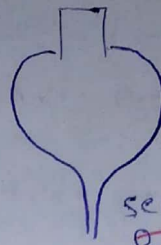


Exp 7

* راجعي الأدوات



Buchner funnel



separatory funnel

Melting point

(m.p) : physical constant

check the purity

pure solid

(0.5-1)°C

سكنج

شده

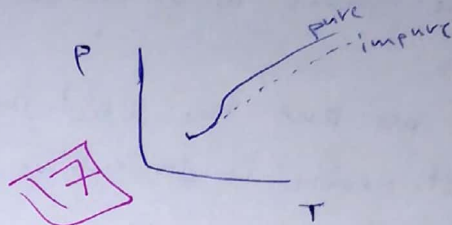
- sharp (m.p)

impure solid

(m.p.r) → اقل

(2-20°C)

* (m.p) → doesn't affect by pressure



equilibrium at 1 atm

impurities

soluble

↓
affect on (m.p)

How ↓

it ↓ lower the m.p

* Broaden (m.p range)

insoluble

↓
don't affect

because its not enter in crystal lattice

oil bath

* in this exp we use oil that don't affect on the (m.p)

for example → silicon oil
paraffin oil

} → should be high boiling & stable.

* thermometer is not immersed in oil → lower m.p

* Rapid heating → increase the m.p

* impurities → decrease

المزج المذوب المذوب المذوب

المزج المذوب

- * Many organic are solid at room temperature $\rightarrow$ strong intermolecular forces
- * difference in melting point $\rightarrow$ " " "
- * we can determine if two compounds are the same or different by m.p. 19
- * before we put the solid in a capillary tube we must ground it to a fine particle by spatula
- * melting point range $\rightarrow$ The (T) at which the solid begins to melt and ~~the~~ which is completely $\rightarrow$ liquid

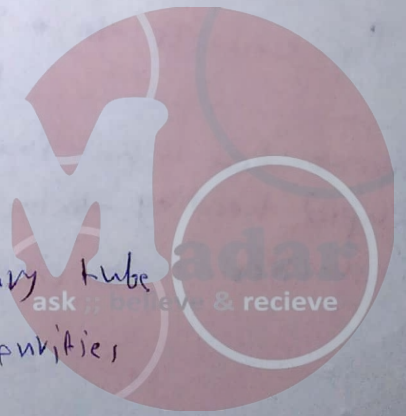
$\Rightarrow$ the factor that affect the (m.p range) :

- particle size
- amount of materials 20
- density
- thickness of capillary tube
- the rate of heating $\rightarrow$ most critical factor

* Mid point $\rightarrow$ m.p. range (a-b) $\frac{a+b}{2}$

- * $\rightarrow$ large sample $\rightarrow$ increases m.p.
- * high rate of heating $\rightarrow$ " "

-
- To lower m.p $\rightarrow$
- (a) thick-walled capillary tube
 - (b) soluble ~~materials~~ impurities
 - (c) larger size crystal



2

Boiling point and Distillation

B.P $\rightarrow$ a temperature at which

Vapor pressure = external pressure

Normal B.P $\rightarrow$ " " "

Vapor pressure = external (1 atm)
760 mmHg

* B.P affect by changing in (P)

$T \uparrow P^v \uparrow$



21

external P $\uparrow$

B.P $\uparrow$

Vapor pressure $\downarrow$

intermolecular forces $\rightarrow$ Hydrogen Bonding H- (N O F)
 $\rightarrow$ Dipole-Dipole (between polar molecules)
 $\rightarrow$ London force (non-polar)

((كَيْفِيَّةُ التَّأثير)) $\Rightarrow$ ① Inter molecular force

H.Bonding > Dipole-Dipole > London

for pure liquid

② Mw

Mw $\uparrow$ B.P $\uparrow$

22

② الشكل

Branching $\uparrow$ B.P $\downarrow$

HF $\rightarrow$ H-bonding

Solutions

Solid Solute and non volatile

زيت الخ والي
" السكر "

Solute $\uparrow$ B.P $\uparrow$

Amount of Solute

B.P $\uparrow$

شكليه لانك

ذائبة ببعده (completely miscible)

ومستطير (Volatile)



$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

$$P_{\text{Solution}} = X_A P_A^0 + X_B P_B^0$$

$$X_A + X_B = 1$$

B.P for Solution is between A, B

P^v " " " " " " " " " " " "

Distillation → purification separation

بزرگوار حدث
7
مندی درجه حراره
0-100

① Simple distillation

* یکبار مرتبه و جد

* we use it when the B.P of component is 80°C or more ..
المرتبه في درجه الحراره

23

② Fractional distillation

* تسخين وتكثيف اكثر من مرة

* we use fractional column → provides a large surface area for continuous heat exchange between hot vapor and cool liquid.

* " " it when the B.P

is less than 80°C →
در المرتبه كبر

* more efficiency

③ Vacuum distillation بالإجبار

$P_{\text{external}} \downarrow$ B.P $\downarrow$

We use it in ① distillation of high boiling liquid

② Distillation of compound that decomposes at P_{atm}.

24

* Boiling stones → To prevent bumping

* grease: الشحمة → to ensure a completely sealed system.

* Thermometer should be below the opening → to measure the (T) at which we have equilibrium between liquid and gases

* The water enter the ^{lower} ~~upper~~ side and going out from the upper side

↓

condenser is always full of water

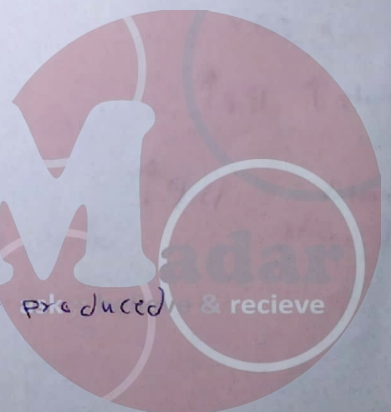
* we use water bath → ① for low boiling liquid

② flammable liquid

volatile.

