

Inductive effect. (1)

⇒ permanent effect.

⇒ Applicable for σ bonded system.

⇒ Two kinds of effects are possible.

a) -I effect (electron withdrawing effect)

b) +I effect (electron donating effect).

Condition for -I effect: (group)

$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{ClH}_2 \rightarrow G$ [If G has e⁻ withdrawing effect,

G must have such atom which is more electro-

negative than sp³ carbon].

for example -OH; -NH₂; -OCH₃; -NHR; -N^{CH₃}

- All (ex. oxygen, nitrogen containing neutral group has -I effect. because O & N more e⁻ than sp³ C).

- Cl, -F (nucleophile group has more -I effect).

sp² C en (electronegativity) > sp³ C en (electronegativity)

sp C en (electronegativity) > sp³ C en (electronegativity)

so -^{sp²}O⁻H; -^{sp²}N⁺H₃; -^{sp²}Cl; -^{sp²}C=H₂; -^{sp²}C=C₂H₃;

-^{sp}O⁻H₂; -C≡N; -C≡CH;

n have -I effect.

n have -I effect: (groups having -I effect)

: Ordering -I effect: (groups having -I effect)

-NMe₂ > -NH₃⁺ > -SM₂ > -NO₂ > -CN > -CO₂H

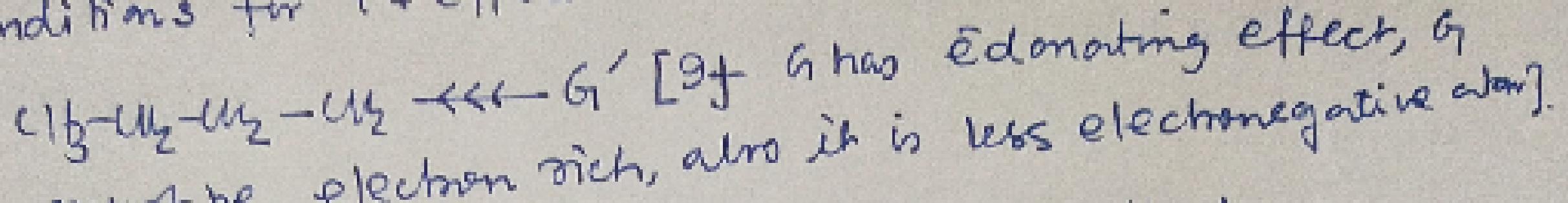
> -F > -Cl > -Br > -I > -OR > -OR > -OH

> -NH₂ > -C≡CH > -PH > -CH=CH₂ > -H.

⇒ positively charged ion is more electron deficient than neutral group. So it has +I effect.

- ⇒ Among halides, most electronegative atom F has highest (2) -I effect & least electronegative atom I has least -I effect. Similarly $-OH$ has more -I effect than $-NH_2$.
 ⇒ sp carbon has more -I effect than sp² carbon.

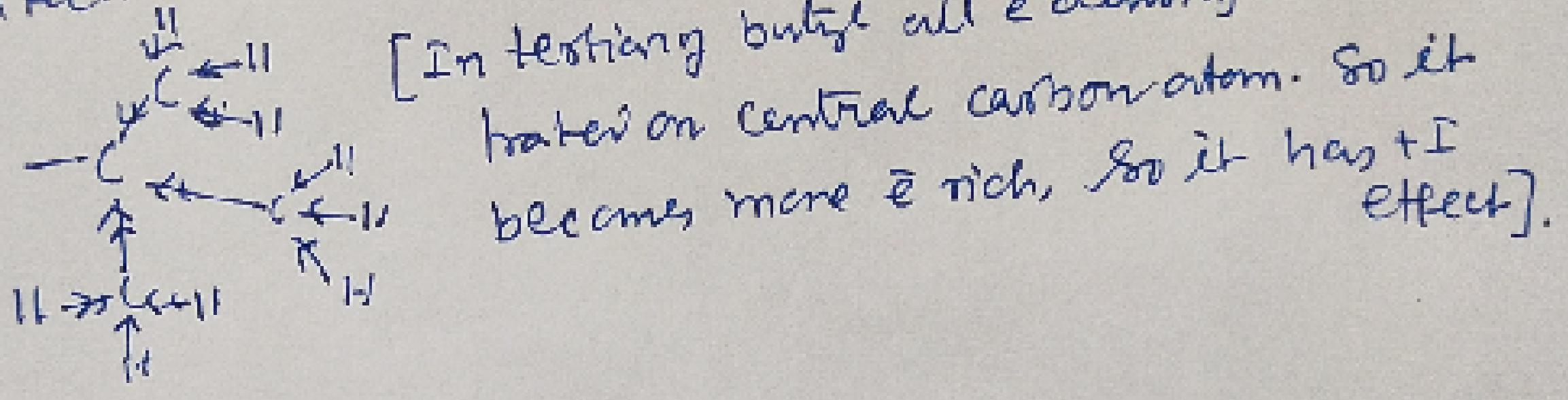
Conditions for +I effect:



