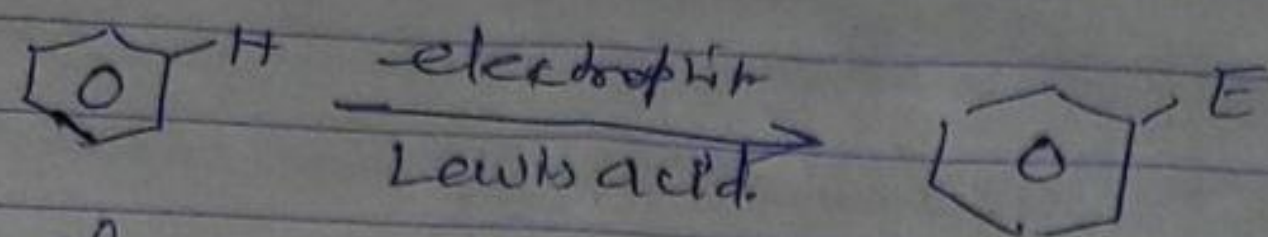


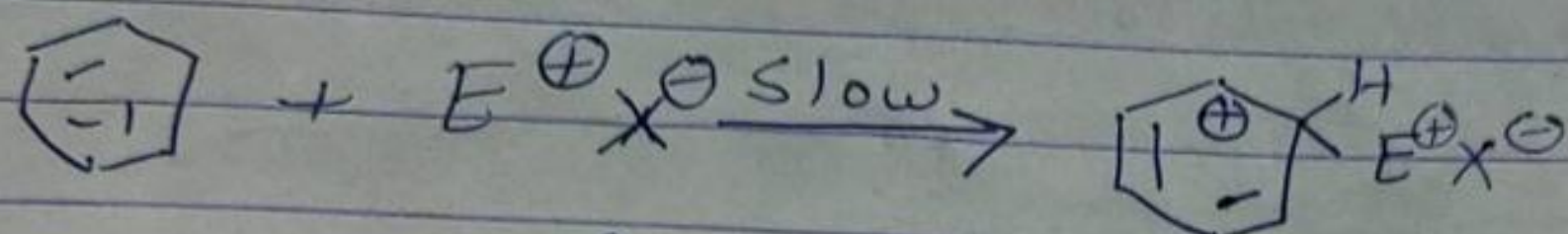
Electrophilic aromatic substitution:

- (SE₂)
- Bimolecular, formation of intermediate
- electron cloud of benzene ring
- arenium ion
- Common Mechanism



- electron donating substituents increase the rate
- electron withdrawing " decrease " "
- Proceeds through carbocation
- Breakage of C-H is not the slow step. The first step is the rate determining step.

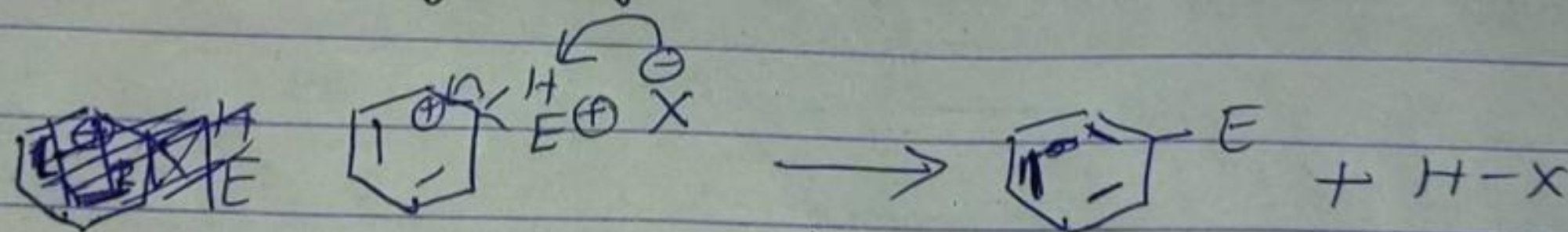
Step 1 → Attack of electrophile - π bond of the aromatic ring.



