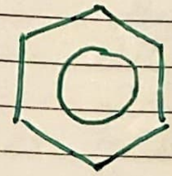
Electrophilic Substitution Rxn Mechanisms

1. B - $AlCl_3$ accepts an electron pair from Br_2 to generate Br^+ electrophile
2. B - NO_2^+ is electrophile in nitration of benzene
3. B - delocalized e^- in benzene ring

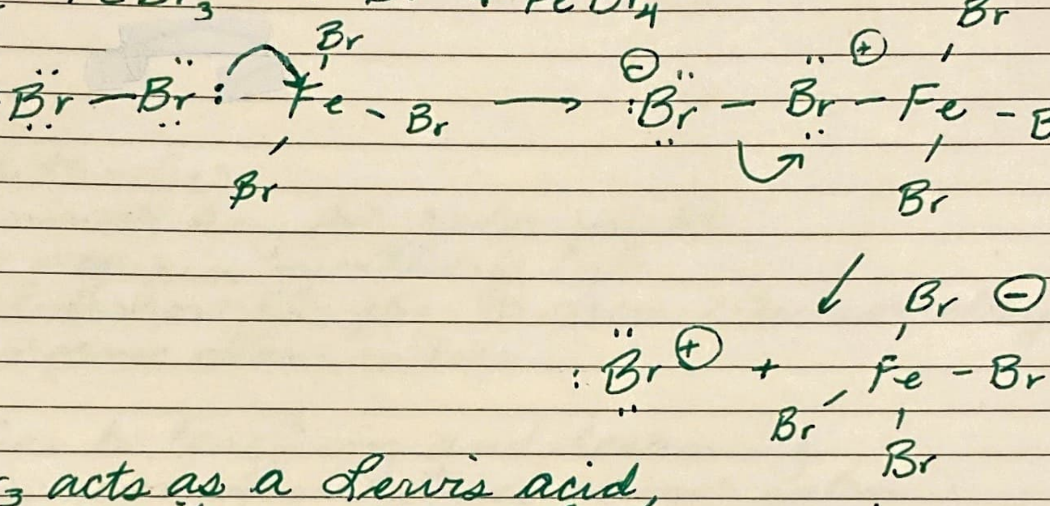
4. a)



b) benzene's delocalized e^- ring makes it too stable to undergoe addition rxns, which would disrupt aromaticity

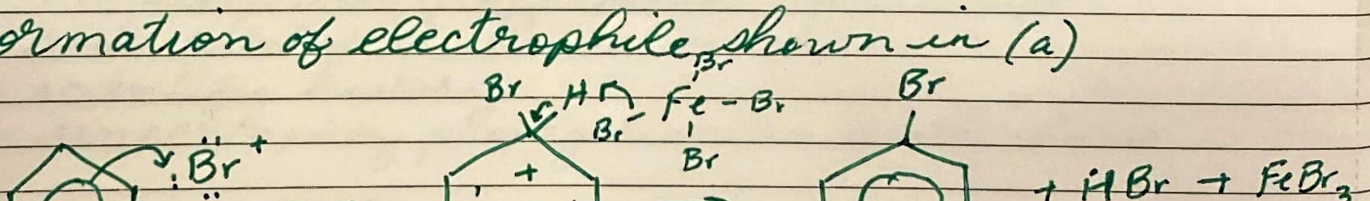
5.

a) $Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$



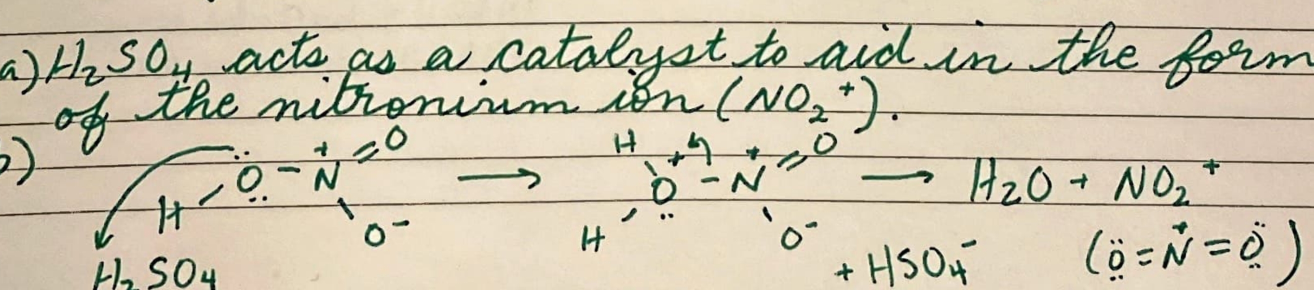
b) $FeBr_3$ acts as a Lewis acid because it accepts an electron pair
Br_2 acts as a Lewis base, losing an electron pair to become Br^+.

