



Organic Chemistry

Dr. Eman Ahmed

AROMATICITY

العطرية



Aromaticity

• هناك أربع شروط للحكم على المركب بأنه عطري:

1. ان يكون مركب حلقي **Cyclic**.

2. جميع ذرات المركب تقع في مستوى واحد **planar**.

3. يحتوى على اوربيتالات P متبادلة ومتعاقبة **Fully Conjugated**.

4. يتبع قاعدة هوكل.

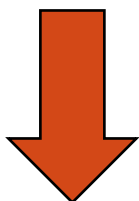
Huckel's rule :The molecule has $4n + 2\pi$ electrons

$n = 0$ or any positive integer.

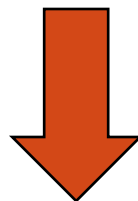
قاعدة Huckel's

$$4n + 2\pi \text{ electrons}$$

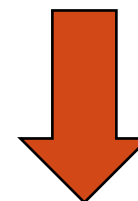
Flat , Cyclic, Completely conjugated	Flat , Cyclic, Completely conjugated	Not Flat ,Not Cyclic Not Completely conjugated
2,6,10,14,..... . π electrons	4,8,12,16,..... π electrons	



Aromatic



Anti-aromatic



Non-Aromatic

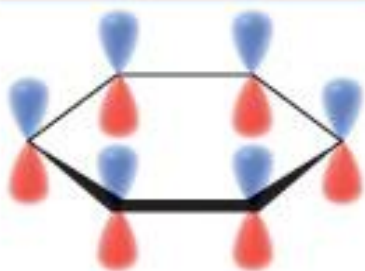
Aromaticity

هناك أربع شروط للحكم على المركب بأنه عطري:

[1] A molecule must be cyclic.

ان يكون مركب حلقى

Cyclic compound

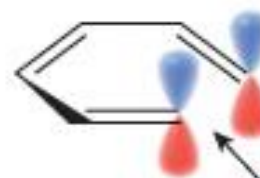


benzene

Every p orbital overlaps with two neighboring p orbitals.

aromatic

Acyclic compound



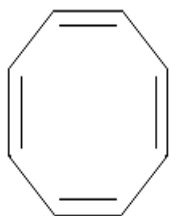
no overlap

1,3,5-hexatriene

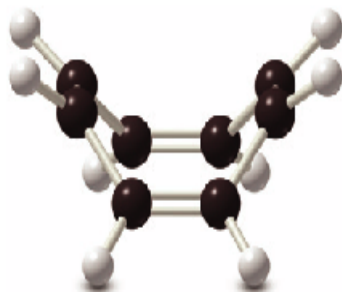
There can be no overlap between the p orbitals on the two terminal C's.

not aromatic

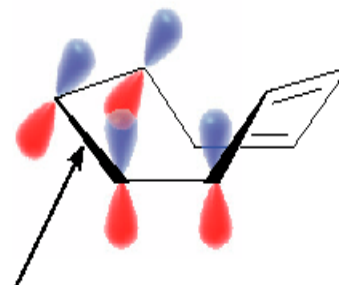
[2] A molecule must be planar. جميع ذرات المركب تقع فى مستوى واحد



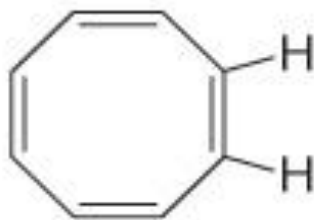
cyclooctatetraene
not aromatic



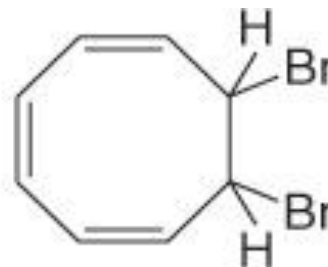
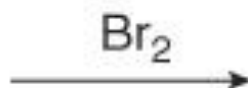
a tub-shaped,
eight-membered ring



Adjacent *p* orbitals cannot overlap.
Electrons cannot delocalize.



cyclooctatetraene

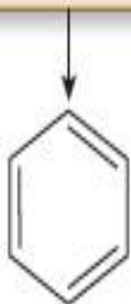


addition product

[3] A molecule must be completely conjugated.

يحتوى على اوربيتالات P متبادلة ومتعاقبة

A completely conjugated ring



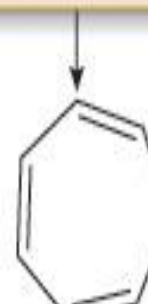
benzene
a *p* orbital on **every** C
aromatic

These rings are not completely conjugated.



no *p* orbitals

1,3-cyclohexadiene
not aromatic



no *p* orbital

1,3,5-cycloheptatriene
not aromatic

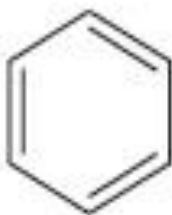
[4] A molecule must satisfy **Hückel's rule**, and contain a particular number of π electrons.

يتبع قاعدة هوكل

Hückel's rule: $4n + 2\pi$ electrons

Benzene

An aromatic compound



$$4n + 2 = 4(1) + 2 = 6 \pi \text{ electrons} \\ \text{aromatic}$$

Cyclobutadiene

An antiaromatic compound



$$4n = 4(1) = 4 \pi \text{ electrons} \\ \text{antiaromatic}$$

Huckel's قاعدة

$$4n + 2\pi \text{ electrons}$$

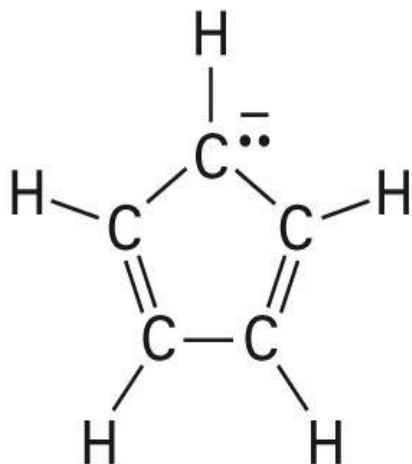
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Table 17.2

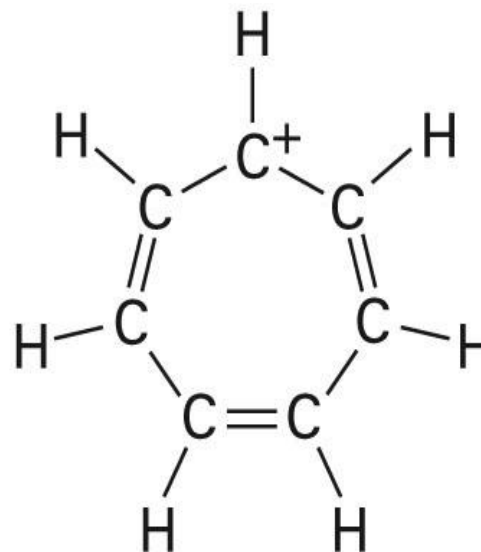
The Number of π Electrons
That Satisfy Hückel's Rule

