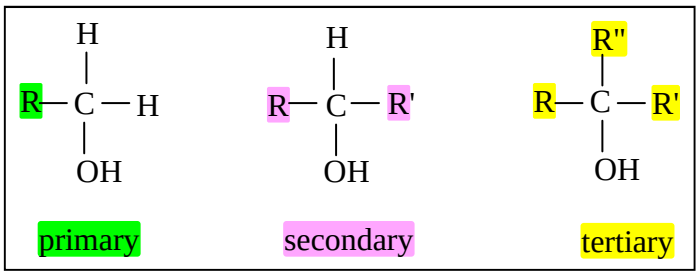
ALCOHOLS AND PHENOLS

Classification and Tests

I. ALCOHOLS

Alcohols are classified as primary, secondary and tertiary according to the number of alkyl groups directly attached to the carbinol carbon.



1) OH bond عند مفاعلة الكحول مع القواعد أو في تفاعلات الأسترة

تفاعل الكحول يتضمن كسر أحد هذه الروابط

2) C-OH bond : في تفاعلات إزالة الماء وتفاعلات الاستبدال

Reactions of alcohols involve the breaking of either of two bonds: the O-H bond as in reactions with bases and esterification reactions, or the C-OH bond leading to dehydration and substitution reactions. In breaking the C-OH bond, protonation of the -OH group is essential to convert it from a poor leaving group to a better one.

Some physical and chemical properties of alcohols are examined in the following tests.

EXPERIMENTAL

MATERIALS NEEDED	Glassware: 4 Test tubes. Chemicals: 1 mL each of: ethanol,1-butanol, 2-butanol, 2-methyl-2-propanol, ethylene glycol,, sodium metal, phenolphthalein indicator, 15 mL potassium dichromate (1%), 0.5 mL sulfuric acid, 6.0 mL Lucas reagent, 15 mL iodoform reagent, 6 mL NaOH (10%),

1. Solubility in Water

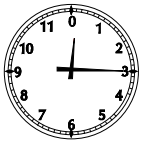
Alcohols of low molecular weight are water soluble due to their ability to form hydrogen bonds with water. Solubility in water decreases with

الكحول الي كتلته المولية قليلة يذوب في الماء لانه قادر يعمل روابط هيدروجينية فى الماء

كلما زادت الكتلة المولية قلت ذائبية الكحول في الماء (علاقة عكسية)

وكلما زادت التفرعات وعدد "OH" مجموعات الهيدروكسيل زادت ذائبية الكحول في الماء (علاقة طردية)

increasing molar mass but increases with branching and with the number of hydroxyl (OH) groups.



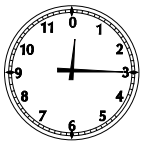
Procedure. To each of four test tubes, add 10 drops of one of the following alcohols: ethanol, 1-butanol, 2-methyl-2-propanol and ethylene glycol. Add 2 mL of water to each test tube and observe the results.

2. Acid Properties of Alcohols Na منتجة غاز الهيدروجين H2

Alcohols react with metallic sodium with the evolution of hydrogen. The relative acidities of alcohols and consequently their relative rates of reaction with sodium are in the order: primary > secondary > tertiary.

الترتيب حسب الحامضية وشدة التفاعل مع الصوديوم

$$2R{-}OH + 2Na \longrightarrow 2RO^{-}Na^{+} + H_2$$



Procedure. To each of three test tubes containing a small piece of sodium, add 2 mL of dry 1-butanol, 2-butanol or 2-methyl-2-propanol. Compare the rates of evolution of hydrogen gas and record your results. After all the sodium has reacted in the test tube containing the 1-butanol, add 3 drops of phenolphthalein indicator solution and observe the color change.

للكشف عن اللون

3. Chromic Acid Oxidation of Alcohols

الكحول الثالثي **tertiary** لا يتفاعل تحت نفس ظروف الأولى والثانوي

Primary and secondary alcohols are oxidized by chromic acid to the corresponding carboxylic acids (Primary) and ketones (Secondary) respectively (على الترتيب). Tertiary alcohols are generally unreactive under similar conditions. When alcohols are oxidized they reduce chromium (VI) to Cr (III) changing the color of the solution from orange to green. Oxidation therefore offers a method for distinguishing primary and secondary alcohols

