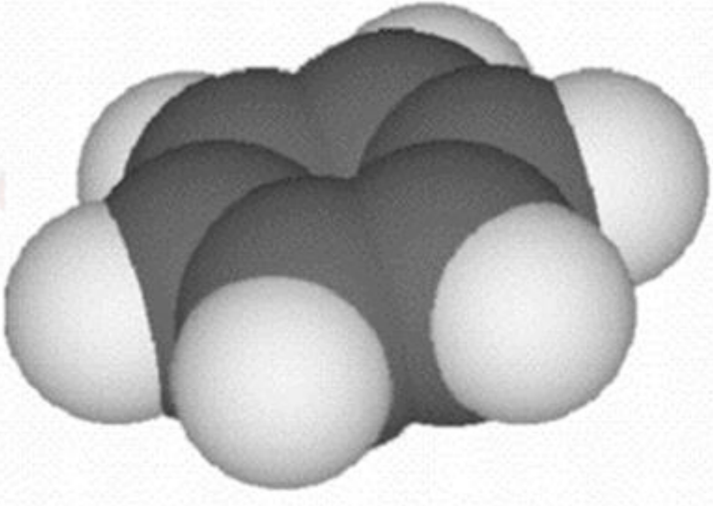
المركبات الأروماتية



الدكتور مهند عامر

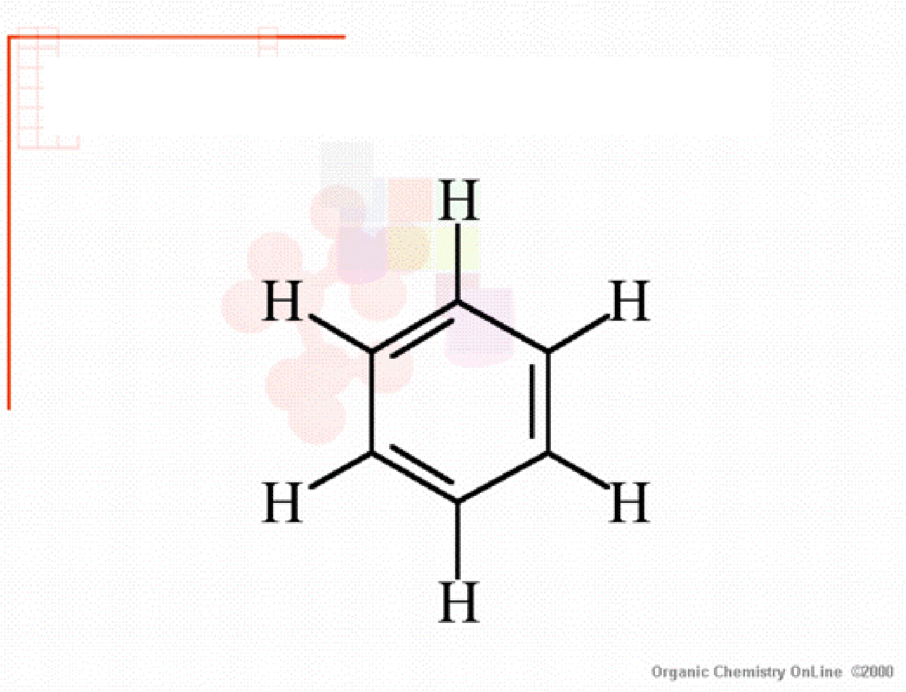
كلية تربية عبري

٢٠٠٦/٢٠٠٥

الهيدروكربونات الأروماتية

المركبات الأروماتية هي :

عبارة عن مركب حلقي مستوي الشكل



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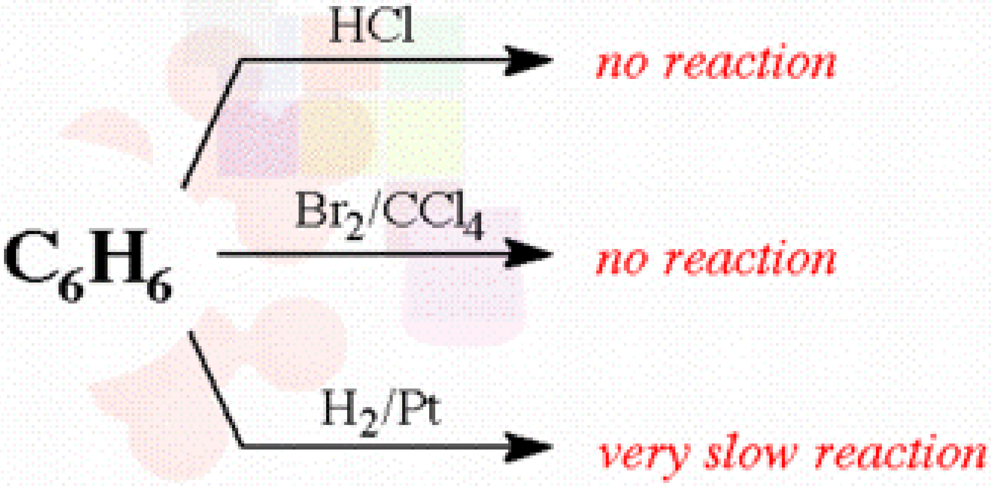
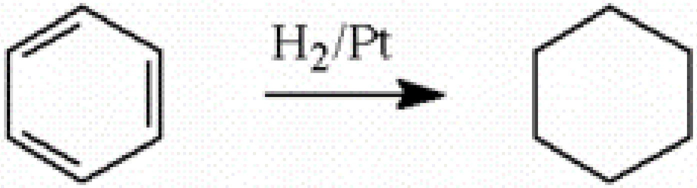
البنزين ومركبات الألكين



$C_6H_6 \xrightarrow{HCl}$ *no reaction*

$C_6H_6 \xrightarrow{Br_2/CCl_4}$ *no reaction*

$C_6H_6 \xrightarrow{H_2/Pt}$ *very slow reaction*



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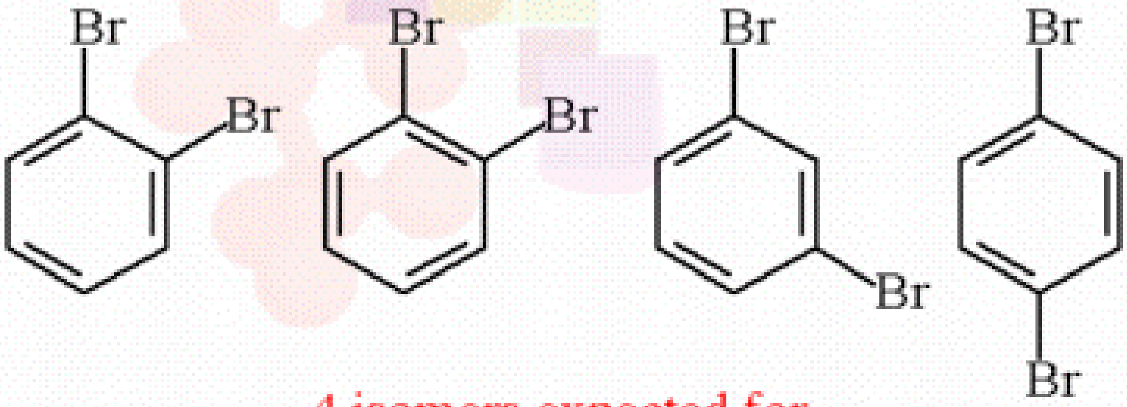
المتشكلات المتوقعة للبنزين

Benzene $\xrightarrow{Br_2/FeBr_3}$ 3 dibromo isomers



4 isomers expected for
Kekulé benzene

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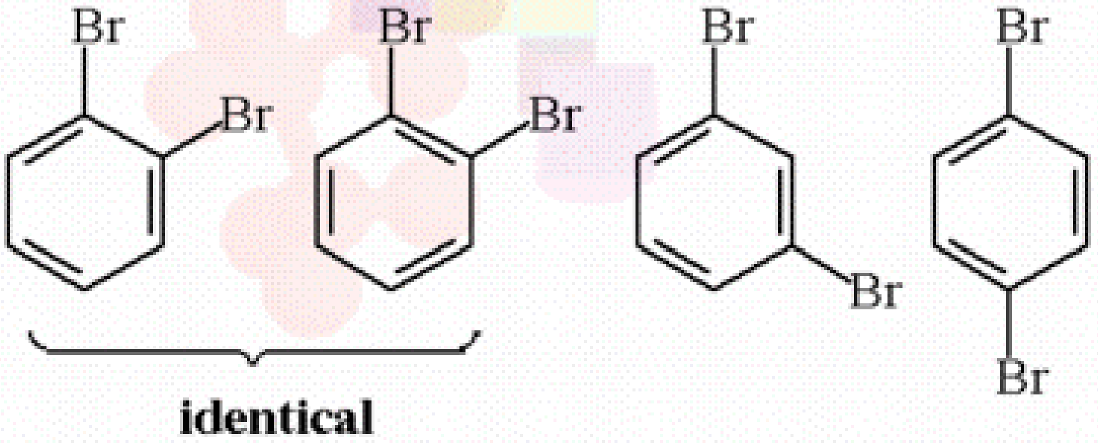
Benzene $\xrightarrow{Br_2/FeBr_3}$ **3 isomers**


Br
Br
Br
Br
Br
Br
Br
Br
identical

3 isomers expected

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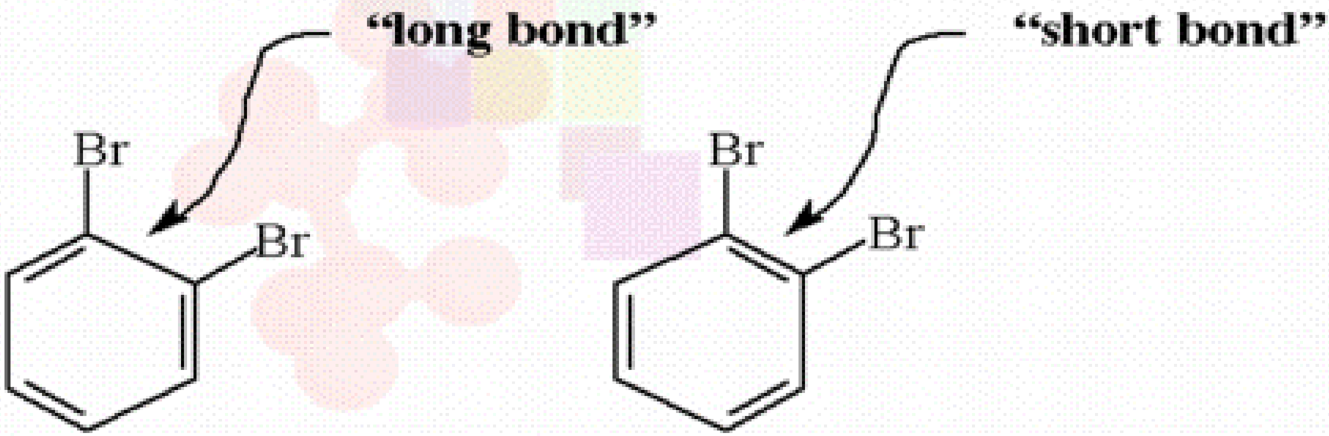
"long bond"
Br
Br
"short bond"
Br
Br

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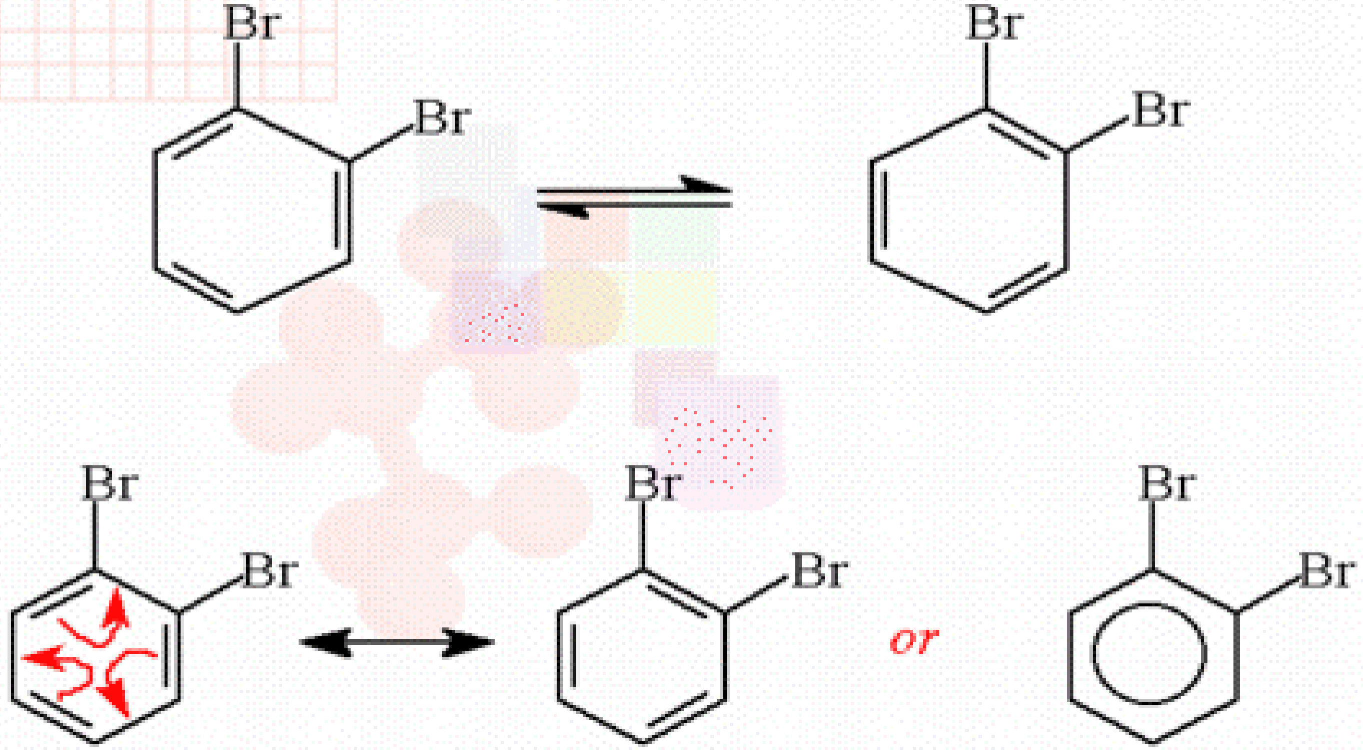
اشكال الرنين في البنزين


Br
Br
Br
Br
Br
Br
Br
Br
or
Br
Br

...today we recognize the two structures Kekulé drew as simple resonance forms.

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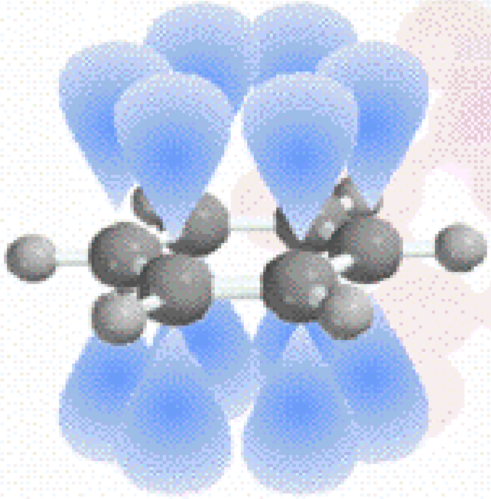
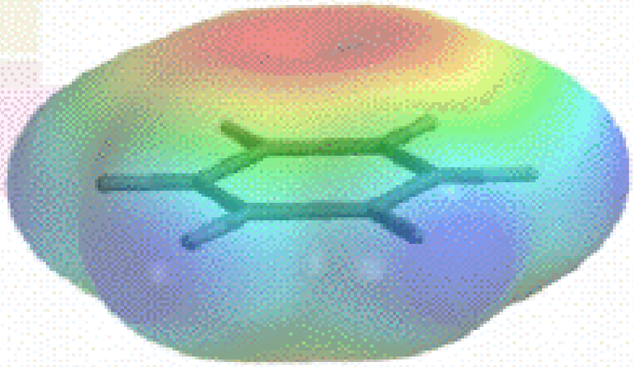
The conjugated system in the benzene ring results in the formation of a continuous π-cloud, above and below the plane of the ring.





An electrostatic potential map of benzene showing enhanced electron density above and below the ring plane.

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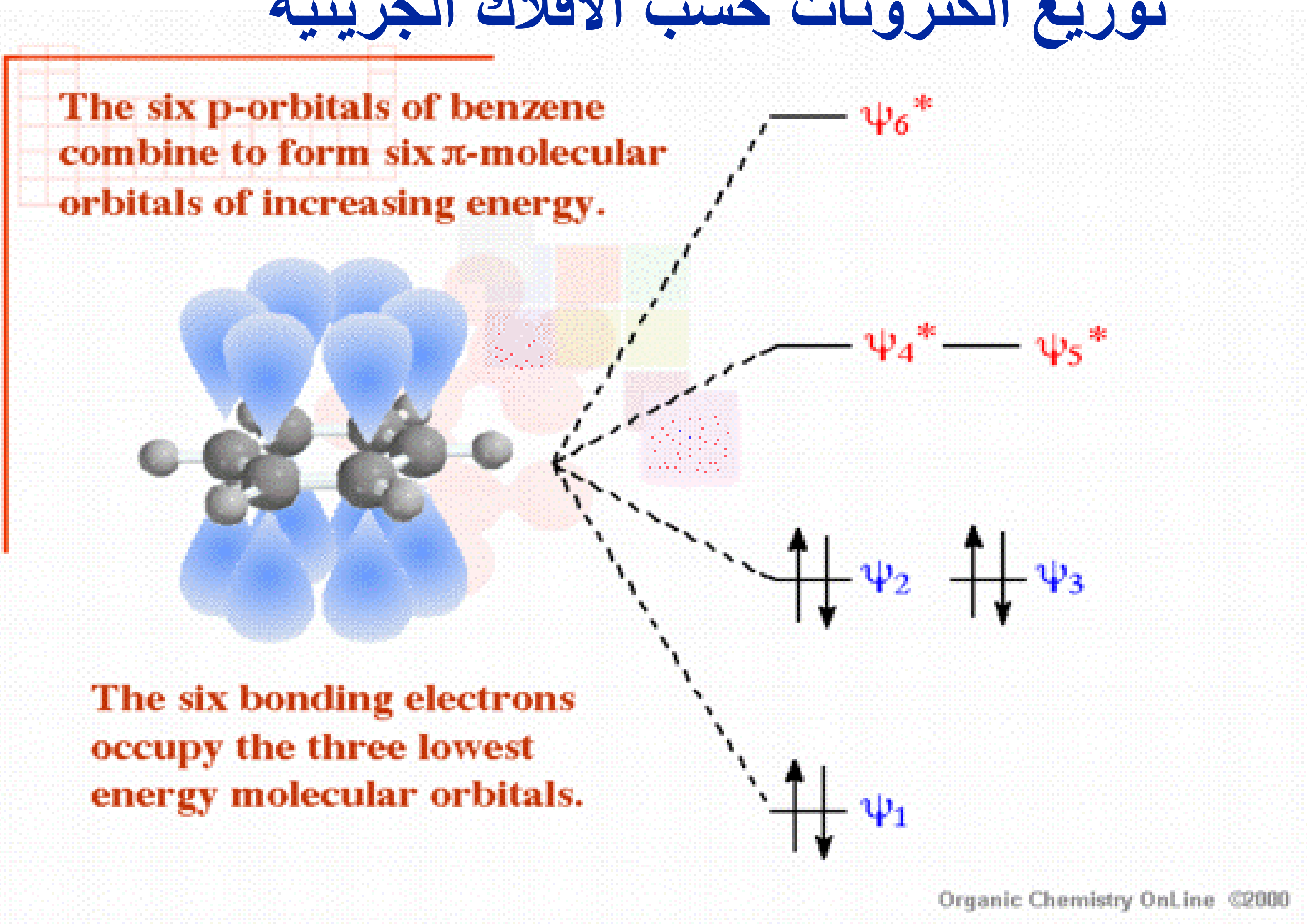
توزيع اُلكترونات حسب الأفلاك الجزيئية



The six p-orbitals of benzene combine to form six π-molecular orbitals of increasing energy.

The six bonding electrons occupy the three lowest energy molecular orbitals.