n	$4n + 2$
0	2
1	6
2	10
3	14
4, etc.	18

Aromatic Ions



Cyclopentadienyl anion



Cycloheptatrienyl cation

Six π electrons; aromatic ions

© 2007 Thomson Higher Education

Aromaticity of the Cyclopentadienyl Anion

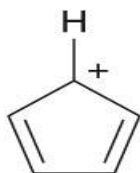


Cyclopentadiene

$-\text{H}^-$

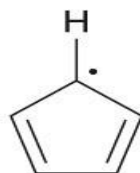
$-\text{H}^\cdot$

$-\text{H}^+$

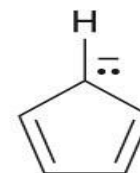


Cyclopentadienyl
cation: **four π electrons**

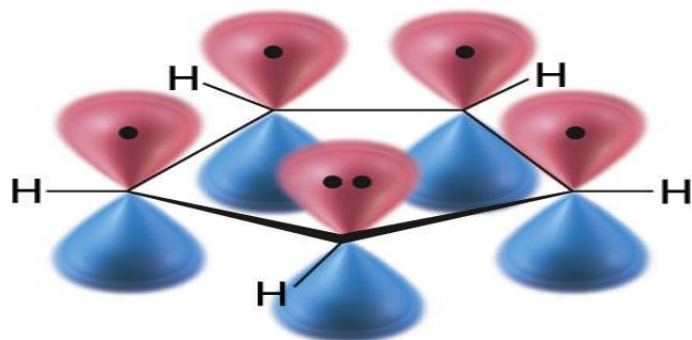
© 2007 Thomson Higher Education



Cyclopentadienyl
radical: **five π electrons**

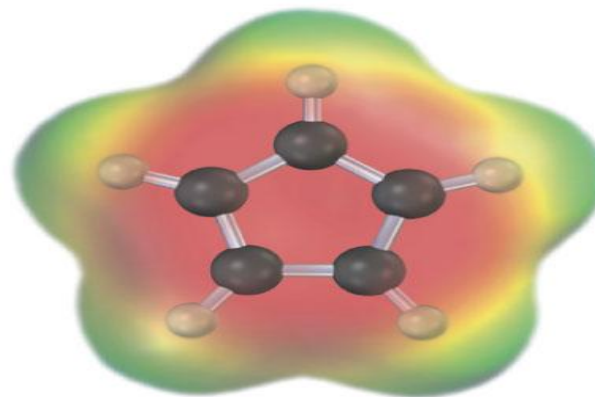


Cyclopentadienyl
anion: **six π electrons**

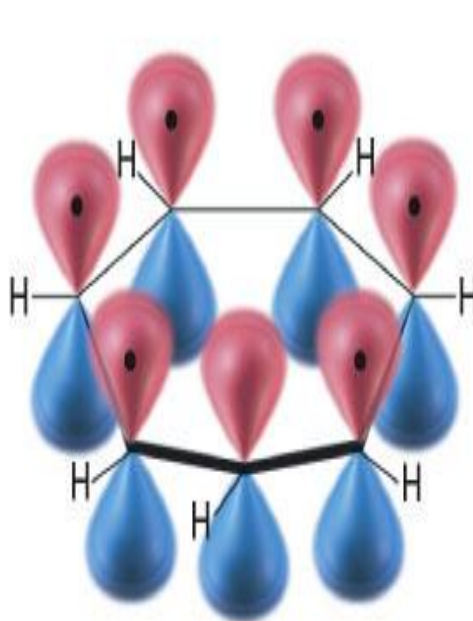
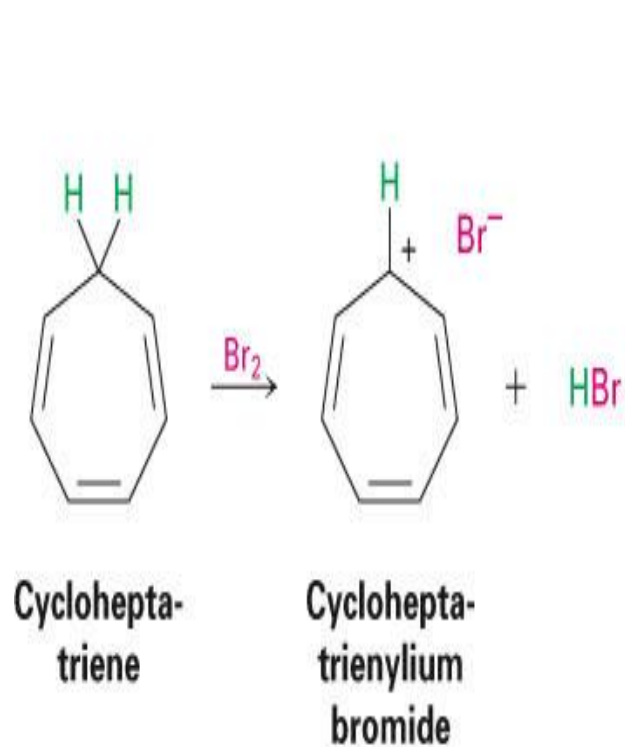


**Aromatic cyclopentadienyl anion
with six π electrons**

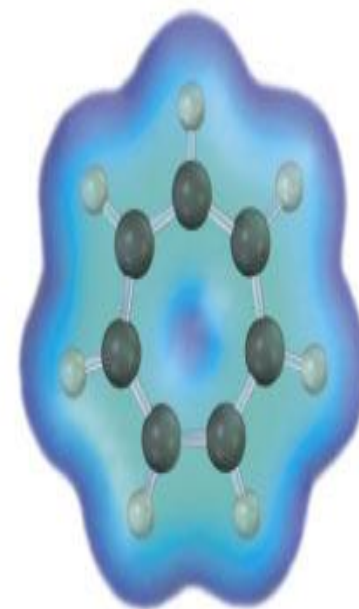
© 2007 Thomson Higher Education



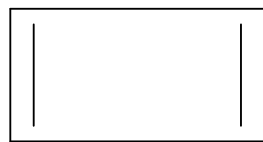
Cycloheptatriene



six π electrons

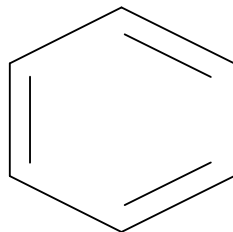


حدد عدد الألكترونات π في المركبات التالية ثم حدد أى من المركبات التالية
Aromatic, Anti-aromatic, Not aromatic