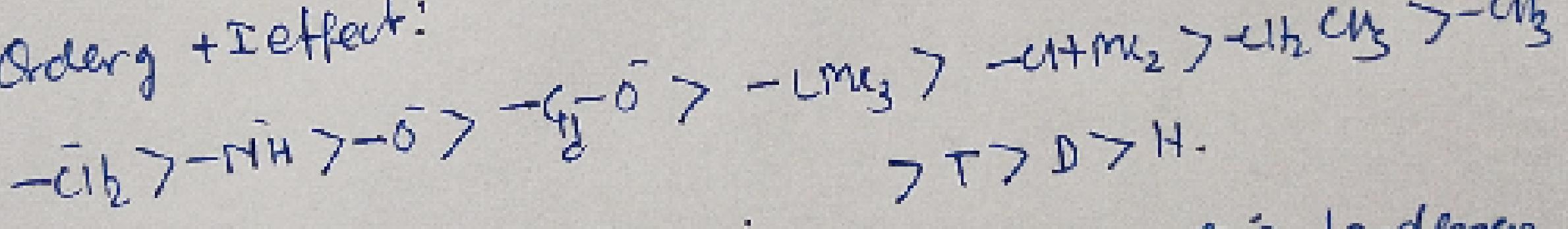
⇒ Small negatively charged ion has +I effect.
 e.g. $-O^-$; $-Cl^-$; $-NH^-$; $-Cl_2^-$

⇒ All alkyl groups show +I effect. $-CH_3$, $-CH_2-CH_3$, $-CH_3$ all have +I effect.
 So $-CH_3$, $-CH_2-CH_3$; $-CH_3$, $-CH_3$ all have +I effect.

Also more alkyl groups, more +I effect.



Order of +I effect:



⇒ As en $O > N > C$. So less is the electronegativity, more is the δ donating tendency.

more is the +I effect.

⇒ Among alkyl group, more carbon atoms, more branching, more +I effect.

⇒ $-O^-$ (100% -ve charged) $\xrightarrow{\text{so electron density}} -O^- > -Cl^-$

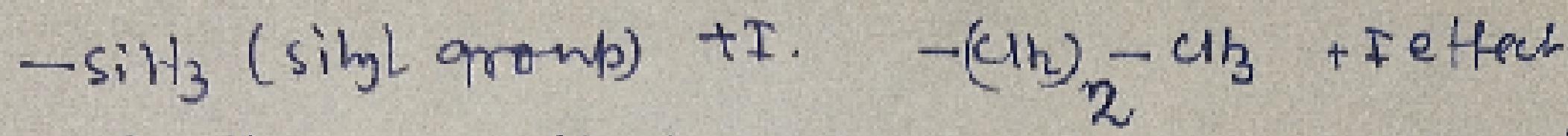
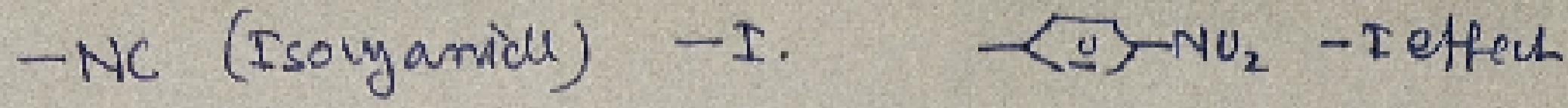
$-Cl^-$ (-ve charge is reduced / partial) $\xrightarrow{\text{+I effect}} -O^- > -Cl^-$

⇒ More heavier isotope, more +I effect.

⇒ More heavier isotope, more +I effect.
 $-T > -D > -H$. $T \Rightarrow$ Tritium; $D \Rightarrow$ Deuterium

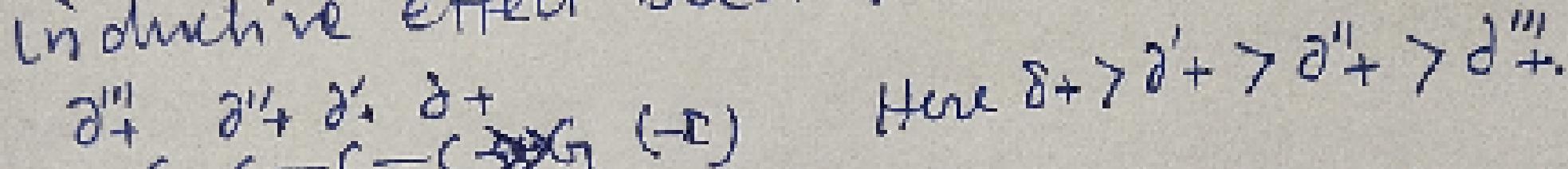
Q. Which group has which effect?