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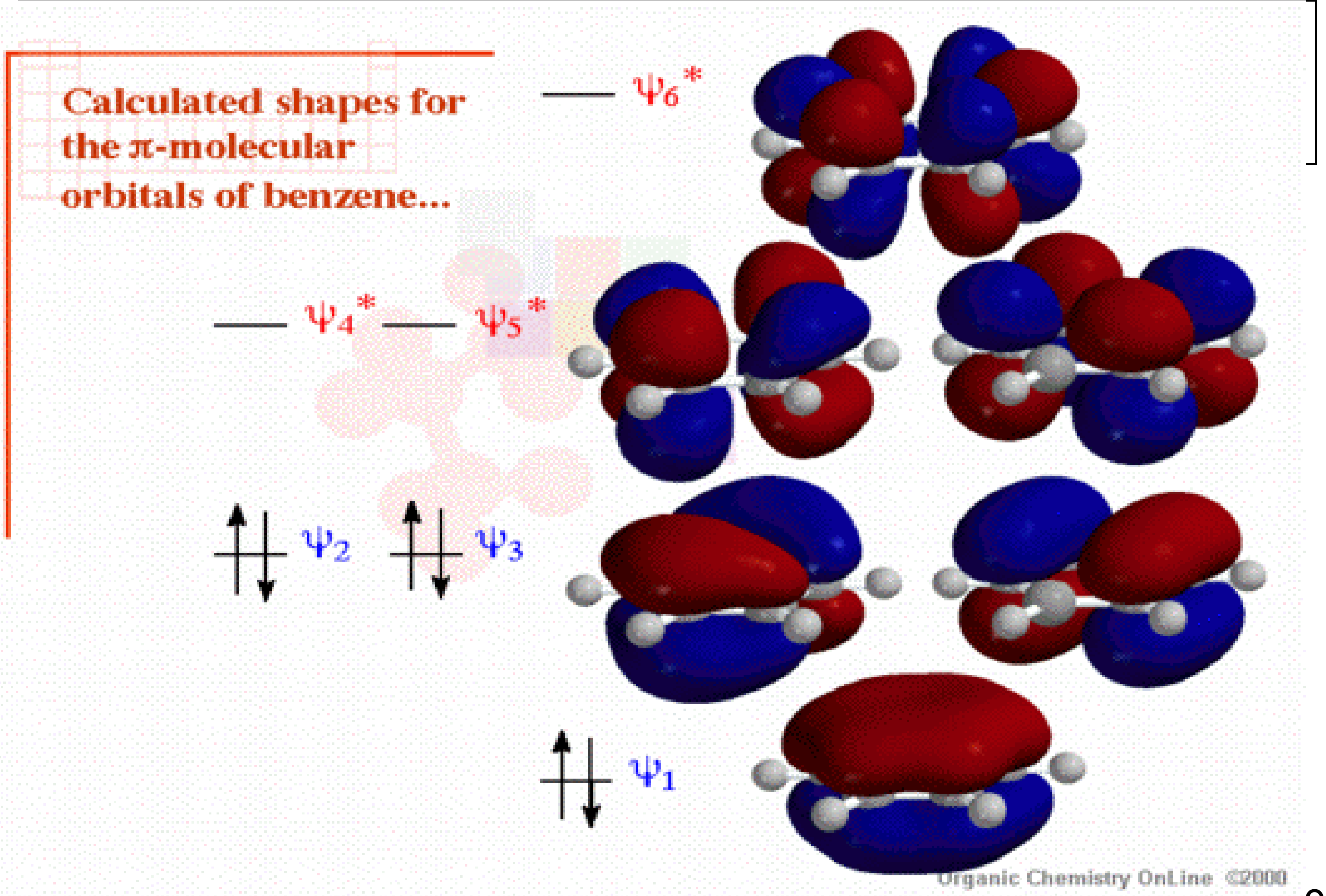

Calculated shapes for the π-molecular orbitals of benzene...

ψ_6^*
ψ_4^*
ψ_5^*
ψ_2
ψ_3
ψ_1

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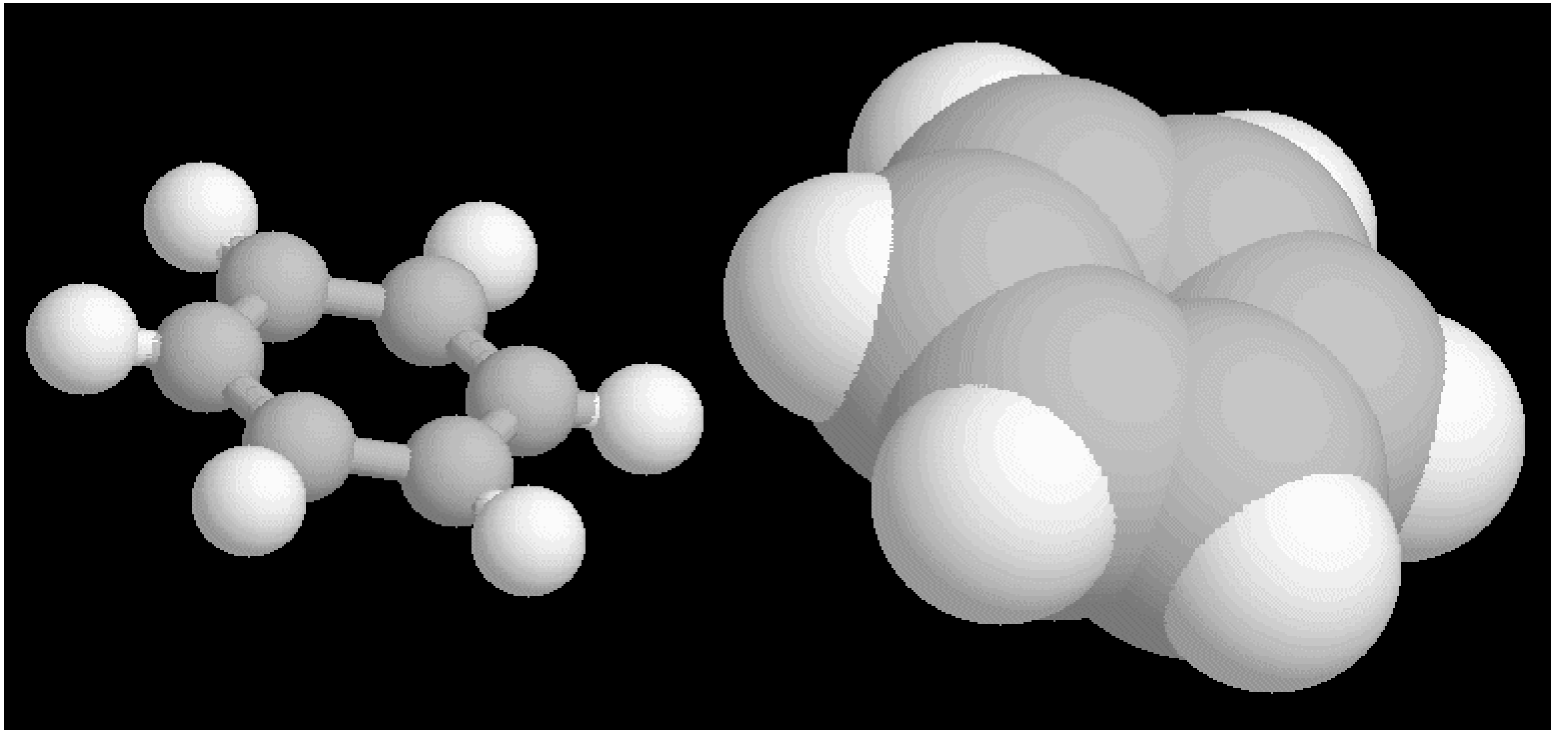
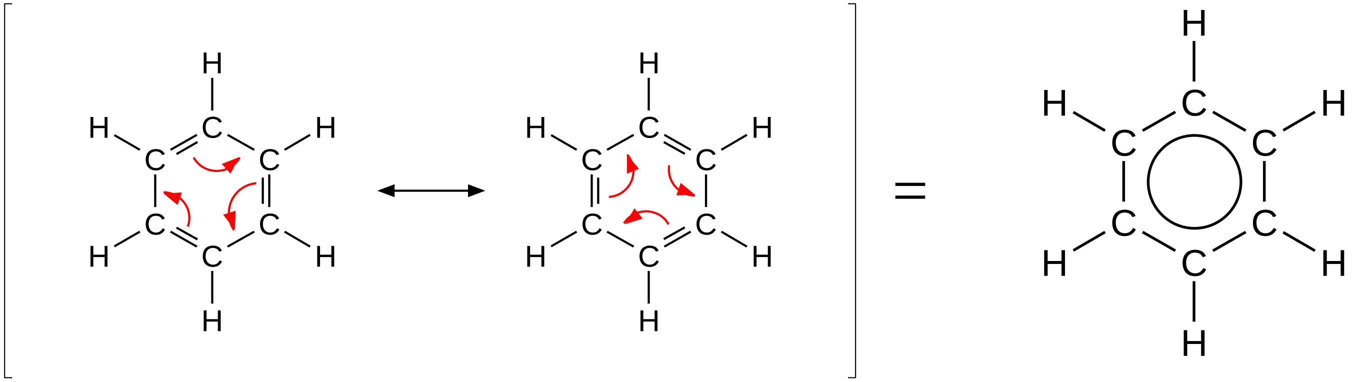
البناء الأروماتي



تفسير بناء البنزين بالطنين

اشكال الطنين هي تخيلية وليست حقيقية

- البناء الحقيقي للبنزين بناء واحد غير متغير التهجين وهو شكل مدمج لهيآت الطنين كما هو مبين في الشكل .



بناء الطنين لمركب البنزين

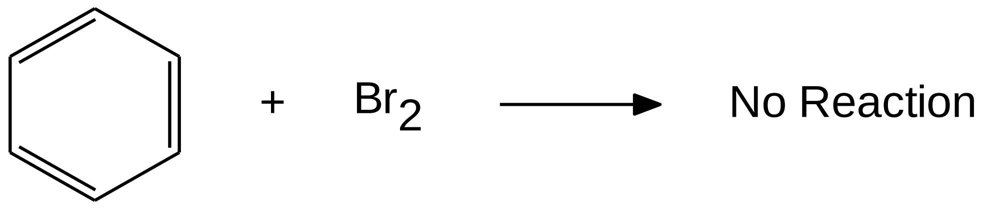
الشكل الممثل للبنزين

تفسير بناء البنزين بالطنين

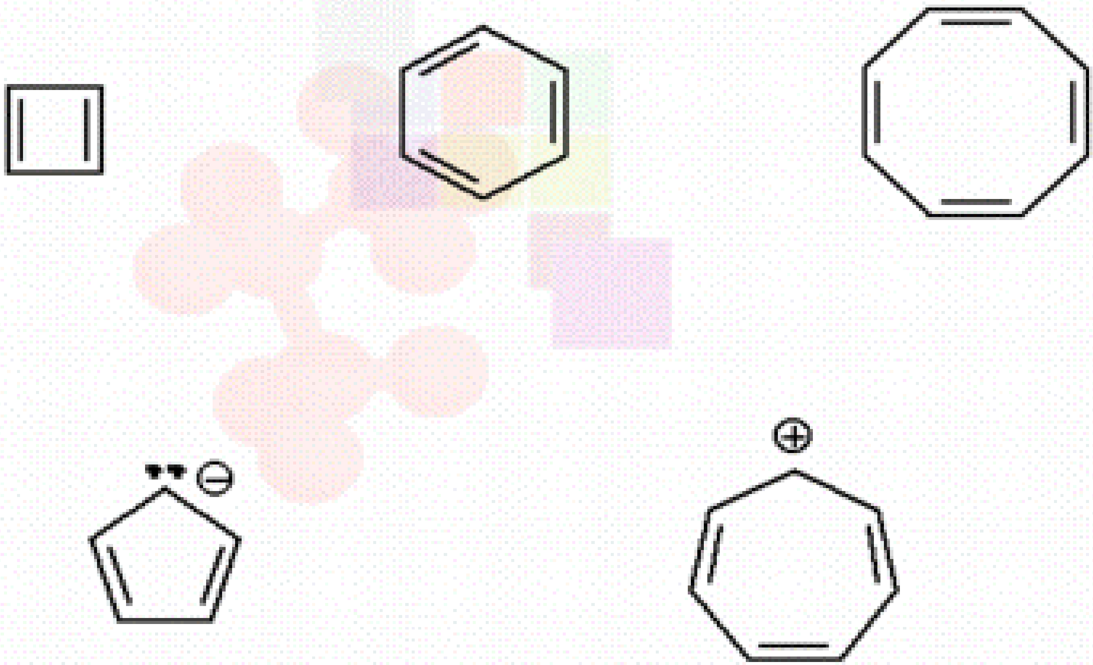
- بناء الطنين يختلف فقط في مواقع الإلكترونات . مواقع الذرات لا تتغير من بناء طنين وآخر
- في البنزين , ذرات الكربون الستة تكون شكل سداسي الأضلاع والزوايا , الكترونات باي π تتشارك بشكل متساوي فيما بينها .جميع روابط كربون – كربون طولها متساوٍ = (1.39 Å) , وهي بين طول روابط C-C = 1.54 Å و C=C (1.34 Å)

الظاهرة الأروماتية

- تحتوي على (4n + 2) الكتروناً على شكل أفلاك π (2,6,10,....الخ) في الحلقة
- تحتوي على سحابة من الكترونات π
- مركبات اكثر استقراراً



4*n* + 2 Rule



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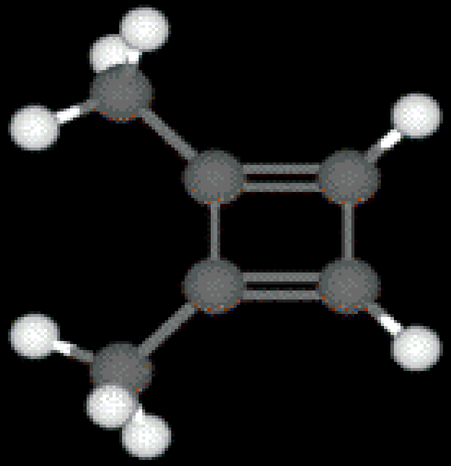
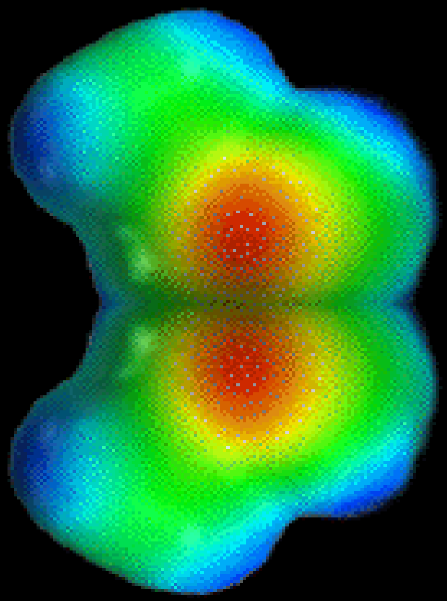
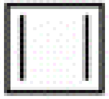
2,3-Dimethylcyclobutadiene





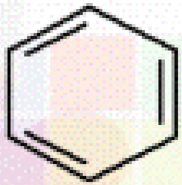
Planar…
4 π electrons,
therefore **not aromatic** *(antiaromatic)*

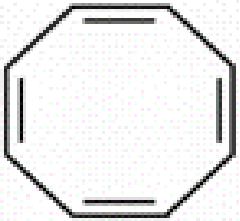
$4n + 2$ Rule

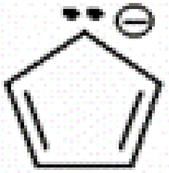


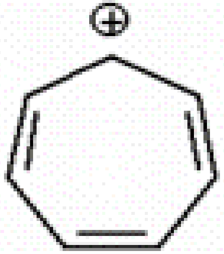
4 π electrons

antiaromatic









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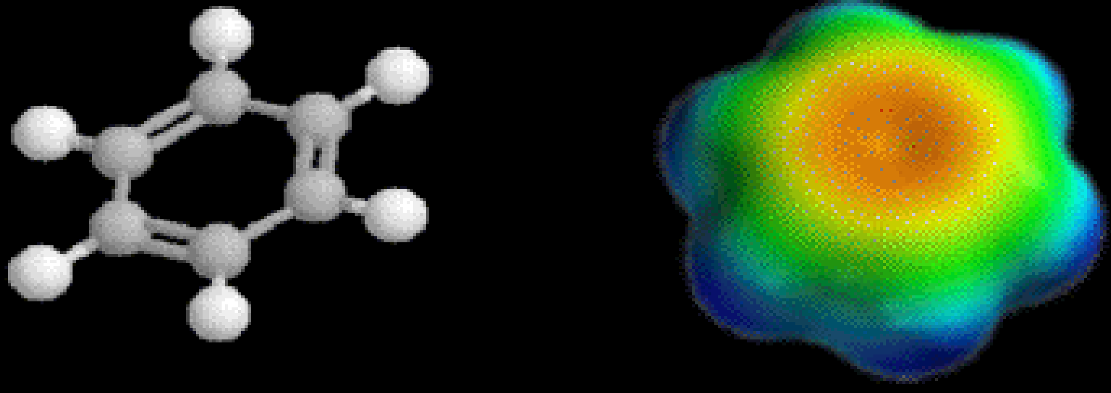
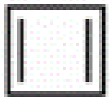
Benzene



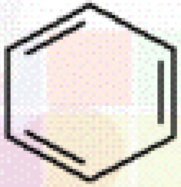
Planar...
6 π electrons,
therefore **aromatic**

4*n* + 2 Rule



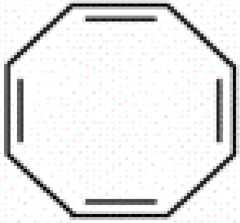
4 π electrons

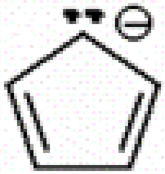
not aromatic

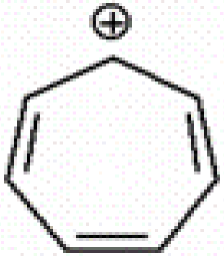


6 π electrons

aromatic







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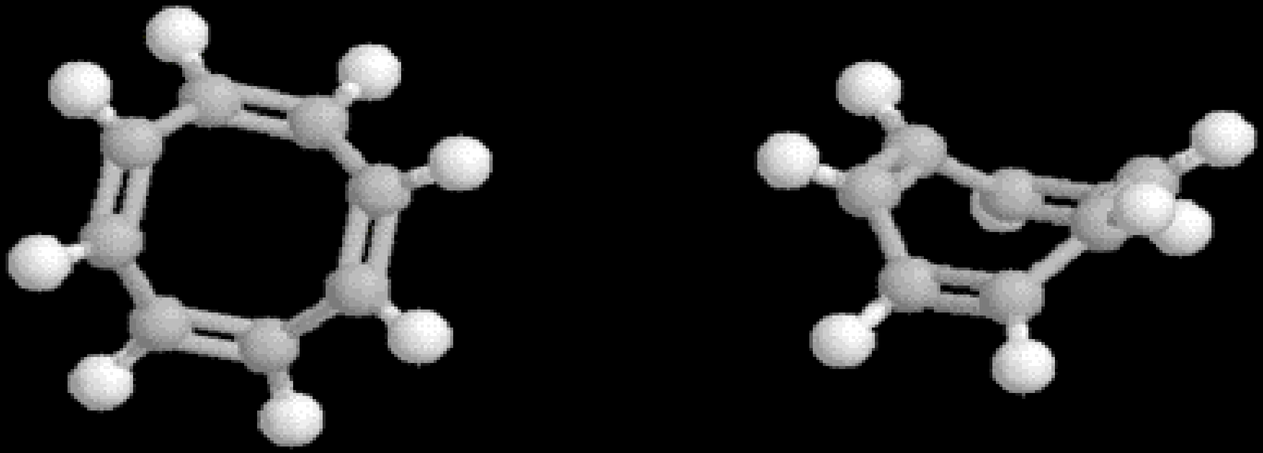
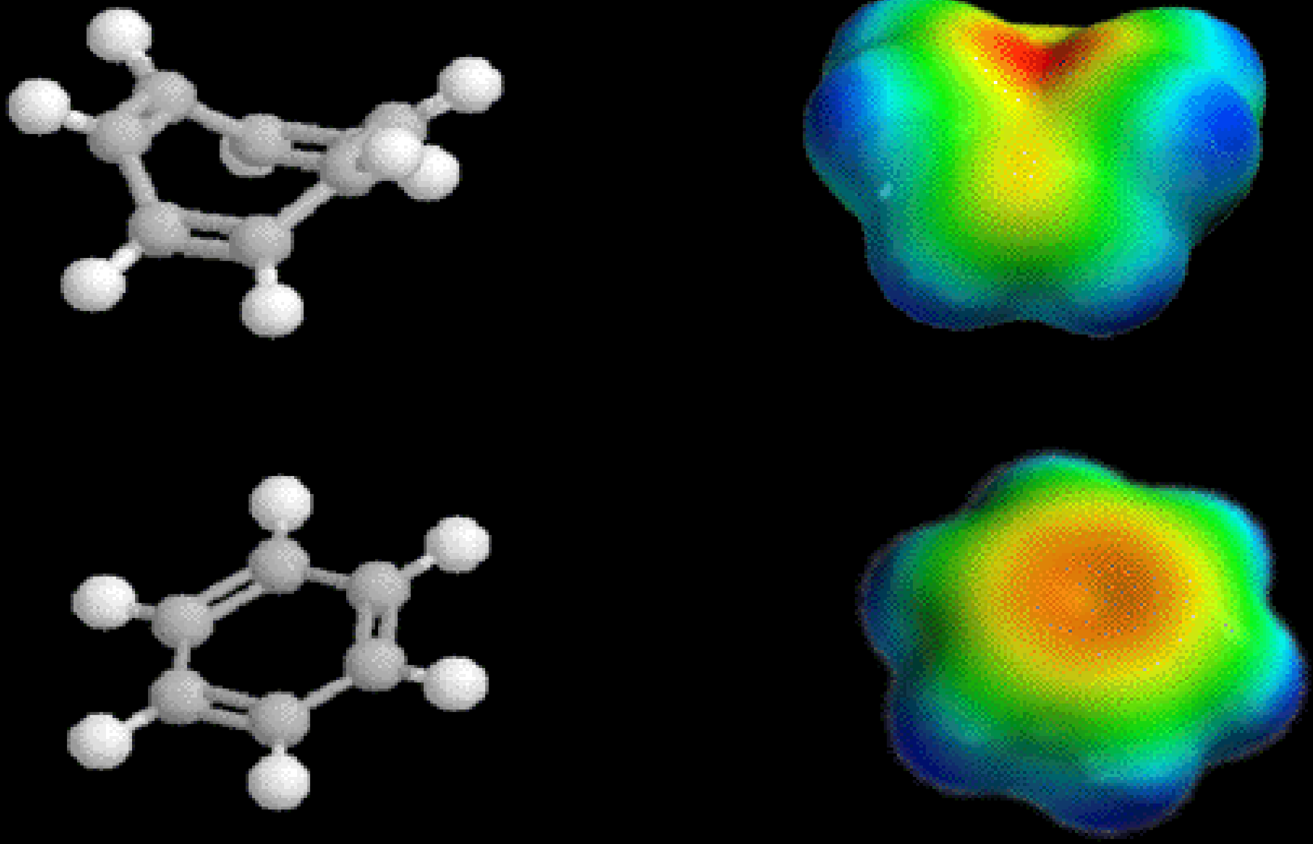
Cyclooctatetraene