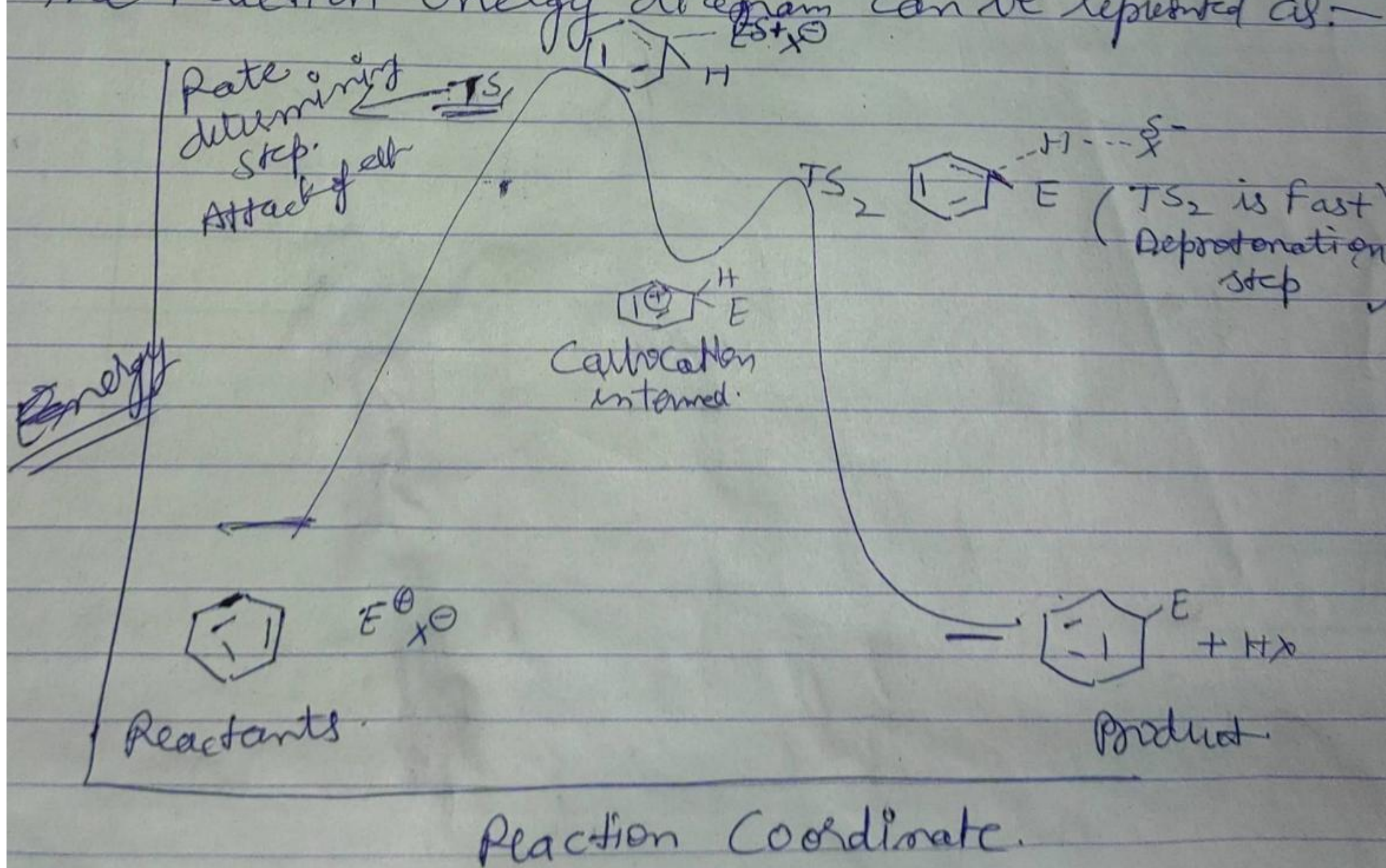
Formation of Carbocation intermediate

It is known as → arenium ion, benzenonium ion, Wheland intermediate

Step 2 → Breakage of C-H bond to restore aromaticity