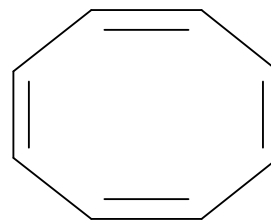
4π

Anti-aromatic



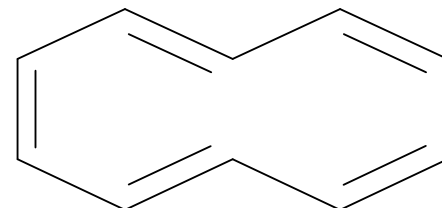
6π

Aromatic



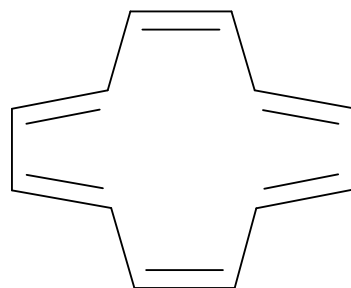
8π

Anti-aromatic



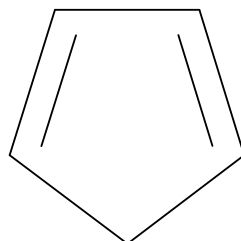
10π

Aromatic



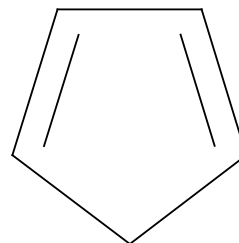
12π

Anti-aromatic



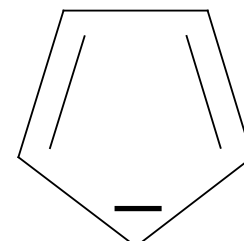
4π

Not aromatic



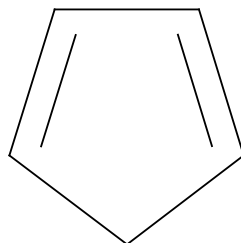
4π

Anti-aromatic



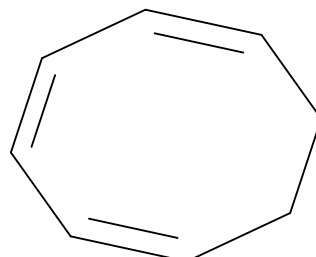
6π

Aromatic



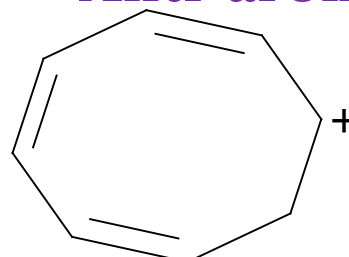
5π

Not aromatic



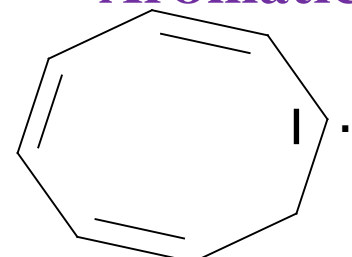
6π

Not aromatic



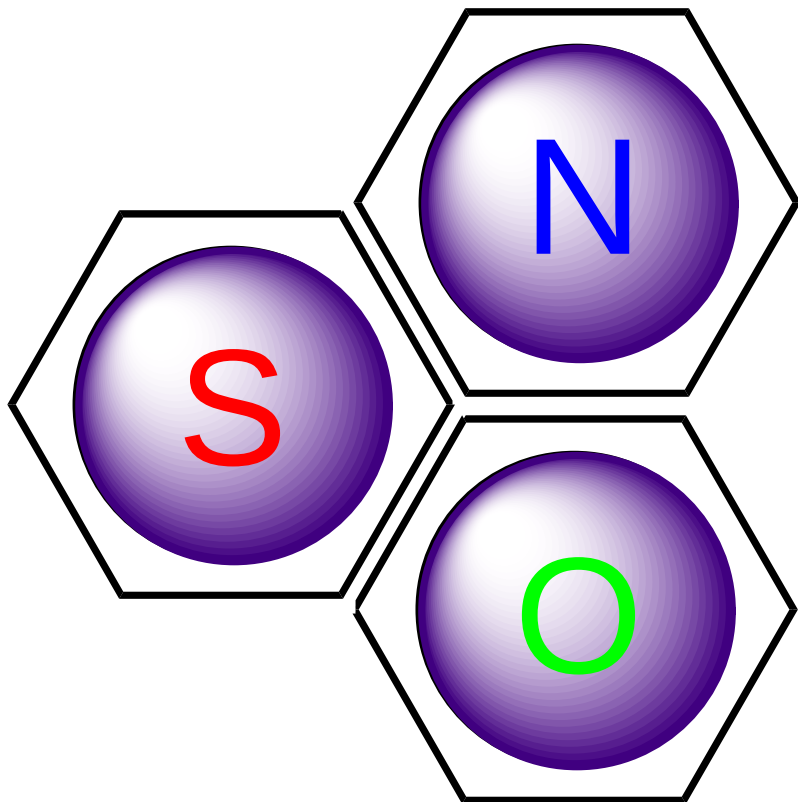
6π

Aromatic



8π

Anti-aromatic



Aromatic Heterocycles

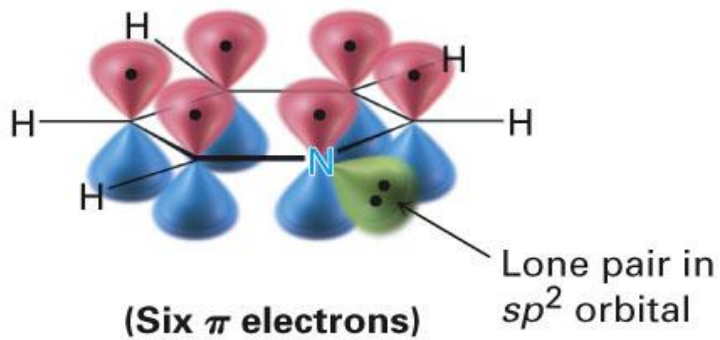
تعرف هذه المركبات على انها مركبات عضوية حلقية تحتوى على ذرات اخرى بجانب الكربون مثل الأوكسجين والنيتروجين والكبريت وقد تكون هذه المركبات عطرية أو غير عطرية.

Aromatic Heterocycles: Pyridine and Pyrrole

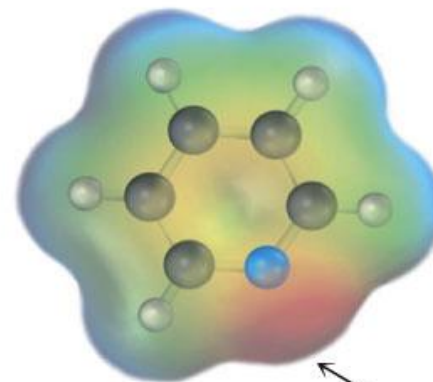
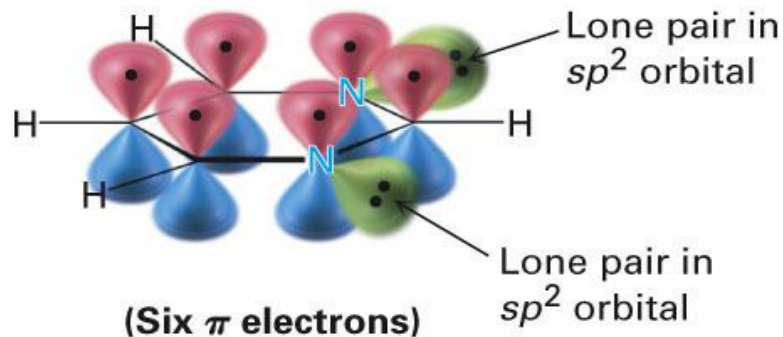
Pyridine & Pyrimidine:



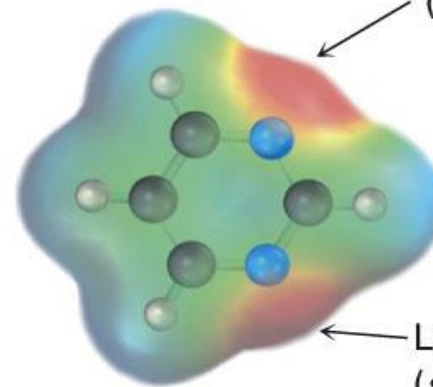
Pyridine



Pyrimidine



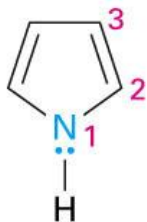
Lone pair (sp^2)



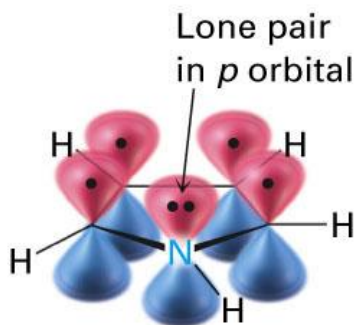
Lone pair (sp^2)

Aromatic Heterocycles: Pyridine and Pyrrole

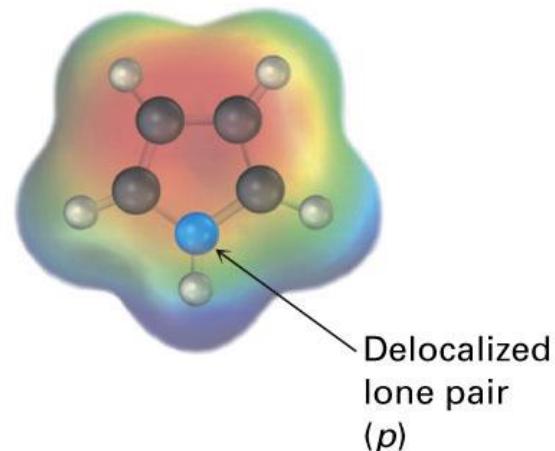
Pyrrole & Imidazole:



