شيمي فيزيك آلي

(مبانی مکانیسم واکنشهای آلی)

جی.میلتون هریس
کارل.سی .ومسر

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دکتر مهدي بکاولي

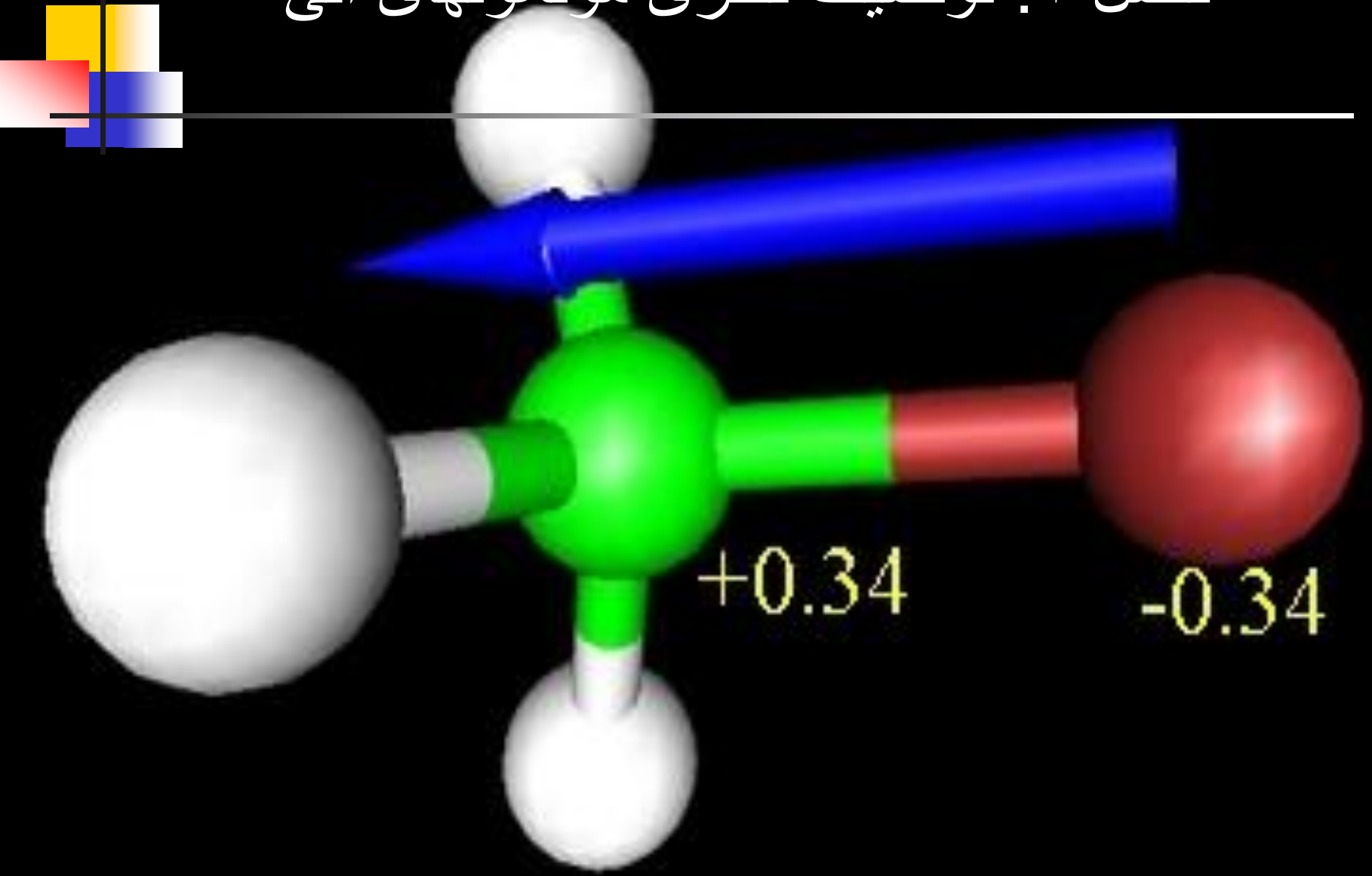
نام درس: شيمي فيزيك آلي

تعداد واحد :۳ واحد

مولف : جي. ميلتون هريس- كارل.سي.ومسر

تهيه كننده : مجيد حليمي دستيار علمی مركز بجنورد

فصل ۱: توصیف نظری مولکولهای آلی

