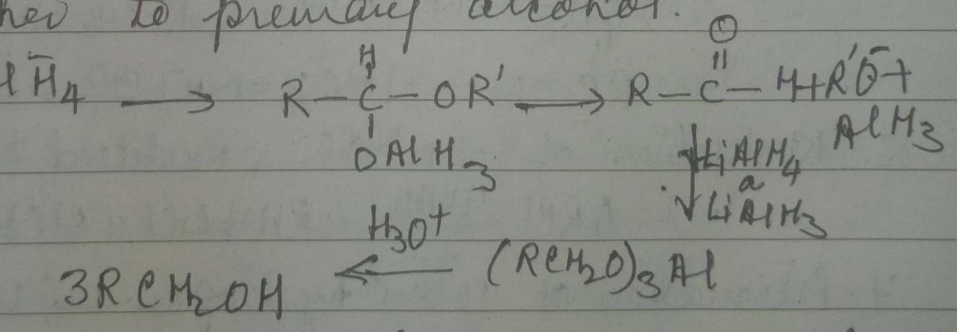
$$(CH_3)_3C.COOH \xrightarrow{LiAlH_4} (CH_3)_3C.CH_2OH$$

<u>Acid Chloride</u> →

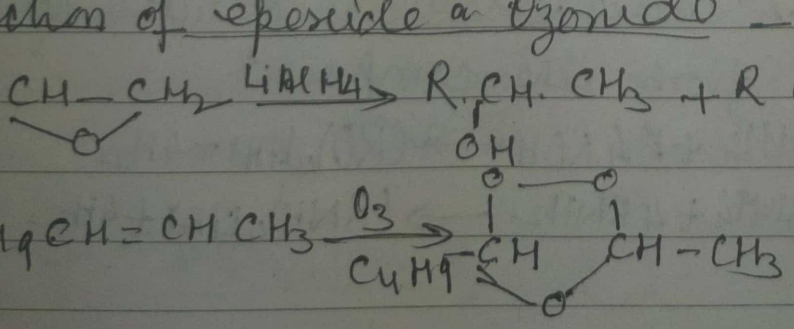
$$CH_3COCl \xrightarrow{LiAlH_4} CH_3CH_2OH$$

Ester → $C_6H_5-COOC_2H_5 \xrightarrow{LiAlH_4} C_6H_5-CH_2OH$

Reduction of ester starts with nucleophilic attack ~~reagent~~ by AlH_4 on the carbonyl group, the intermediate formed eliminate alkoxide ion and then aldehyde reduced further to primary alcohol.



3. <u>Reduction of epoxide a Ozonide</u> – Reduced to Alcohol



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Saturday, January 20

Nitration Reduction → Aliphatic nitro compound reduces to aliphatic primary amine whereas aromatic nitrocompounds are reduces to azobenzene.

$CH_3CH(NO_2)CH_2CH_3 \xrightarrow{LiAlH_4} CH_3CH(NH_2)CH_2CH_3$ 2-Aminobutane

$C_6H_5NO_2 \xrightarrow{LiAlH_4}$ (i) C_6H_5NO (Nitrosobenzene) (ii) $C_6H_5\overset{+}{N}HOH$ $\xrightarrow{-H_2O}$ $C_6H_5-N \rightarrow O$ $\xrightarrow{LiAlH_4}$ C_6H_5-N Azoxybenzene

Azobenzene $C_6H_5N = N-C_6H_5$

Azide also reduced to primary amine by $LiAlH_4$

5. Reduction of nitrile → Nitriles are reduced in specific manner. (a) If the compound is added to the reagent an amine is formed. (b) But if the reagent is added to the compound aldehyde is formed.

$$C_6H_5C\equiv N \xrightarrow{LiAlH_4} C_6H_5CH_2NH_2$$

$$RC\equiv N \longrightarrow [RCH=NH] \xrightarrow{H_2O} RCHO$$

6. Reduction of halide → Reduced to parent H.C. by $LiAlH_4$

$$4RCl \xrightarrow{LiAlH_4} 4RH + LiCl + AlCl_3$$

7. Estimation of active hydrogen → used in analytical determination because evolve molecular hydrogen from the compound.

Sunday, January 21

$$LiAlH_4 + 4ROH \longrightarrow (RO)_4LiAl + 4H_2$$

$$LiAlH_4 + 4RNH_2 \longrightarrow (RNH)_4LiAl + 4H_2$$