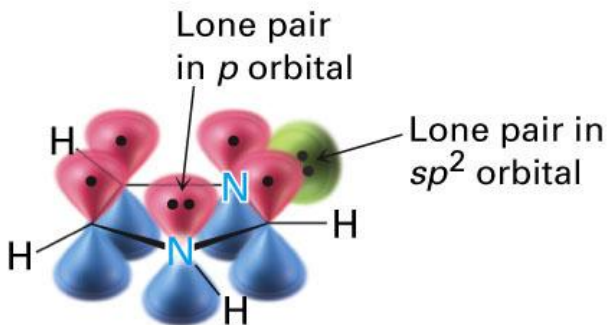
Pyrrole



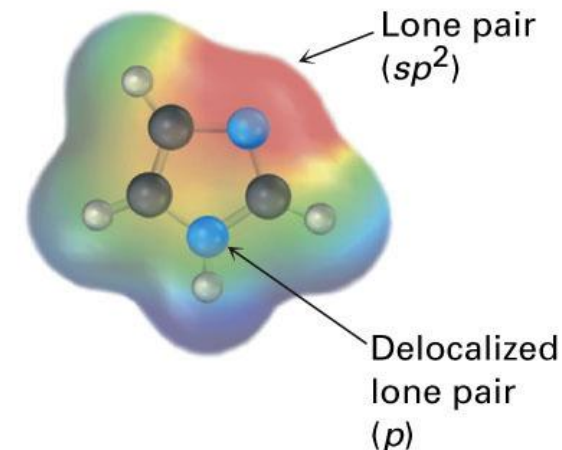
(Six π electrons)



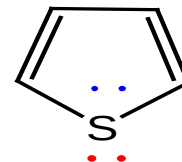
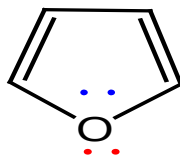
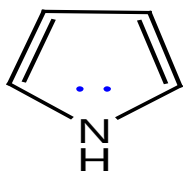
Imidazole



(Six π electrons)



Pyrrole, Furan, and Thiophene



Blue electron pair participate in the aromaticity
Red electron pair does not participate in aromaticity

Six π electrons

Six π electrons

Six π electrons

❖ ترتب هذه المركبات على حسب العطرية كما يلي:

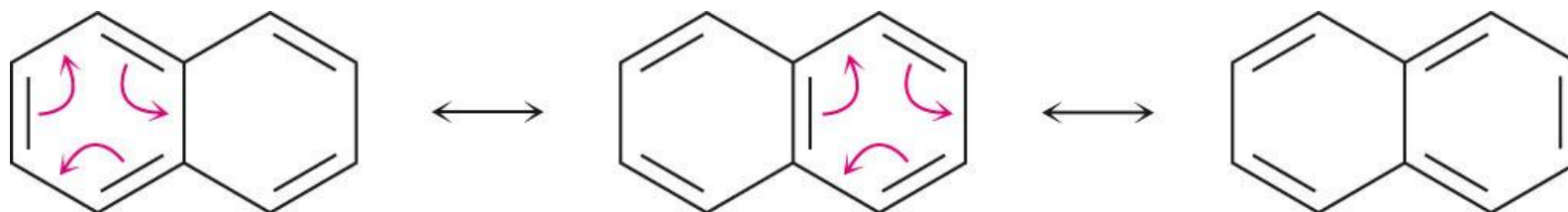
Thiophene > pyrrole > Furan

وذلك لأن سالبية:

$O > N > S$

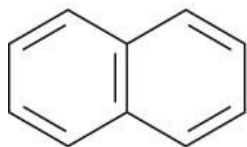
Bicyclic Aromatic Compounds

Naphthalene Orbitals



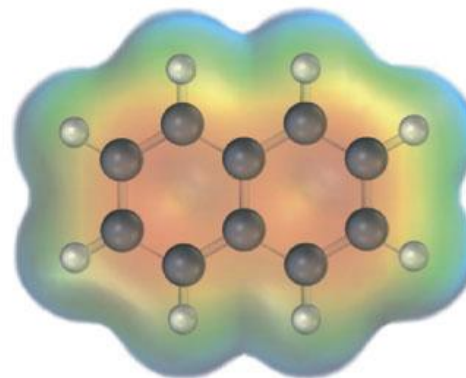
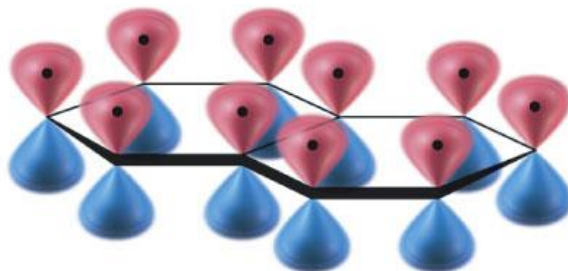
Naphthalene