c) formation of electrophile shown in (a)



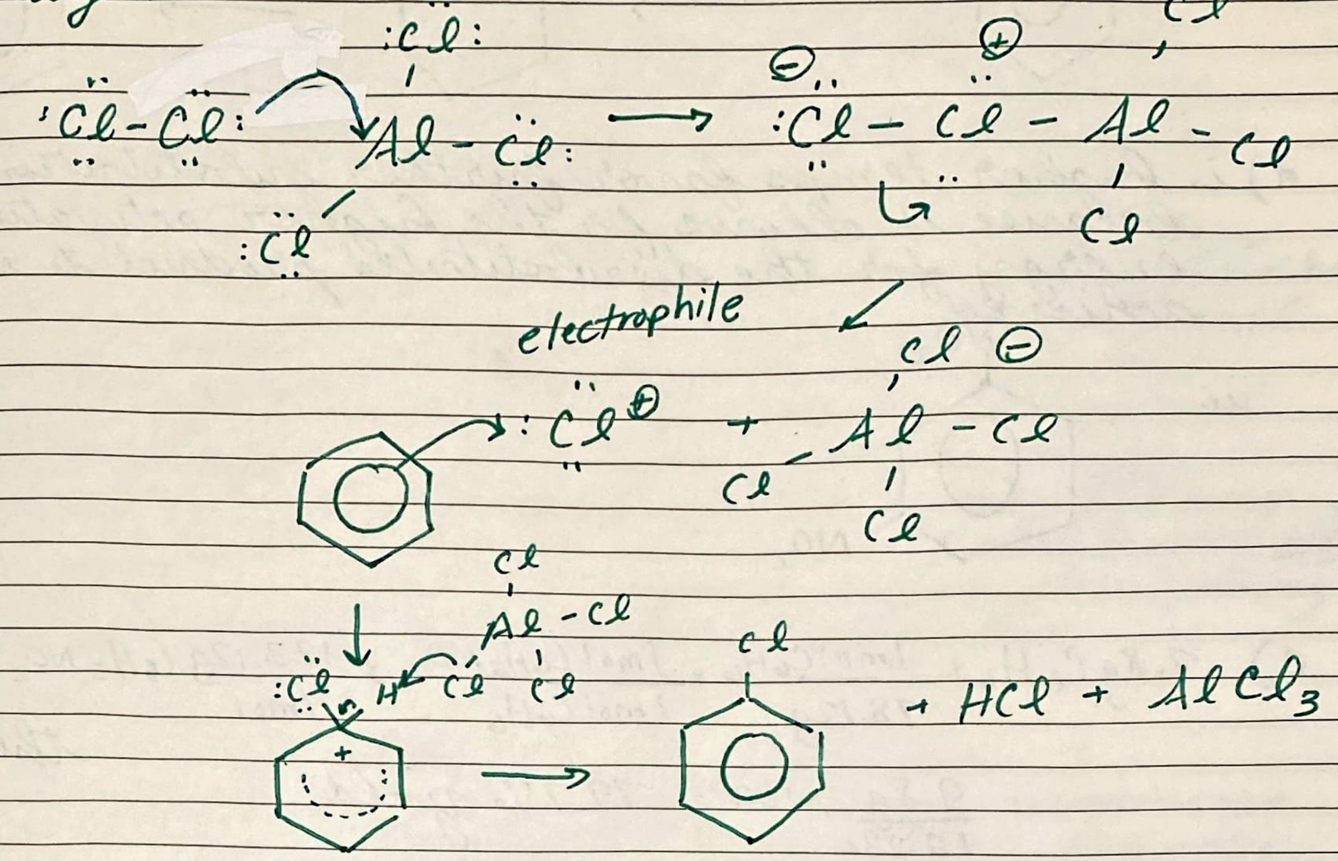
6. a) H_2SO_4 acts as a catalyst to aid in the formation of the nitronium ion (NO_2^+).

b)



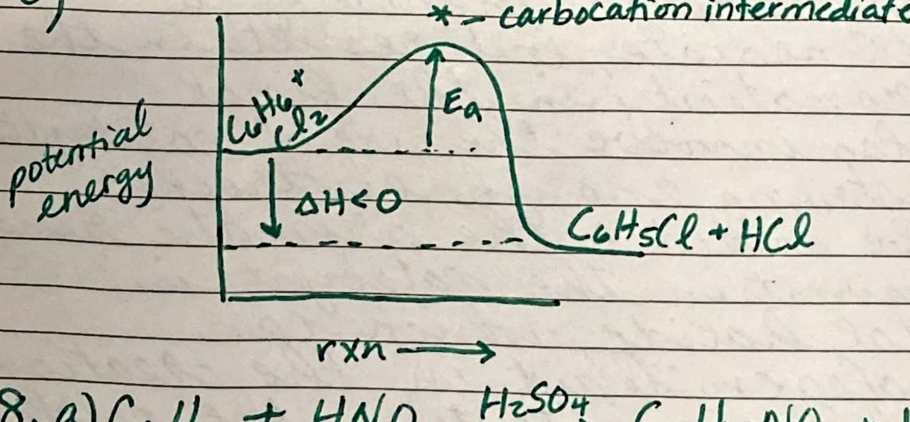
c) solvent, production of explosives, manufacture of dyes

7. a)



b) The intermediate is less stable than benzene due to the disruption of the aromatic ring. Benzene is more stable due to the delocalized electron cloud.