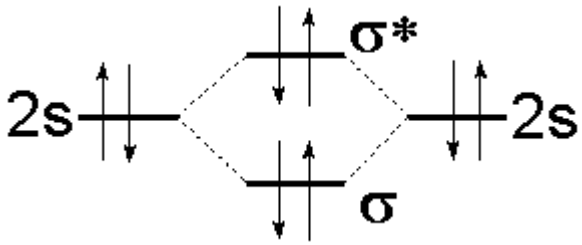


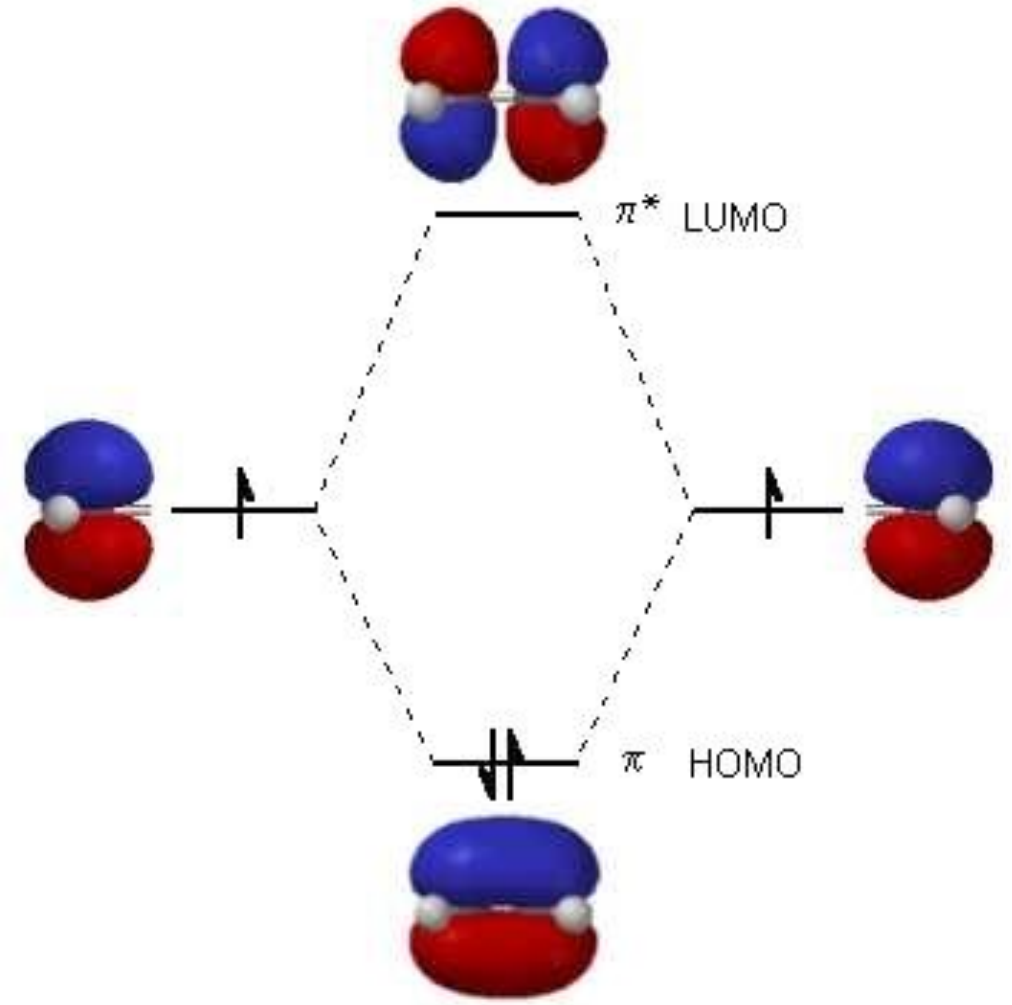
هدفهای کلي :

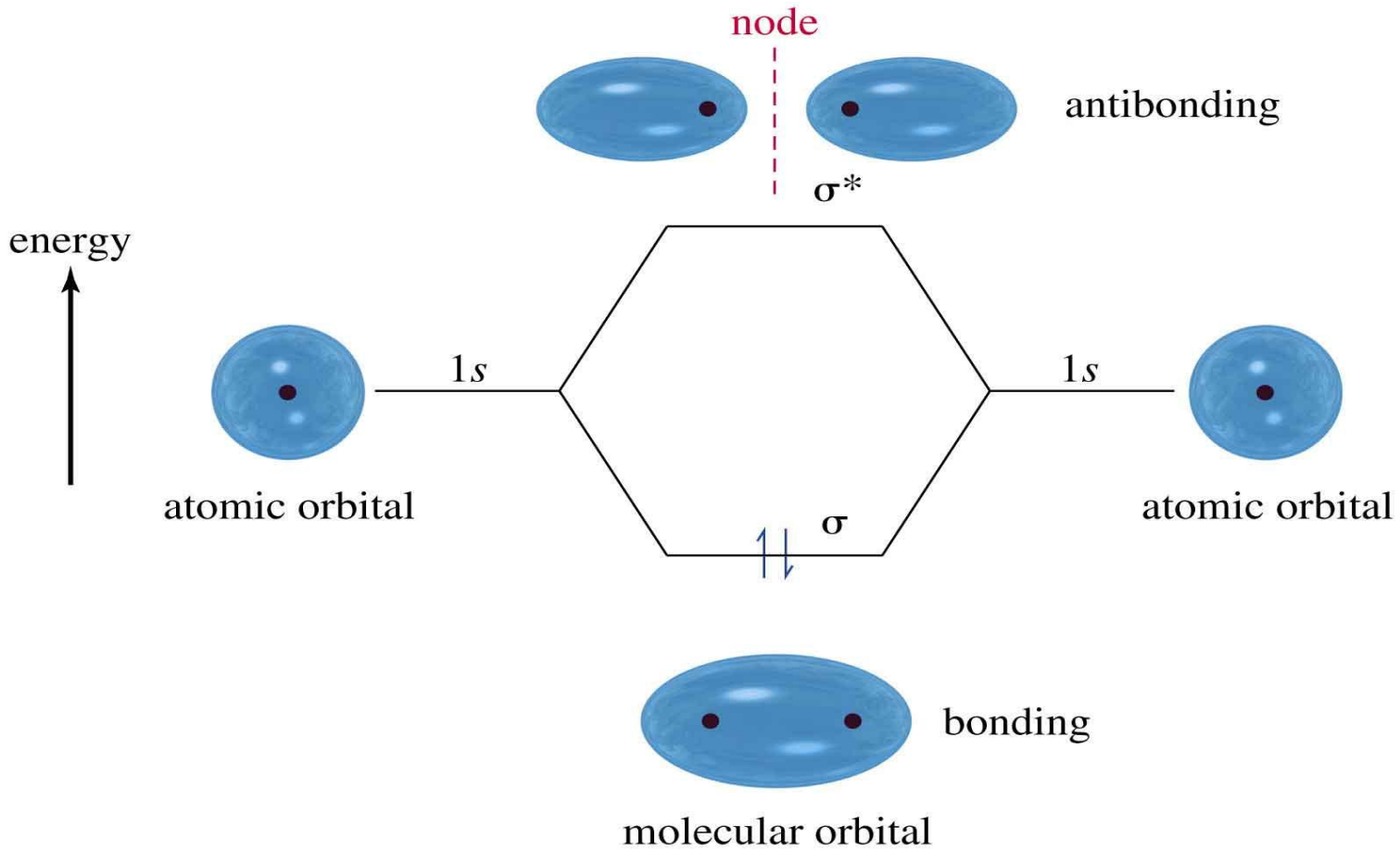
در این مبحث دانشجویان با توجه به مطالب شیمی کوانتوم ، مبحث اوربیتال مولکولی را منطبق با معادلات بکار رفته در شیمی کوانتوم (معادله شرودینگر) فرا گرفته و برای مولکولهای بزرگتر انرژی سیستم را محاسبه می کنند .