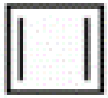


Not planar…
8 π electrons,
therefore **not aromatic**

Cyclooctatetraene

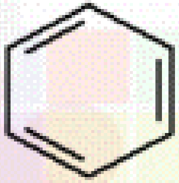


4*n* + 2 Rule



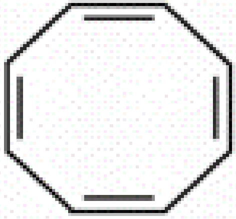
4 π electrons

not aromatic



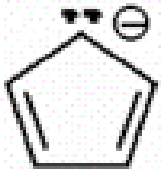
6 π electrons

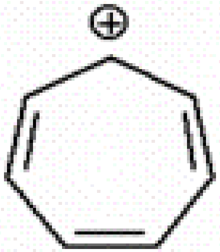
aromatic



8 π electrons

not aromatic





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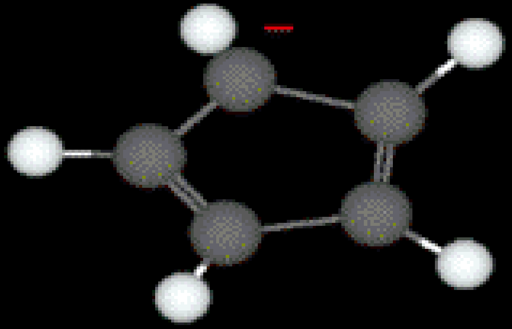
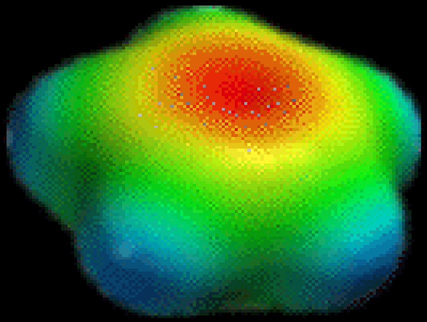
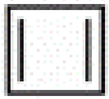
Cyclopentadienyl Anion





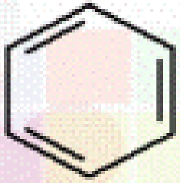
Planar…
6 π electrons,
therefore **aromatic**

4*n* + 2 Rule



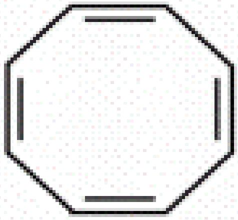
4 π electrons

not aromatic



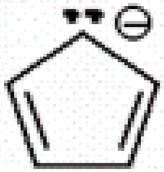
6 π electrons

aromatic



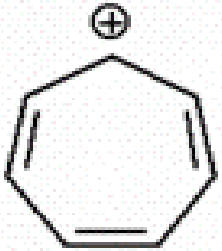
8 π electrons

not aromatic



6 π electrons

aromatic



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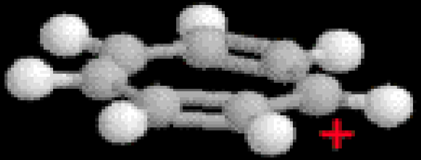
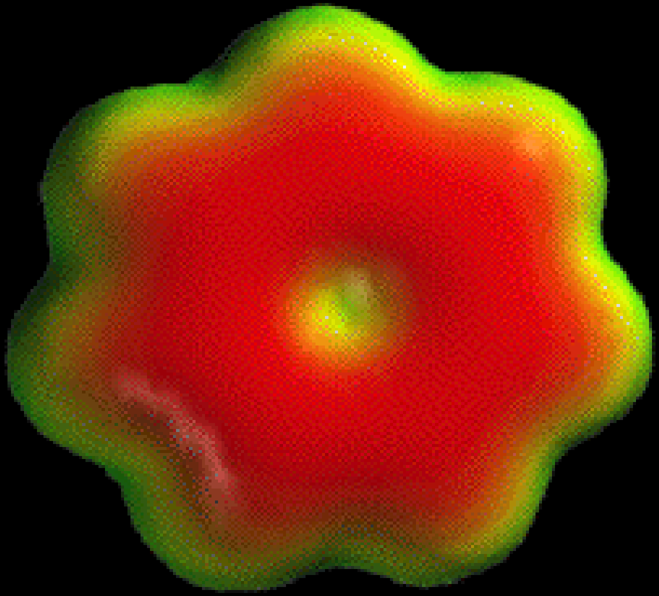
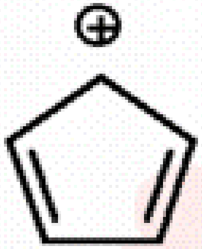
Cycloheptatrienyl Cation





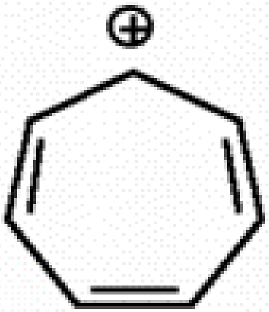
Planar…
6 π electrons,
therefore aromatic

$4n + 2$ Rule



4 π electrons

not aromatic



6 π electrons

aromatic

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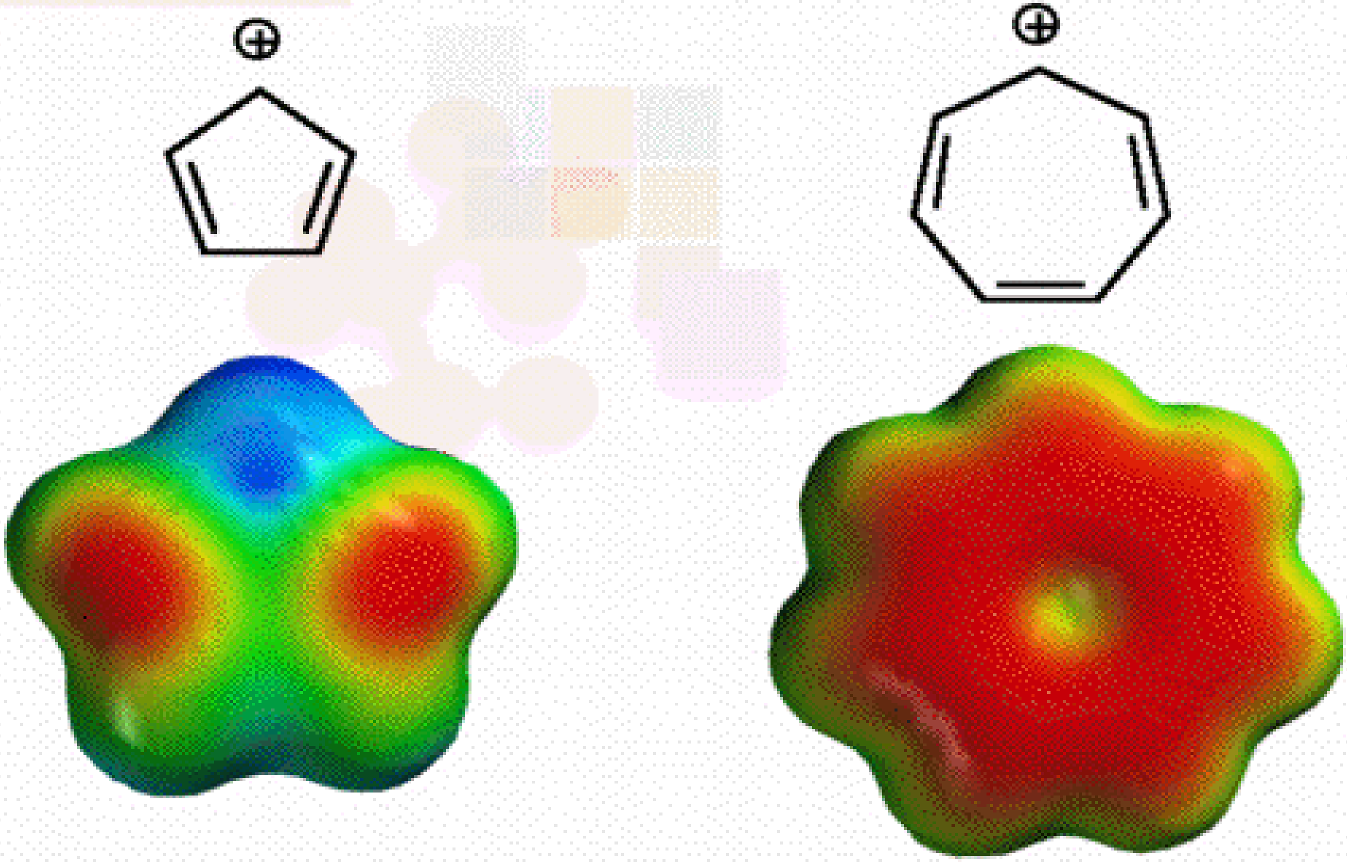
4*n* + 2 Rule



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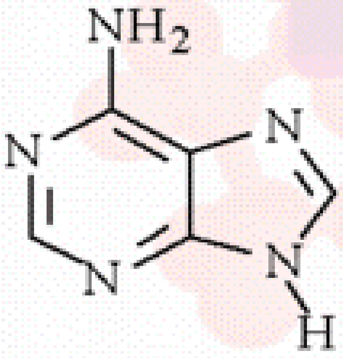
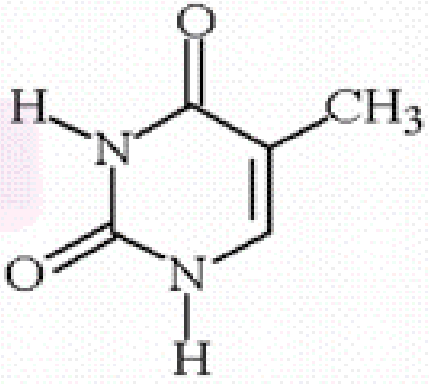
4*n* + 2 Rule



Adenine



Uracil

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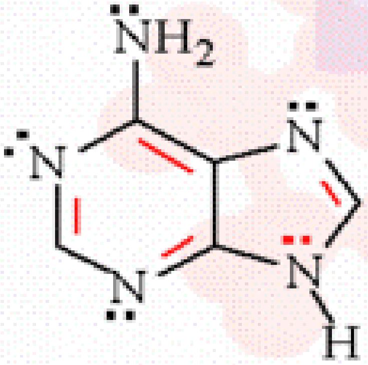
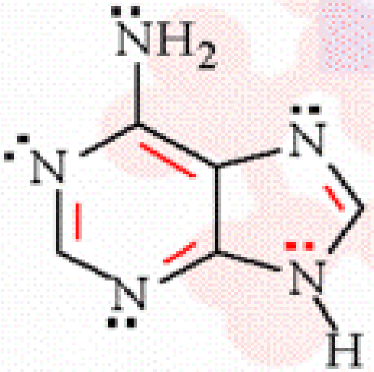
$4n + 2$ Rule



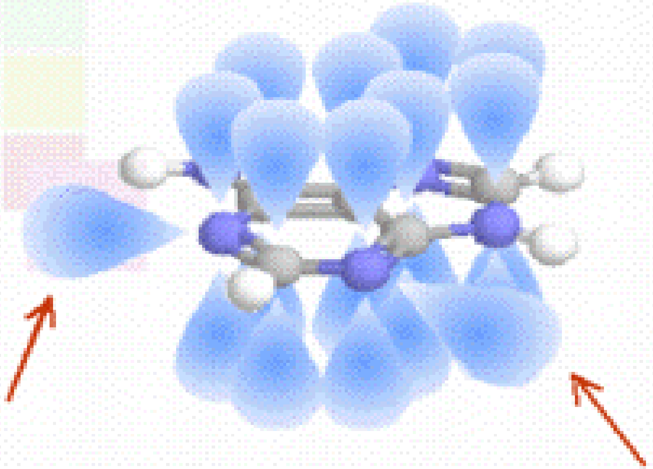
Adenine:
10 π electrons
Aromatic

Organic Chemistry OnLine ©2000

4*n* + 2 Rule



Adenine:
10 π electrons
Aromatic



The lone pairs on the nitrogens are orthogonal to the π-system and do not participate in the π–molecular orbital.

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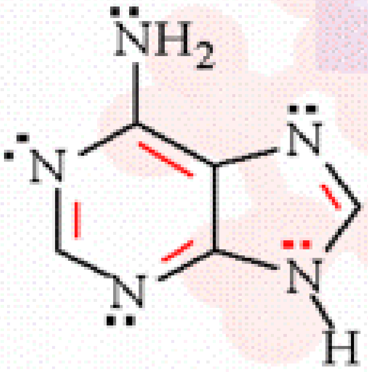
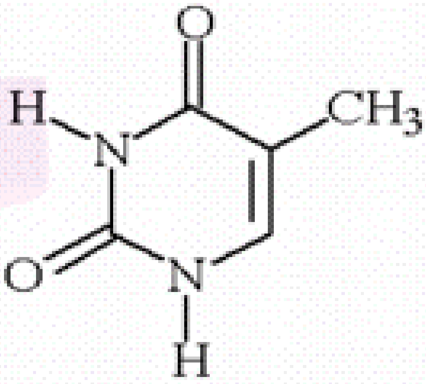
4*n* + 2 Rule


$\ddot{N}H_2$
N
N
N
N
H

Adenine:
10 π electrons
Aromatic



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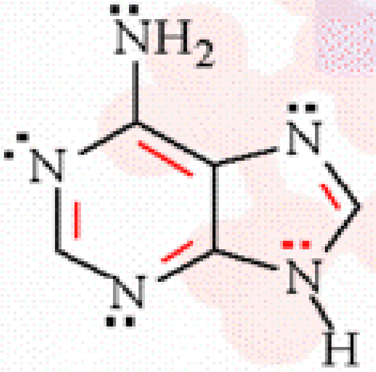
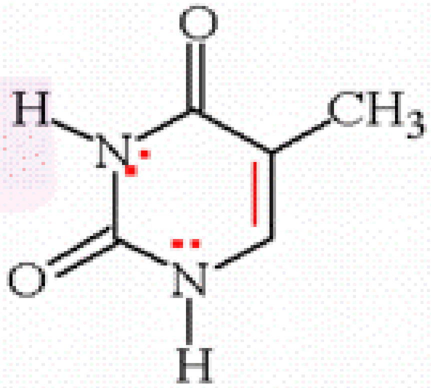
4*n* + 2 Rule



Adenine:
10 π electrons
Aromatic

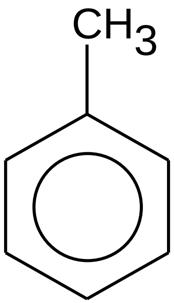


Uracil:
6 π electrons
Aromatic

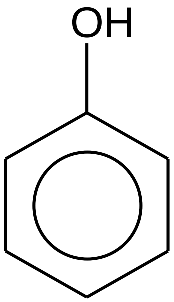
Organic Chemistry OnLine ©2000

تسمية المركبات الأروماتيـة

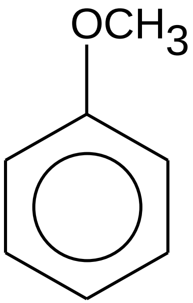
اسماء شائعة تستخدم كما هي :



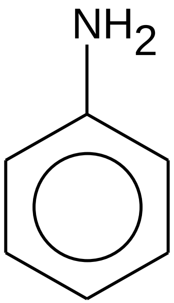
toluene



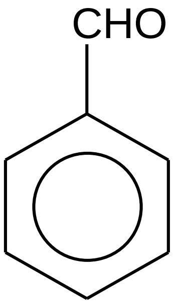
phenol



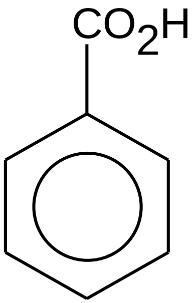
anisole



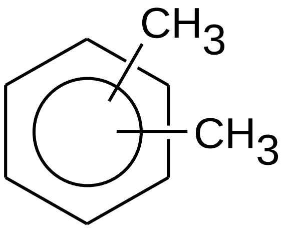
aniline



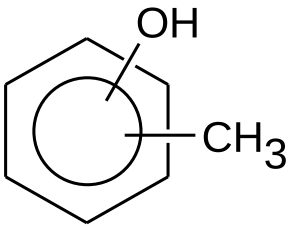
benzaldehyde



benzoic acid



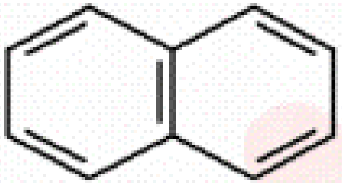
xylene



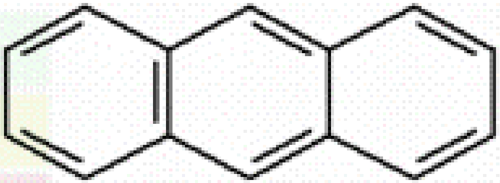
cresol

جميعها مقبولة حسب قواعد الأيوباك IUPAC.

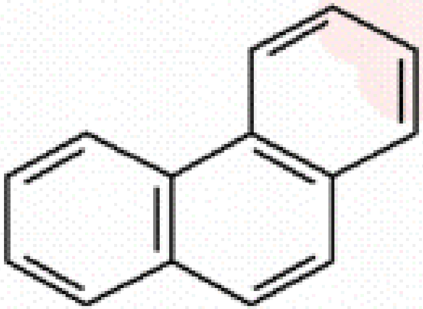
بعض المركبات الأروماتية عديدة الحلقات



napthalene



anthracene



phenanthrene

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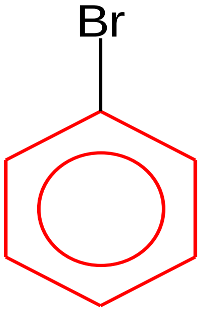
اوجد اسم الأصل

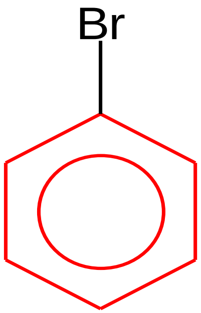
- نستخدم كلمة البنزين فقط للحلقة



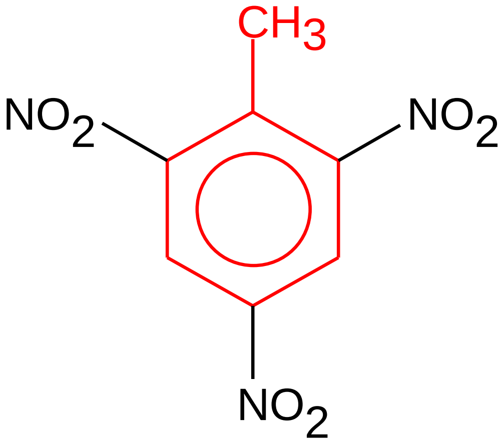
bromobenzene

اوجد اسم الأصل

- نستخدم البنزين فقط للحلقة
- وتستخدم هنا الأسماء الشائعة



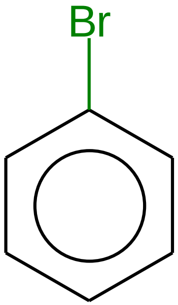
bromobenzene


CH_3
NO_2
NO_2
NO_2

2,4,6-trinitrotoluene

سم البدائل

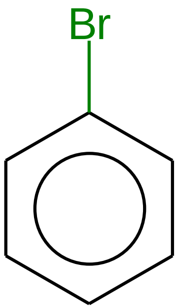
- مثلما ذكرنا سابقاً



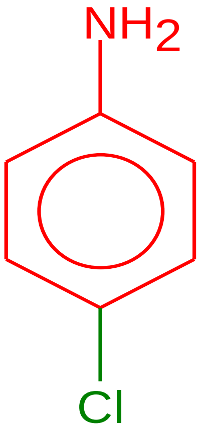
bromobenzene

سم البدائل

- مثلما ذكرنا سابقاً
- في حالة وجود بديلين نستخدم الكلمات التالية للمواقع ortho, meta, para

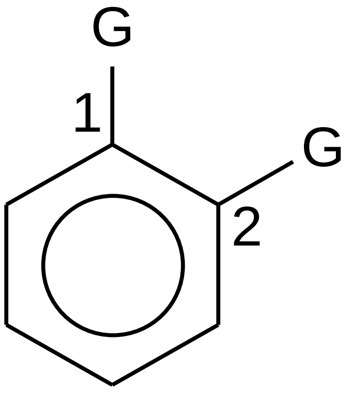


bromobenzene

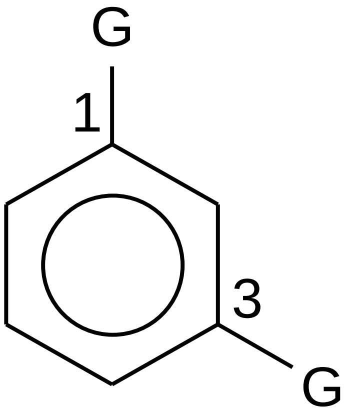


para-chloroaniline

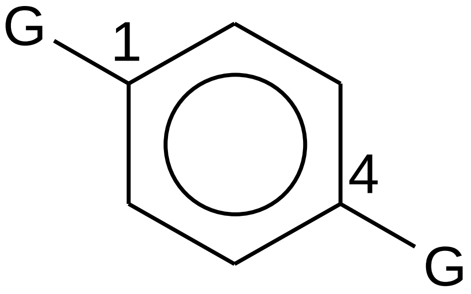
Ortho, meta, & para



ortho



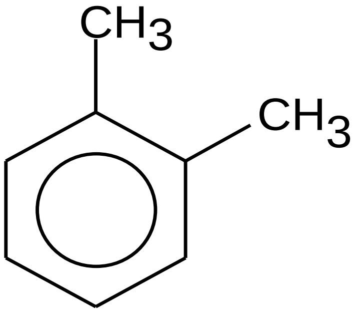
meta



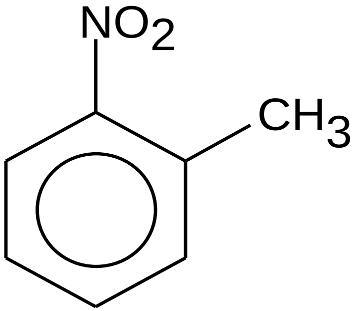
para

سؤال 1

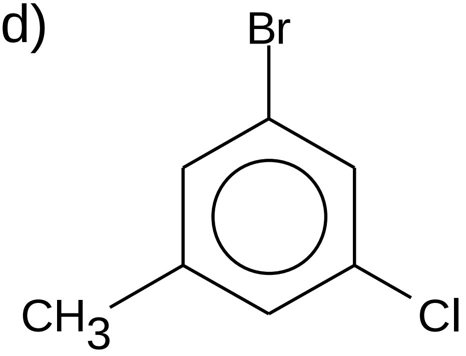
(a)