© 2007 Thomson Higher Education

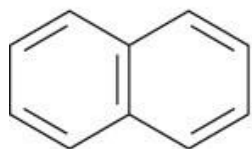


Naphthalene

© 2007 Thomson Higher Education

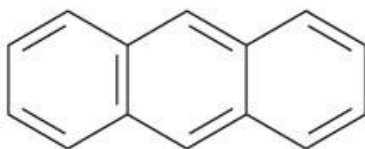


Polycyclic Aromatic Compounds

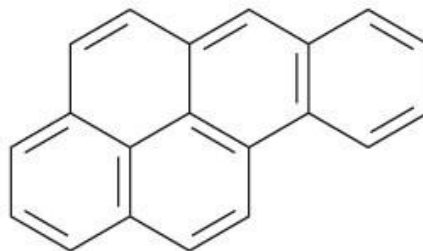


Naphthalene

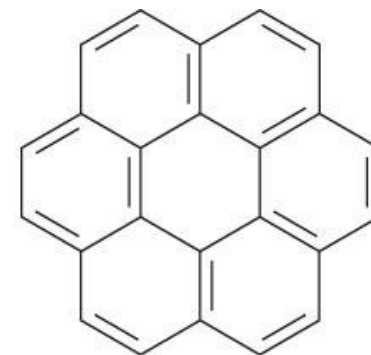
© 2007 Thomson Higher Education



Anthracene

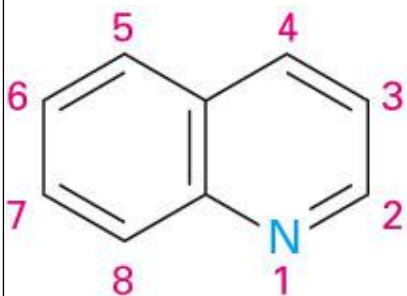


Benzo[a]pyrene

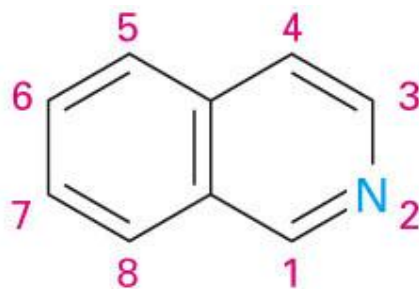


Coronene

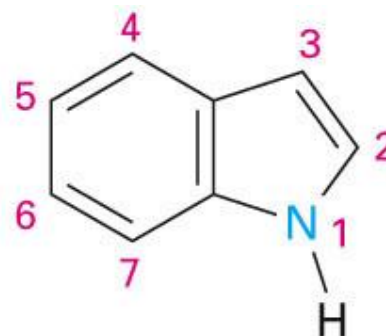
Aromatic Heterocycles



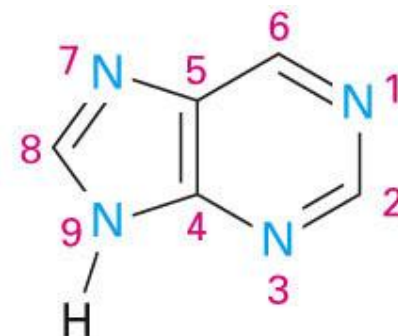
Quinoline



Isoquinoline



Indole

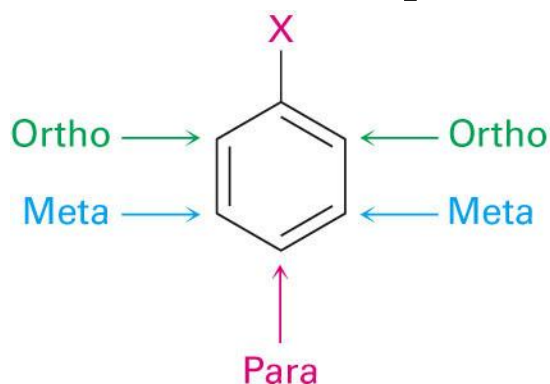


Purine

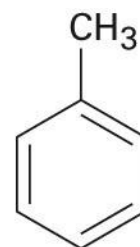
© 2007 Thomson Higher Education

الاستبدال في حلقة البنزين

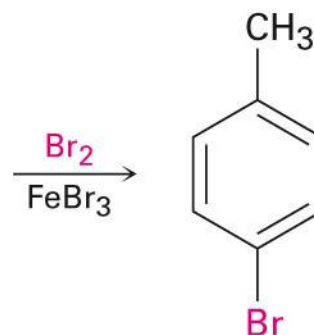
- *ortho-* (*o*) on adjacent carbons (1,2)
- *meta-* (*m*) separated by one carbon (1,3)
- *para-* (*p*) separated by two carbons (1,4)
- Describes reaction patterns (“occurs at the para position”)



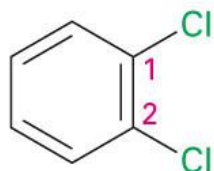
© 2007 Thomson Higher Education



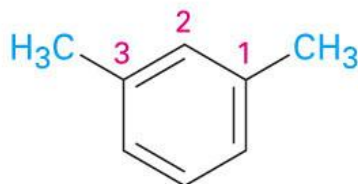
Toluene



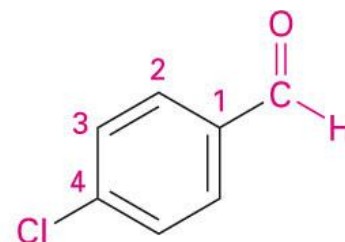
***p*-Bromotoluene**



***ortho*-Dichlorobenzene**
1,2 disubstituted

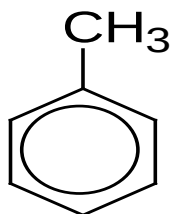


***meta*-Dimethylbenzene**
(*meta*-xylene)
1,3 disubstituted

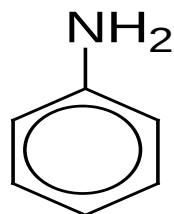


***para*-Chlorobenzaldehyde**
1,4 disubstituted

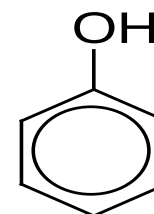
تسمية البنزين



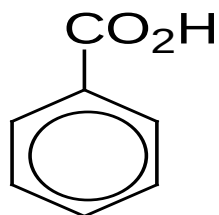
toluene



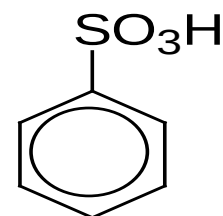
aniline



phenol



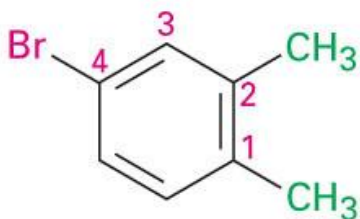
benzoic acid



benzenesulfonic acid

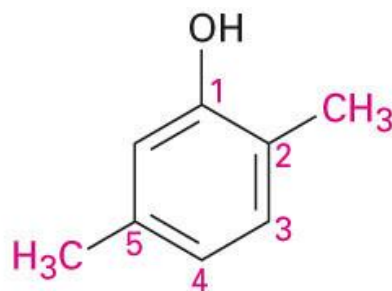
تسمية البنزين في حالة وجود أكثر من أستبدال على الحلقة

- تأخذ الأستبدلات اقل الأرقام الممكنة.
- ترتب الأستبدلات ترتيبا هجائيا.
- يمكن استخدام الأسماء الشائعة في تسمية المركبات (as in TNT).



4-Bromo-1,2-dimethylbenzene

© 2007 Thomson Higher Education

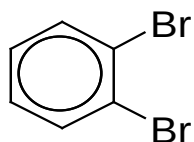


2,5-Dimethylphenol

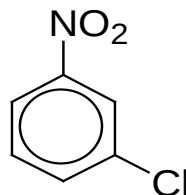


2,4,6-Trinitrotoluene (TNT)

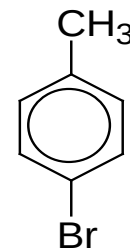
تسمية البنزين في حالة وجود أكثر من استبدال على الحلقة



o-dibromobenzene
1,2-dibromobenzene

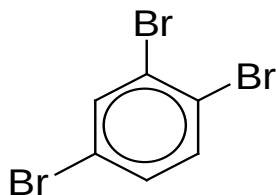


m-chloronitrobenzene
3-chloro-1-nitrobenzene

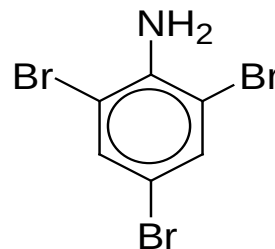


p-bromotoluene
4-bromotoluene

If more than two groups on the ring, use numbers!