نظريه اوربيتال مولكولي:

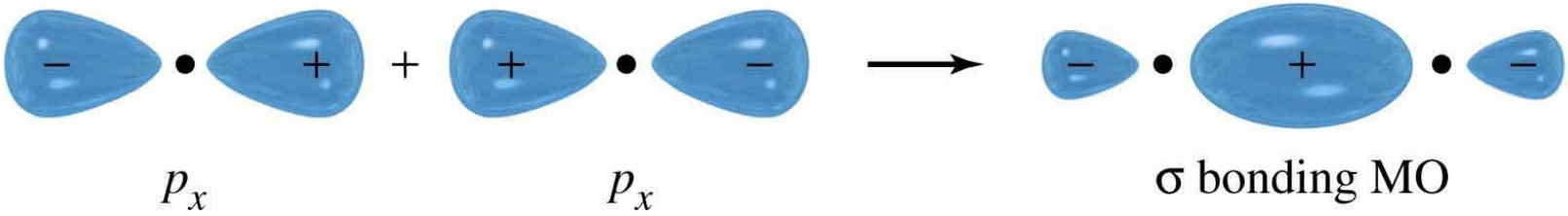
از همپوشاني اوربيتالهاي اتمي , اوربيتالهاي مولكولي به وجود مي آيد اين اوربيتالها وضعيت الكترونها را در يك محيط مولكولي كه تحت تاثير بيش از يك هسته هستند , توصيف مي كنند.



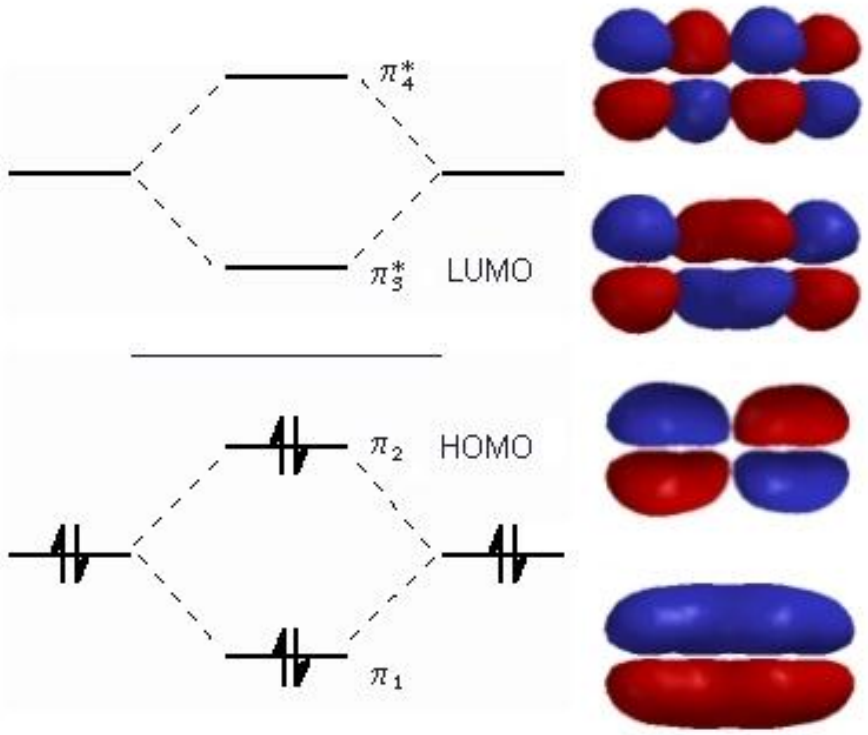

π* LUMO
π HOMO


node
antibonding
σ*
energy
1s
1s
atomic orbital
atomic orbital
σ
bonding
molecular orbital

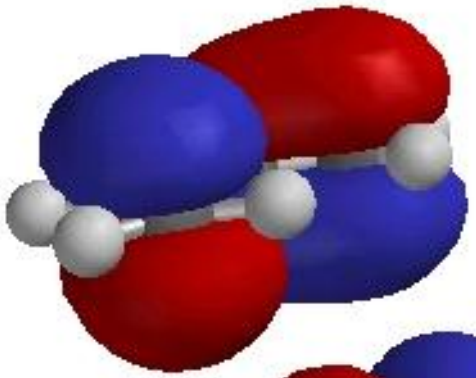
همپوشانی اوربیتال های p



ترازهاي انرژي بوتادي ان :