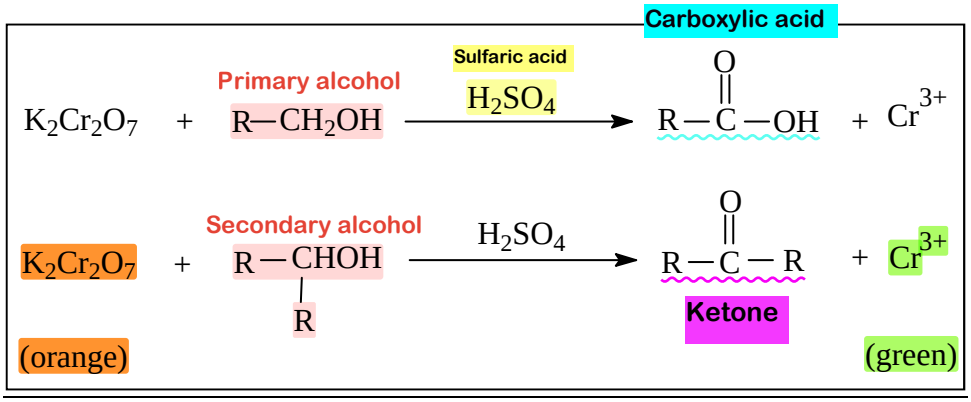
عندما يتم أكسدة الكحول يقوم الكحول باختزال الكروم **Cr+6 to Cr+3** وينغير اللون من البرتقالي إلى الأخضر

بالتالي هذه الطريقة تميز الكحول الأولى والثانوي معاً عن الكحول

Mechanism of reaction غير مطلوب

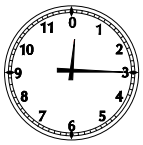
Tertiary مع ال Chromic acid
No reaction (Negative)
يبقى orange

from tertiary alcohols.



Primary & secondary
Give a Positive result

K2Cr2O7



Procedure. Place 5 mL of 1% potassium dichromate solution and 2 drops of concentrated sulfuric acid in each of three test tubes. Mix thoroughly and add 2 drops of one of the following alcohols: 1-butanol, 2-butanol, or 2-methyl-2-propanol. Shake the tubes and observe any change in color.

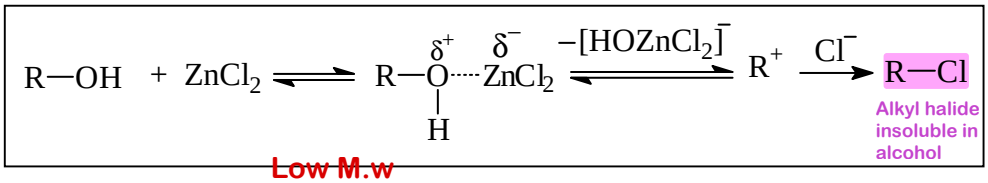
مفاعلة الكحول مع كلوريد الزنك الموجود في محلول مخفف من HCL

تترتب الكحول من حيث سرعة التفاعل
3 > 2 > 1 (SN1)

4. The Lucas Test

A solution of zinc chloride in concentrated hydrochloric acid (Lucas reagent) can be used to distinguish between primary, secondary and tertiary alcohols. With this reagent the order of reactivity is typical of compounds reacting by the S_N1 mechanism. The zinc chloride (a Lewis acid) assists in breaking the C-OH bond as illustrated in the equation below:

للتمييز بين الكحول الأولي والثانوي والثالثي



Alcohols (of no more than six carbons) are soluble in the Lucas reagent while the corresponding alkyl chlorides are not. Tertiary alcohols react rapidly with the reagent forming an insoluble alkyl chloride layer almost

الكحول الثالثي يتفاعل بشكل سريع جداً مشكلاً طبقة غير ذائية من هاليد الألكيل
Very fast formation of 2 laye

الثانوي أبطئ يحتاج وقت اكثر
ليكون طبقتين منفصلات ١٠-٥ دقائق

immediately. Secondary alcohols react within 5-10 minutes, while primary alcohols require several hours to react at room temperature (S_N2 mechanism).

الكحول الأولي هو الابطئ ويحتاج لعدة ساعات

Procedure. Place 2 mL of Lucas' reagent in each of three test tubes and add 6 drops of the alcohol to be tested. Close the tubes with a cork, shake and allow them to stand. Record the time required for the tubes to acquire a cloudy appearance. Carry out the test on 1-butanol, 2-butanol, and 2-methyl-2-propanol.

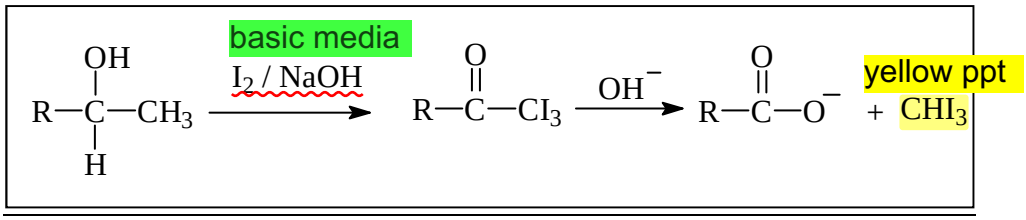
Water path نحتاج للأولى والثانوي

يستخدم للكشف عن terminal methyh (الطرفية)

5. The Iodoform Test

This is a test for methyl carbinols having the structure CH_3CHOH- (carbinol) and methyl ketones (CH_3CO-) (ketone). Methyl carbinols are first oxidized by the reagent to methyl ketones which become iodinated and then cleaved by base to give a bright yellow precipitate of iodoform.