1,2,4-tribromobenzene



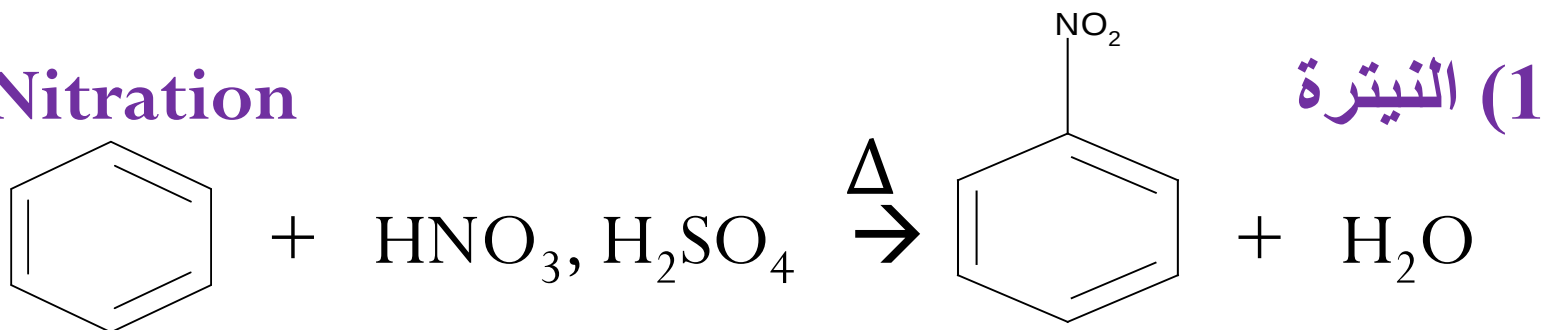
2,4,6-tribromoaniline

Reactions of benzene

تفاعلات البنزين

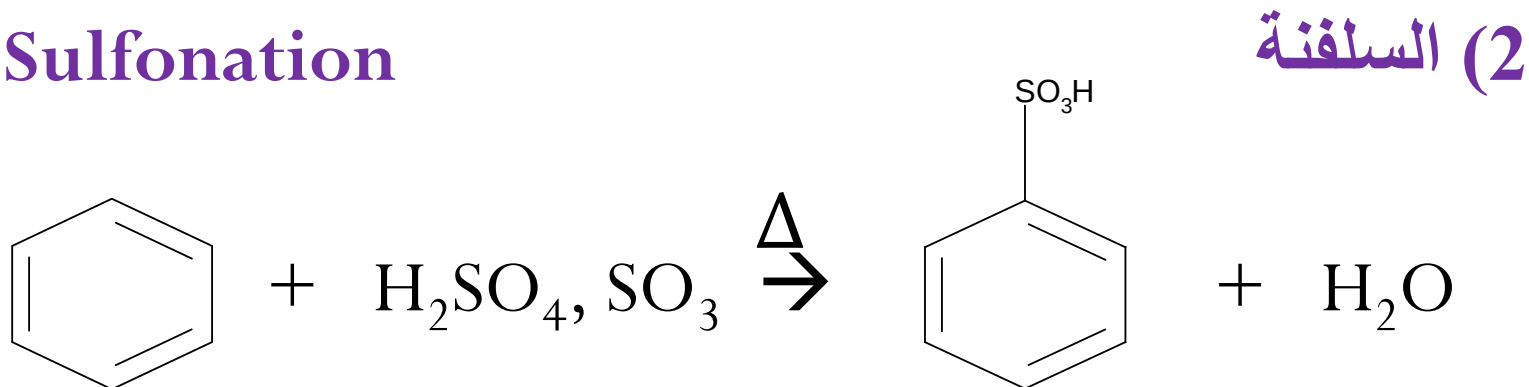
Reactions of benzene

1. Nitration



Nitro benzene

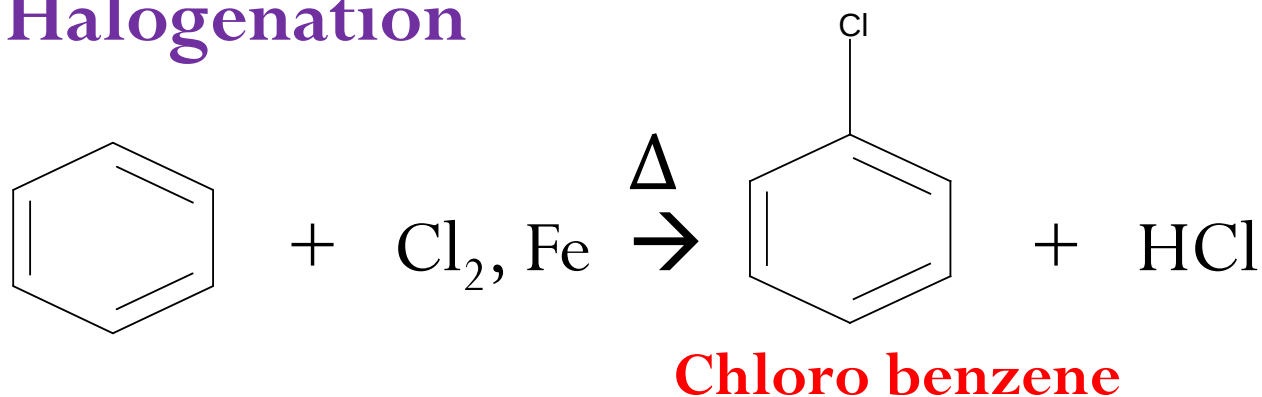
2. Sulfonation



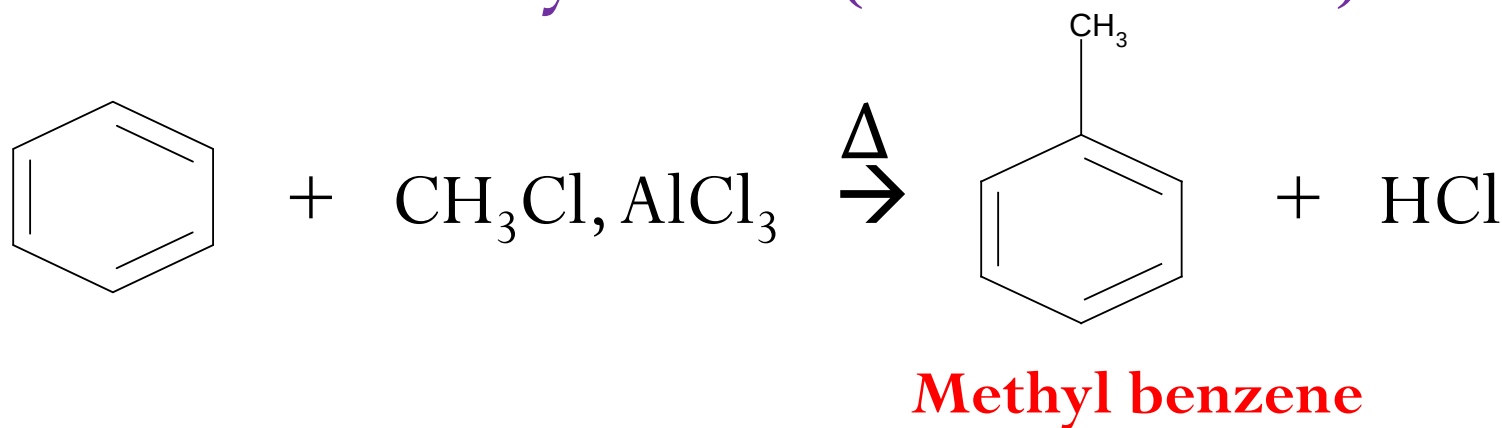
Benzenesulphonic acid

3. Halogenation

(3) الهلجنة