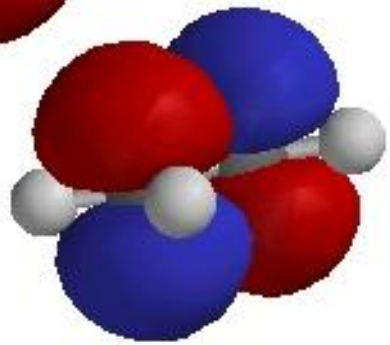


1,3-butadiene HOMO



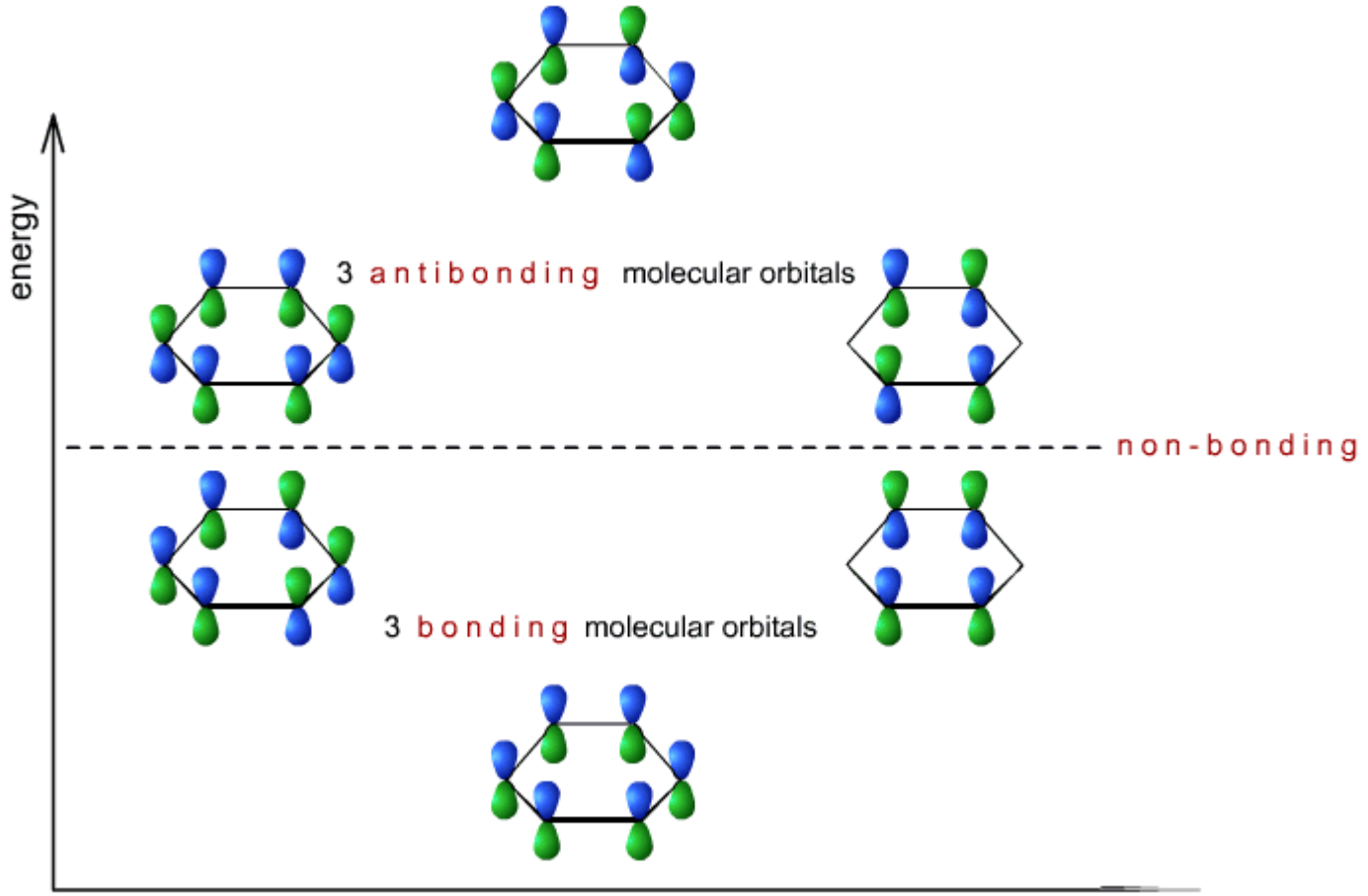
Bonding interaction

Bonding interaction



ethene LUMO

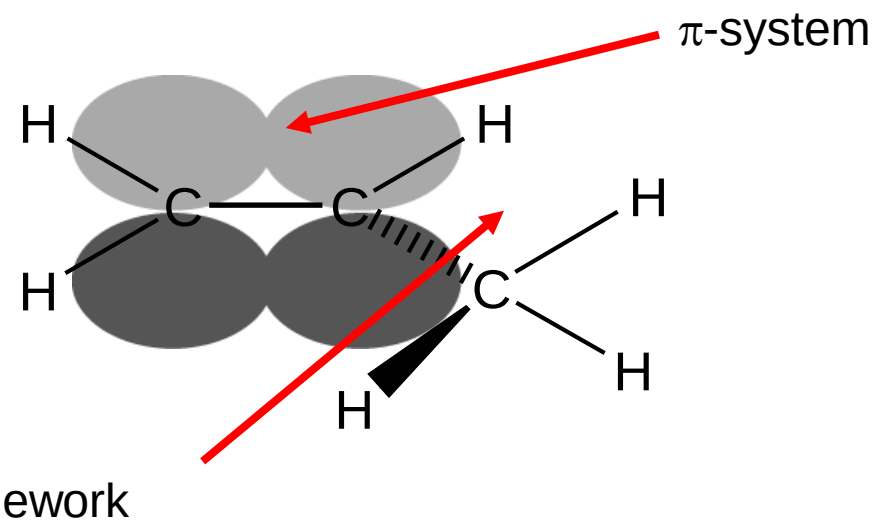
سیستم بنزن:


energy
3 antibonding molecular orbitals
non-bonding
3 bonding molecular orbitals

نظريه اربيتال مولكولي هوكل :

Hückel Molecular Orbital Theory

نظريه اوربيتال مولكولي هوكل (HMO) در سال ۱۹۳۱ عرضه شد و كاربرد آن به همراه نظريه پيوند ظرفيتي عامل اصلي استفاده از نظريه كوانتوم به عنوان ابزار در مطالعه شيمي آلي بوده است.

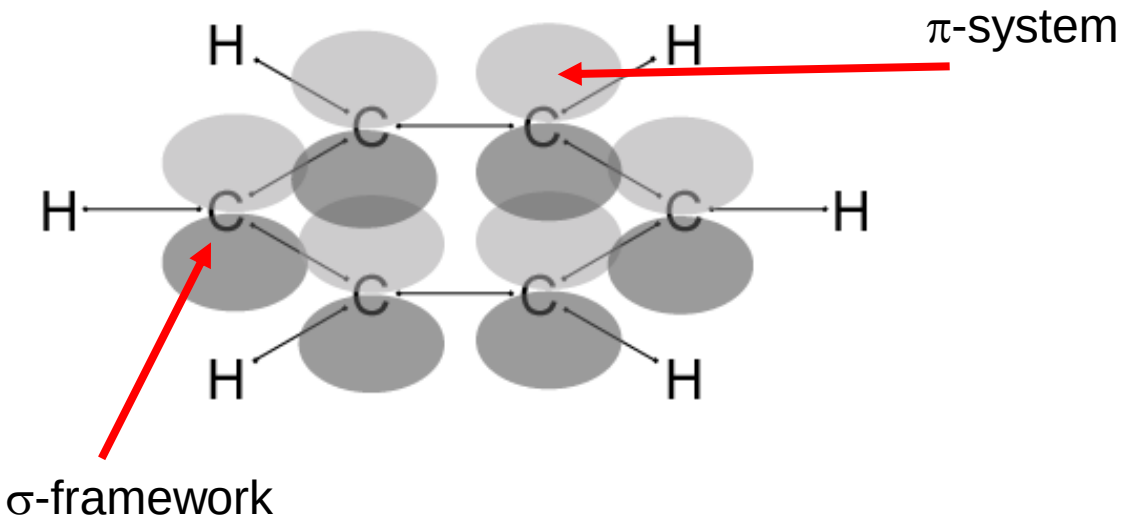


Erich Hückel (1896-1980)

Benzene

سيستم بنزن شامل ۶ الكترون غير مسقر مي باشد.