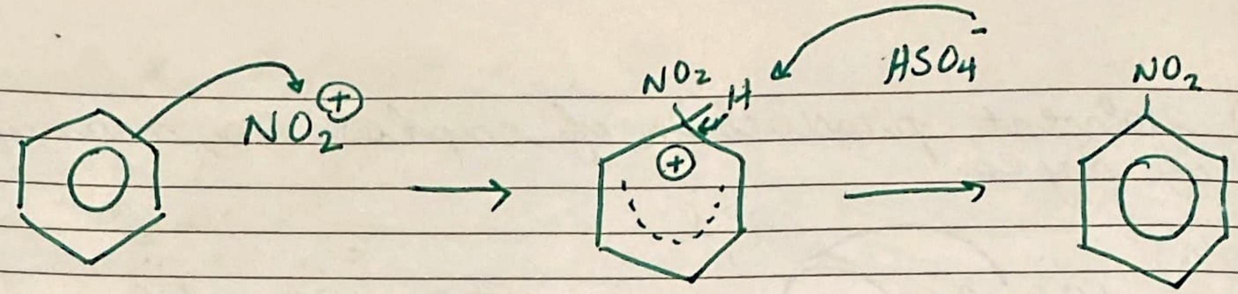
c)



8. a) $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$

b) same mechanism as 6(b). H_2SO_4 protonates HNO_3. H_2O leaves protonated HNO_3 to form nitronium ion.

c)



d) i. higher temps favor further substitution because it allows for the higher activation energy for the disubstituted product to be achieved

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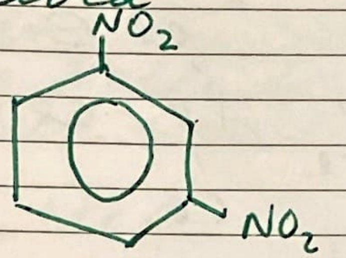


e) $7.8g\,C_6H_6 \times \frac{1mol\,C_6H_6}{78.12g} \times \frac{1mol\,C_6H_5NO_2}{1mol\,C_6H_6} \times \frac{123.12g\,C_6H_5NO_2}{1mol} = 12.29g$
theoretical

$\frac{9.8g}{12.29g} \times 100 = 79.7\%$ yield

9. Both bromination and nitration of benzene involve electrophilic substitution mechanisms that result in the temporary disruption of the aromatic ring through the use of a carbocation intermediate, but results in the restoration of aromaticity in the final product. They also involve the use of catalysts to generate a strong enough electrophile to be able to be added to the aromatic ring. However, in bromination the catalyst is usually a metal halide, which can polarize the halogen to aid in the creation of the electrophile. In nitration, the catalyst is sulfuric acid, which protonates the nitric acid, which produces the hydronium electrophile as well as water. In both mechanisms, the catalyst is regenerated

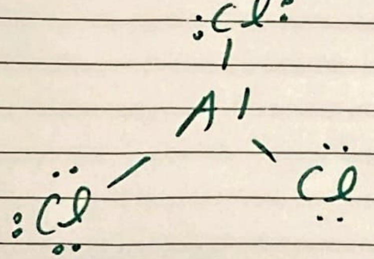
through the loss of the hydrogen on the benzene ring to restore aromaticity.
Bromination of benzene can also occur at room temp, whereas nitration requires moderate heating to aid in the formation of NO_2^+.

10. a) The substitution with iodine is endothermic which means it would require additional input of heat. This could be due to the lower electronegativity of iodine compared to other halogens, which means it is more difficult for it to produce a strong enough electrophile

→ due to incomplete octet

b) $AlCl_3$ can act as a Lewis acid, accepting an electron pair to generate the electrophile.

c)



Aluminum only has 3 valence electrons, meaning it forms 3 covalent bonds with an incomplete octet. This makes Al electron-deficient.

d) Fluorination of benzene is <u>more</u> exothermic than chlorination. This is because fluorine is more electronegative than other halogens, which makes the C-F bond that forms more polar and stable than those of larger halogens. A more stable product would be lower in energy than a less stable one, resulting in more energy release.