* fill flask to two third → To leave space for vapor produced & relieve

* if the thermometer not kept moist → B.P ↑



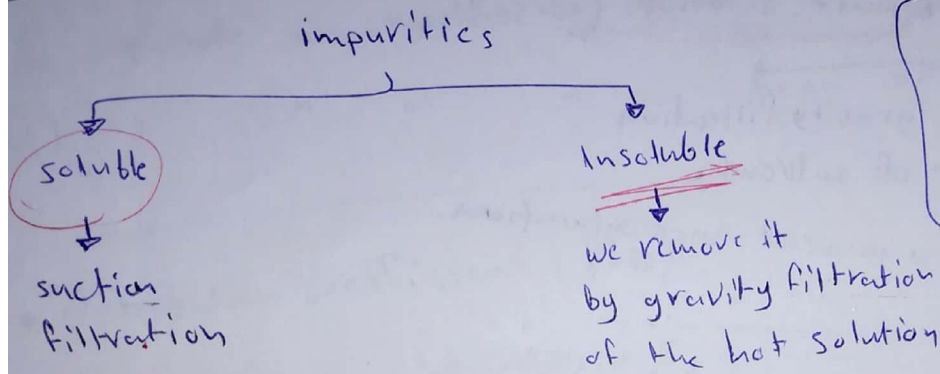
Recrystallization

↳ solid compound precipitates from saturated solution in form of crystal

To increase the precipitation : (1) cooling
(2) evaporation

we use Recrystallization : (1) For purification of solid
(2) separation of solid mixture

25



لattice energy ↑
m.p ↑
Solubility ↓

properties of solvent which we use

it in crystallization : (1) No react with substance to be purified

(2) No flammable

(3) Evaporate easily from crystals

(4) Dissolve large amount of solid at high (T)
" small " " " " low (T)

(5) less toxic

Large volatility

if we use two solvent they must be miscible in each other

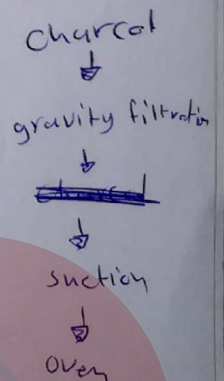
we add Charcoal → to remove colored impurities

gravity filtration → to remove charcoal
" " insoluble impurities

we use oven → For solids which has high m.p

Fluted filter paper → to make the rate of filtration fast

Why the flask and filter paper... should heated after filtration → to prevent precipitation of sub, to have easy filtration



→ purification by recrystallization depends on :

- ① different solid have different solubilities
- ② Most solids are more soluble in hot

→ Solubility determine by two factors :

- ① like dissolve like
- ② The lattice energy

if a substance soluble in one solvent
and insoluble in other → poor solvent (miscible)

* evaporation during the gravity filtration
will reduce the amount of solvent.
and we minimize it to prevent supersaturation



separation of sub. from mix.
by using solvent prefer dissolve the sub

+ extraction
 → solid-liquid → فصل مادة صلبة من المواد السائلة باستخدام مذيب سائل
 → liquid-liquid → فصل السائل من السائل
 من المواد السائلة باستخدام مذيب سائل
 CH₂Cl₂

[illegible]

to Distribution coefficient (H.D)

تركيز الماء المراد فصلها
بالذئب العصوي
تركيزها بالماء

$$k_D = \frac{S_0}{S_w} \cdot \frac{\frac{w_0}{v_0}}{\frac{w_w}{v_w}}$$

Handwritten: Δ $\rightarrow$ Δ

$$C_s = \frac{m}{V}$$

4. الادوية بإيرج الست الخصم الخصم

- ~~1~~ Immiscible with liquid in which the solute
- 2 dissolve the solute to be extracted
- 3 No flammable.

→ Sulphing out (مبدأ الكبريت)
→ ① NaCl
② Na_2CO_3

- ↳ 1) decrease the solubility of organic
2) breaking up emulsion.

Compound in water
ask :: believe & receive

we can remove the emulsion by 3)

- 1) salting out
- 2) centrifugation
- 3) stirring the layer with glass rod.

Salting out $\rightarrow$ we use Na_2CO_3 , NaCl



1) salting out

2) using to remove the acidic tannis ^{acid}
by converting them to water soluble salts

30

drying agent $\rightarrow$ anhydrous CaCl_2
anhydrous MgSO_4
anhydrous Na_2SO_4

to remove traces of
water from organic layer



5 Steam Distillation

↳ separation of slightly volatile, water insoluble sub from non volatile by using steam

"Bromo Benzene in water"

* sub that we want to separate them must be :

- ① slightly volatile
- ② insoluble in water
- ③ Inert toward steam and stable

31

we use steam distillation :

- ① separation compound from mix which contain non volatile impurities
- ② separation of organic compound from its natural source.

* essential oil

① Anise oil

② Caraway

③ Cummin

④ Clove

$$P_{\text{total}} = X_A P_A^{\circ} + X_B P_B^{\circ} \quad \rightarrow \text{miscible}$$

$$(X_A + X_B = 1) \rightarrow P_{\text{total}} = P_A^{\circ} + P_B^{\circ}$$

Constant

↳ B.p constant

↳ immiscible

كسالة (P.V)

ما يغير في
هكونا هالول
به رجدة
مؤثرات



essential oil
Anise
clove
caraway
cummin

* B.p → انتد التقطير كونه
اقل من اقل درجة كليا

B.P → يكون ثابتا
اقل من اقل درجة كليا

$$\frac{n_A}{n_B} = \frac{P_A^{\circ}}{P_B^{\circ}}, \quad \frac{m_A}{m_B} = \frac{P_A^{\circ} M_{wA}}{P_B^{\circ} M_{wB}}$$

B.P →

اقل من اقل

P.V

→

اقل من اقل



* to extract most of essential oil we add salt (up 7) salt out

* last fraction contains the same amount

* all fraction have the same composition in steam distillation.

steam distillation (hexane + acetone & water + bromobenzene)

Simple

B.p variable

B.p between

acetone and water.

$$P_{\text{total}} = P_A X_A + P_B X_B$$

Different

Steam

B.p constant

B.p is less than B.p of water and water

Bromobenzene and water

$$P_{\text{total}} = P_A + P_B$$

Composition kept constant

steam dist. is used high-boiling steam volatile organic compound at temp below b.p of water



Chromatography

(Technique) → أداة

- ① separate the compound from the mix.
- ② Identify the organic sub.
- ③ To check the purity

34

Chromatography depend on : ① Adsorption : depend on selective of component (TLC, column)

② partition : depend on partition of component between
(Paper, liquid-liquid, gas-liquid)

⇒ TLC chromatography

Stationary phase : Silica
Alumina

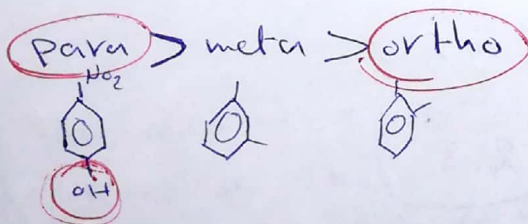


35

Factors that affect R_f :

① polarity of compound

polarity ↑ R_f ↓ m.p ↑



② polarity of stationary phase

polarity ↑ R_f ↓

③ polarity of mobile phase

polarity ↑ R_f ↑

راجع الزيت

$$R_f = \frac{\text{distance by compound}}{\text{distance by solvent}}$$

$R_f \leq 1$

* if the spots isn't colored :

- ① UV-light
- ② Iodine
- ③ sulfuric acid

ask & believe & recieve

→ Paper chromatography.