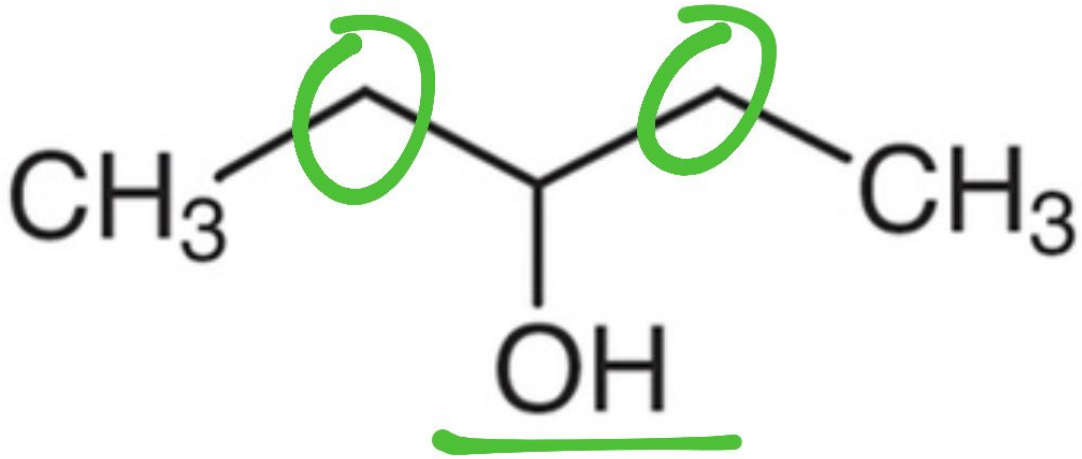
الكربونة الي عليها ال OH لو كان عليها CH3 بعطيني positive راسب اصفروغير ذلك الناتج Negative



Procedure. To each of three test tubes add 2 mL of 10% NaOH solution. Add 5 drops of one of the following alcohols: 1-butanol, 2-butanol or 2-methyl-2-propanol. To each test tube add, dropwise with shaking, 5 mL of iodine-KI solution. Observe any changes and record your results.

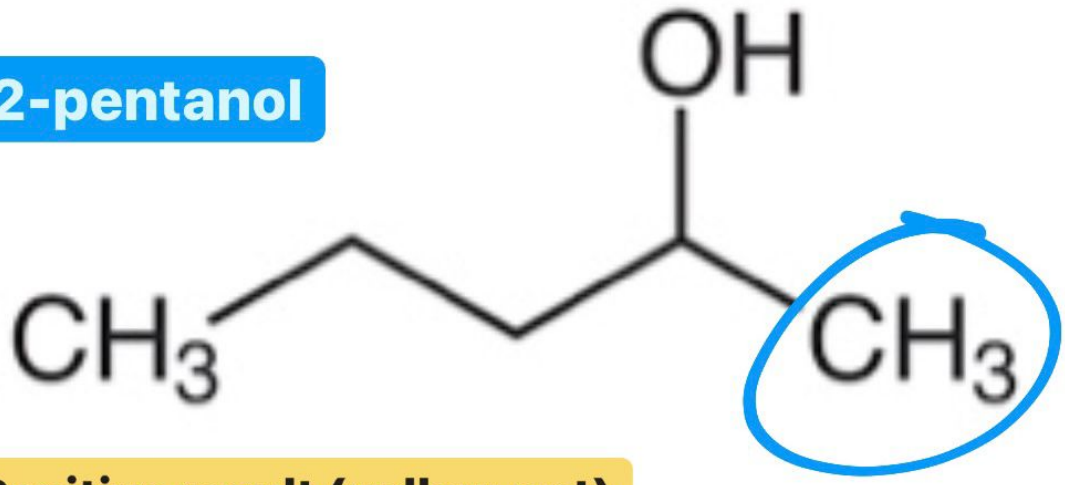
II. PHENOLS

3-pentanol



Negative result (No yellow ppt) ❌

2-pentanol



Positive result (yellow ppt)

يمتلك حلقة بنزين

Aromatic alcohol

The most common reactions of phenols involve breaking the O-H bond and the usual electrophilic aromatic substitution at the aromatic ring. Protonation of the hydroxyl group and loss of a water molecule as in alcohols would give a phenyl cation which is very unstable and difficult to form. Since the aromatic nucleus is electron rich, direct attack by nucleophiles as in $S_N1$or S_N2 reactions is not possible. Consequently, phenols do not undergo substitution of the hydroxyl group either by the S_N1 or S_N2 mechanisms.