اين شش الكترون تشكيل ۳ پيوند π مي دهند.



معادلات عام براي سيستم هاي ٢ اتمي :

$$H_{ij} = \int \Phi_i H \Phi_j d\tau$$

$$S_{ij} = \int \Phi_i \Phi_j d\tau$$

$$\sum_J a_j \left(H_{ij} - E S_{ij} \right) = 0$$

$$ij = 1,2,.....n$$

دترمینان عام :

$$\left|H_{ij} - E_{ij}\right| = o$$

$$\left|H_{ij} - E_{ij}\right| = \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots\cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots\cdots & H_{2n} - ES_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots\cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

روش هوکل :

به جاي حل دترمينان عام و انتگرالهاي H_{ij}, S_{ij} انتگرالها به صورت پارامتر در نظر گرفته مي شوند.

۱. $H_{ij} = \alpha$

۲. اگر i, j بهم متصل باشند $H_{ij} = \beta$ واگر نباشند $H_{ij} = 0$

۳. براي $S_{ii} = 1, i = j$ و براي $S_{ii} = 0, i \neq j$

۴. پيوند هاي سيگما متمركز بوده , مي توان آنها را به عنوان يك چها ر چوب براي الكترونهاي پي در نظر گرفت

دترمينان عام براي سيستم هاي ٢ اتمي:

$$\begin{pmatrix} \alpha-\varepsilon & \beta \\ \beta & \alpha-\varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{vmatrix} \alpha-\varepsilon & \beta \\ \beta & \alpha-\varepsilon \end{vmatrix} = 0$$

محاسبه انرژي براي سيستم هاي ٢ اتمي:

$$\begin{vmatrix} \alpha - \varepsilon & \beta \\ \beta & \alpha - \varepsilon \end{vmatrix} = 0$$

$$(\alpha - \varepsilon)^2 - \beta^2 = 0$$

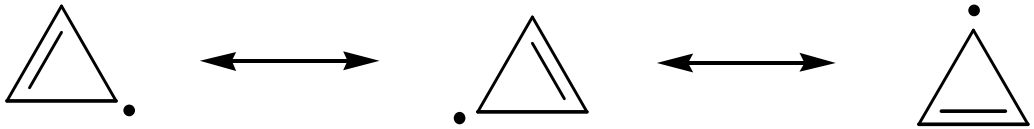
$$(\alpha - \varepsilon - \beta)(\alpha - \varepsilon + \beta) = 0$$

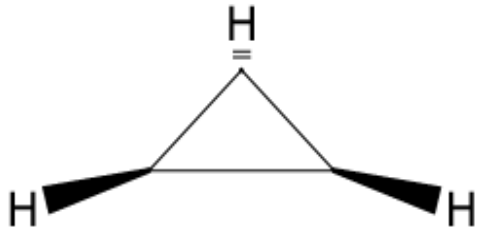
$$\varepsilon = \alpha \pm \beta$$

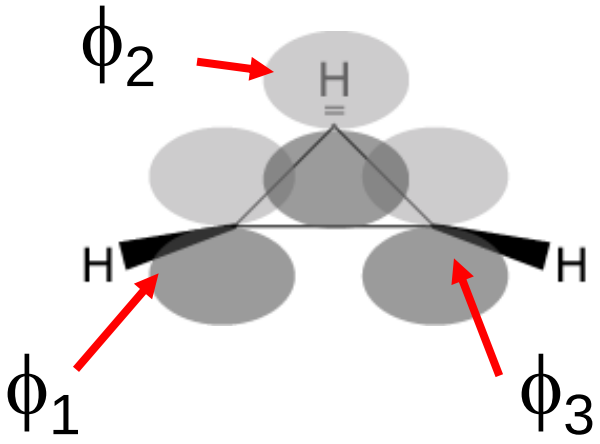
This is the energy of an isolated π-bond

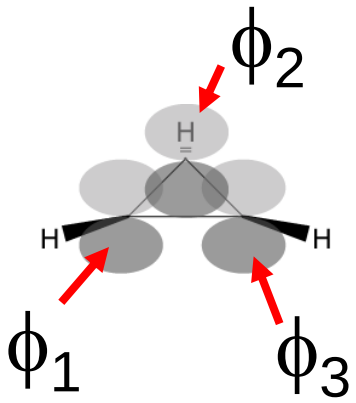
Cyclopropenyl radical – C_3H_3

سیستم رادیکال سیکلوپروپنیل:









$$\hat{H}(c_1\phi_1 + c_2\phi_2 + c_3\phi_3) = \epsilon(c_1\phi_1 + c_2\phi_2 + c_3\phi_3)$$

Left multiplying by ϕ_1 and integrating gives us

$$c_1 \int \phi_1 \hat{H} \phi_1 \mathrm{d}\tau + c_2 \int \phi_1 \hat{H} \phi_2 \mathrm{d}\tau + c_3 \int \phi_1 \hat{H} \phi_3 \mathrm{d}\tau = \epsilon \left(c_1 \int \phi_1 \phi_1 \mathrm{d}\tau + c_2 \int \phi_1 \phi_2 \mathrm{d}\tau + c_3 \int \phi_1 \phi_3 \mathrm{d}\tau \right)$$

assuming no overlap ($\int \phi_1 \phi_2 \mathrm{d}\tau = 0$) and normalization ($\int \phi_1 \phi_1 \mathrm{d}\tau = 1$), this may be simplified to