(3)



Depending factor on inductive effect:

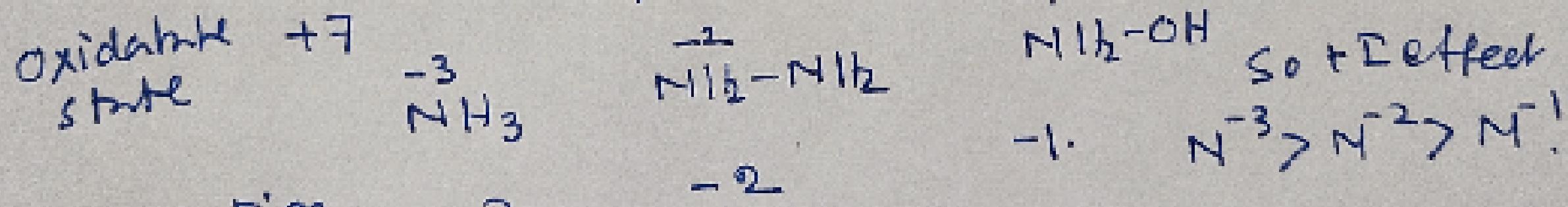
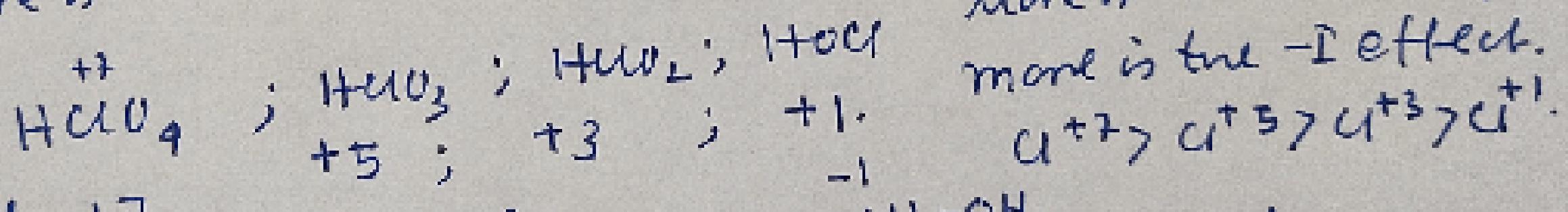
\Rightarrow Inductive effect is distance dependent, more is the distance, less is the \pm I effect. After 3 carbon atoms inductive effect becomes zero.



δ δ δ δ G (-I) δ δ δ δ G (-I)
Here -I effect of G on α carbon is higher, then on β carbon, then on γ carbon & almost negligible on δ carbon.

More is the -recharge, more is the -I effect.

\Rightarrow More is the +recharge, more is the +I effect.
More is the -recharge (e^- rich), more is the +I effect.



Oxidation state of N -3

\Rightarrow More is the branching of alkyl groups more is the +I effect.

so isopropyl group has more +I effect than n-propyl group.

so tertiary butyl group has more +I effect

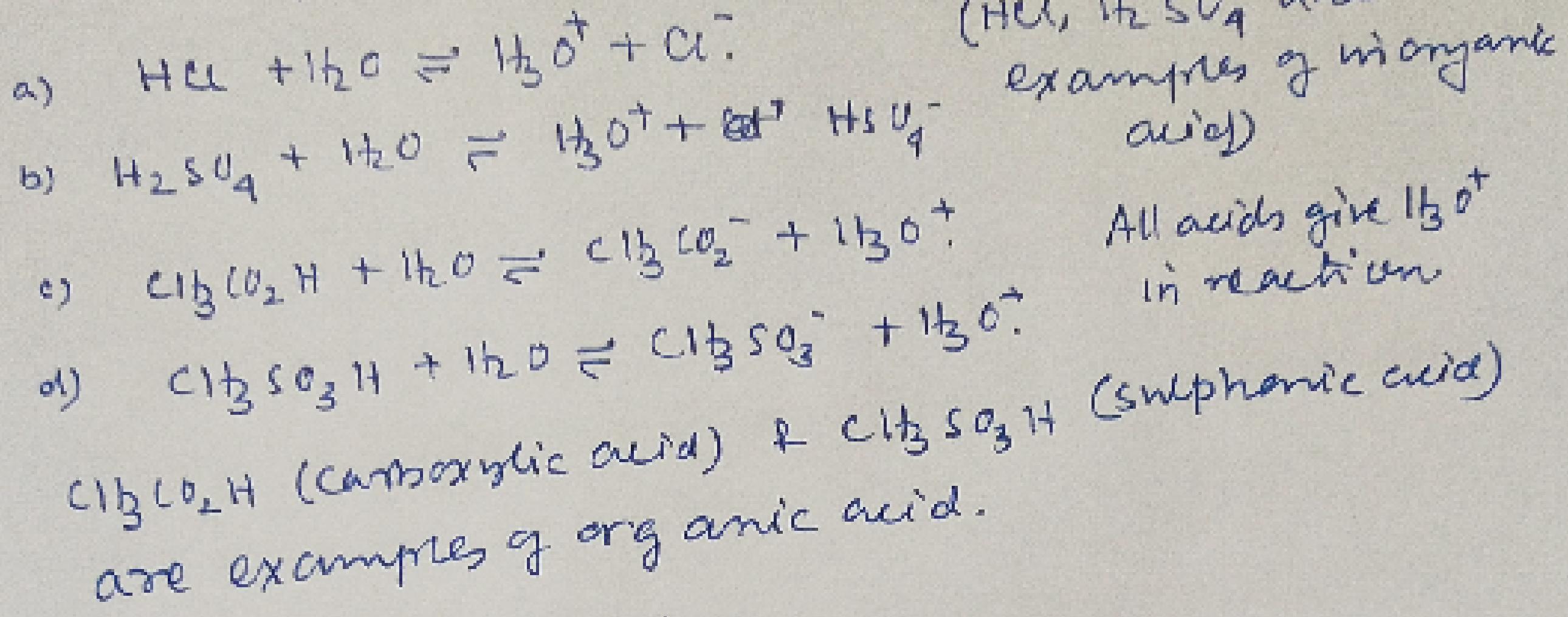
than isobutyl & isobutyl has more +I effect