* we use (petri dish.)

↓
stationary: water

yellow → R_f less

blue → R_f more

36

* eluent → solvent → mobile phase

$$P_t = P_A + P_B$$

$$= P_B \cdot \frac{x_A}{x_B} + P_B \cdot \frac{x_B}{x_B}$$

$$P_t =$$

2:3

ask & believe & recieve

در 30 درجات برده

در 1°, 2° بدفع تر كز عالي
من الحمة و بدفع حرارة عالية
30° < 1° < 2°

1

Dehydration of alcohols

از الالان

alcohols → 1°, 2°, 3°

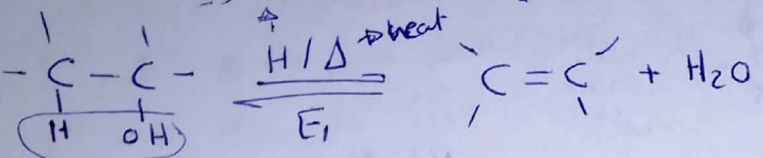
حسب الكربنة المرتبطة مع OH

مرتبطة مع كم مجموعة R

* remove H₂O from alcohol

to become alkene

(H₂SO₄, H₃PO₄) حمض قوي



3° > 2° > 1° > CH₃OH

Dehydration reaction

Why we use H₂SO₄, H₃PO₄ instead of HBr, HCl — ?

because when it dissociate it give (HSO₄⁻, H₂PO₄⁻)

weak nucleophiles

↓
minimize substitution

but HCl, HBr → Cl⁻, Br⁻

will convert alcohol to alkyl halides.

تقابل بازجاسيت و سانه
از يد كيم المواتج بدفعه للميت
من خلال ازالة الاكسجين

by distillation

because it has lower b.p

* after distillation

but the product in ice
to minimize loss of highly
volatile product by
evaporation.

2

→ separatory funnel

↓
بعد
بإضافة NaOH
→ to remove acid
to prevent alkene
to back to alcohol

E₁ → 2°, 3° (E₁)

E₂ → 1°

بإضافة H⁺ بعد ذلك بترى H₂O بعد ذلك
بترى H⁺ E₁

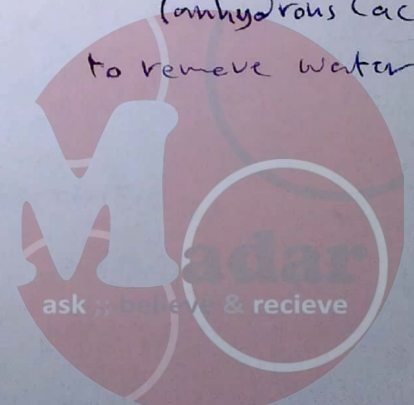
→ after extraction : put drying agent
(anhydrous CaCl₂)
to remove water

المواد
المتبقلة → distillation → extraction

percent yield = $\frac{\text{mass actual}}{\text{mass theoretical}} \times 100\%$

actual → V, m

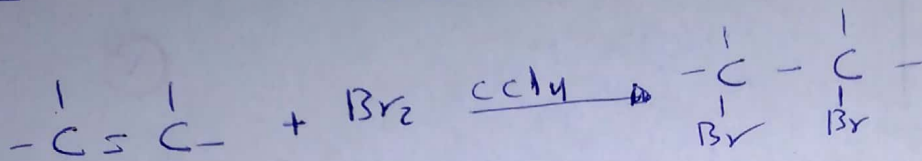
theoretical → حسب التقابل



Test of unsaturation = 1, 2

[1] Bromine $\rightarrow$ alkene ✓
alkene X

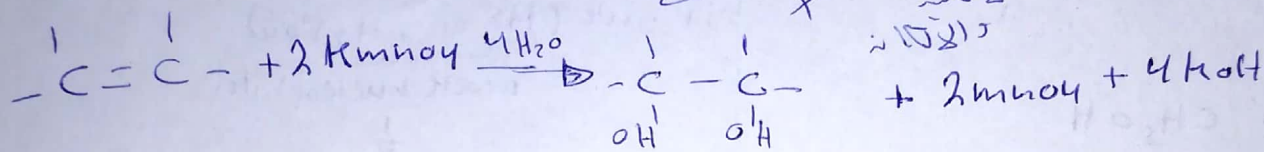
التركيب
الالكين والالكين



[2] potassium permanganate (KMnO₄)

alkene ✓
alkene X

التركيب
الالكين
والالكين



major $\rightarrow$ مركب
مركب

التركيب $\rightarrow$ no $\rightarrow$ H₂SO₄ H₃PO₄ لا يكون



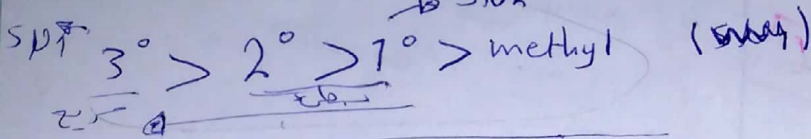
Electrophilic Substitution

Exp 8

reaction of alcohols with halides.

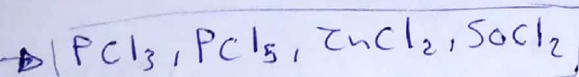


SN2



2°, 1° → we use catalyze

3° → we use HX



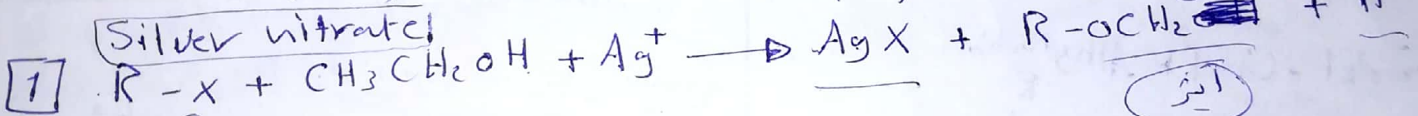
OH → Cl



in preparation of alkyl halide



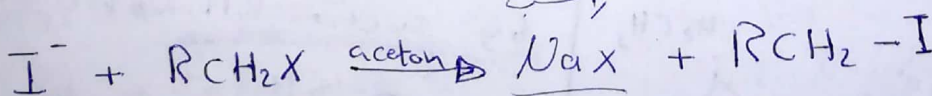
تفاعلات هاليدات الألكيل (R-X)