$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon.$$

We now have three equations

$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon$$

$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon$$

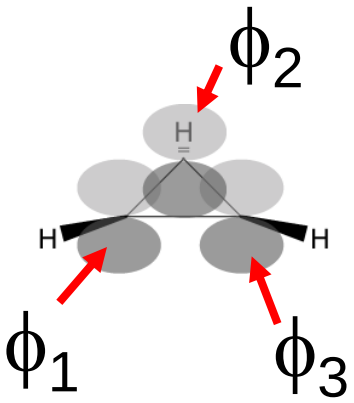
$$c_1\beta + c_2\beta + c_3\alpha = c_3\epsilon$$

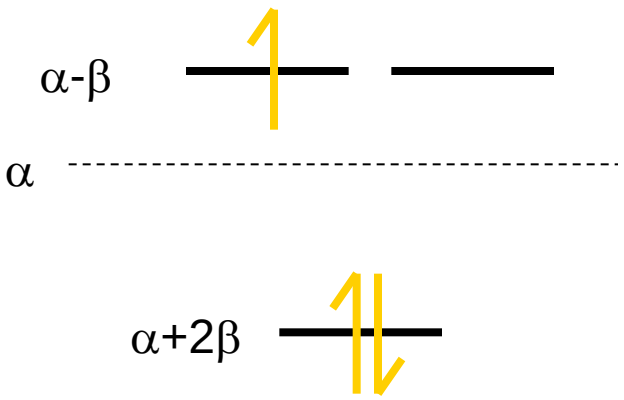
$$\begin{vmatrix} \alpha-\epsilon & \beta & \beta \\ \beta & \alpha-\epsilon & \beta \\ \beta & \beta & \alpha-\epsilon \end{vmatrix} = 0$$

Dividing the matrix by β and substituting $x = (\alpha - \epsilon)/\beta$ we get

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

$$x(x^2-1) - 1(x-1) + 1(1-x) = 0$$
$$x^3 - 3x + 2 = 0$$
$$(x-1)(x-1)(x+2) = 0$$
$$x = 1, 1, -2$$
$$(\alpha-\epsilon)/\beta = 1, 1, -2$$
$$\epsilon = \alpha + 2\beta, \alpha - \beta, \alpha - \beta$$



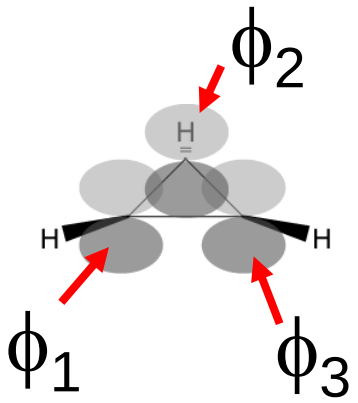


We have three equations

$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon \qquad (1)$$

$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon \qquad (2)$$

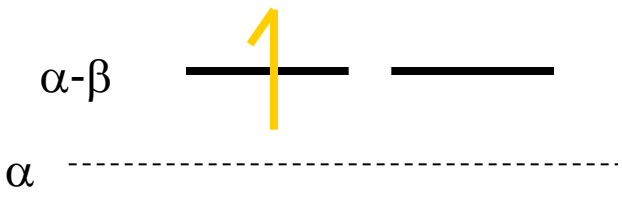
$$c_1\beta + c_2\beta + c_3\alpha = c_3\epsilon \qquad (3)$$



(1)-(2) and (1)-(3)

$$(\alpha - \epsilon - \beta)c_1 + (\beta - \alpha + \epsilon)c_2 = 0$$

$$(\alpha - \epsilon - \beta)c_1 + (\beta - \alpha + \epsilon)c_3 = 0$$



substitute $\epsilon = \alpha + 2\beta$

$$-3\beta c_1 + 3\beta c_2 = 0$$

$$-3\beta c_1 + 3\beta c_3 = 0$$

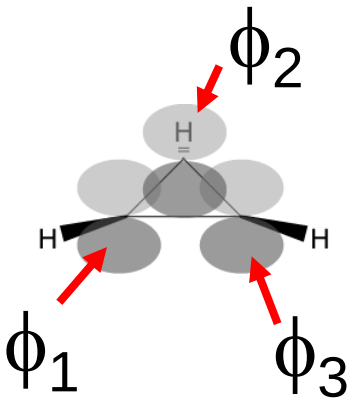
$$c_1 = c_2 = c_3$$

We have three equations

$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon \quad (1)$$

$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon \quad (2)$$

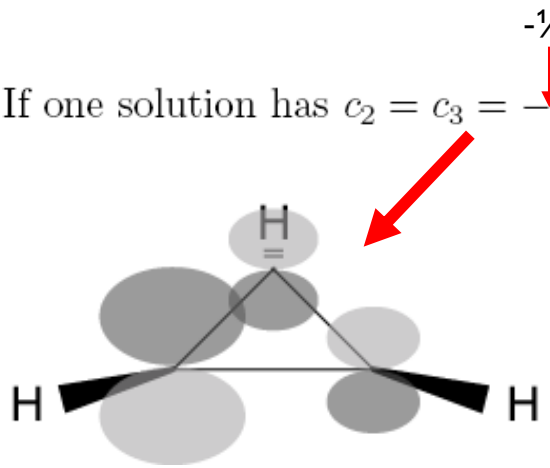
$$c_1\beta + c_2\beta + c_3\alpha = c_3\epsilon \quad (3)$$