than n-butyl group.

Effect of inductive effect on property of molecule: (4)

: Acidic strength:

We talk about Brønsted acid which give H_3O^+ & hydroxide ion (OH^-) in water. [Acids are $\text{H}^+/\text{H}_3\text{O}^+$ donors].



$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

$$K_{\text{eq}} = \text{equilibrium constant} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

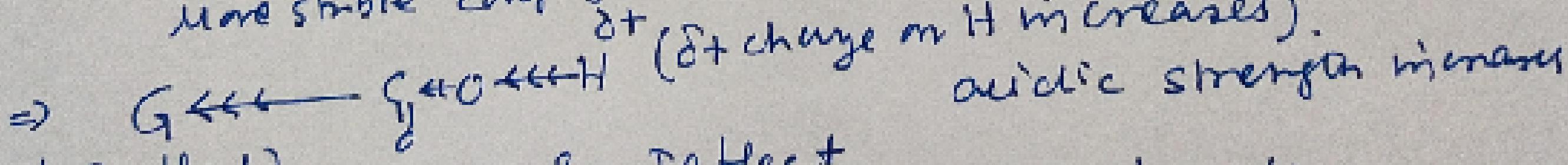
$$K_{\text{eq}} [\text{H}_2\text{O}] = K_a = \text{acid dissociation constant}$$

$$= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

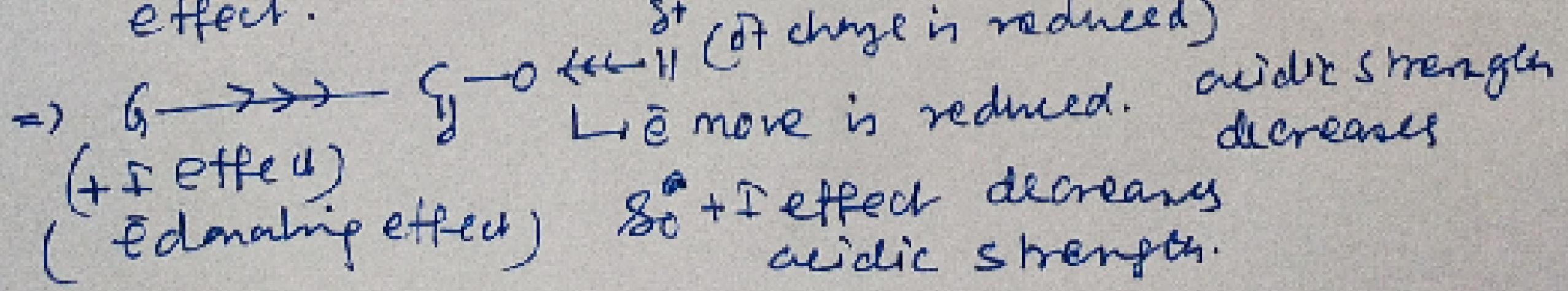
A^- is called conjugate base.

If acidic strong acid, it will give more H_3O^+ in H_2O , so $[\text{H}_3\text{O}^+] \uparrow$; $K_a \uparrow$; More is the acidic strength more will be K_a . As $pK_a = -\log K_a$, more is the acidic strength, less will be pK_a .

More stable conjugate base; stronger will be acid.



(-I effect) So -I effect increases acidic strength
@ withdrawing effect.



\Rightarrow More is the $-I$ effect, more is the acid strength. (5)
 \Rightarrow More is the $+I$ effect, less is the acid strength.