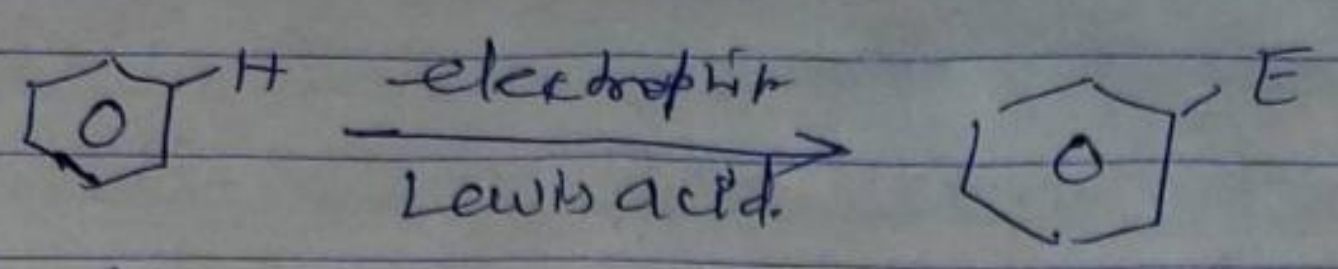


The Reaction energy diagram can be represented as:-



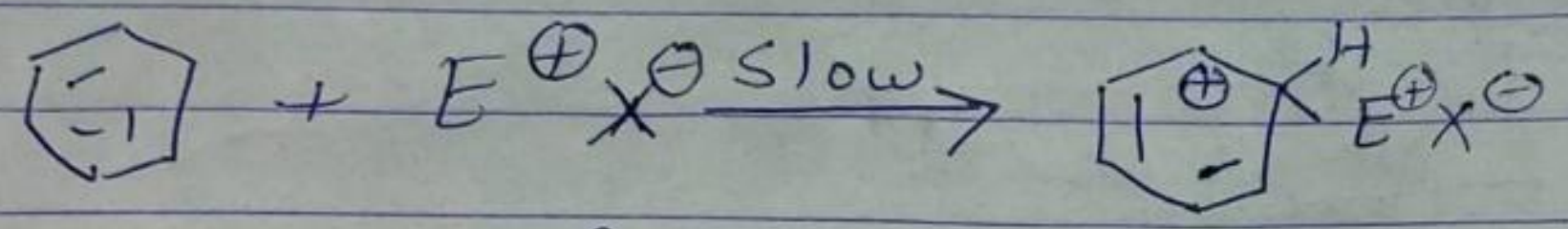
Electrophilic aromatic substitution: (SE₂)