(b)

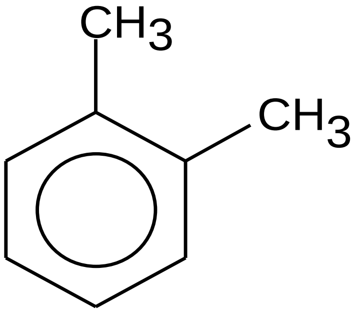


(d)



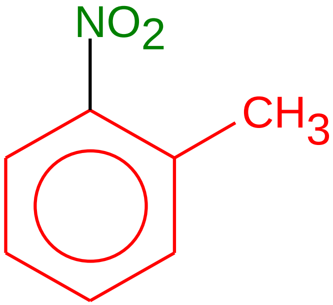
سؤال 1

(a)



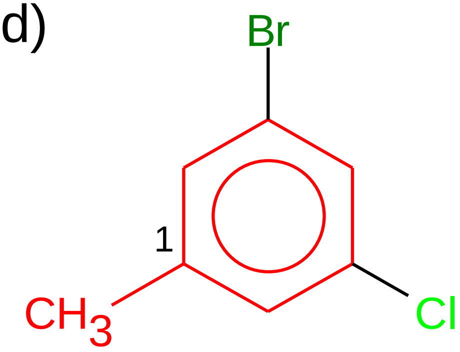
ortho-xylene

(b)

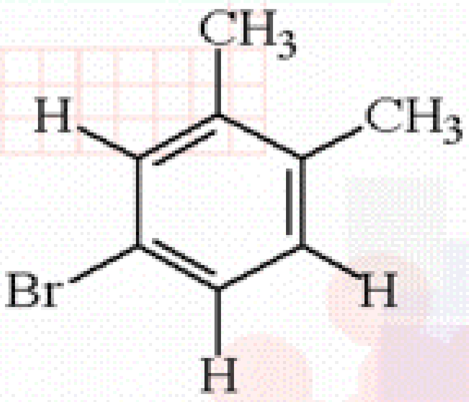


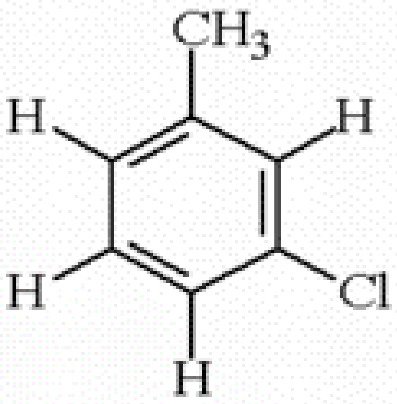
ortho-nitrotoluene

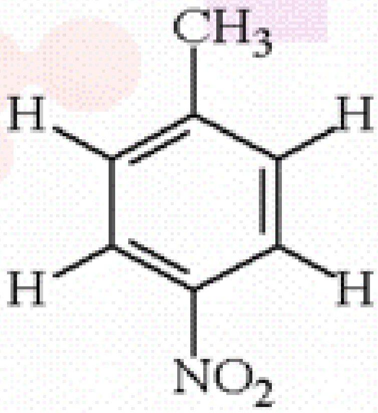
(d)



3-bromo-5-chlorotoluene


CH3
H
CH3
Br
H
H




CH3
H
H
H
H
NO2

سم المركبات التالية طبقا لقواعد أيوباك ؟

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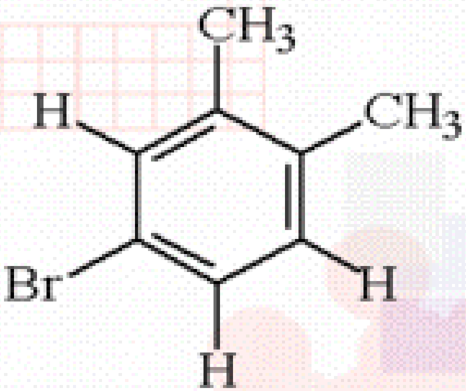
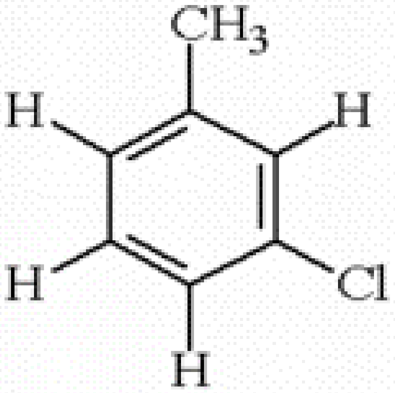
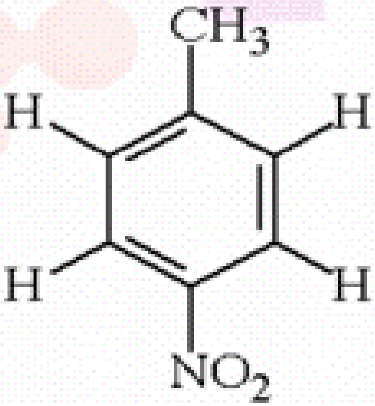

CH3
CH3
H
Br
H
H

4-bromo-1,2-dimethylbenzene




CH3
H
H
H
H
NO2

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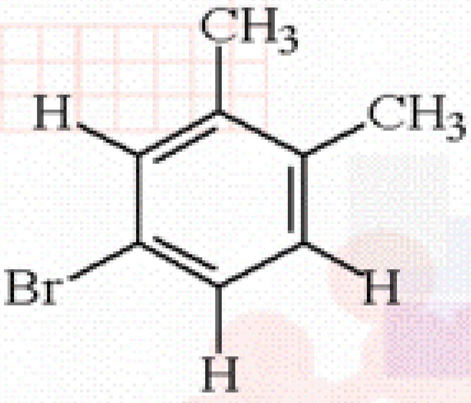
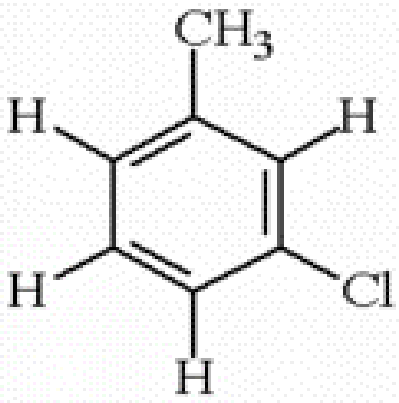
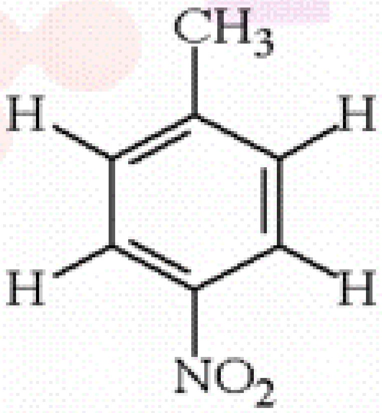


4-bromo-1,2-dimethylbenzene



1-chloro-3-methylbenzene *or*
3-chlorotoluene



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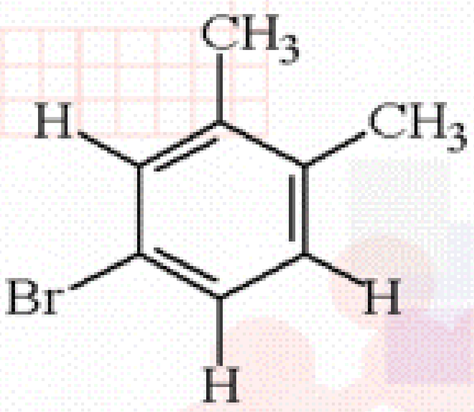
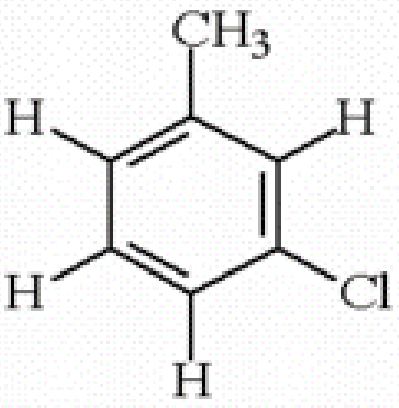
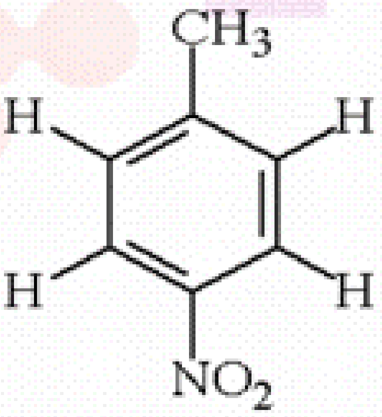

CH$_3$
CH$_3$
H
H
Br
H

4-bromo-1,2-dimethylbenzene



1-chloro-3-methylbenzene *or*
3-chlorotoluene


CH$_3$
H
H
H
H
NO$_2$

1-methyl-4-nitrobenzene *or*
4-nitrotoluene

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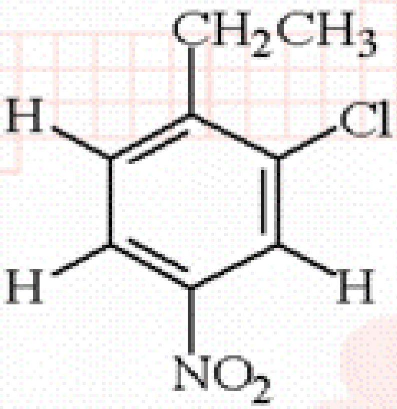
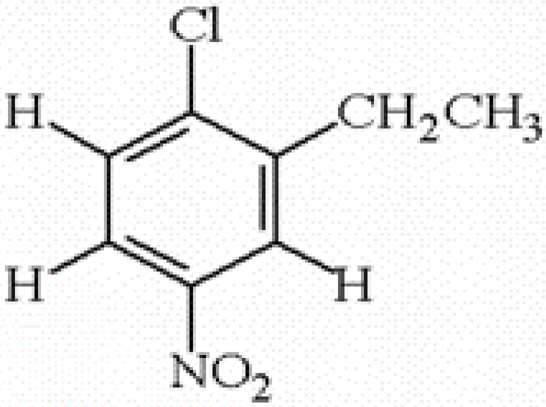
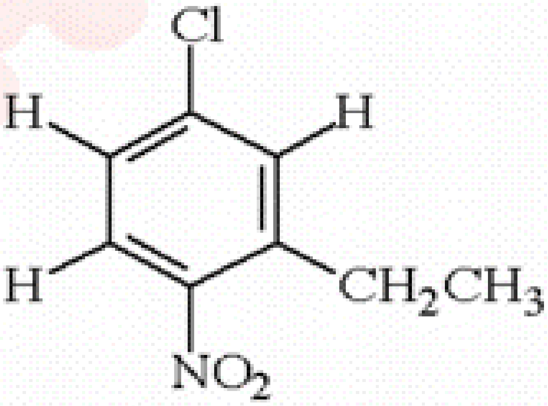
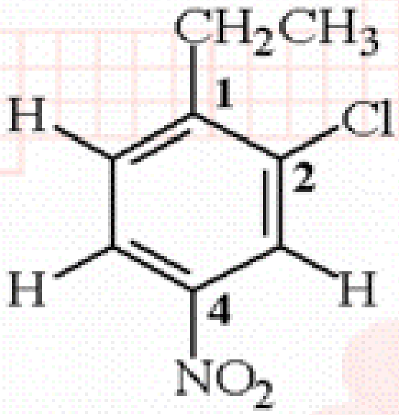

CH2CH3
H
Cl
H
H
NO2

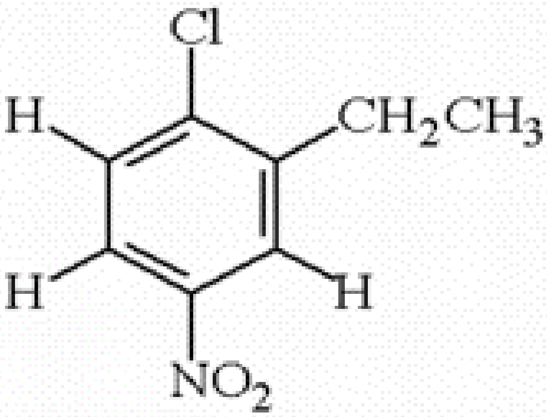

Cl
H
CH2CH3
H
H
NO2

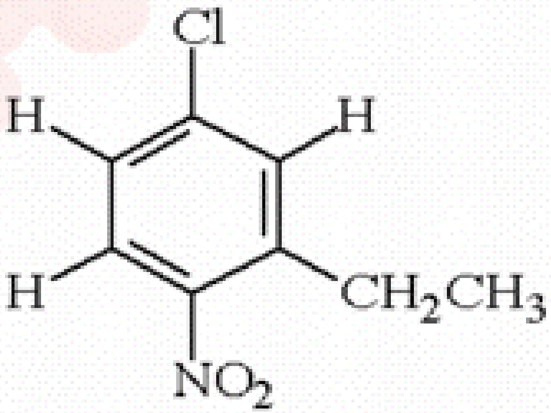

Cl
H
H
H
CH2CH3
NO2

سم المركبات التالية طبقا لقواعد أيوباك ؟

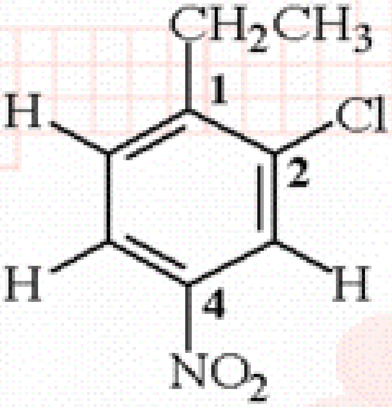

CH2CH3
H
1
Cl
2
H
H
4
NO2

2-chloro-1-ethyl-4-nitrobenzene

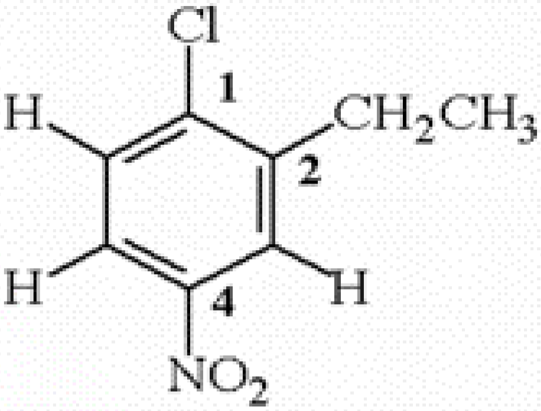

Cl
H
CH2CH3
H
H
NO2


Cl
H
H
H
CH2CH3
NO2

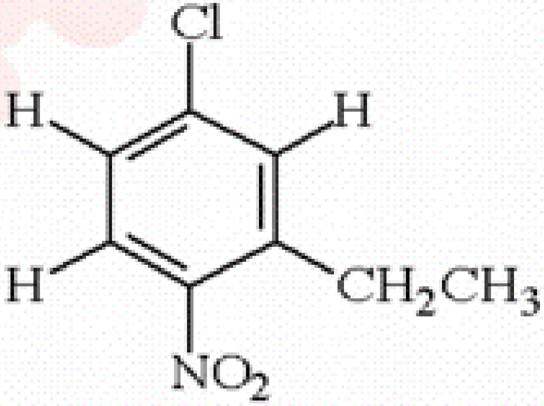
Organic Chemistry OnLine ©2000


CH2CH3
1
H
Cl
2
H
H
4
NO2

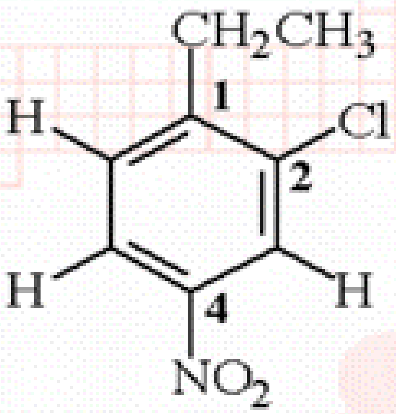
2-chloro-1-ethyl-4-nitrobenzene


Cl
1
H
CH2CH3
2
H
H
4
NO2

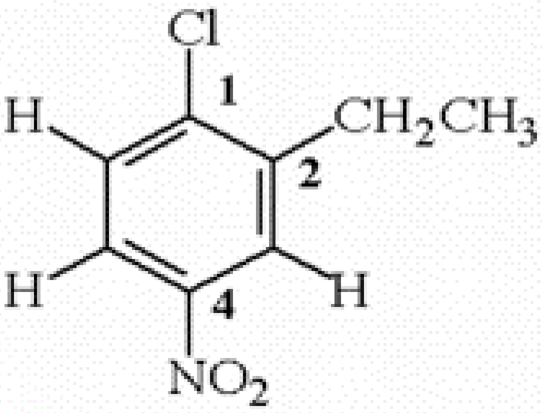
1-chloro-2-ethyl-4-nitrobenzene


Cl
H
H
H
CH2CH3
NO2

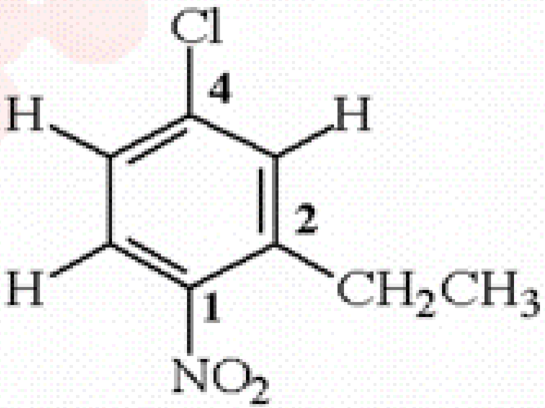
Organic Chemistry OnLine ©2000


CH2CH3
1
H
Cl
2
H
H
4
NO2

2-chloro-1-ethyl-4-nitrobenzene


Cl
1
H
CH2CH3
2
H
H
4
NO2

1-chloro-2-ethyl-4-nitrobenzene


Cl
4
H
H
2
H
CH2CH3
1
NO2

4-chloro-2-ethyl-1-nitrobenzene

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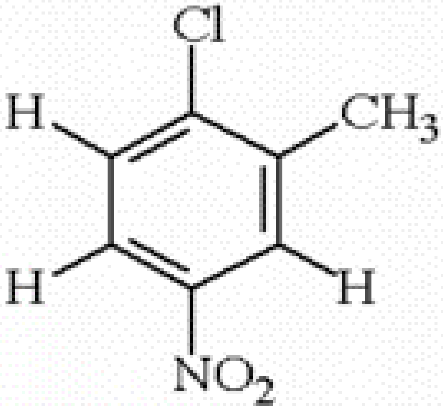
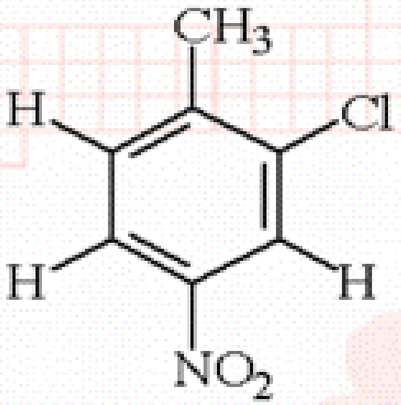
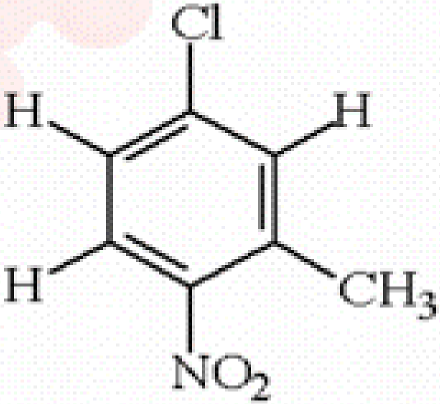
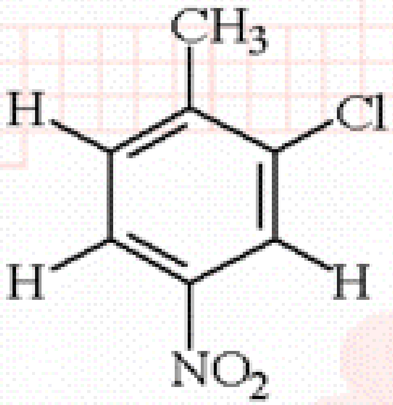