SN1 3° > 2° > 1°

SN1 → يحدث في خطوتين
① carbocation (slow)
② AgX

2 Sodium Iodide

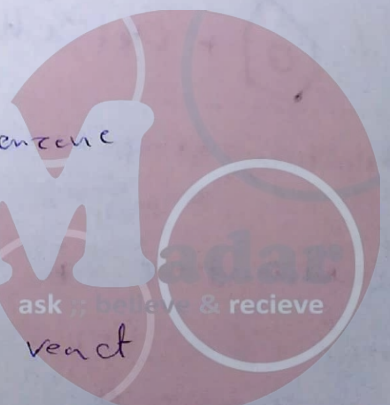


SN2 1° > 2° > 3°

in mechanism

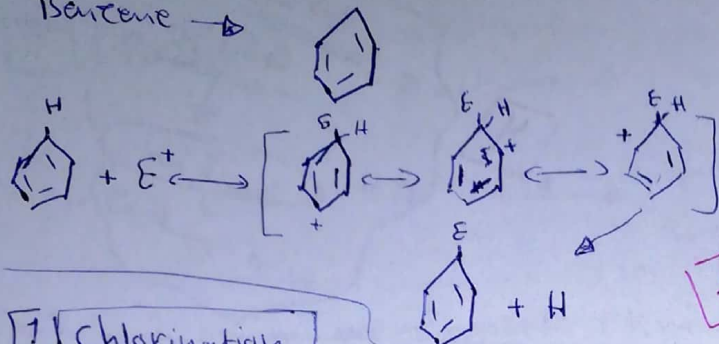
Low reactivity of chlorobenzene towards silver nitrate?

because phenyl halide don't react by SN1 or SN2

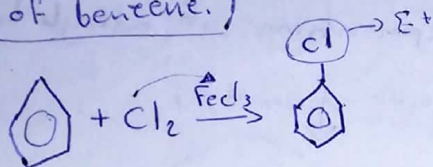


Exp 9 Electrophilic Substitution

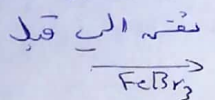
Benzene →



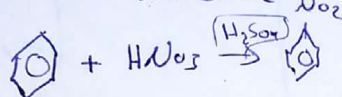
1 Chlorination of benzene.



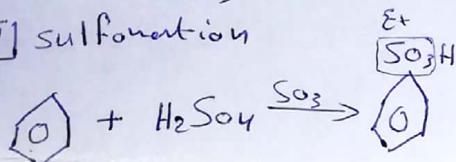
2 Bromination of benzene



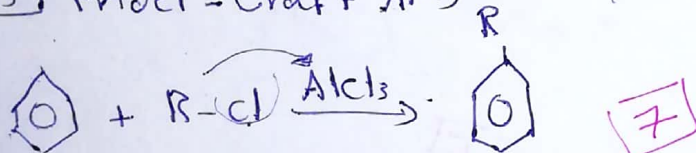
3 Nitration of benzene



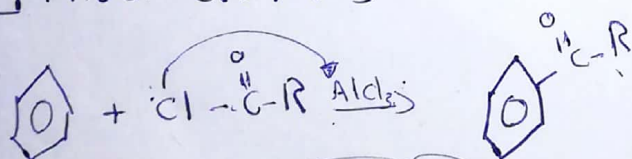
4 sulfonation



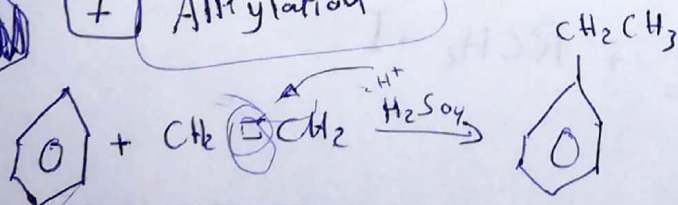
5 Friedel-Craft Alkylation



6 Friedel-Craft Acylation



7 Alkylation



Activating group →

إذا كانت الذرة المتصلة C, H, ...

deactivating group →

إذا لم تكن الذرة المتصلة C, H, ...
إذا كانت الذرة الأخرى (+)

بالرجوع

→

* activating group

+ (Cl, Br, I)

ortho, para

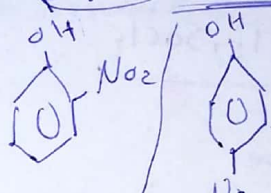
* deactivating group

+ (Fe, Cl, Br, I)

meta

Notes :

separation of ortho and para nitro phenol



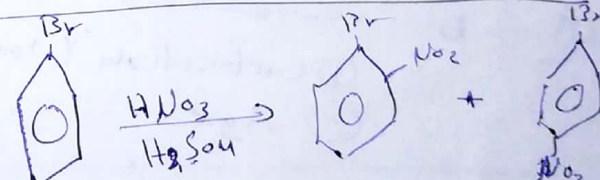
by Steam distillation

التي يتم فصلها بالترسيب البخاري

para has very low P^v / B.p ↑
because of H-bonding

* When we increase T →

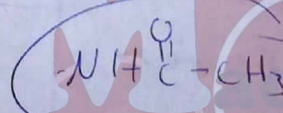
- Di and Tri nitration might
- oxidation of phenols by nitric acid



separation of ortho and para by suction filter → recrystallization

O > P solubility

acetanilide



ask, share & recieve

10 Alcohols and Phenols

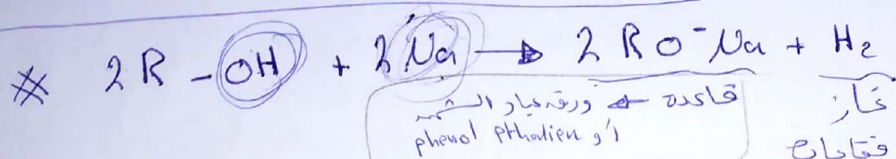


this exp. to study the physical and chemical properties.

Solubility in water

alcohol is soluble in water.