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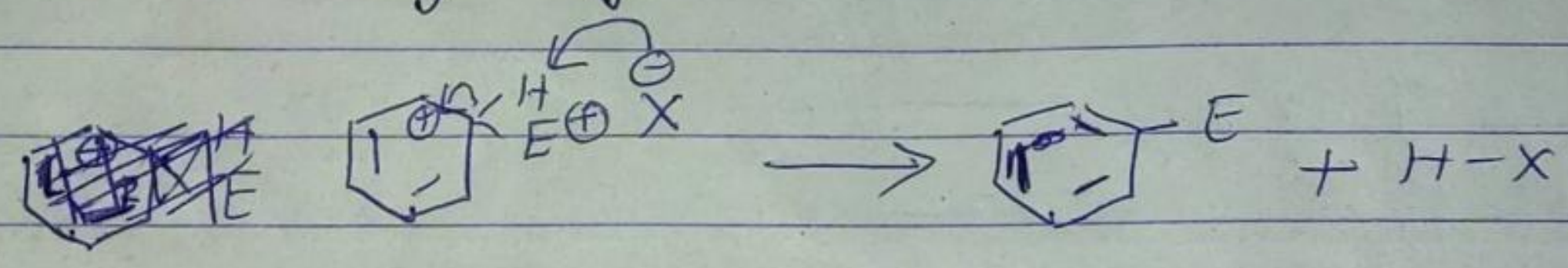
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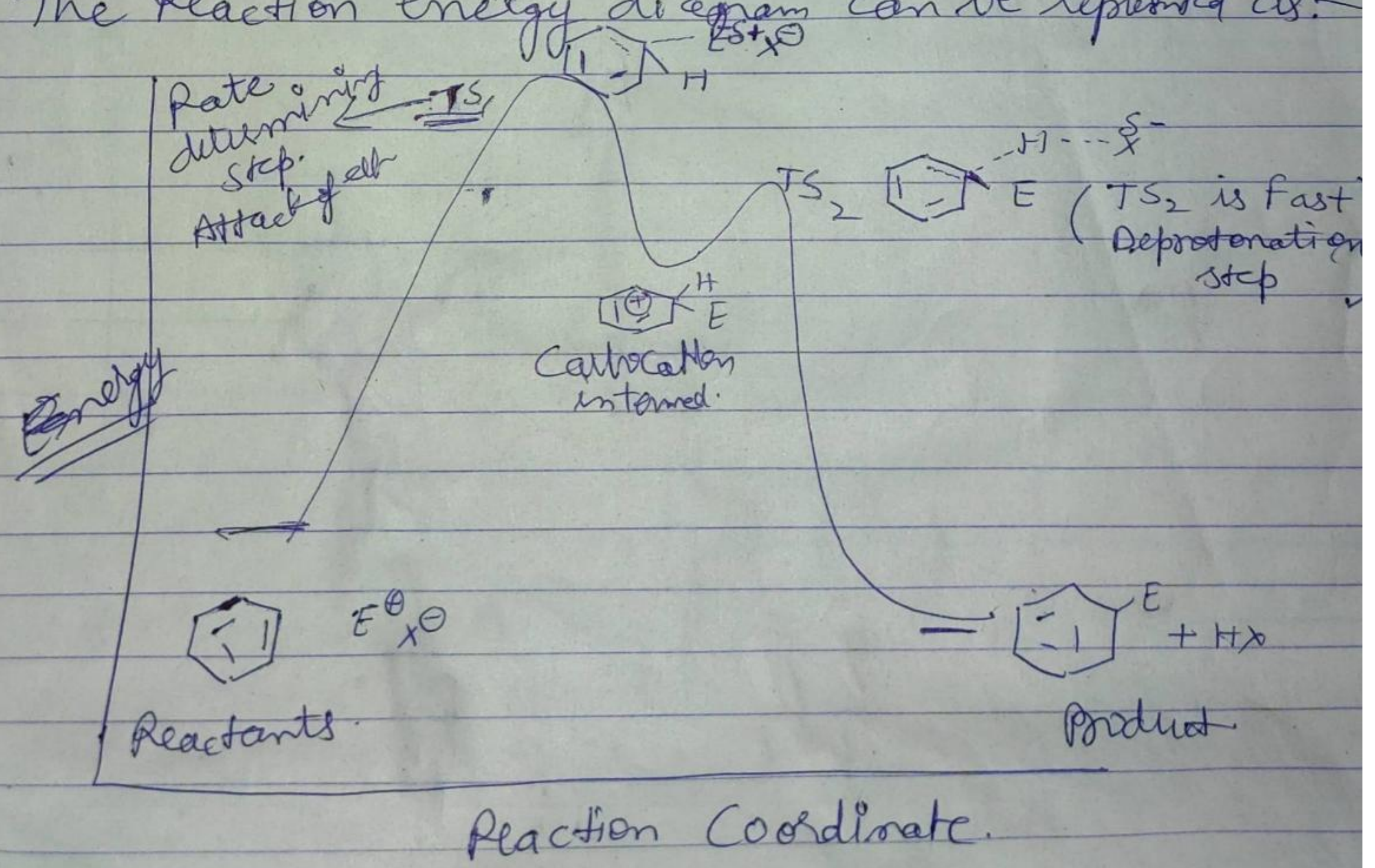
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The Reaction energy diagram can be represented as:-