Example $\text{Fe(OH)}_3 + \text{Cu}^{2+} \rightarrow \text{Fe(OH)}_3 + \text{Cu(OH)}_2$

Example a) $\text{FeCl}_2 + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2$ b) $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

$$0) \quad \epsilon_1 = \epsilon_0 = 0.14$$

$$b) \quad \alpha - \alpha_2 - \zeta_2 = 0.1$$

e) Br-CH₂-Cl - 0 II

$$d) \quad \Gamma = c\mu - 4 - 0.11$$

$$(2) \text{ H}_3\text{N}^+ - \text{CH}_2 - \text{CO}_2\text{H}$$

$$b \quad \text{D}_2\text{N} \rightarrow \text{CH}_2 - \text{CO}_2\text{H}$$

$\text{H}_2\text{NC}-\text{CH}_2-\text{CH}_2\text{NH}_2$

$$d) \quad Br = M_2 - (v_2)$$

Answer: a > b > c > d.

As-I effect - $H_3^{+} > H_2O_2 > -CN$
 order $> -CO_2H.$

so ad'st're strength $a > b > c > d$

$$\text{Q}_2 \left(-\overset{\alpha}{\underset{\beta}{\text{C}}} - \text{C} = \text{O} \right) \text{H} \quad (\alpha\text{-Chloro aceto})$$

Position A has highest -I effect, then B, then C position

b) $\text{C}_6\text{H}_5\text{COCl}$ (B-chloro acid) has acidic strength order $a > b > c$

c) $\text{C}_6\text{H}_5\text{COOCl}$ (F-chloro acid)

Oxyacid: (Acid containing oxygen is called oxy acid)
An acid molecule may contain one or more
oxygen atoms.

More +ve oxidation state of central atom,
-1.0 and -0.5 will be

i) HClO_4 More +ve Oxychlorine S will be
more will be -e effect, more will be

$$2) \text{H}_2\text{O}_2 + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_2$$

Acidic Strength

c) H_2S_2 $a > b > c > d.$ 2) $\text{H}_2\text{SO}_4 > \text{H}_2\text{S}_2\text{O}_3$

d) HOCl^+

: Hydronium: [H directly attached with central atom in H_3O^+ it is called Hydronium].

If it acts as acid, then it is called hydronium ion.
If elements are in same group.

a) H_2 among
 HF , He , HBr , HF

in H₂O, H₂S, H₂Se, H₂Te.

\rightarrow RSH

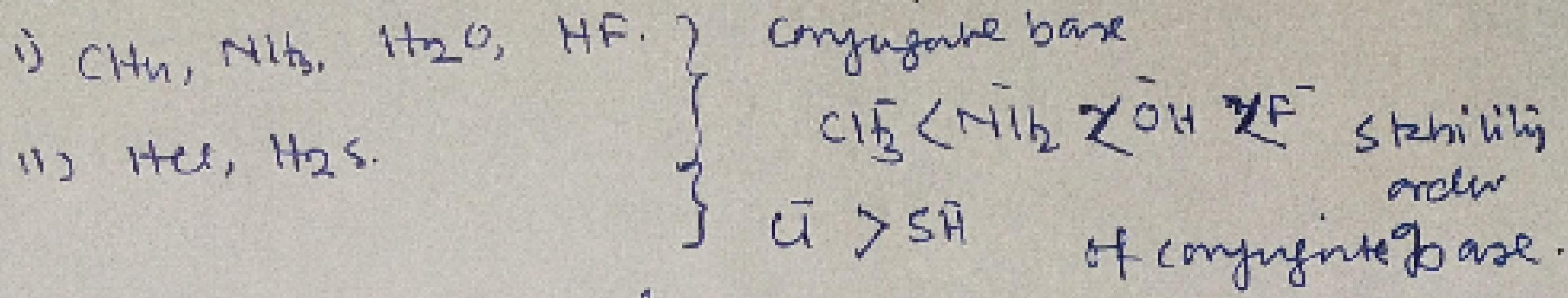
iii) Rolt,
Down the grants, size is the } deciding factor. - we change on large sized ones is
more stable. More stable aggregate back styles in the acid.