1. No. of (OH) ↑ solubility ↑
2. Mw ↑ solubility ↓
3. Branching ↑ solubility ↑

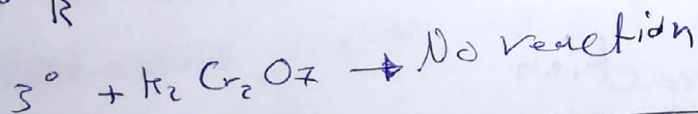
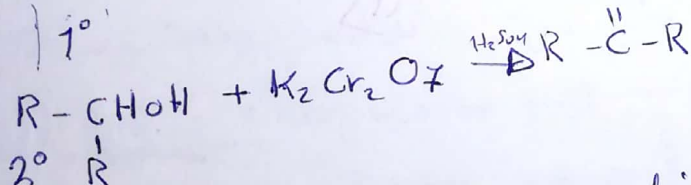
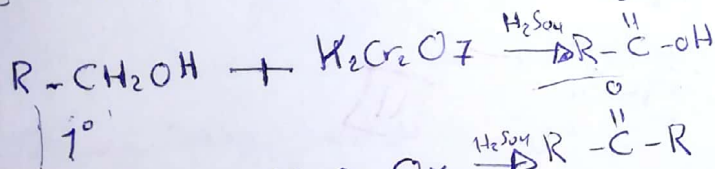


Methyl alcohol > 1° > 2° > 3°

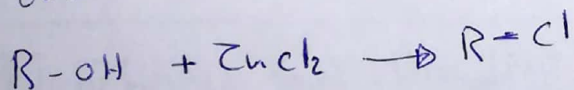
acidity
Reaction with Na

Chromic acid oxidation of alcohols

(K₂Cr₂O₇) → carboxylic acid



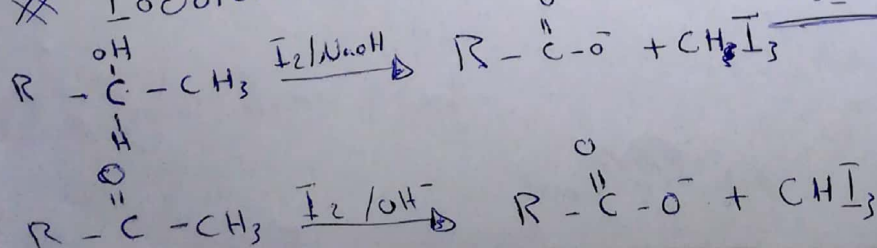
Lucas test



الترتيب
1°, 2°, 3°
حسب سرعة التفاعل

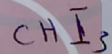
3° > 2° > 1° > methyl

Iodoform test (I₂)



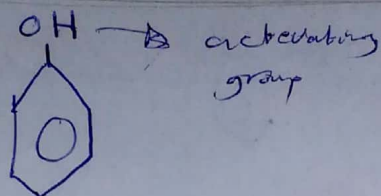
بمحتوى انا اوكسى في الميثيل
الجزئية للكحول والكيون
يوحنا قادري

give yellow precipitate.



اذا ما في ملاحظة
No reaction

phenols



* aromatic

* SN1, SN2 or else

E_1 , E_2 ~

* it react $\rightarrow$ Electrophilic Substitution

* insoluble in water

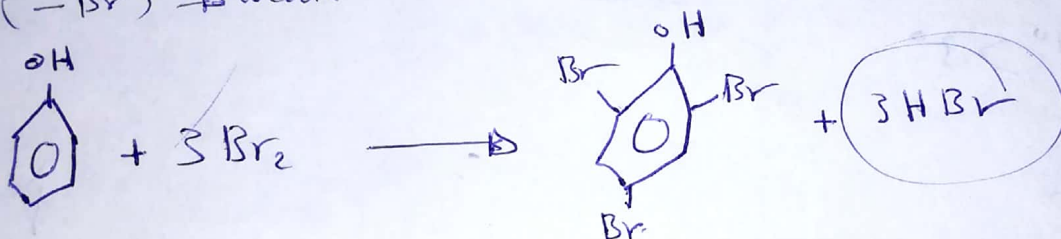
ethanol $\rightarrow$ more acidity than water

10

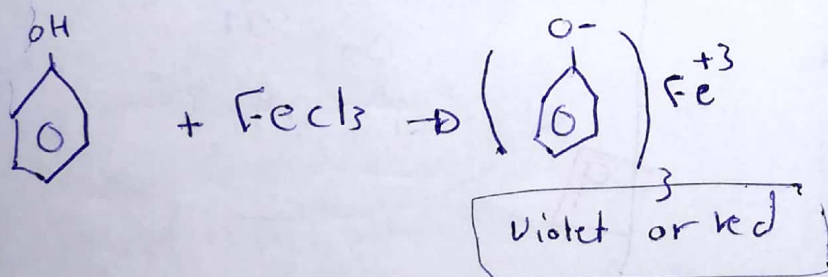
[1] Bromination of phenols

(-OH) $\rightarrow$ strong

(-Br) $\rightarrow$ weak

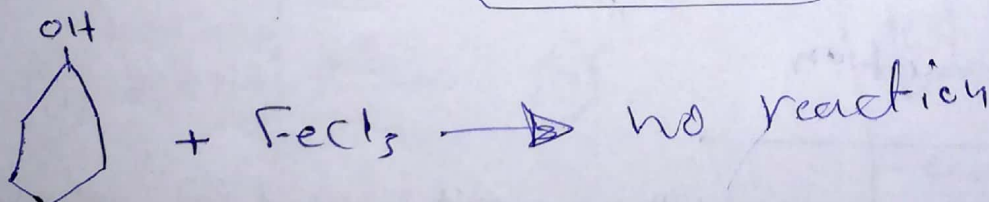


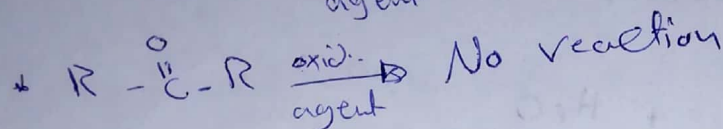
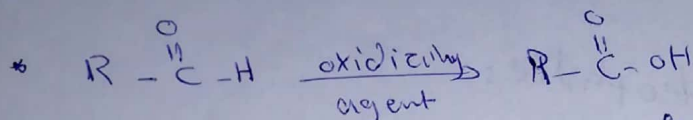
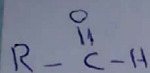
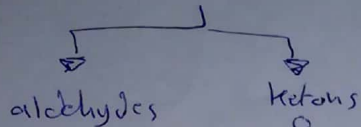
[2] Ferric chloric test