Cl
H
CH_3
H
H
NO_2

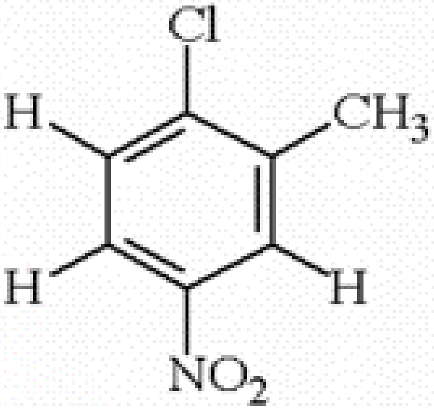

CH_3
H
Cl
H
H
NO_2

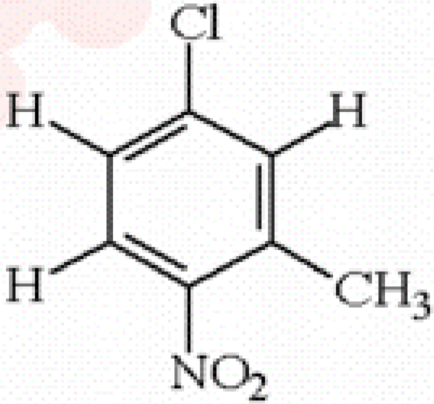

Cl
H
H
H
CH_3
NO_2

سم المركبات التالية كمشتقات للتولوين ؟

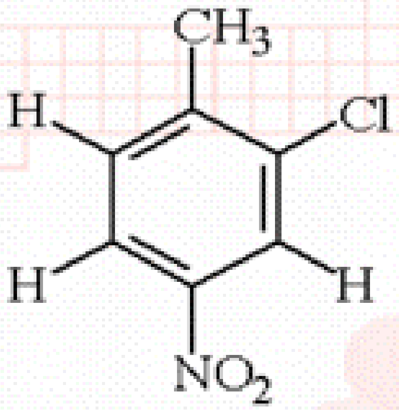

CH$_3$
H
Cl
H
H
NO$_2$

2-chloro-4-nitrotoluene

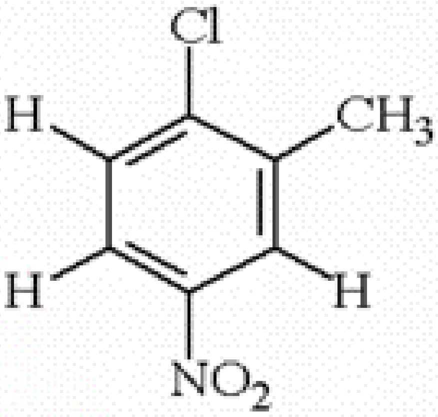

Cl
H
CH$_3$
H
H
NO$_2$


Cl
H
H
H
CH$_3$
NO$_2$

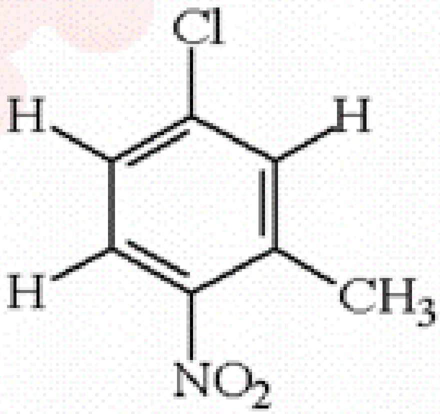
Organic Chemistry OnLine ©2000


CH3
H
Cl
H
H
NO2

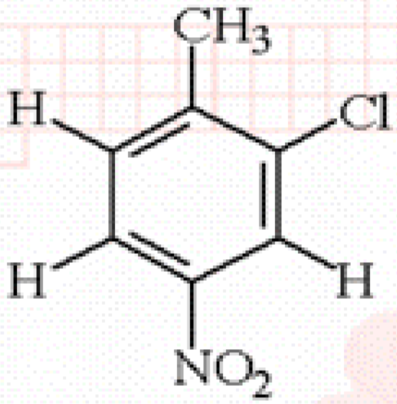
2-chloro-4-nitrotoluene


Cl
H
CH3
H
H
NO2

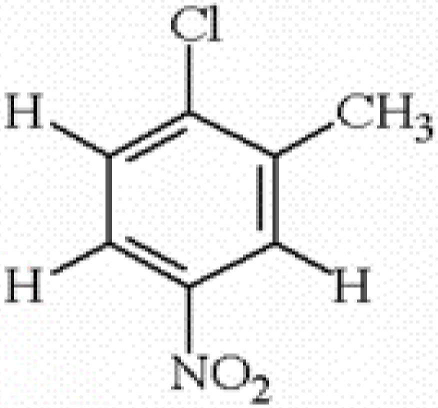
2-chloro-5-nitrotoluene


Cl
H
H
H
CH3
NO2

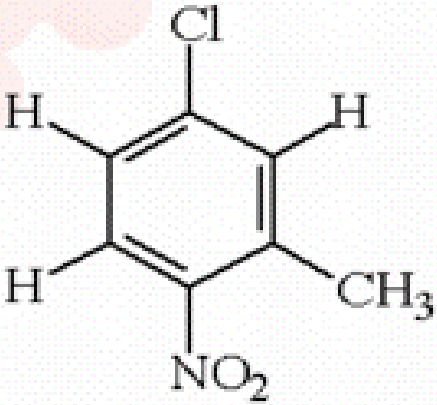
Organic Chemistry OnLine ©2000


CH_3
H
Cl
H
H
NO_2

2-chloro-4-nitrotoluene


Cl
H
CH_3
H
H
NO_2

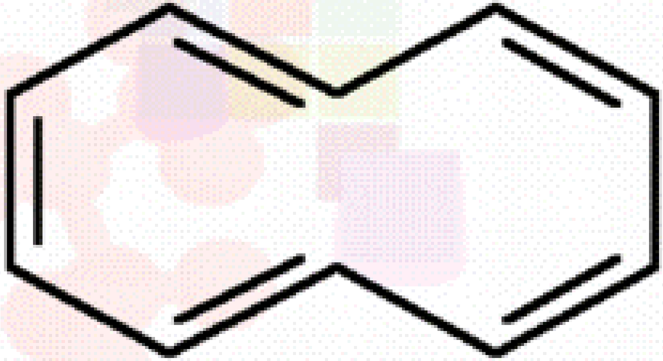
2-chloro-5-nitrotoluene


Cl
H
H
H
CH_3
NO_2

5-chloro-2-nitrotoluene

Organic Chemistry OnLine ©2000

Would you predict cyclodecapentaene to be an aromatic compound?

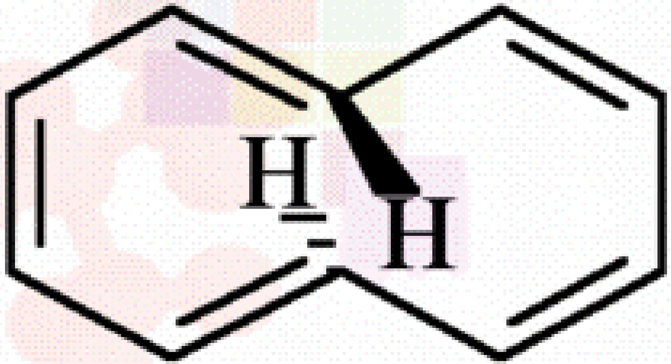


...consider the geometry of the two central hydrogens.

Cyclodecapentaene

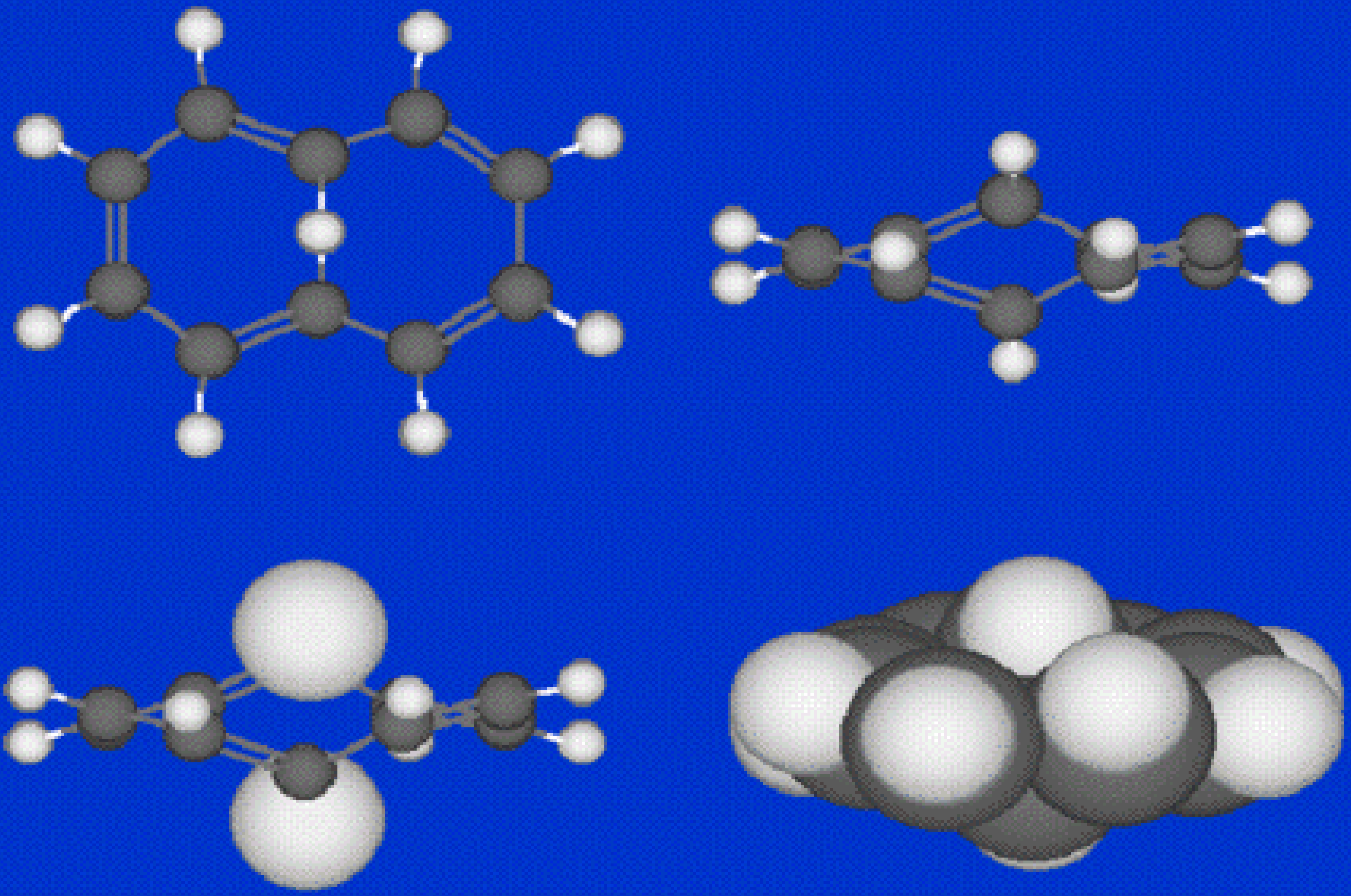
Organic Chemistry OnLine ©2000

Would you predict cyclodecapentaene to be an aromatic compound?



Cyclodecapentaene

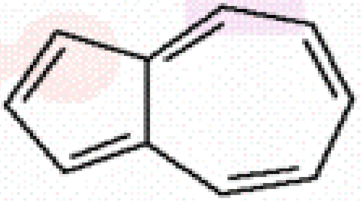
Organic Chemistry OnLine ©2000



Steric repulsion between the opposing hydrogens forces the π system out of planarity, therefore the molecule isnot aromatic.

Azulene, $C_{10}H_8$, is a deep blue hydrocarbon with a large dipole magnetic moment.

a. is azulene aromatic using the Hückel definition?
b. utilize resonance forms for azulene to explain the large dipole moment.



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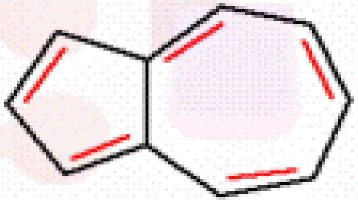
Azulene, $C_{10}H_8$, is a deep blue hydrocarbon with a large dipole magnetic moment.

a. is azulene aromatic using the Hückel definition?

b. utilize resonance forms for azulene to explain the large dipole moment.



10 π-electrons

Aromatic

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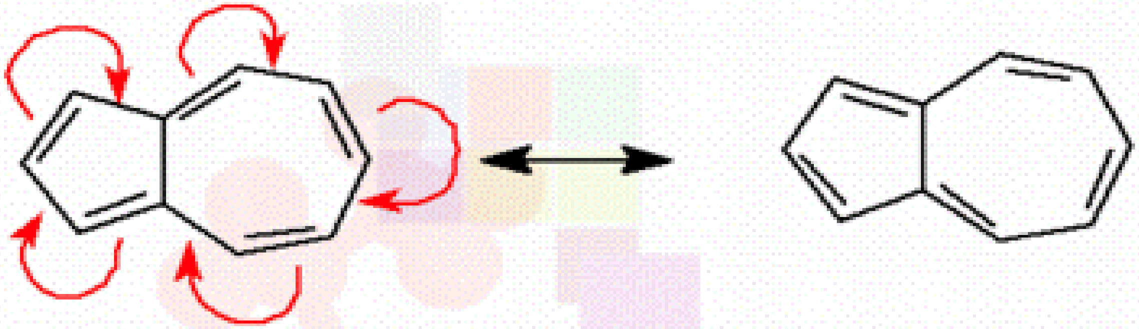
The two major (neutral) resonance forms forazulene...



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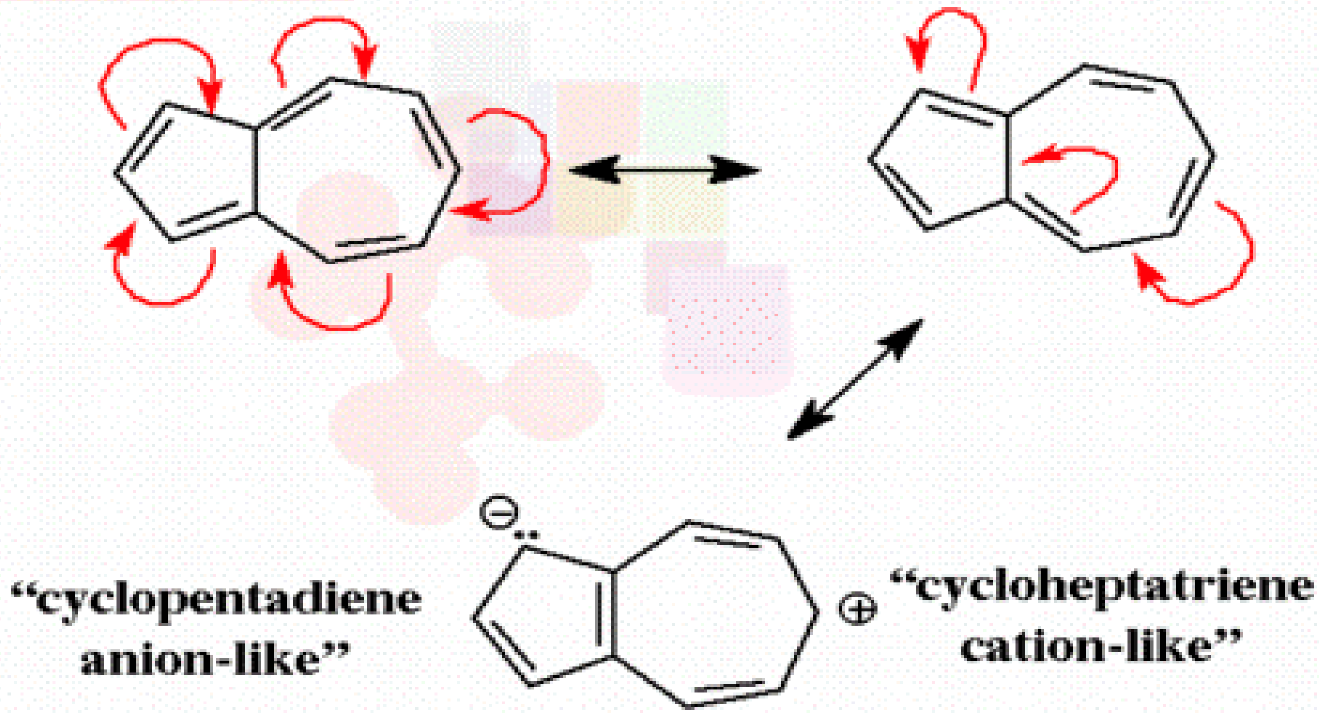
The two major (neutral) resonance forms forazulene...



“cyclopentadiene anion-like”

“cycloheptatriene cation-like”

...and the very stable Zwiterionic form.

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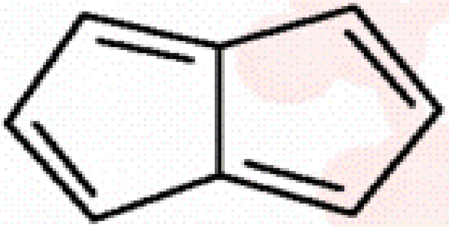
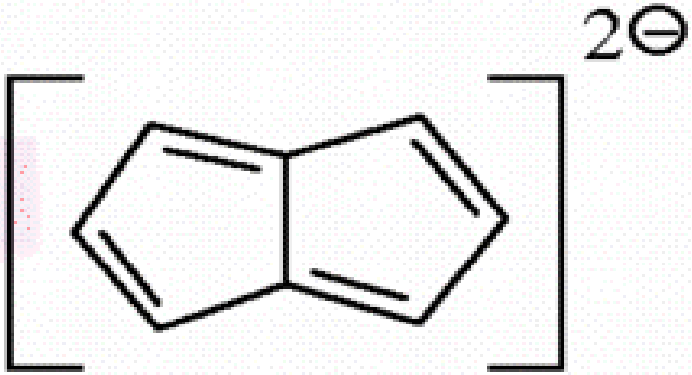
Account for the differences in reactivity betweenpentalene (an unknown compound) and the well-knownpentalene dianion:



very unstable



stable

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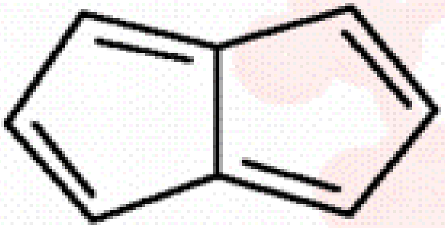
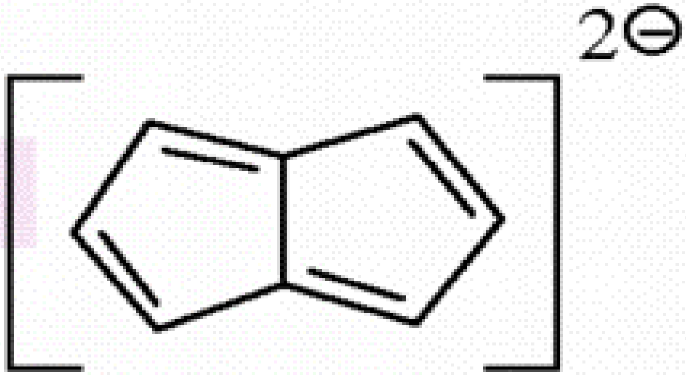


**8 π-electrons;
not aromatic**



**10 π-electrons;
aromatic**

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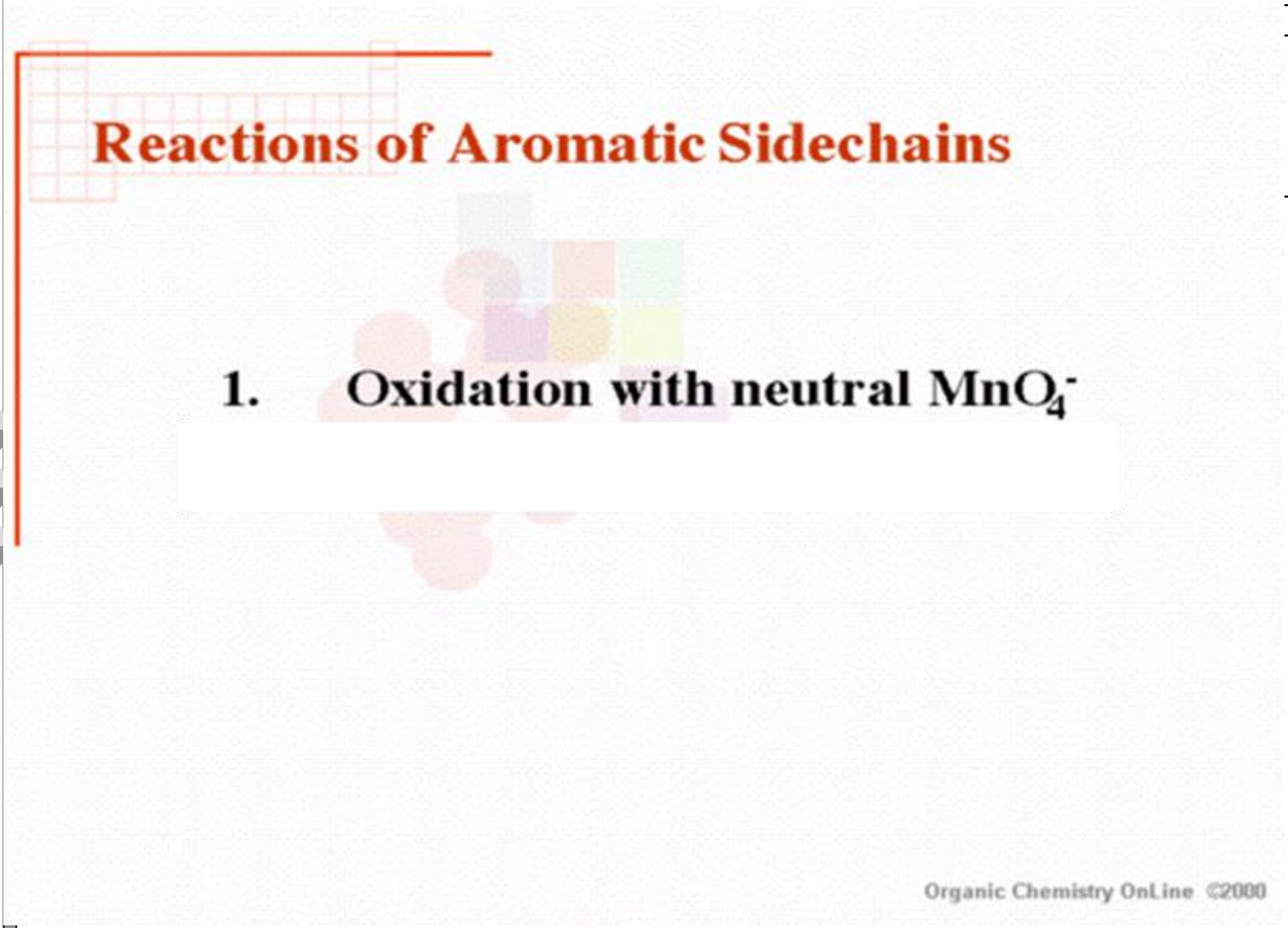