Here we have to write
congruence back of all
and. If stability order is

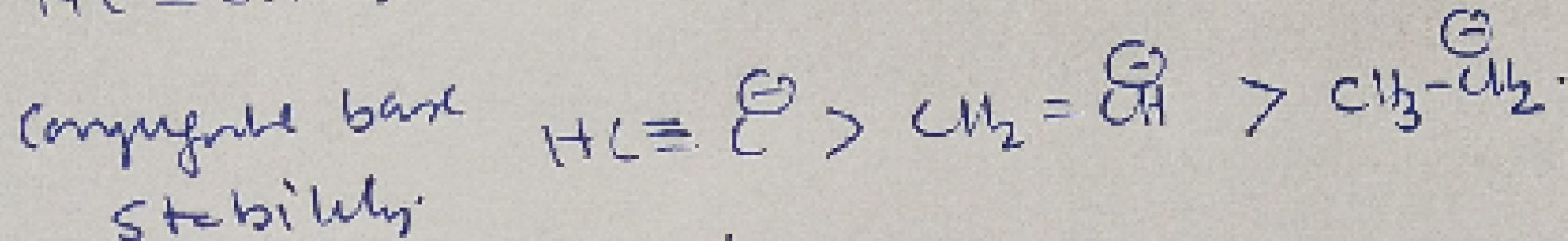
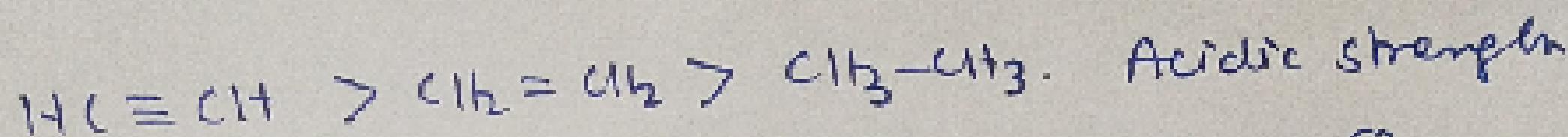
$$F^- < U^- < Br^- < I^-$$

Te⁴⁺ > Se⁴⁺ > S⁴⁺ > O⁴⁻

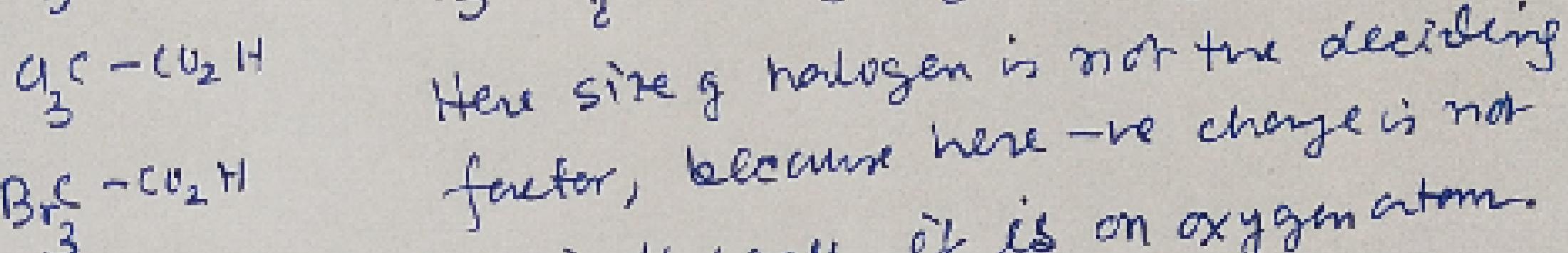
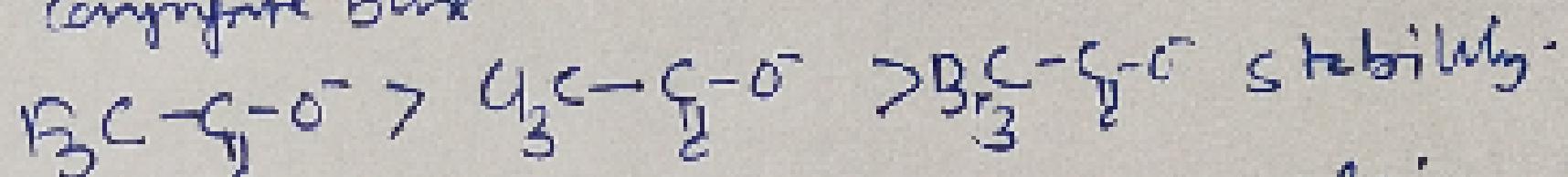
b) If in hydronium, elements are in the same period (6)