Aromatic Electrophilic Substitution:

Orientation and Reactivity in Monosubstituted Benzenes:

- (1) o, p directing and activating gp. (+I effect and +R effect)
- (2) m-directing and deactivating gp. (-R effect)
- (3) o, p directing but deactivating gp. \Rightarrow halogens
 \hookrightarrow Here two opposite effect +R effect.
 -I effect.

(1) Explanation based on charge distribution \rightarrow $\left. \begin{array}{l} +R \\ -R \\ +I \\ -I \end{array} \right\}$ effect.

(2) Explanation based on carbocation stability \rightarrow

(1) o, p directing and activating

\hookrightarrow Resonating str.

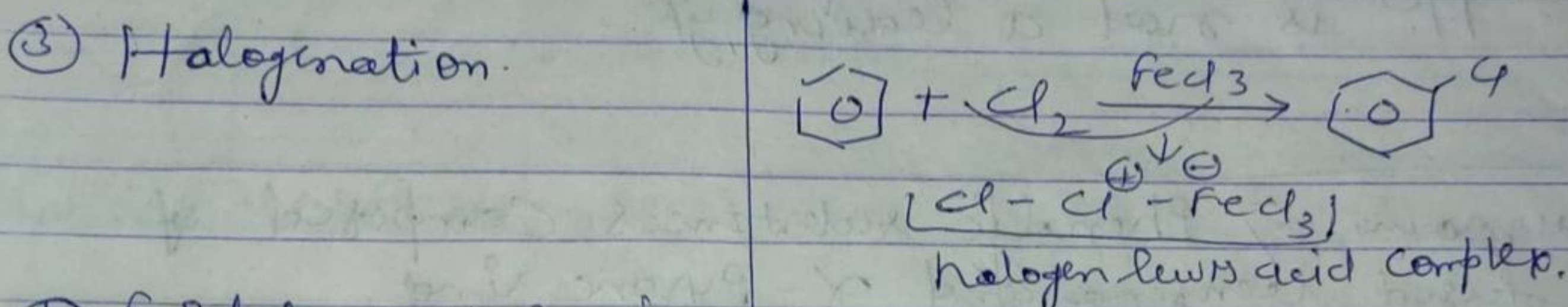
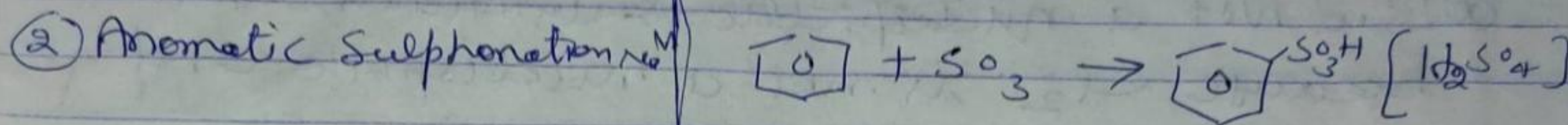
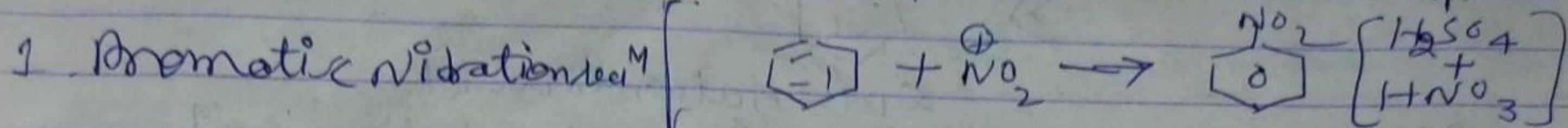