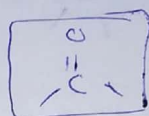
← الفينول
القيتول
كبريتي
مركب آح

11

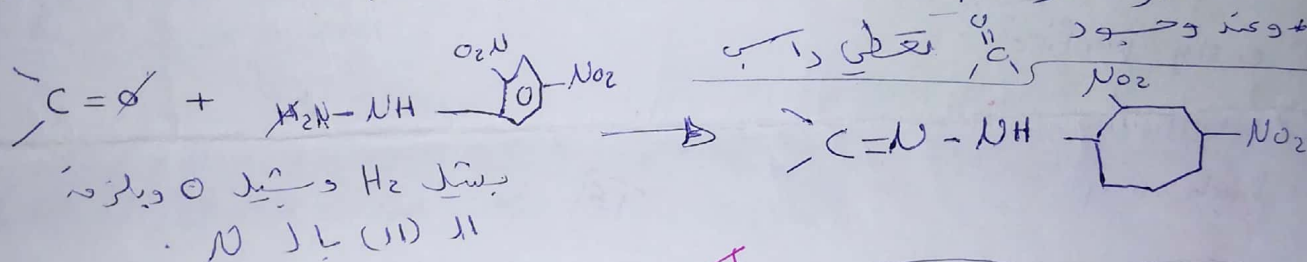




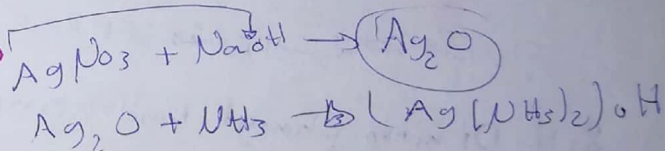
~~XX~~ Test for carbonyl group



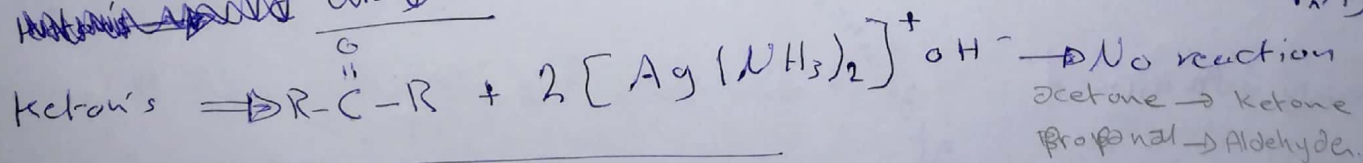
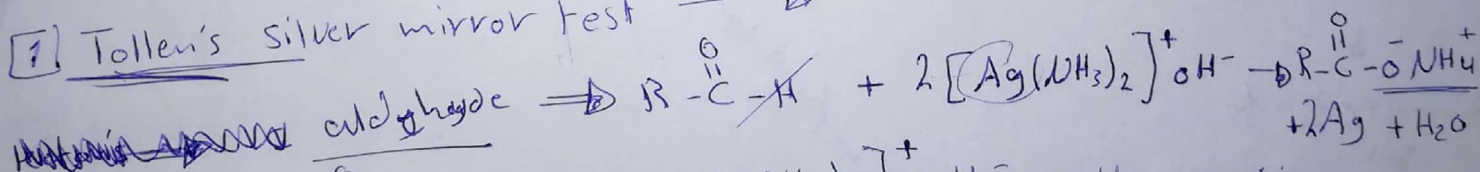
we can test for (carbonyl) $\rightarrow$ 2,4-di nitro phenyl hydrazine



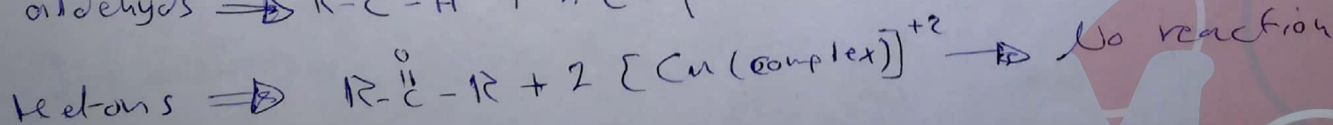
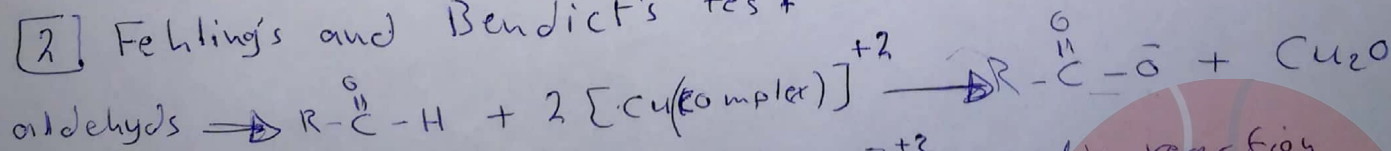
للتيز بيت الالهائيد والكيسون



[1] Tollen's silver mirror test



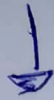
[2] Fehling's and Benedict's test



3] Iodo form test.

$$2[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$$

⇒ صونة يكونه عارفة اذا
الدعايد او كيتونه بست
شعارة حواسه

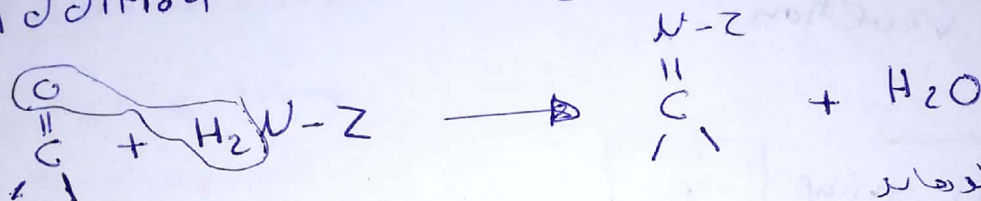


مروج بجره احدى الشفقات
وبطلوه من الجدول

14

⇒ لتخفيف الشفقات

Addition of nitrogen Nucleophiles



سواد الدعايد
او كيتونه

⇒ ليس بجره الشفقات ؟

- (1) easily purified
- (2) Crystalline Solids
- (3) high m.p

15

+ اكر مشقة بحدسه ؟

2,4-Di nitro phenyl hydrazine



لا تجميع شفقات
Solid

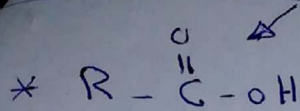
m.p easily determined

2,4 di nitro phenyl hydrazine



12

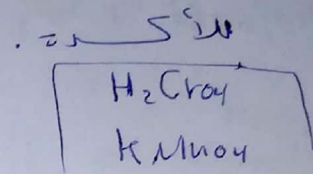
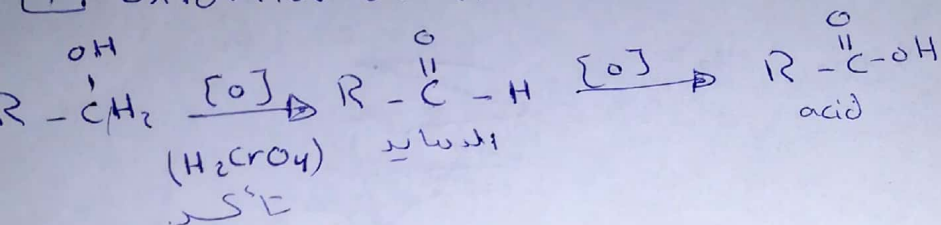
preparation of carboxylic acids