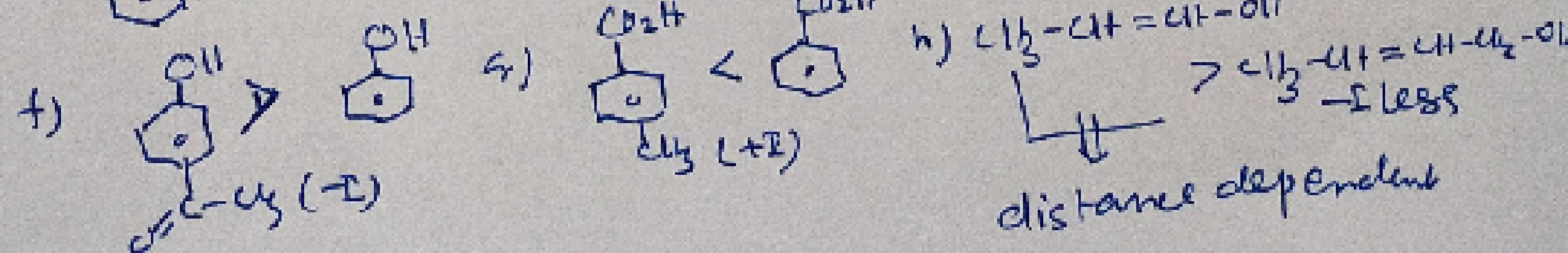
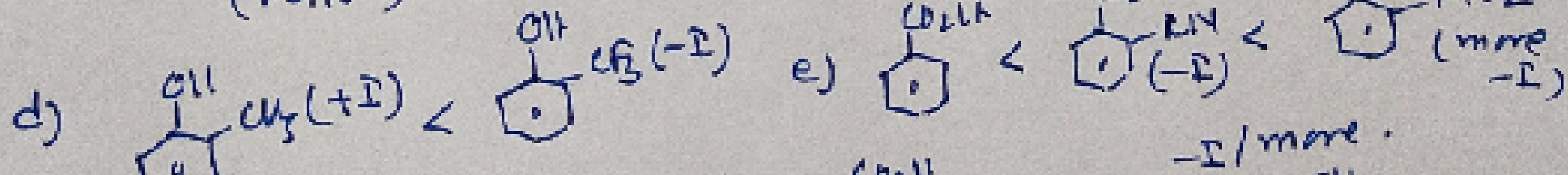
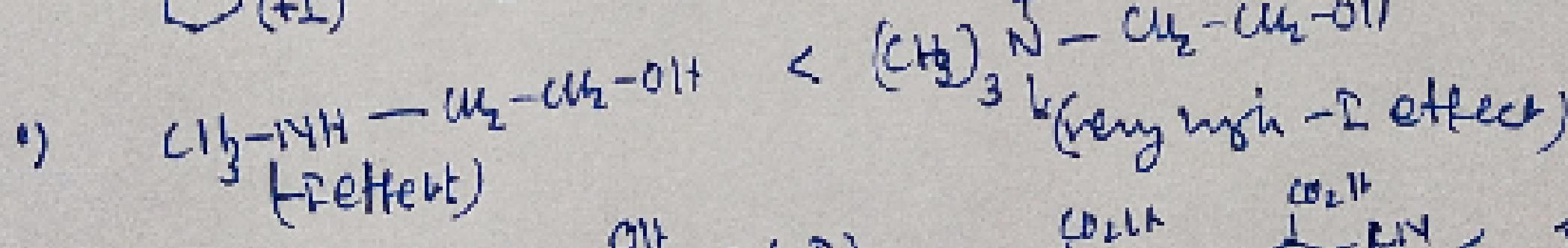
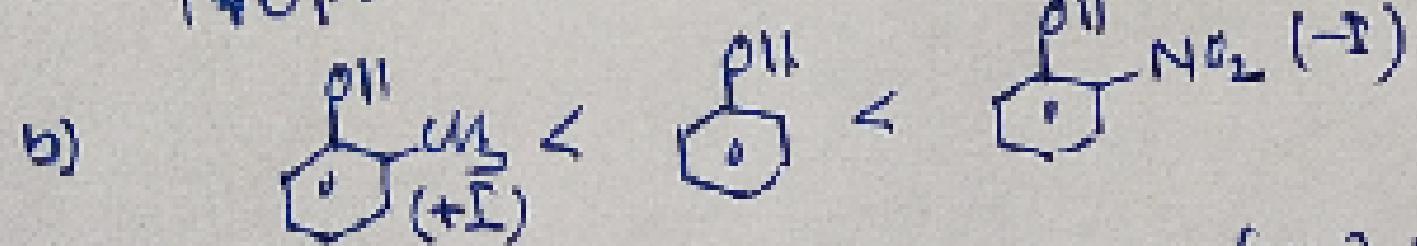
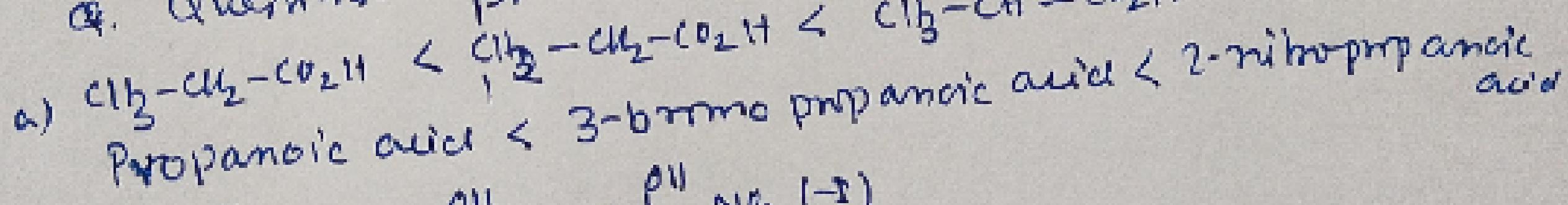
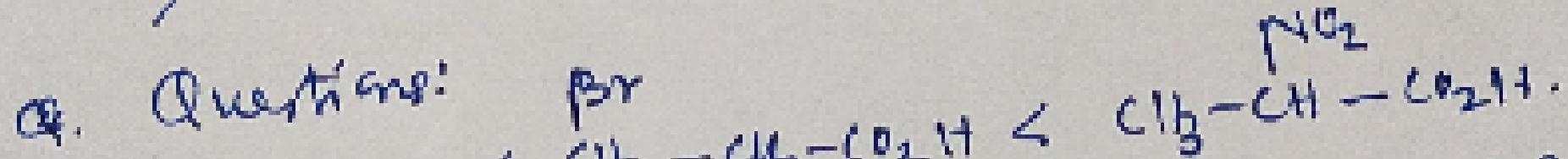
So acidic strength order $\text{H}_2\text{S} > \text{CH}_3 > \text{NH}_3 > \text{HF}$.