Aromatic electrophilic Substitution → 90

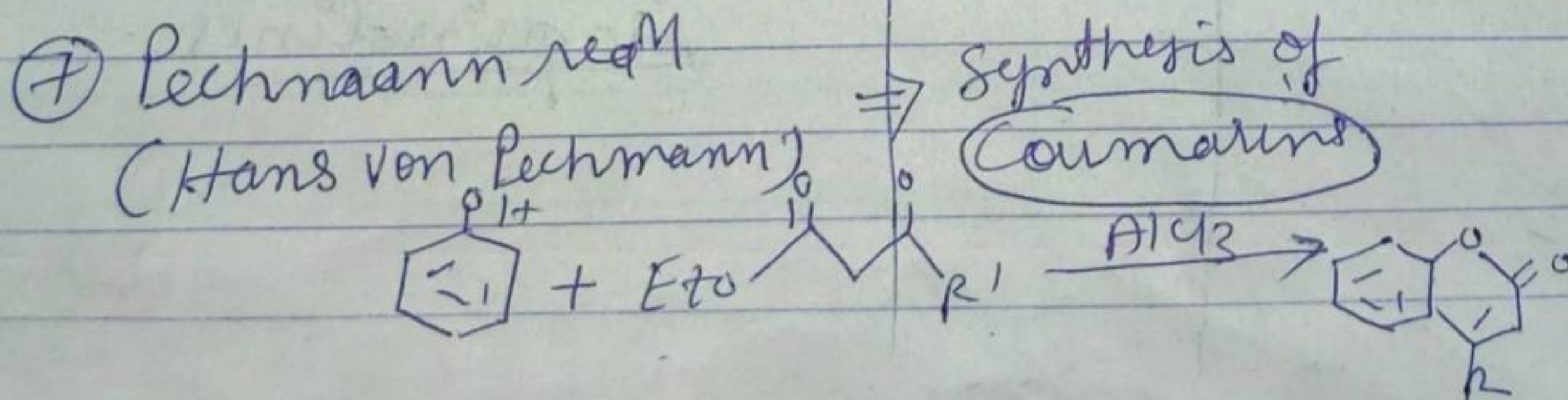
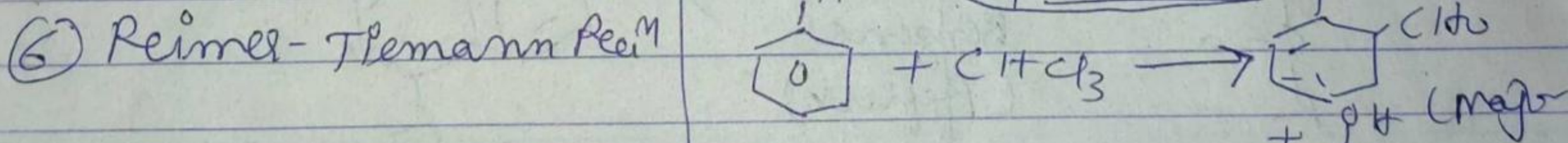