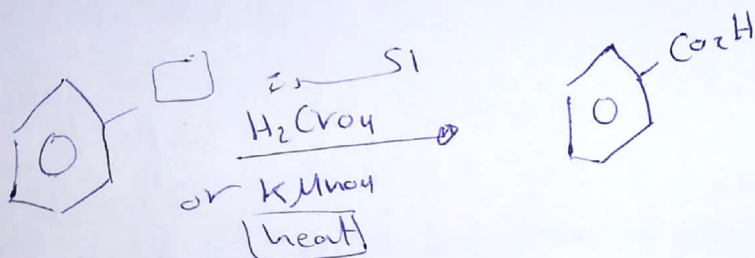
Way to prepare Acids :

16

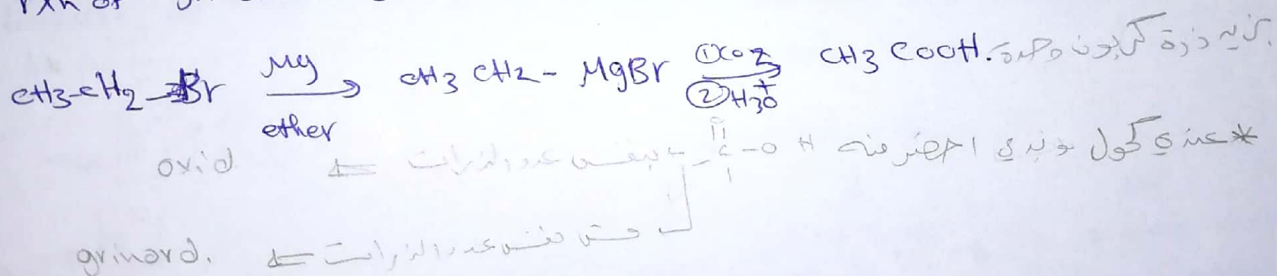
[1] oxidation of (1°) alcohol



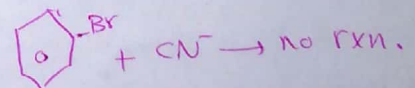
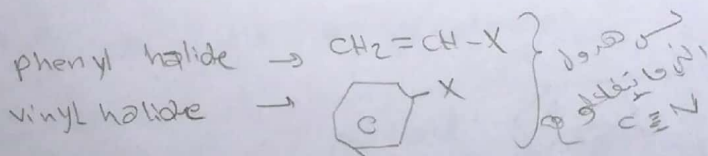
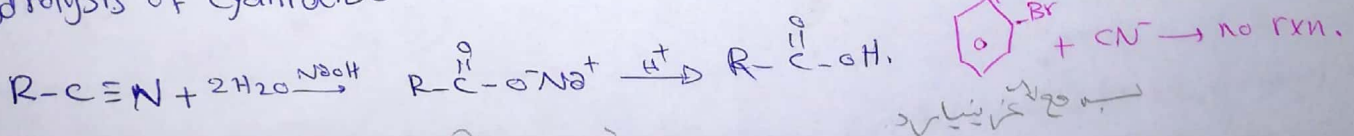
[2] oxidation of aromatic side chain.



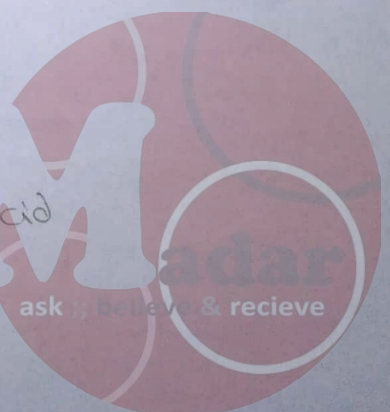
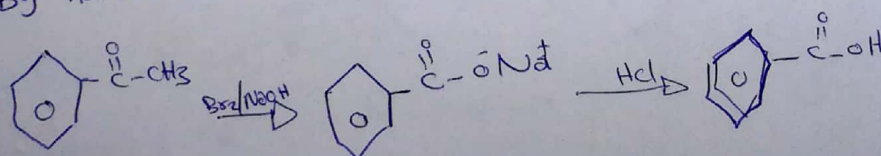
[3] rxn of grignard reagent with carbon dioxide



[4] Hydrolysis of cyanides $C \equiv N$



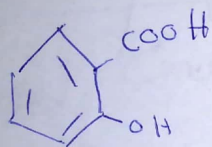
[5] by haloform $[I_2 \text{ or } Br_2]$.



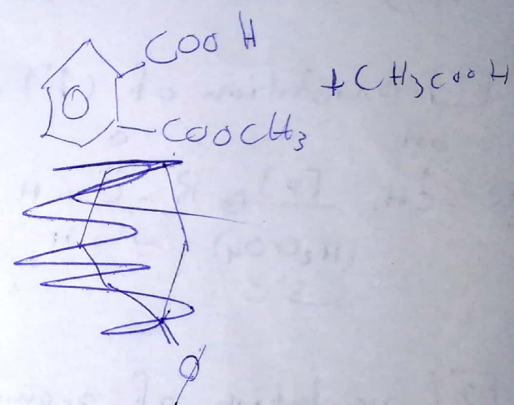
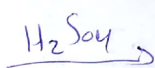
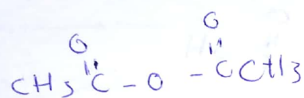
Aspirin



reagent $\rightarrow$ H_2SO_4



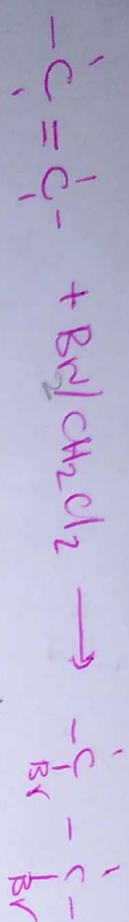
+



Tests

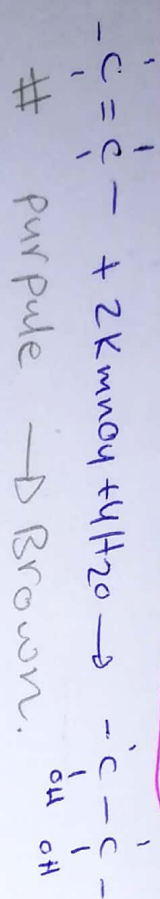
For Alkene & other [ALKANE]

Bromine



red-Brown $\rightarrow$ colorless.