الفينول مثل أي مركب اروماتي لا يقوم بتفاعل SN1 /SN2

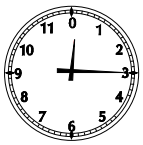
The characteristic property that differentiates phenols from alcohols is acidity. Phenols are stronger acids than alcohols and react with sodium hydroxide, whereas alcohols do not. The reason for this difference is that the phenoxide ion is resonance-stabilized whereas the alkoxide ion is not.

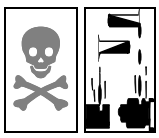
الفينول يتفاعل مع NaoH بينما الكحول لايتفاعل بسبب ال resonance في الفينول وهذا التفاعل يميزهم عن بعض

EXPERIMENTAL

MATERIALS NEEDED	Glassware: 4 Test tubes. Chemicals: cyclohexanol, phenol, *p*-cresol, 4 mL bromine water solution, 0.5 mL ferric chloride solution (1%), 6 mL of 10% NaOH solution .

1. Acidity of Phenols



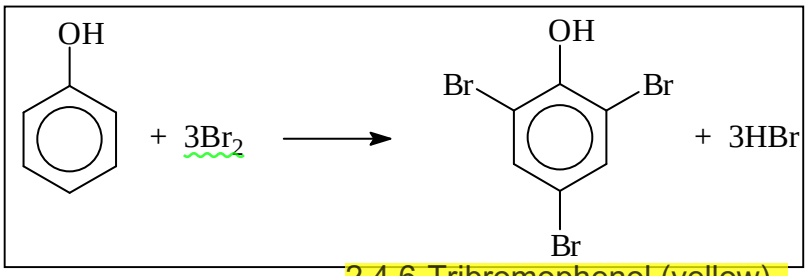


Procedure In each of three test tubes add 0.4 mL or 0.2 g of cyclohexanol, phenol, or *p*-cresol. Add 1 mL of water to each tube, shake and note whether the compound dissolves. If not add 2 mL of 10% NaOH solution and observe the result.

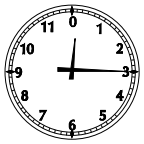
2. Bromination of Phenols with Bromine Water

The hydroxyl group strongly activates the aromatic ring towards electrophilic aromatic substitution. Phenol readily forms a tribromo

derivative when treated with a solution of bromine-water at room temperature.



2,4,6-Tribromophenol (yellow)



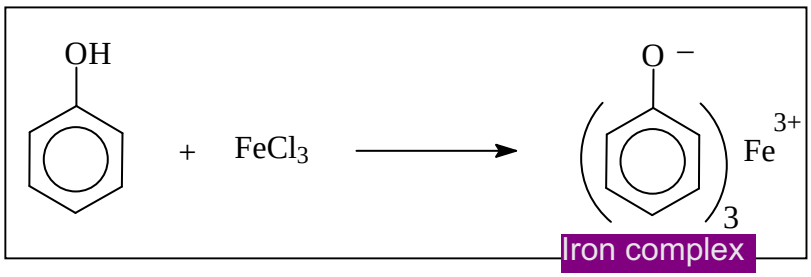
Procedure. In a test tube introduce 1 mL of water and about 0.2 g of phenol. Add enough bromine-water and shake until the yellow color persists. Observe the formation of a precipitate.

يستخدم هذا التفاعل لتمييز الفينول عن أي مركب أخر

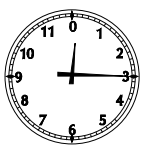
3. Ferric Chloride Test

The presence of a phenolic (or enolic group) in a compound is indicated by the formation of a violet (or red) iron complex when treated with a ferric chloride solution

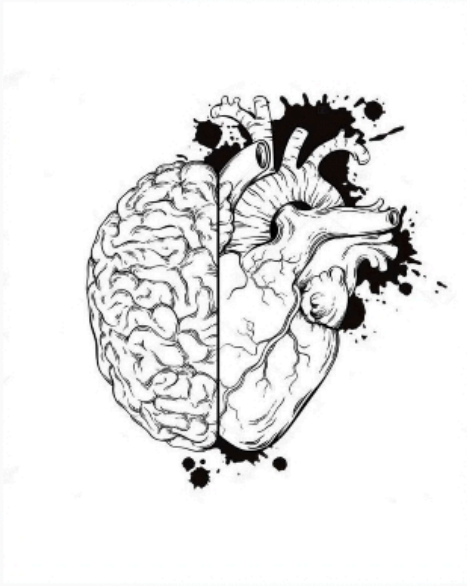
باللاب بيطلع هذا اللون فقط



Iron complex



Procedure. In a test tube dissolve a few crystals of phenol in 5 mL of water. Add 1-2 drops of 1% ferric chloride solution, shake and observe the results. Repeat with cyclohexanol.



Artery Academy