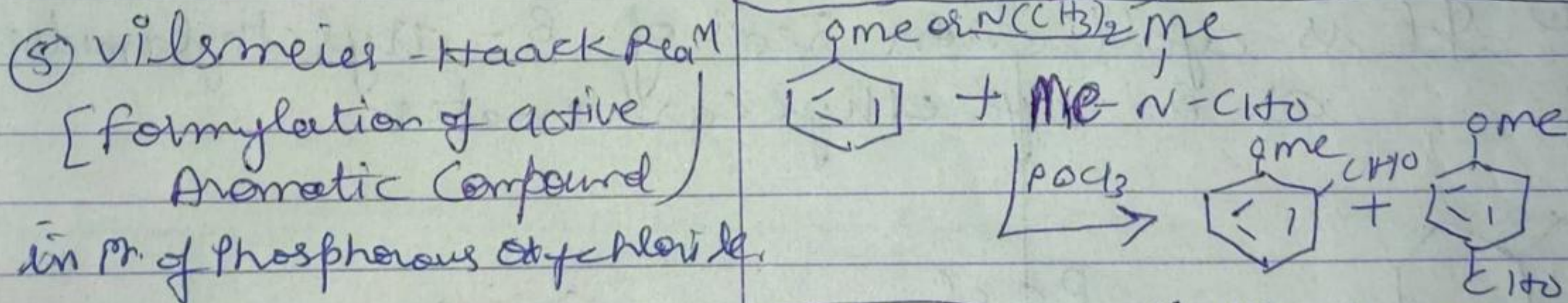
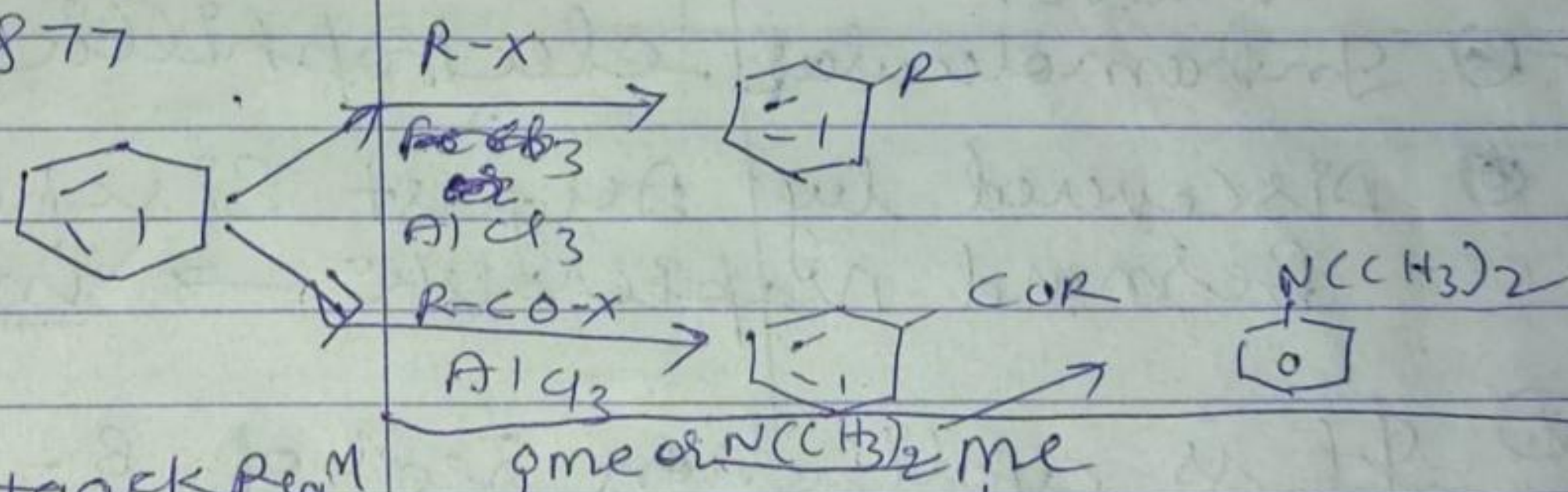
Substitution Ar^{M} (SE_2)
 $\text{R-X} \rightarrow$ Bimolecular