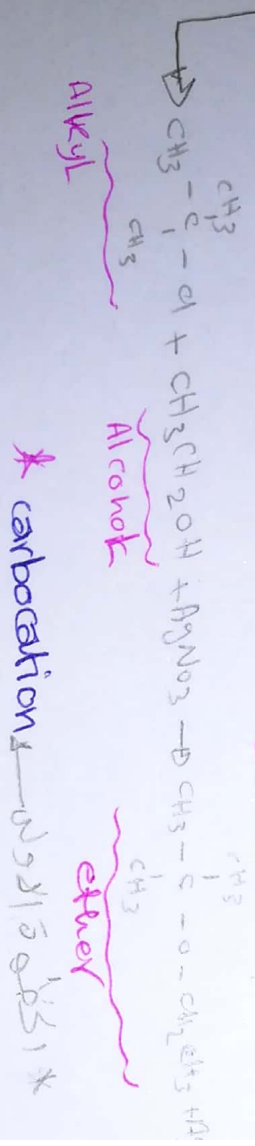
potassium permanganate KMnO_4



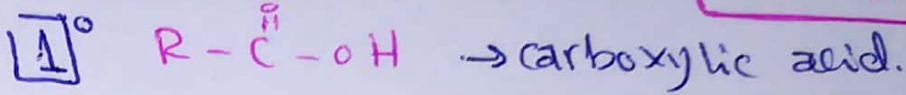
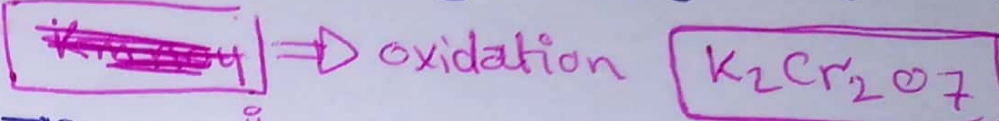
Reactivity for Alcohol $\rightarrow$ Alkyl $\rightarrow$ primary, secondary, tertiary

[I] silver nitrate $[\text{SN}_1]$. $3^\circ > 2^\circ > 1^\circ$

[2] sodium iodine $[\text{SN}_2]$ $1^\circ > 2^\circ > 3^\circ$



* لتأمين بين الكحول الاول والثاني والثالث

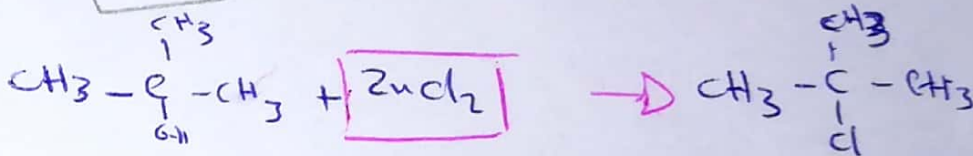


orange → green.



Lucas test for Alcohol. $3^\circ > 2^\circ > 1^\circ$

S_N1

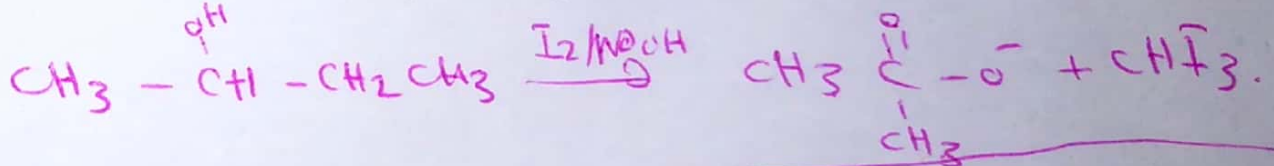


Iodoform test

$I_2/NaOH$ بوسط قلوي

* تلتق عن مجموعة Methyl طرفية

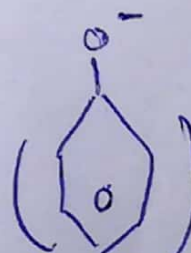
No rxn. ← اذا كانت Methyl طرفية



⇒ ALcohol or Ketone [terminal methyl]

Ferric chloric test

for Phenol



Violet or red

No rxn. او قلة تأمين بين فينول وكون

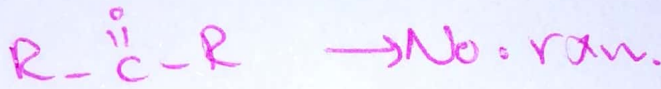
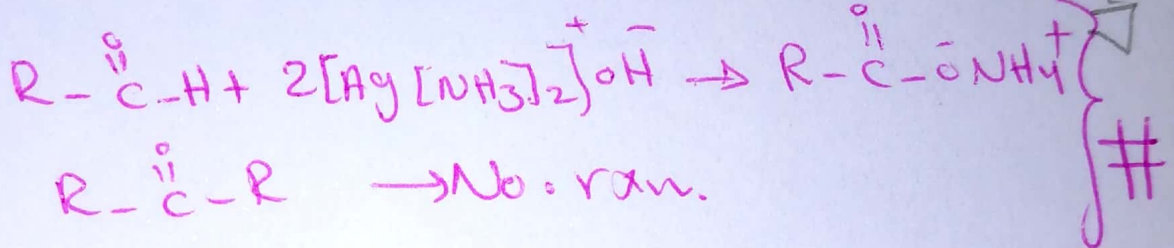
ask & recieve

* 2,4-dinitrophenyl hydrazine → اذائنج راسب
 carbonyl group وجود (C=O)
 $\text{C}=\text{O}$ و $\text{H}_2\text{N}-\text{N}=\text{N}-\text{Ar}$

Tollen's silver mirror test

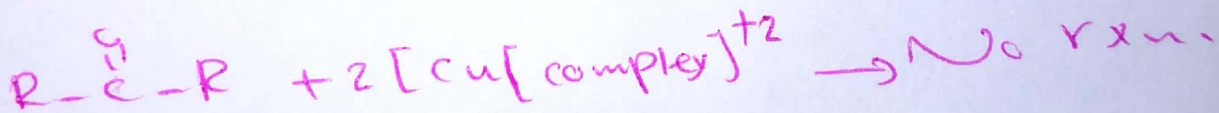
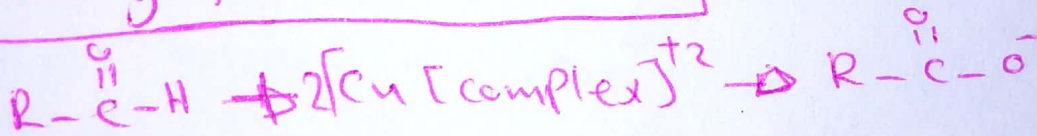
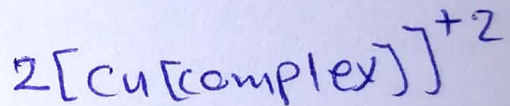


Tollen's test #



تفريق بين كيتون و الد هيد

Fehling & Benedict's test



Red

علاج السكر

⇒ Tollen's & Fehling → mild oxidation agent.

* Iodo Form test → Ketone → Yellow ppt (acetone)

Aldehyd → No rxn.