Reactions of Aromatic Sidechains

1. Oxidation with neutral MnO_4^-

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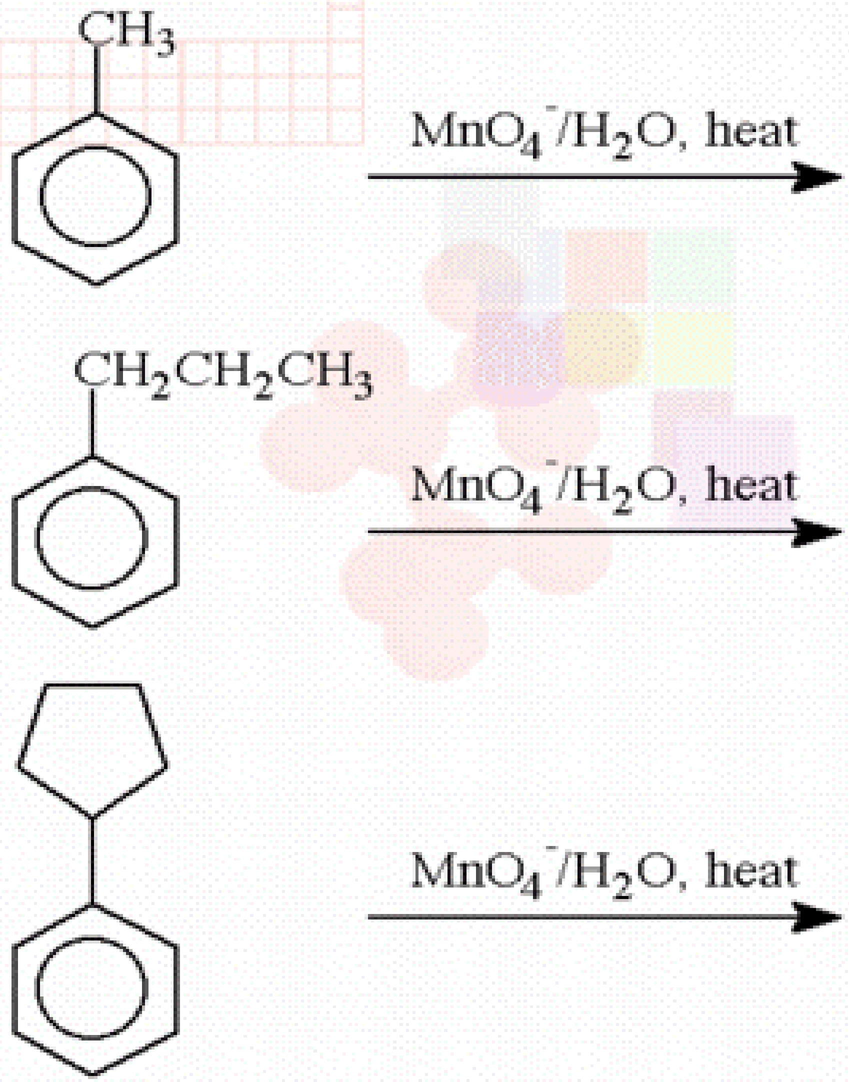
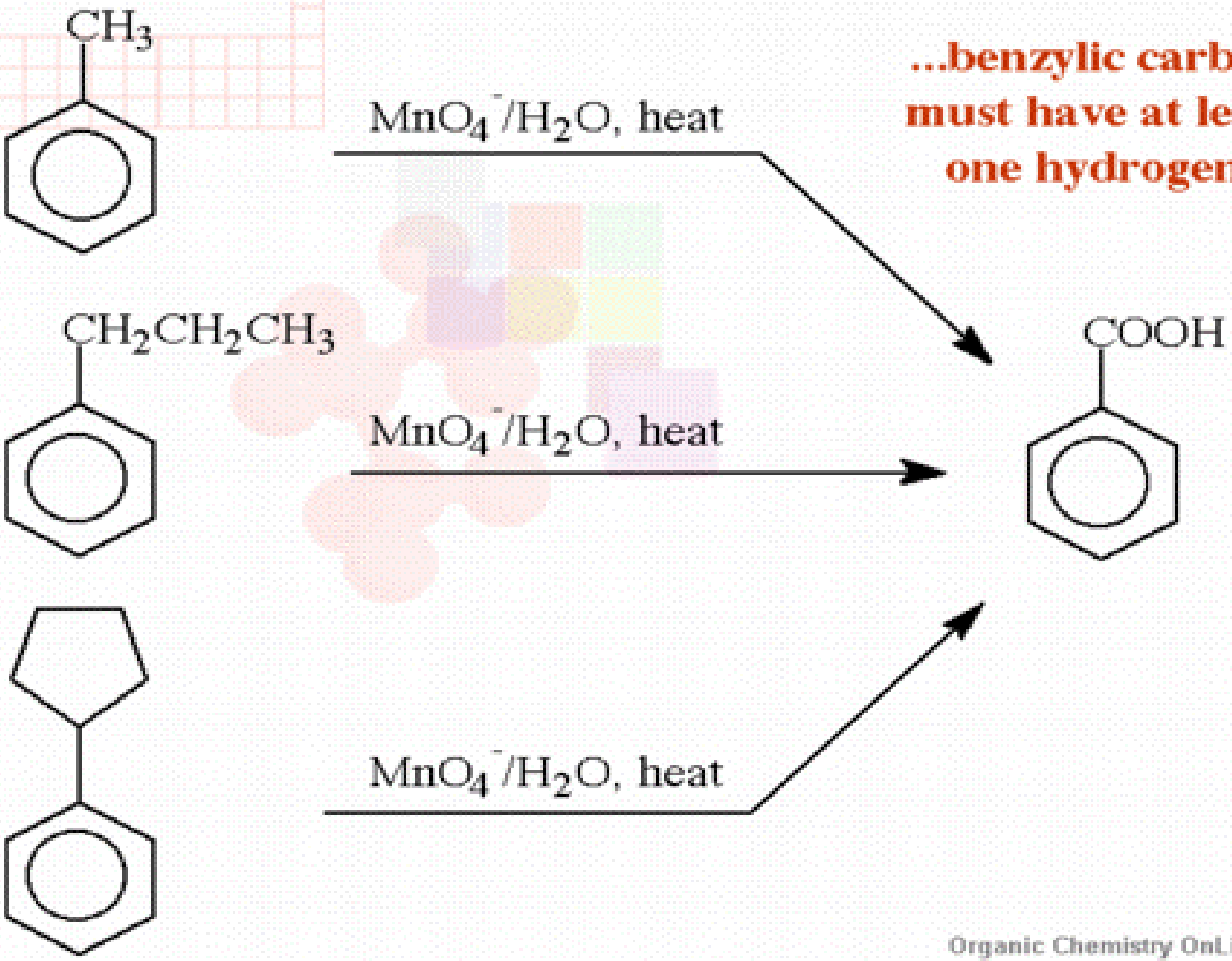
Oxidation with Neutral MnO_4^-

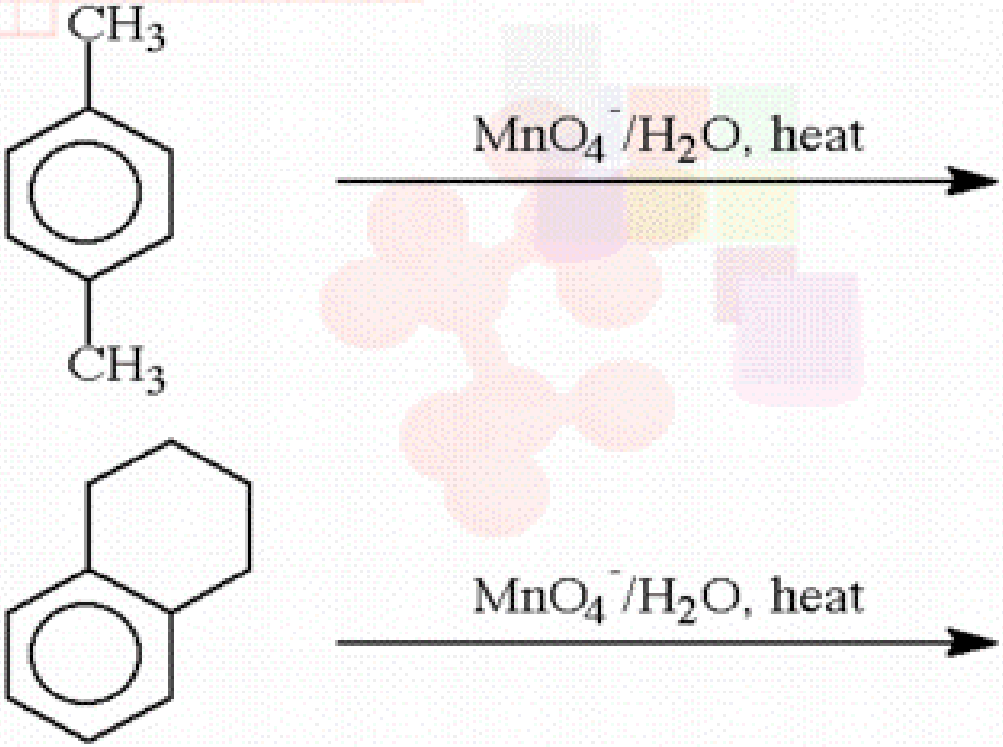

CH_3
MnO_4^-/H_2O, heat
$CH_2CH_2CH_3$
MnO_4^-/H_2O, heat
MnO_4^-/H_2O, heat

Organic Chemistry OnLine ©2000

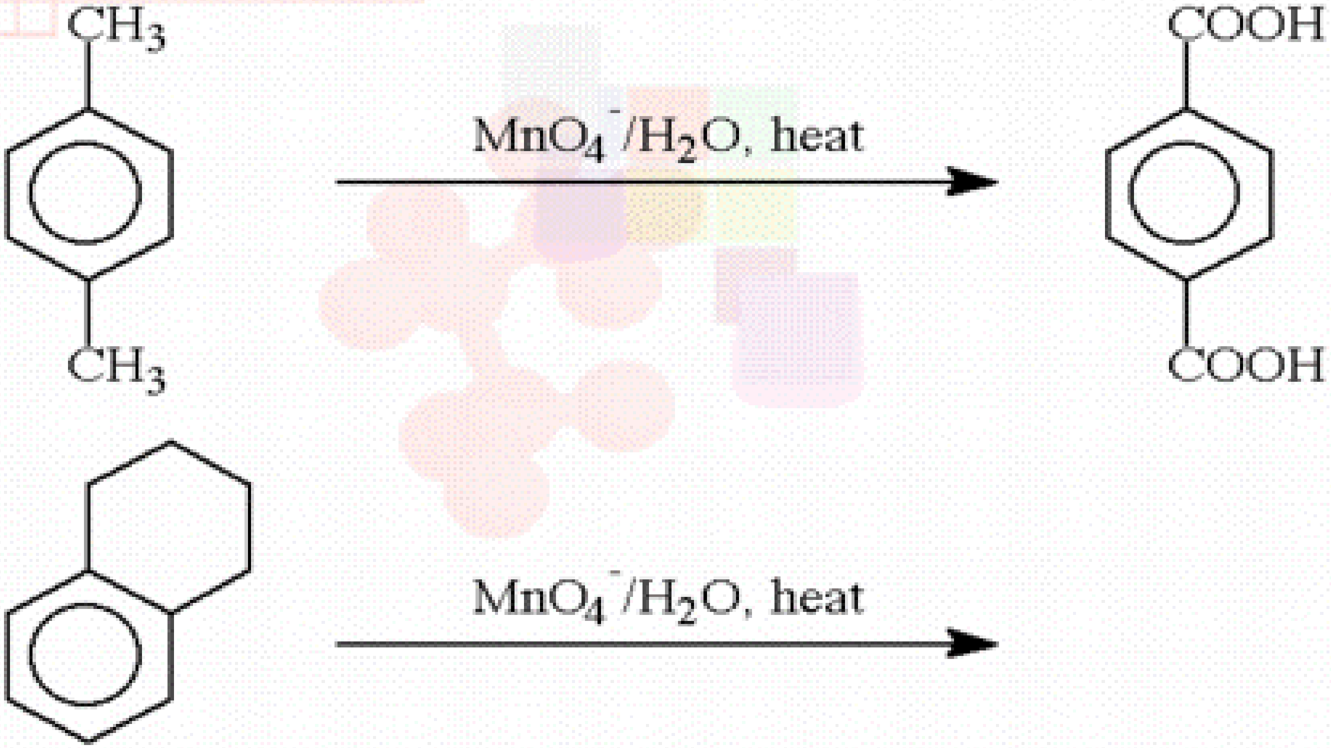

CH3
MnO4-/H2O, heat
CH2CH2CH3
MnO4-/H2O, heat
MnO4-/H2O, heat
COOH

...benzylic carbon must have at least one hydrogen.

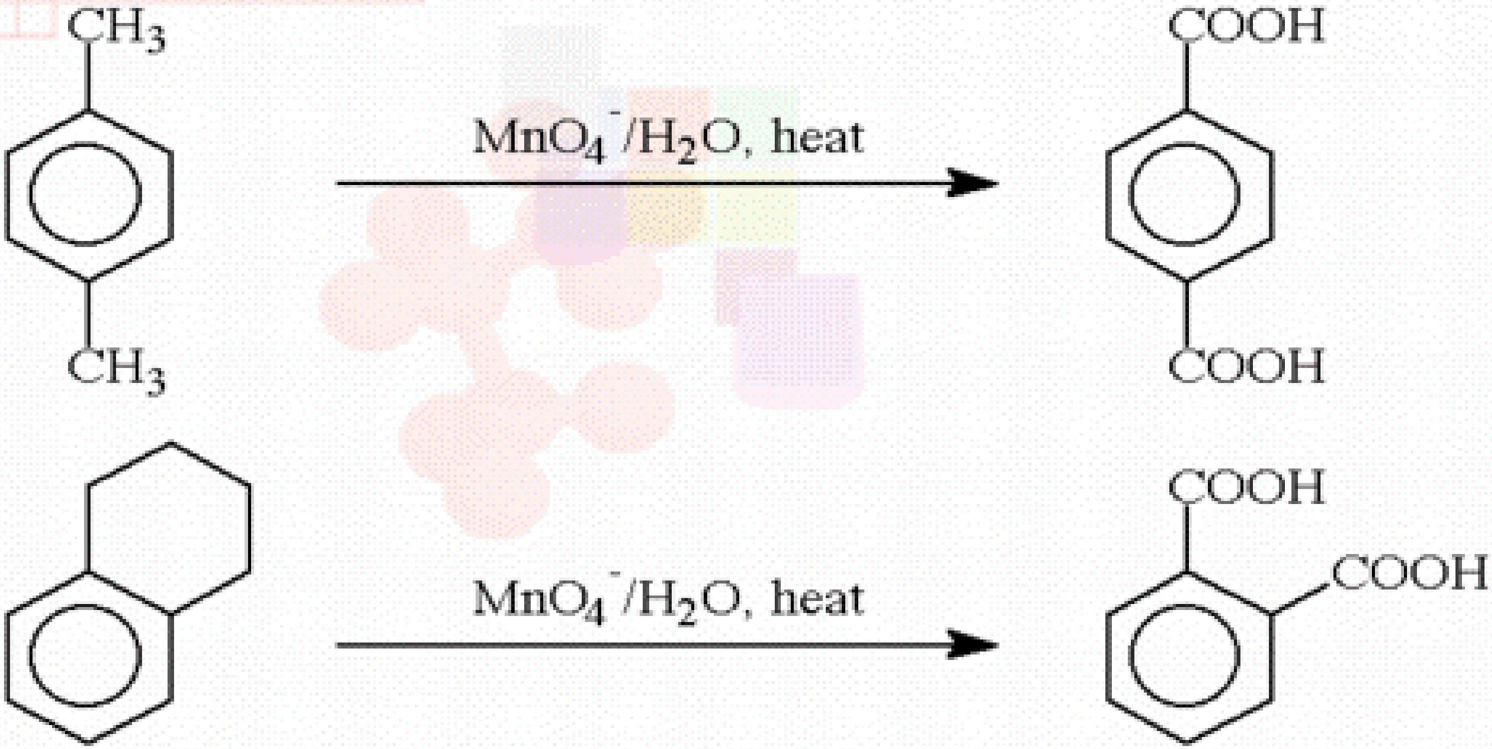
Organic Chemistry OnLine ©2000


CH3
CH3
MnO4-/H2O, heat
MnO4-/H2O, heat

Organic Chemistry OnLine ©2000

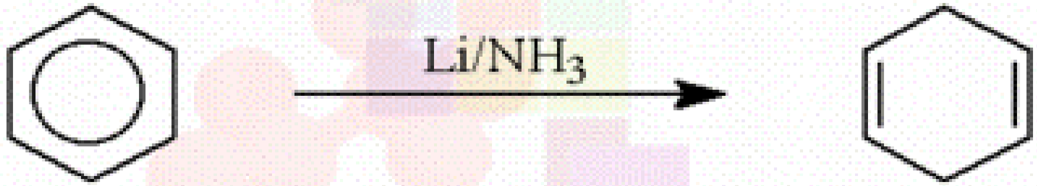

CH3
CH3
MnO4-/H2O, heat
COOH
COOH
MnO4-/H2O, heat

Organic Chemistry OnLine ©2000


CH3
CH3
MnO_4^-/H_2O, heat
COOH
COOH
MnO_4^-/H_2O, heat
COOH
COOH

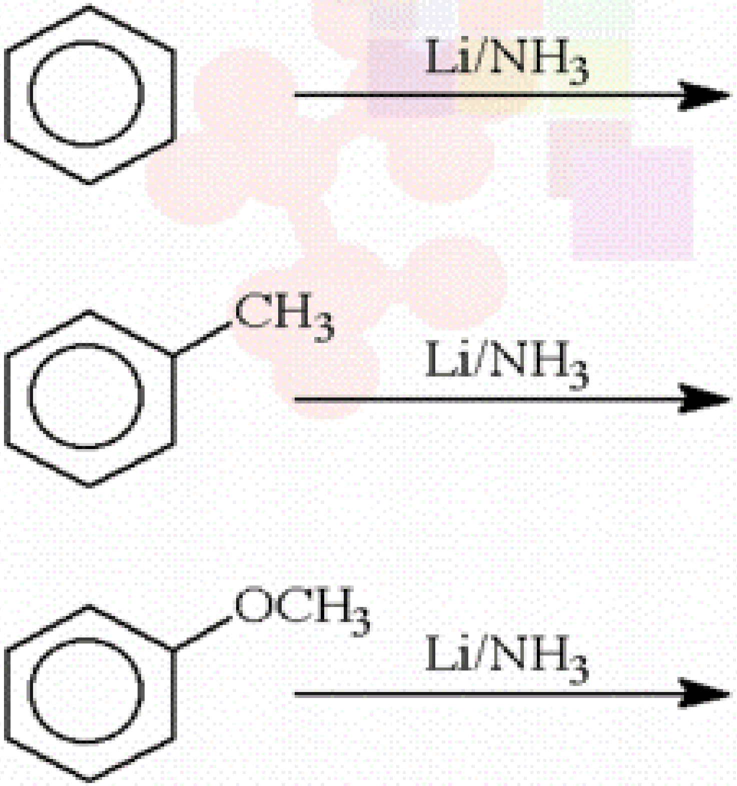
Organic Chemistry OnLine ©2000

Dissolving Metal Reduction of Benzene Derivatives
The Birch Reduction



Organic Chemistry OnLine ©2000

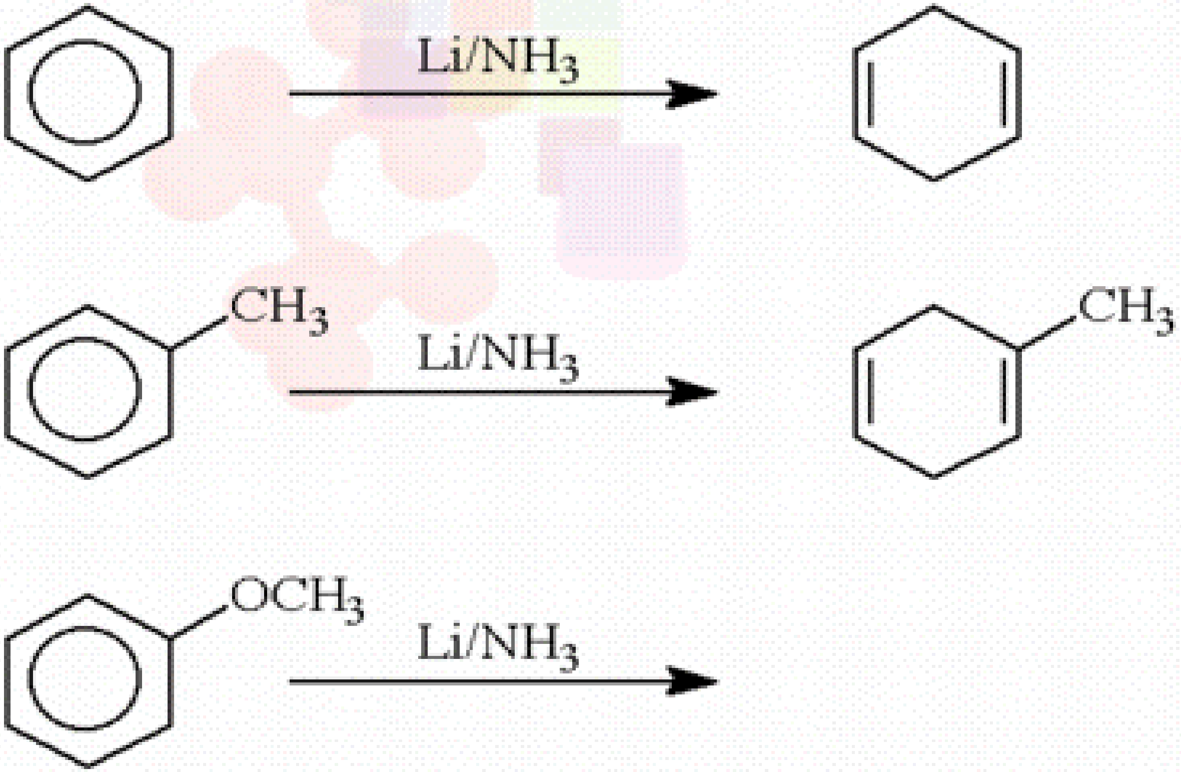
Dissolving Metal Reduction of Benzene Derivatives
The Birch Reduction



With substituted arenes, the Birch Reduction will proceed to place the double bond on a ring carbon which is attached to electron donating substituents...