Atom attached to an aromatic system (usually Hydrogen) is replaced by an electrophile.

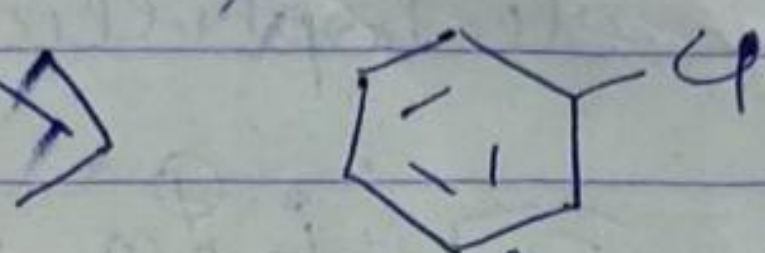
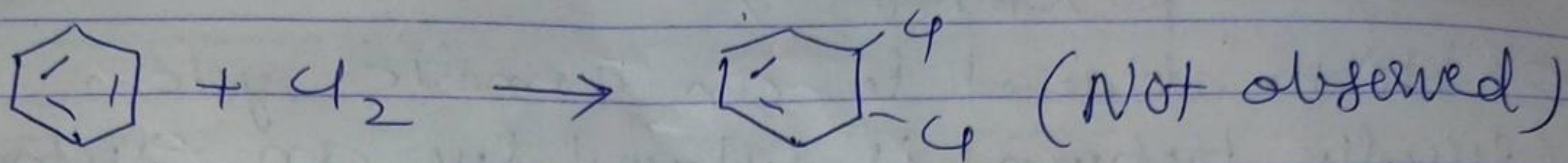
Some Important Aromatic electrophilic substitution - catalysts



4. Friedel-Crafts Reaction
 Charles Friedel in 1877
 James Crafts
 Friedel-Crafts Alkylation
 Friedel-Crafts Acylation



* Like Alkenes \rightarrow Benzene not give addition product



Substitution product.

* But not a nucleophilic substitution rxn.
because Cl_2 is not a nucleophile and H^+ is not a leaving group.

*

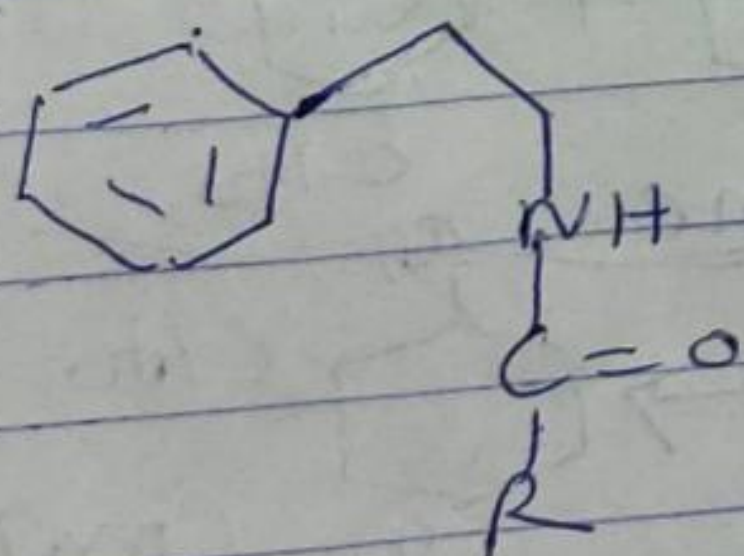
Coumarins \rightarrow Phenolic substances composed of fused benzene and α -pyrone ring.

⑧ Bischler-Napieralski Reaction

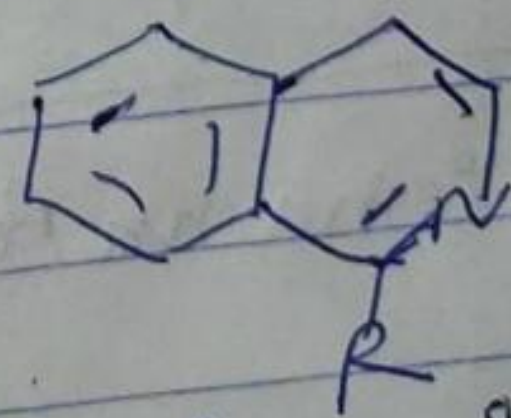
* Intramolecular electrophilic reaction

* Discovered by August Bischler and Bernard Napieralski \rightarrow in 1893

* It is cyclization rxn of β -arylethylamide or β -arylethyl carbamates.



POCl_3
Benzene
(Reflux)



isoquinolines.