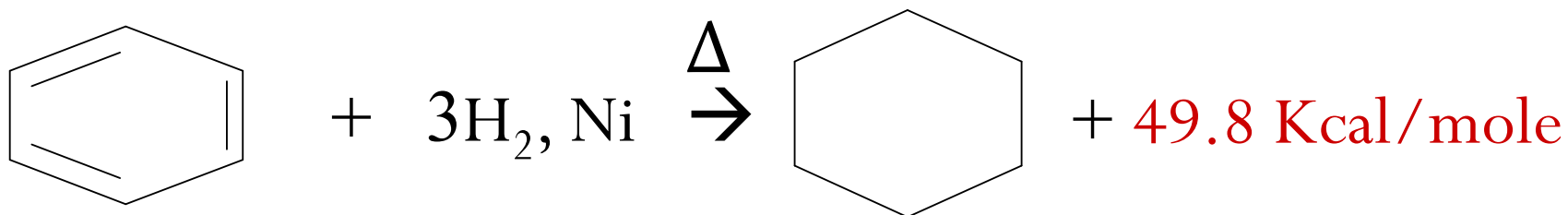
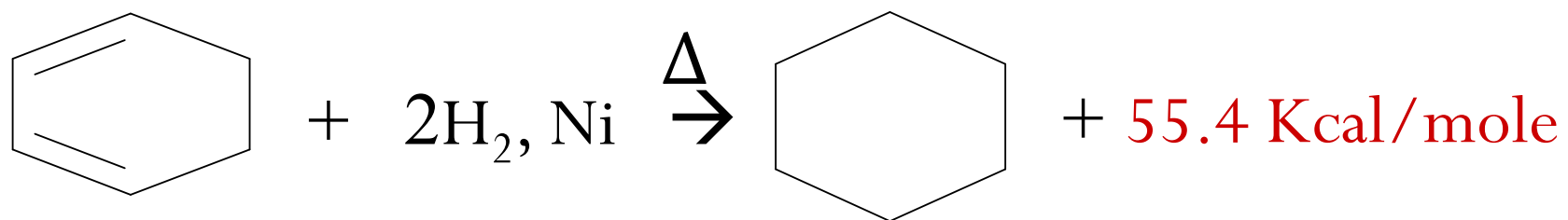
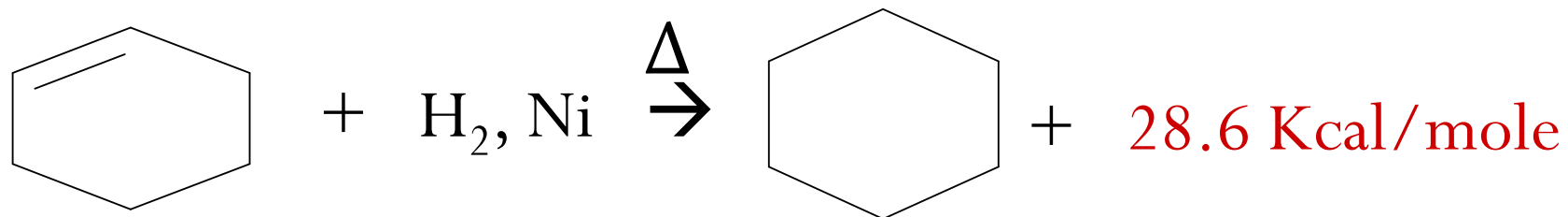


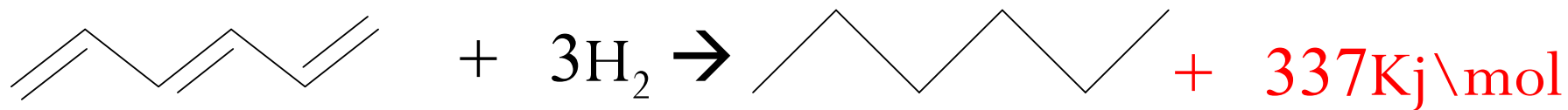
4. Freidel-Crafts alkylation (4) الألكلة (تفاعل فريدل كرافت)



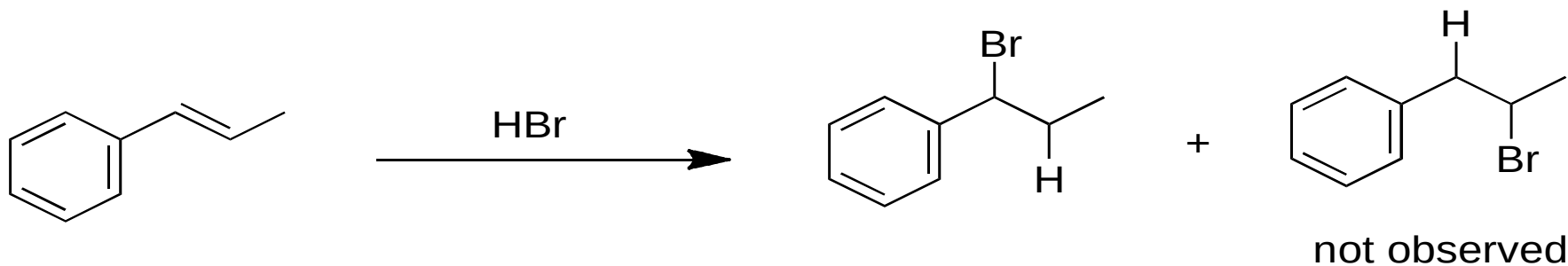
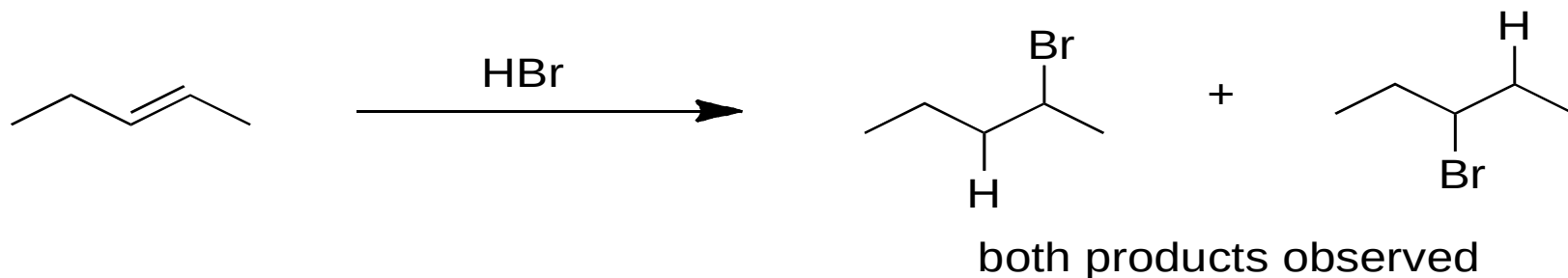
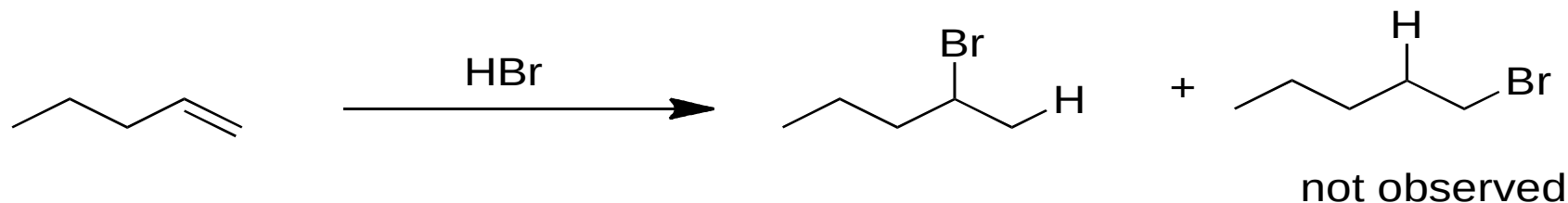
5. Hydrogenation