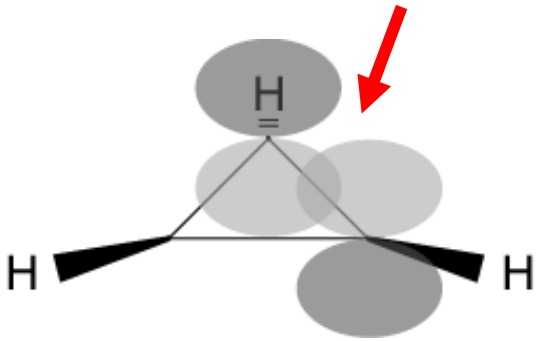


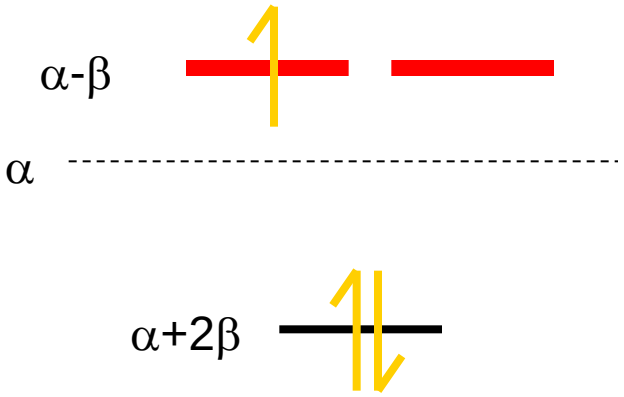
Substitute $\epsilon = \alpha - \beta$ into (1)

$$c_2\beta + c_3\beta = -c_1\beta$$

If one solution has $c_2 = c_3 = -c_1$. The other has $c_1 = 0, c_2 = -c_3$.





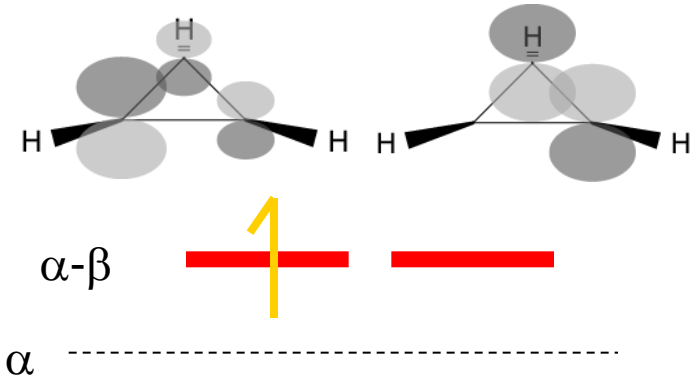


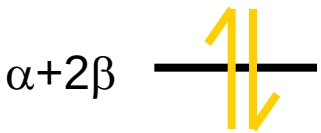
$$E_\pi = 2\times(\alpha+2\beta)+1\times(\alpha-\beta)$$

$$= 3\alpha + 3\beta$$

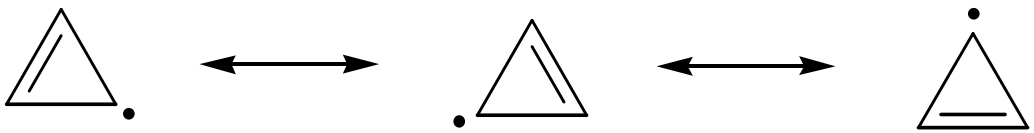
The energy of a normal double bond is $2\alpha+2\beta$ (2 electrons in $\alpha+\beta$)

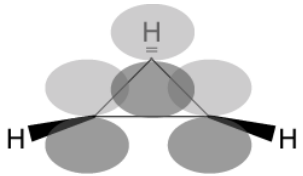
The energy of a lone p-orbital is α





Therefore, the energy of each resonance form is $3\alpha+2\beta$



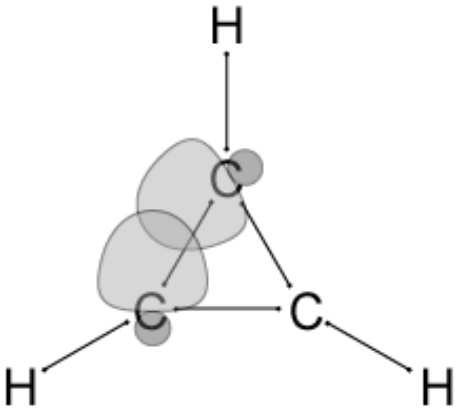


Cyclopropenyl is resonance stabilized! (by β) *i.e.* its *resonance energy* is β

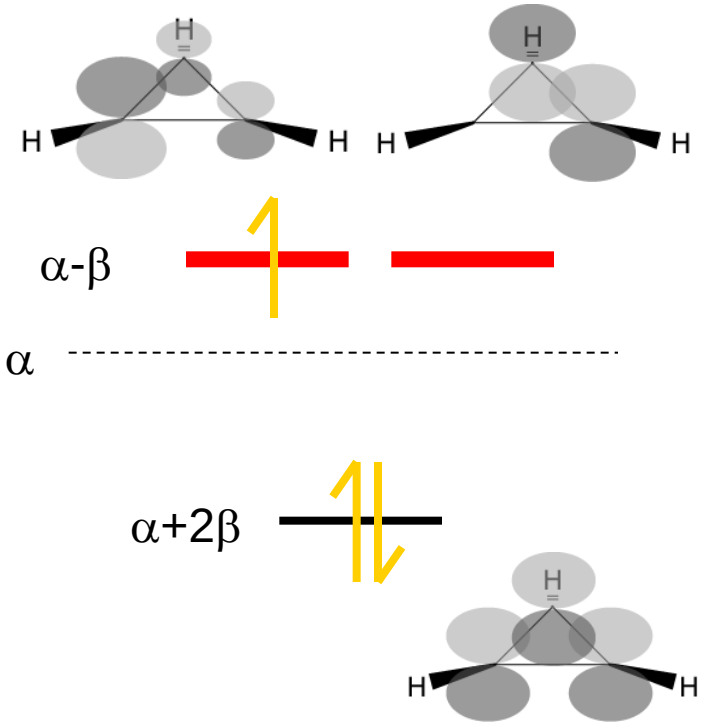
While the cyclopropenyl molecule is stable,

Its σ-bonds are not as strong as they would be in, say, benzene. This is because the overlap between in the sp^2 hybrids is reduced due to the strained geometry of the radical.