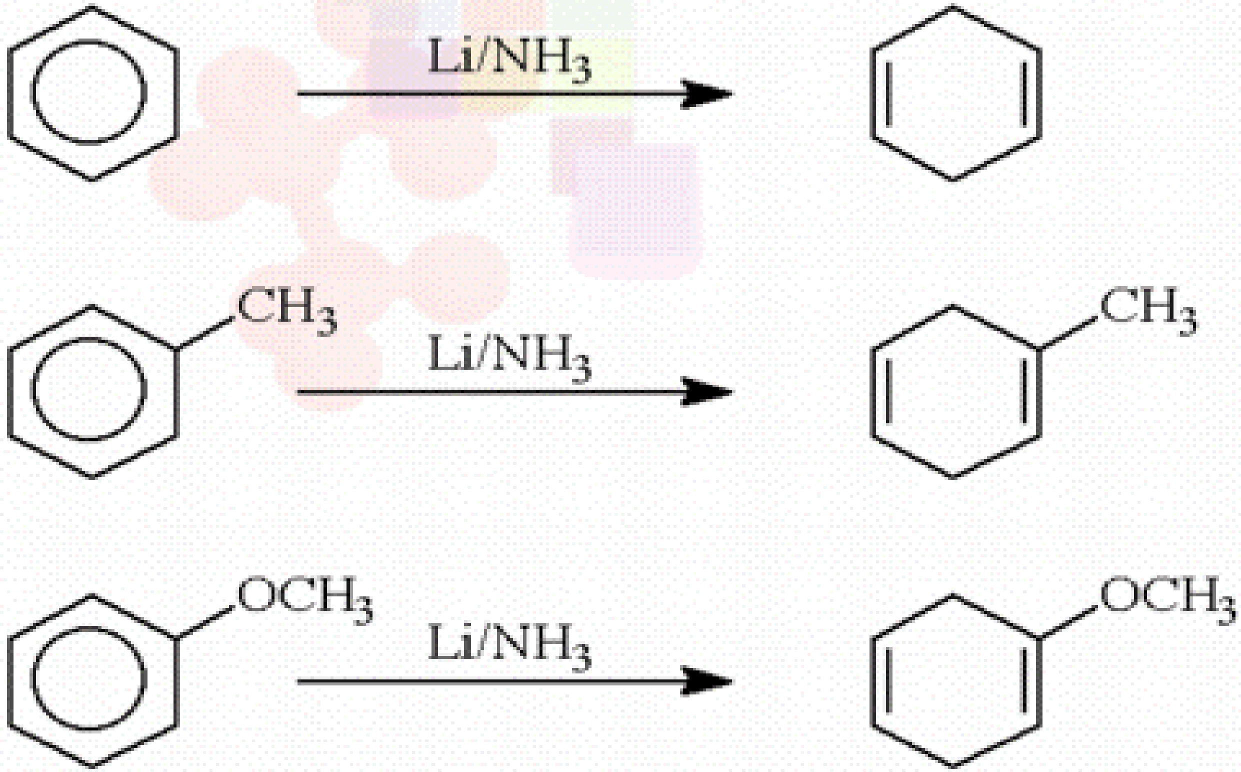
Organic Chemistry OnLine ©2000

Dissolving Metal Reduction of Benzene Derivatives
The Birch Reduction


Li/NH$_3$
CH$_3$
Li/NH$_3$
CH$_3$
OCH$_3$
Li/NH$_3$

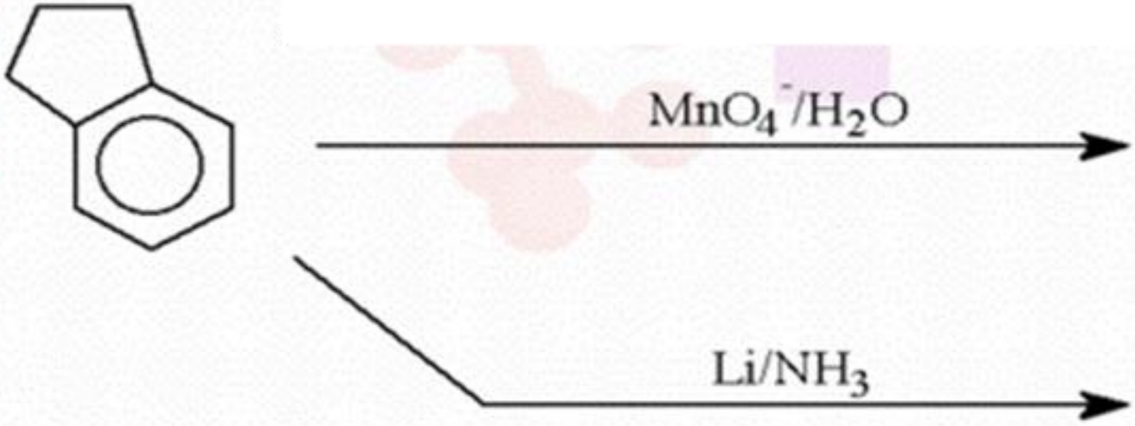
Organic Chemistry Online ©2000

Dissolving Metal Reduction of Benzene Derivatives
The Birch Reduction


Li/NH$_3$
CH$_3$
Li/NH$_3$
CH$_3$
OCH$_3$
Li/NH$_3$
OCH$_3$

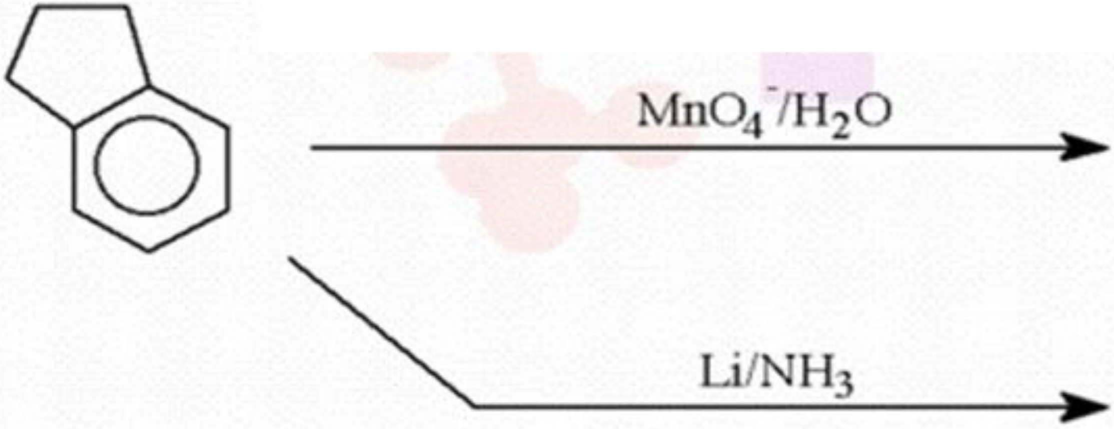
Organic Chemistry OnLine ©2000

Predict the products of the following reactions.


MnO_4^-/H_2O
Li/NH_3

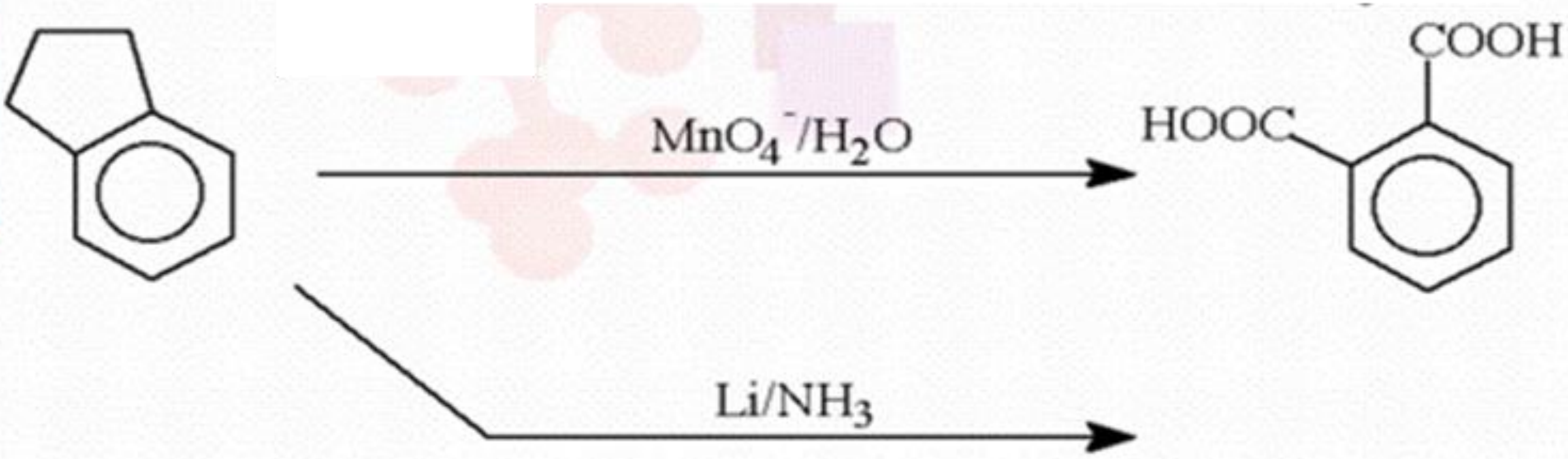
Organic Chemistry OnLine ©2000

Predict the products of the following reactions.


MnO4-/H2O
Li/NH3

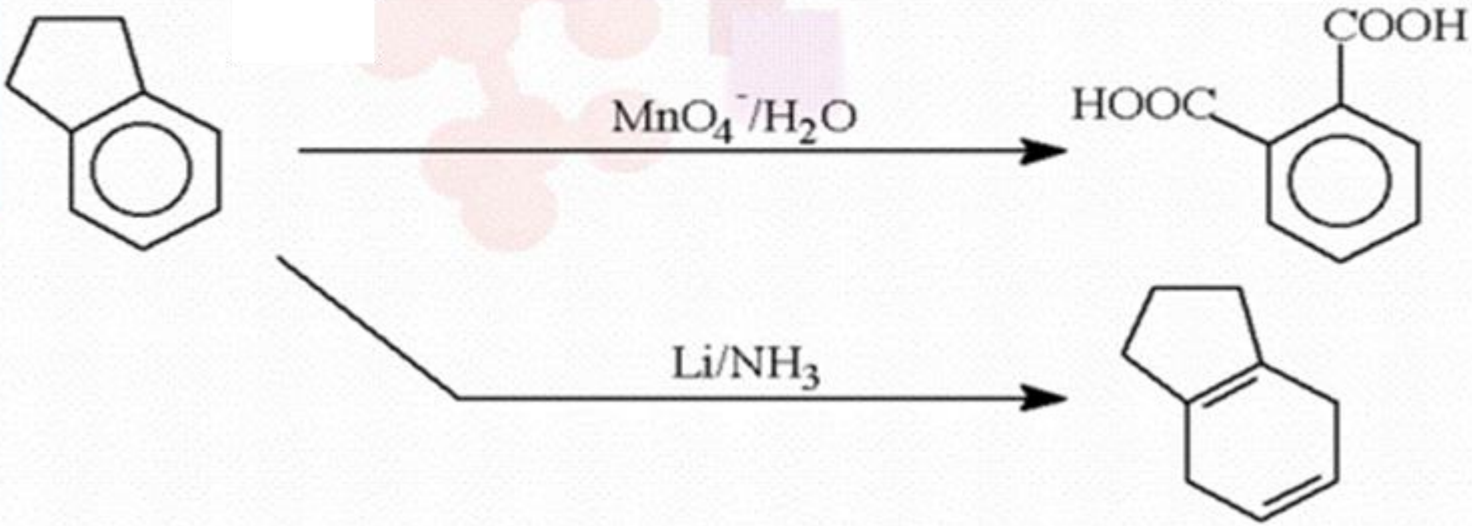
Organic Chemistry OnLine ©2000

Predict the products of the following reactions.


MnO_4^-/H_2O
HOOC
COOH
Li/NH_3

Organic Chemistry OnLine ©2000

Predict the products of the following reactions.

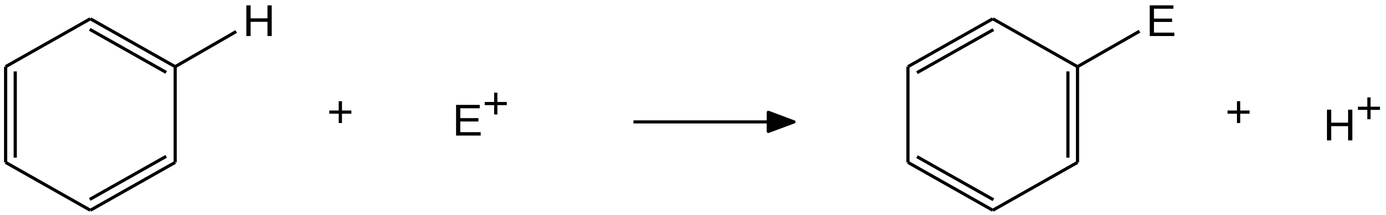

MnO_4^-/H_2O
COOH
HOOC
Li/NH_3

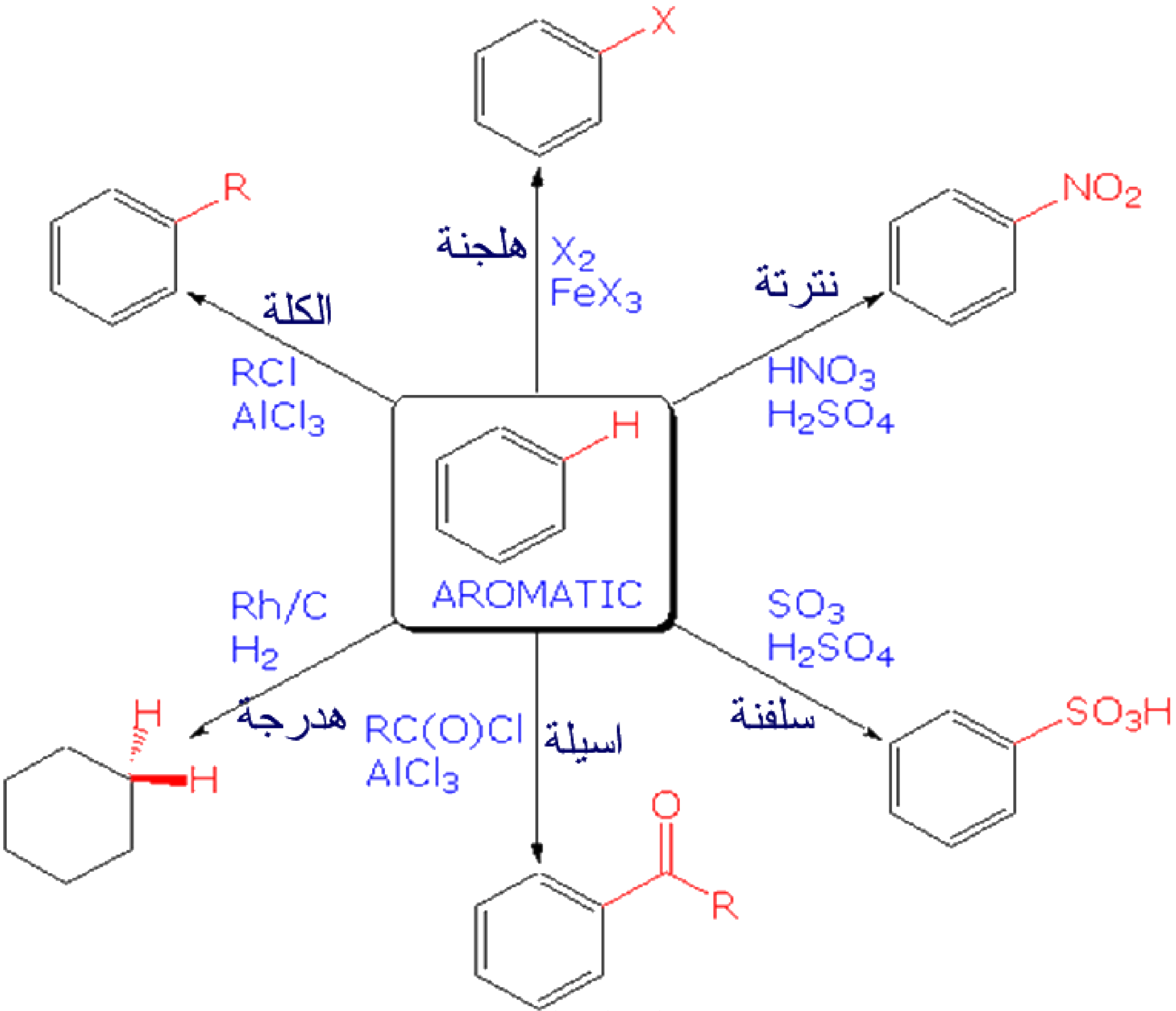
Organic Chemistry OnLine ©2000

تفاعلات الإحلال محل

نوع الإحلال محل " الكتروفيلي "

- الإلكتروفيل يحل محل ذرة الهيدروجين في الحلقة البنزينية



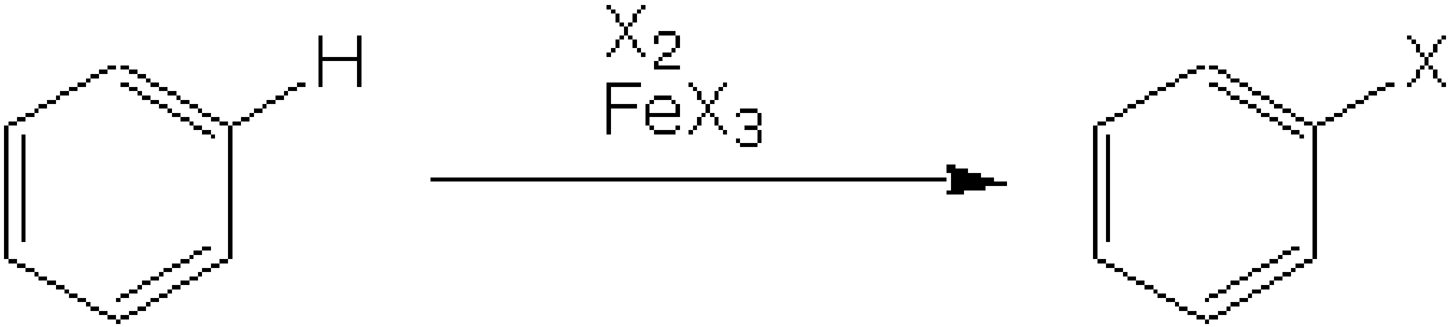

X
هلجنة
X_2
FeX_3
R
الكلة
RCl
$AlCl_3$
NO_2
نترتة
HNO_3
H_2SO_4
H
AROMATIC
Rh/C
H_2
هدرجة
H
H
SO_3
H_2SO_4
سلفنة
SO_3H
RC(O)Cl
$AlCl_3$
اسيلة
O
R

تفاعلات الهلجنة

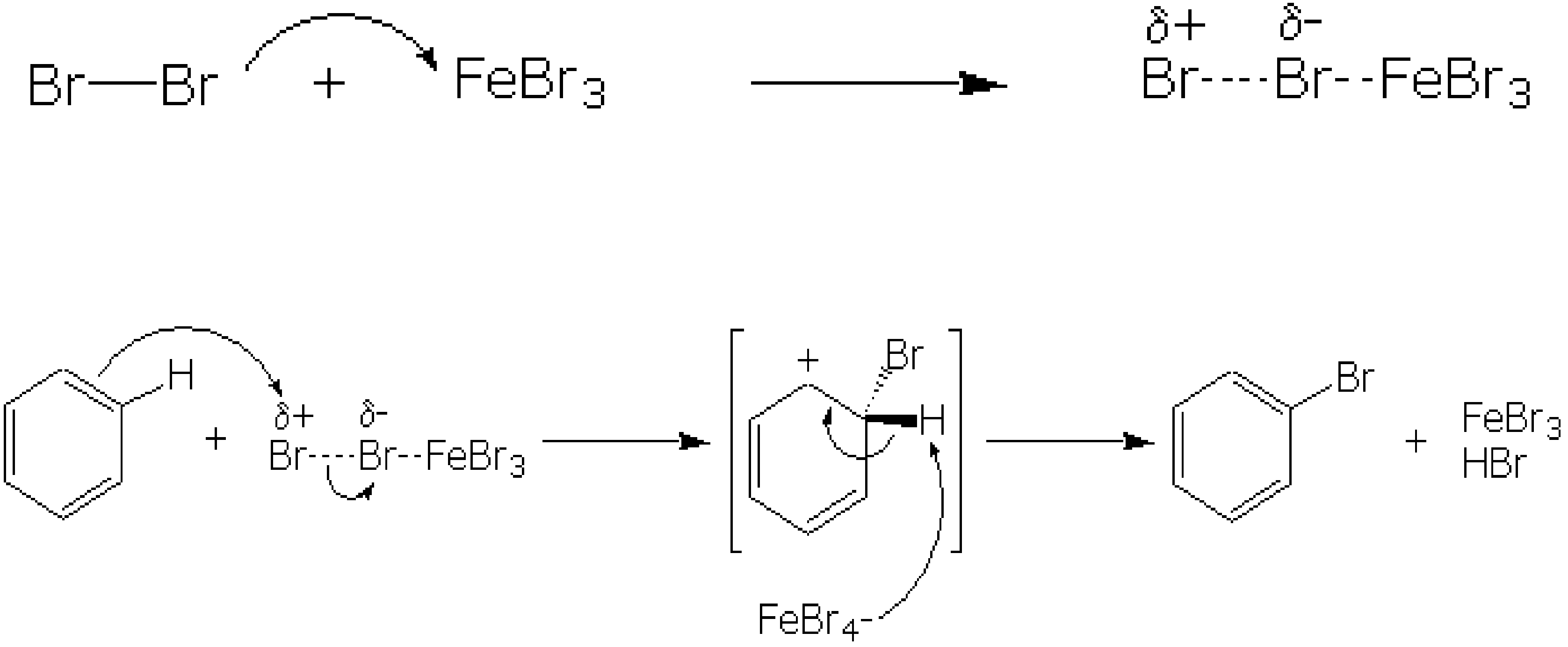
معدن الحديد أو هاليد الحديد يستخدم كعامل مساعد