(5) الهدرجة



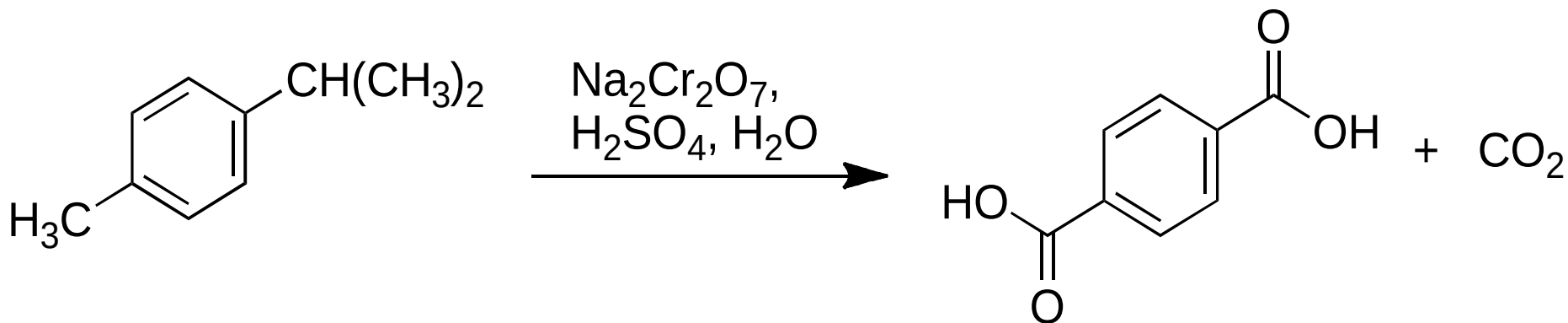
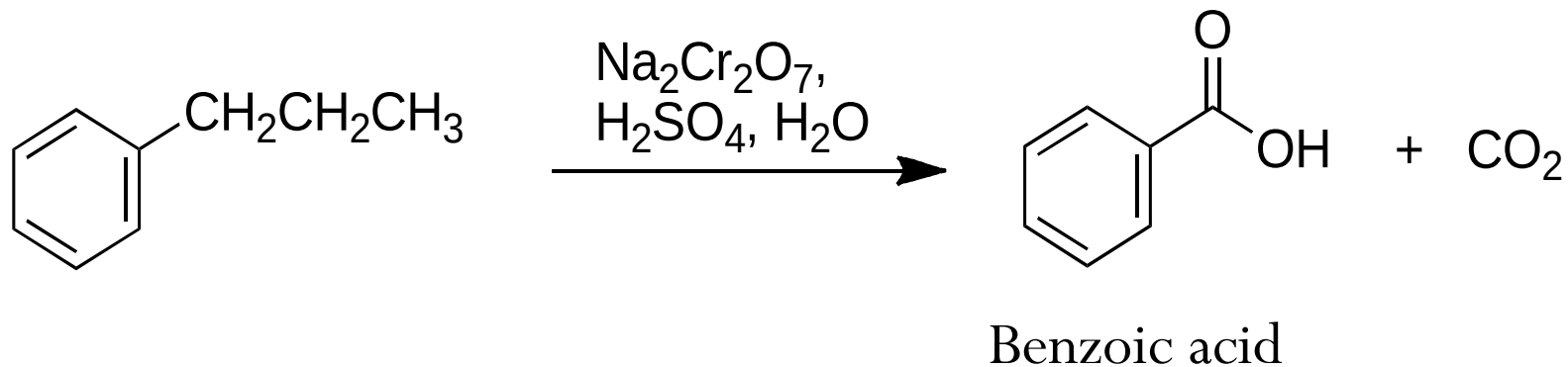


1,3,5-Hexatriene



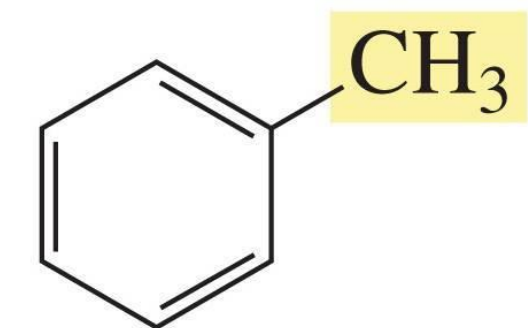
6. Oxidation of Alkylbenzenes

(6) أكسدة الكيالات البنزين

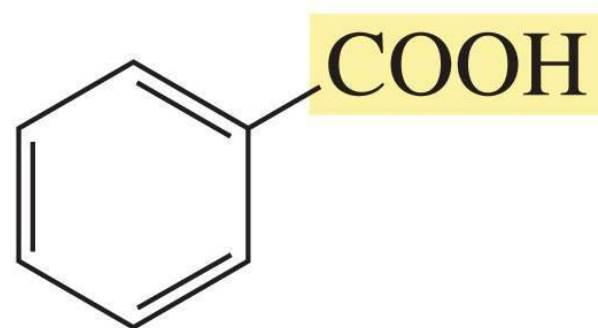
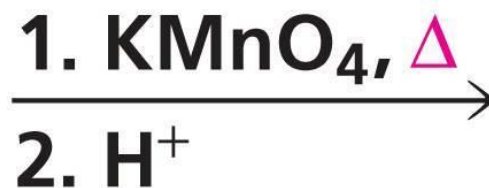


6. Oxidation of Alkylbenzenes

(6) أكسدة الكيالات البنزين



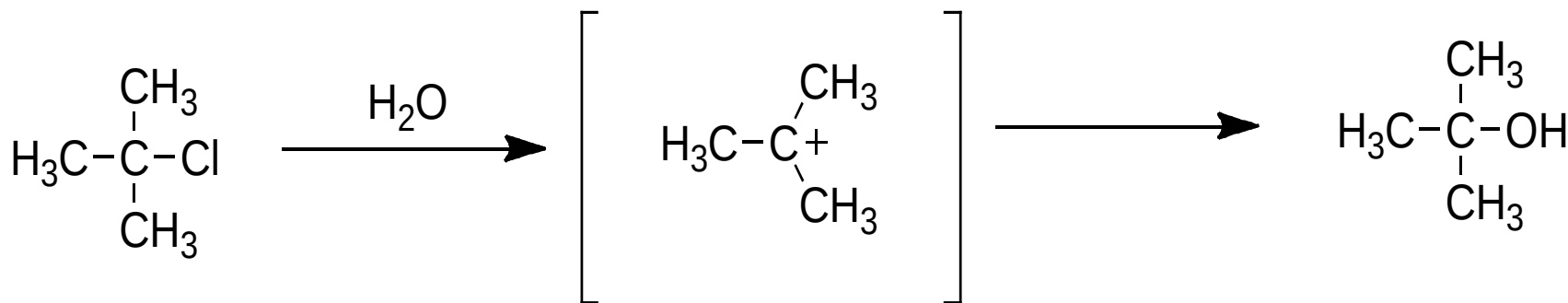
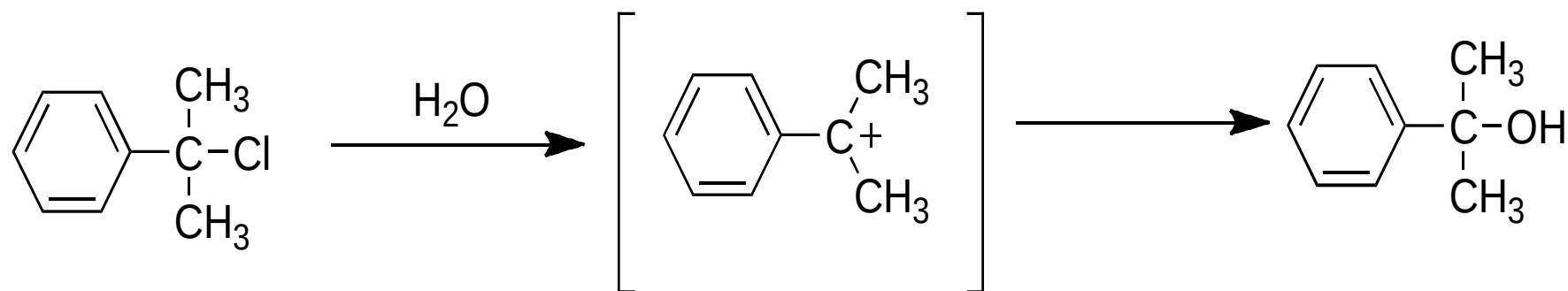
toluene



benzoic acid

7. S_N1 Reactions of Benzylic Halides

(7) تفاعلات هاليدات البنزين



8. Reactions of benzyl bromide