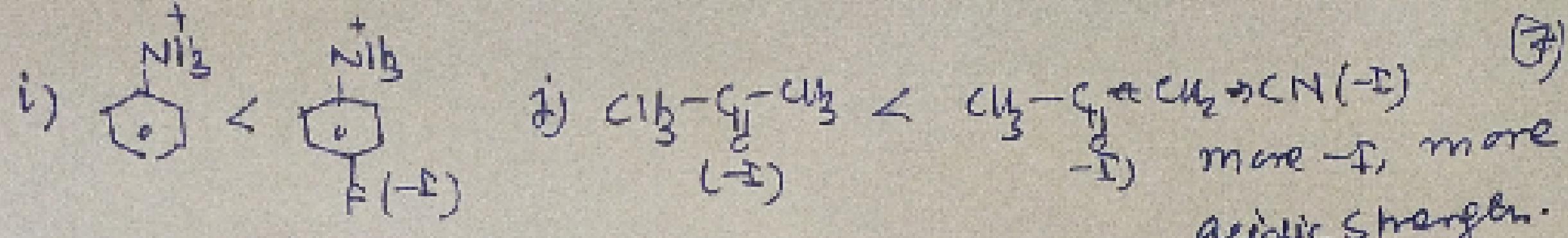
conjugate base



In more is the $-I$ effect, more is the acidic strength.



distance dependent



iii) $\alpha\text{-hydroxy butanoic acid} > \beta\text{-hydroxy butanoic acid} > \gamma\text{-hydroxy butanoic acid}$
 (More distance, less acidic strength)

iv) $\text{CH}\equiv\text{C}(\text{CH}_2\text{CH}_3) > \text{CH}_2=\text{CH}(\text{CH}_2\text{CH}_3) > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 Alkyne is more acidic than alkene & alkene is more acidic than alkane.

v) $\text{CH}_3 > \text{CH}_2$ [More double bond, more -I, more acidic strength]

vi) $\text{CH}_3-\text{C}_2\text{H}_5 < \text{CH}_3-\text{C}_2\text{H}_5\text{O}^-$ [More -CO group, more acidic strength]

vii) $\text{CH}_3-\text{C}_2\text{H}_5 < \text{CH}_3-\text{C}_2\text{H}_5\text{O}^-$ (Tendency to loose H⁺ is more for +ve charge ion than neutral system)

viii) $\text{CH}_3-\text{C}_2\text{H}_5-\text{OH} > \text{CH}_3-\text{C}_2\text{H}_5-\text{NH}_2 > \text{CH}_3-\text{C}_2\text{H}_5-\text{CH}_3$ Acidic strength
 because $\text{O}^- > \text{N}^-$ (env is the deciding factor)
 (As elements are in same period).

($\text{CH}_3-\text{C}_2\text{H}_5-\text{OH} > \text{CH}_3-\text{C}_2\text{H}_5-\text{NH}_2 > \text{CH}_3-\text{C}_2\text{H}_5-\text{CH}_3$) Acidic strength

ix) $\text{CO}_2\text{H} > \text{CH}_2-\text{CO}_2\text{H} > \text{H}_2\text{C}-\text{CO}_2\text{H}$ (succinic acid)

Oxalic acid Malonic Acid
 More is the distance of one -CO₂H group w.r.t other,
 less is the +I effect, less is the acidic strength.

x) $\text{F}(-\text{OH}) > \text{Cl}(-\text{OH}) > \text{Br}(-\text{OH}) > \text{I}(-\text{OH}) > \text{N}_3^-(-\text{OH})$
 -I effect all, -I effect +I effect
 decreases, acidic strength increases → acidic strength decrease.