وهي تساعد الهالوجين ليسلك سلوك الإلكتروفيل (E^+)

$$Cl_2 + FeCl_3 \rightarrow \text{“ } Cl^+ \text{ ”}$$



ميكانيكية التفاعل

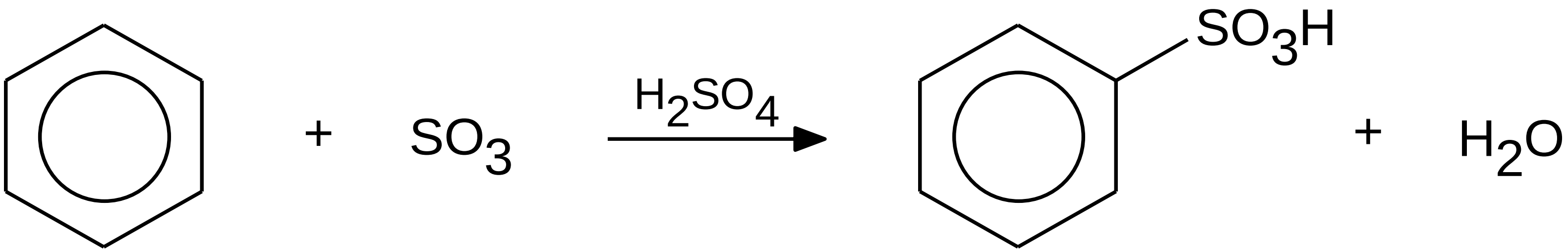

Br—Br + FeBr3 → δ+ δ- Br----Br--FeBr3
H
+
δ+ δ-
Br----Br--FeBr3
+
Br
H
FeBr4-
Br
+
FeBr3
HBr

تفاعل السلفنة

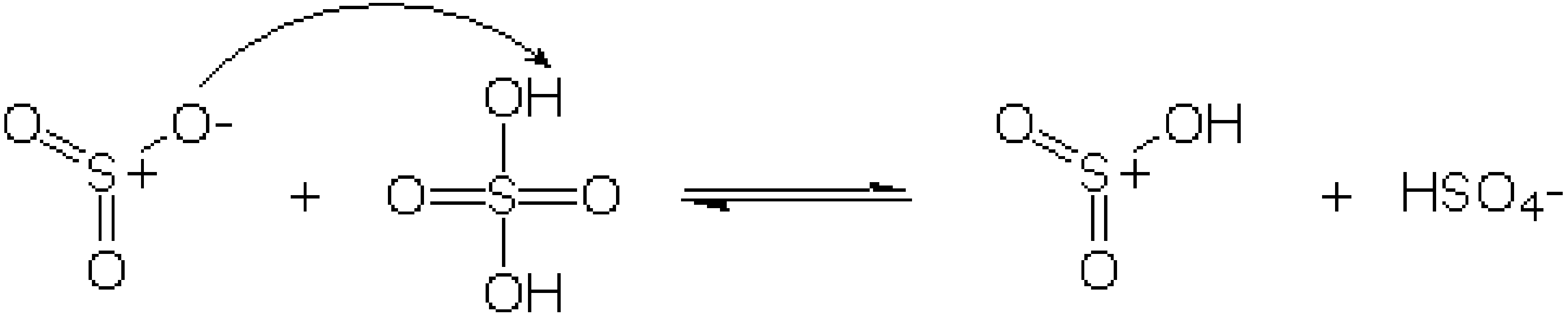
أبخرة حمض الكبريتيك المشبعة بـ SO_3 في H_2SO_4.

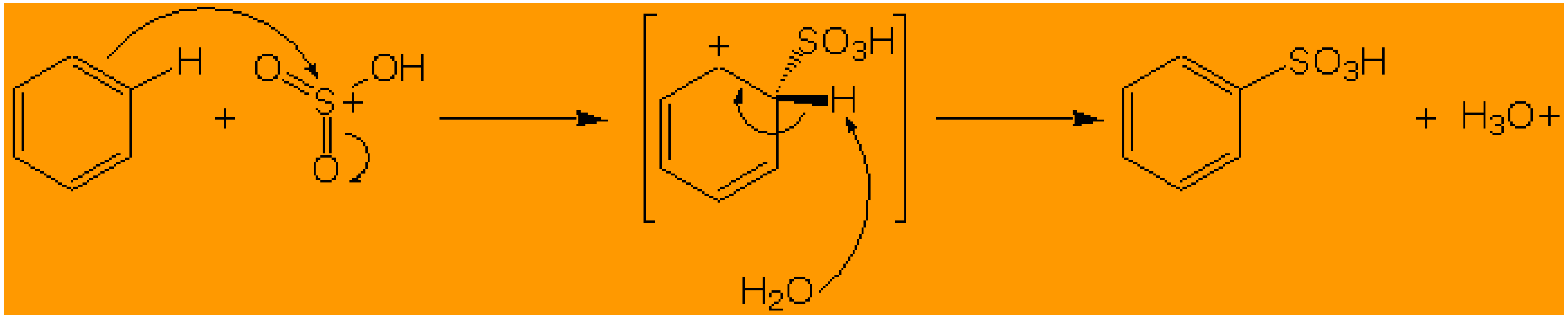
حمض الكبريتيك يلعب دور العامل المساعد لتكوين SO_3H^+ كإلكتروفيل جيد

$$SO_3 + H_2SO_4 \rightarrow \text{“}SO_3H^+\text{”}$$



ميكانيكية تفاعل السلفنة

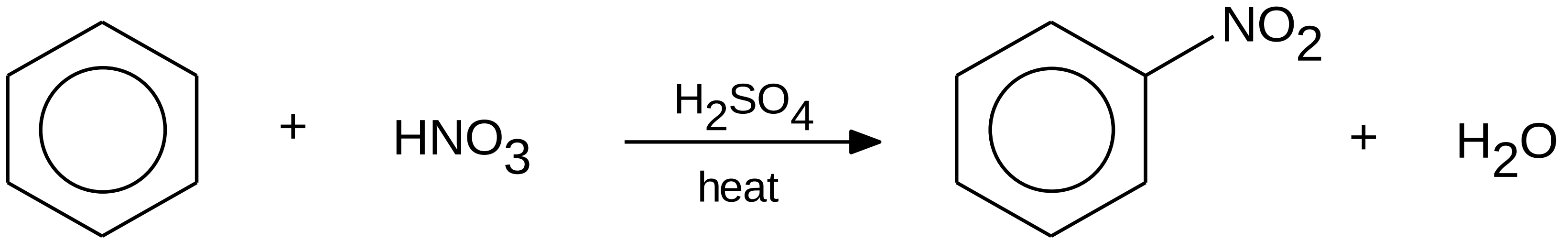

O
S+
O-
O
+
OH
O
S
O
OH
O
S+
OH
O
+ HSO4-


H
+
O
S+
OH
O
+
SO3H
H
H2O
SO3H
+ H3O+

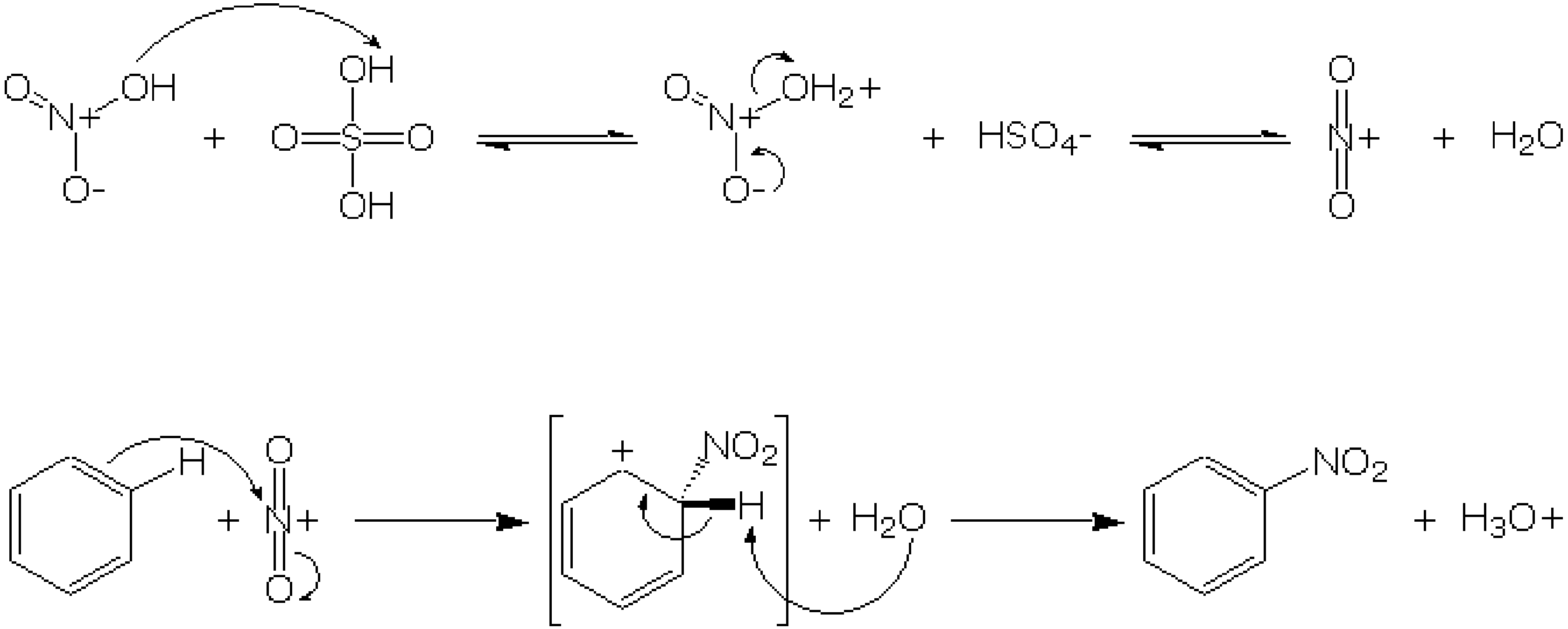
تفاعل النترتة Nitration

حمض النيتريك في حمض الكبريتيك لإنتاج الكتروفيل

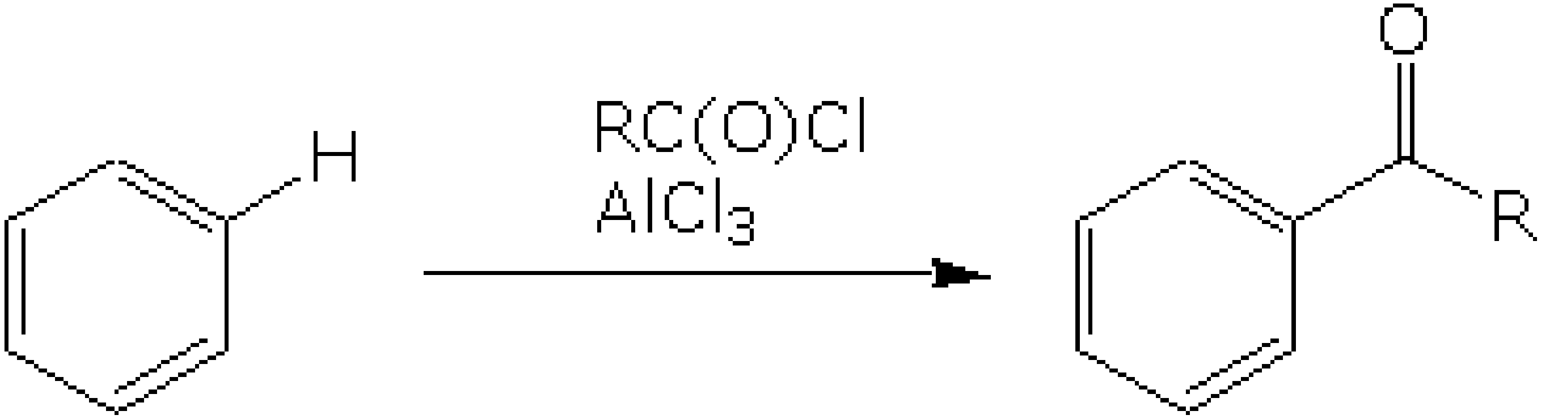
ثاني اكسيد النيتروجين NO_2^+


+
HNO3
H2SO4
heat
NO2
+
H2O

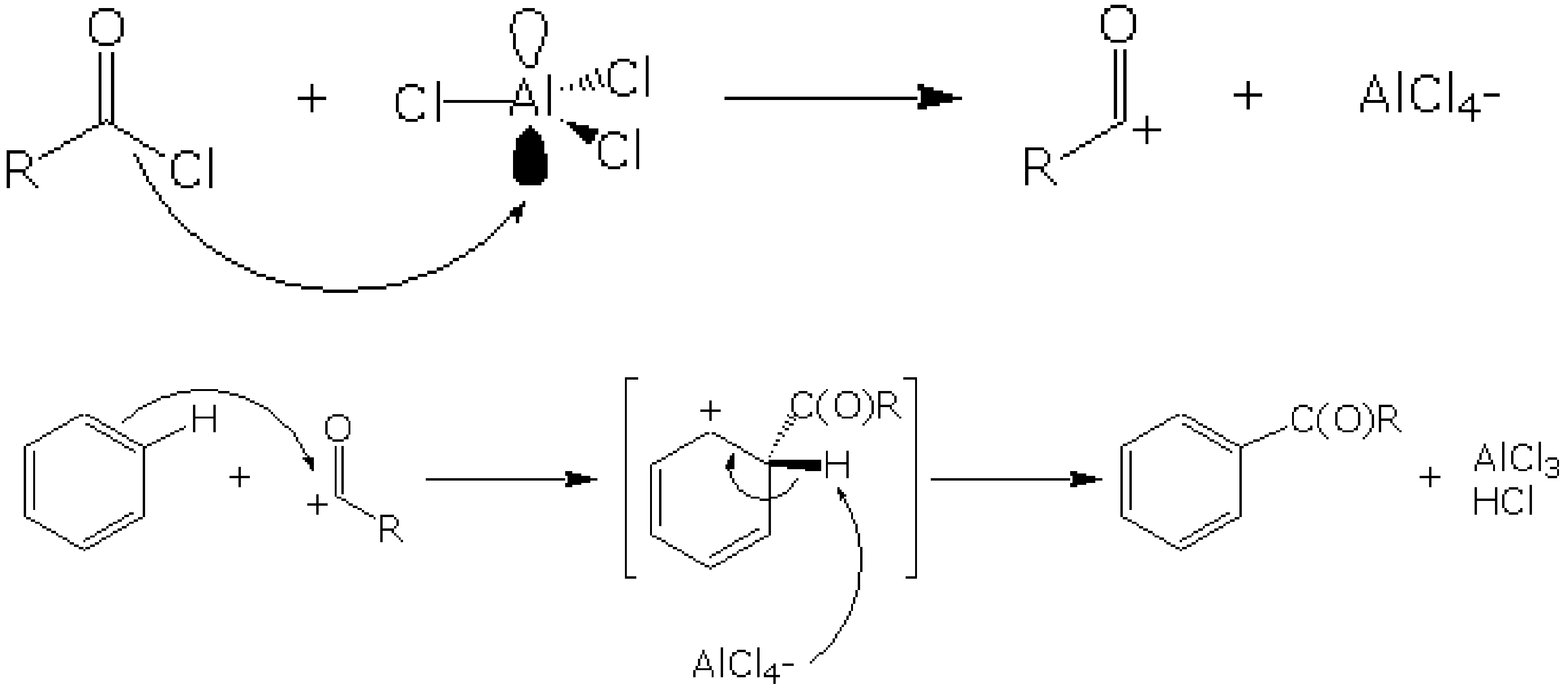
ميكانيكية تفاعل النترتة


O
N+
OH
O-
+
OH
O
S
O
OH
O
N+
OH2+
O-
+ HSO4-
O
N+
O
+ H2O
H
+
O
N+
O
+
NO2
H
+ H2O
NO2
+ H3O+

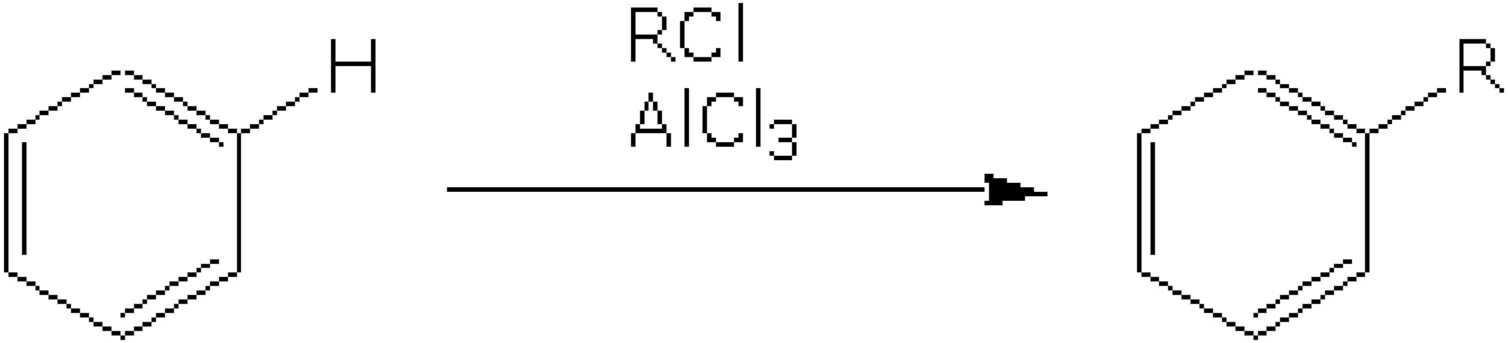
تفاعل الأسايل Acylation


H
RC(O)Cl
AlCl₃
O
R

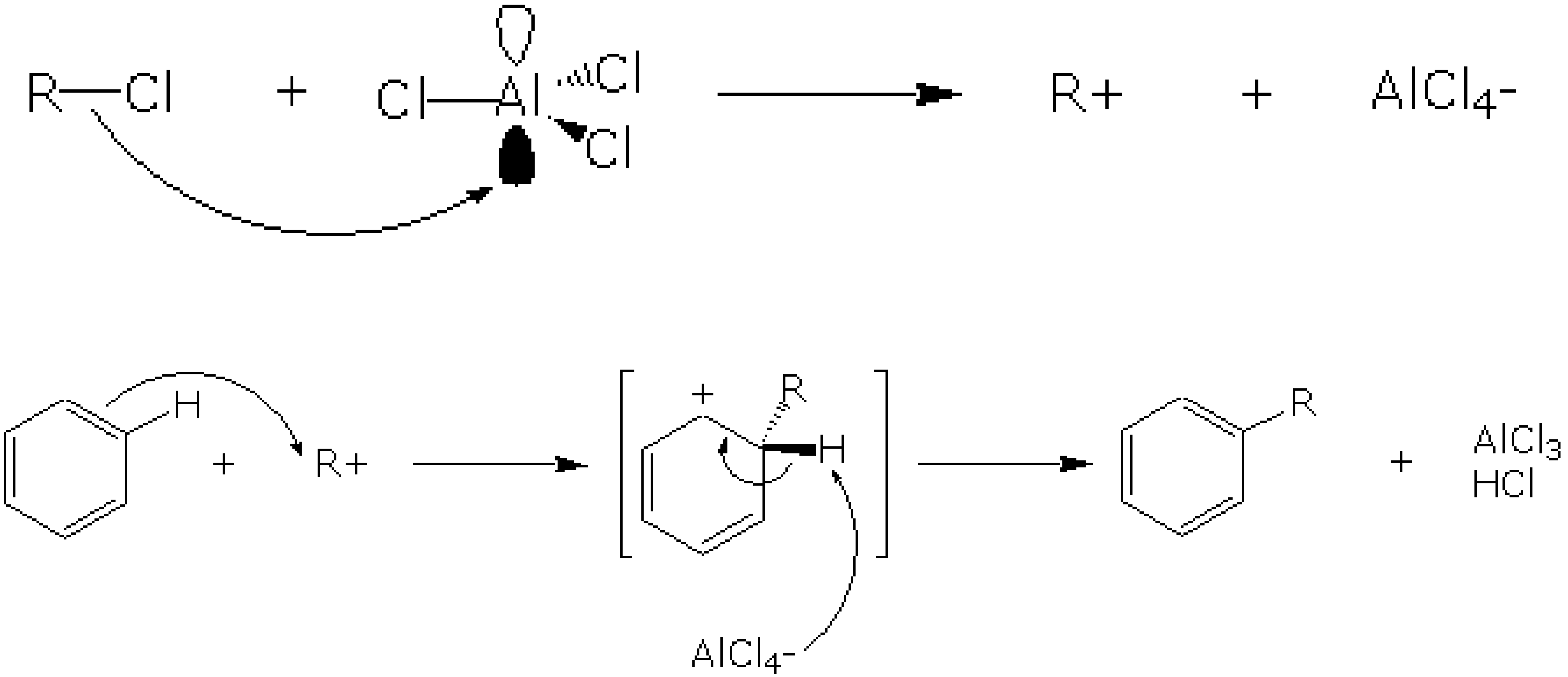
ميكانيكية تفاعل الأسايل


O
R
Cl
+
Cl
Al
Cl
Cl
O
R
+
+
$AlCl_4^-$
H
+
O
+
R
+
C(O)R
H
$AlCl_4^-$
C(O)R
+
$AlCl_3$
HCl

تفاعل الألكلة Alkylation


H
RCl
$AlCl_3$
R

ميكانيكية تفاعل الألكلة


R—Cl
+
Cl—Al
Cl
Cl
R+
+
$AlCl_4^-$
H
+
R+
+
R
H
$AlCl_4^-$
R
+
$AlCl_3$
HCl