This is called σ-strain



This should be taken into account when comparing the stabilities of various isomers

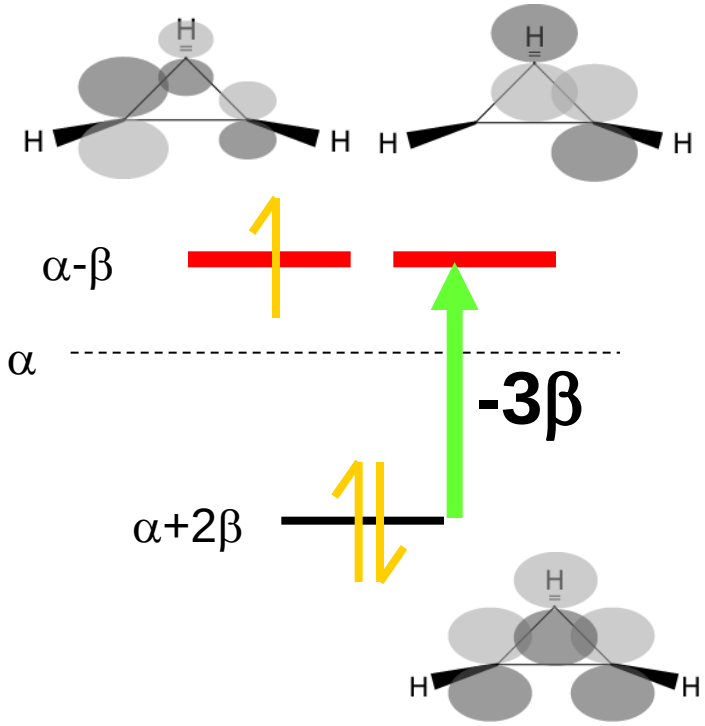


σ-bonding orbitals

The lowest energy transition between the π-orbitals in this system has an energy of -3β.

This transition is well into the UV

The cation is stable and symmetric ($2e^-$) and has 2β of resonance stability (prove yourself)



σ-bonding orbitals

(not examinable)
A note on Jahn-Teller distortion:
The singly occupied MO as drawn on the right may be lowered in energy by decreasing the distance between carbons 2 and 3 while increasing the other two bond lengths. This is energetically favourable and will happen. This is known as Jahn-Teller distortion.

Cyclobutadiene – C_4H_4

سيستم بوتادي ان:

$$\hat{H}(c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4) = \epsilon(c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4)$$

Left multiplying by ϕ_1 and integrating gives us

$$c_1\int \phi_1\hat{H}\phi_1 d\tau + c_2\int \phi_1\hat{H}\phi_2 d\tau + c_3\int \phi_1\hat{H}\phi_3 d\tau + c_4\int \phi_1\hat{H}\phi_4 d\tau$$
$$= \epsilon\left(c_1\int \phi_1\phi_1 d\tau + c_2\int \phi_1\phi_2 d\tau + c_3\int \phi_1\phi_3 d\tau + c_4\int \phi_1\phi_4\right)$$

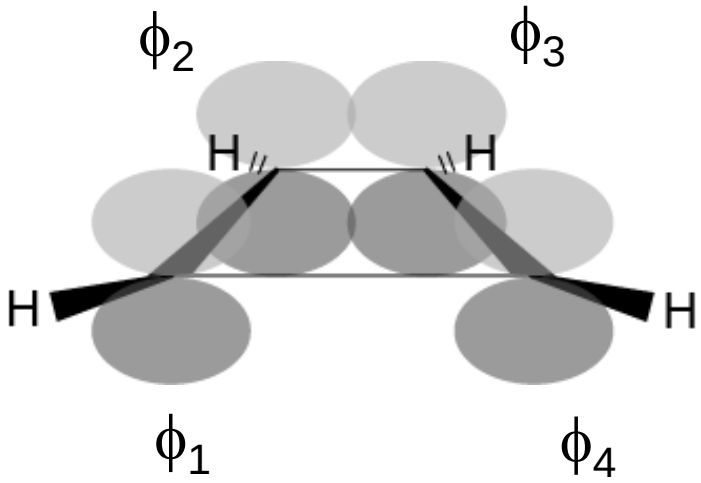
assuming no overlap ($\int \phi_1\phi_2 d\tau$=0) and normalization ($\int \phi_1\phi_1 d\tau = 1$), this may be simplified to

$$c_1\alpha + c_2\beta + c_4\beta = c_1\epsilon.$$

There is no bonding between carbons 1 and 3!

We now have four equations

$$c_1\alpha + c_2\beta + c_4\beta = c_1\epsilon$$
$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon$$
$$c_2\beta + c_3\alpha + c_4\beta = c_3\epsilon$$
$$c_1\beta + c_3\beta + c_4\alpha = c_4\epsilon$$



Dividing the matrix by β and substituting $x = (\alpha - \epsilon)/\beta$ we get

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

x on diagonal

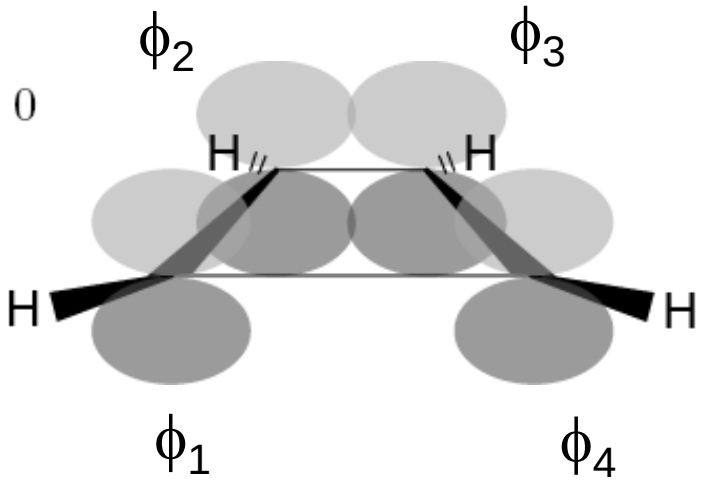
1 off diagonal where there
Is bonding interaction

0 off diagonal where there is no
Bonding interaction; i.e. 1 &3, 2&4

$$x(x(x^2-1)-x)-((x^2-1)+1)-(1-x(-x)-1)=0$$

$$x = -2, 0, 0, +2$$

$$\epsilon = \alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$$



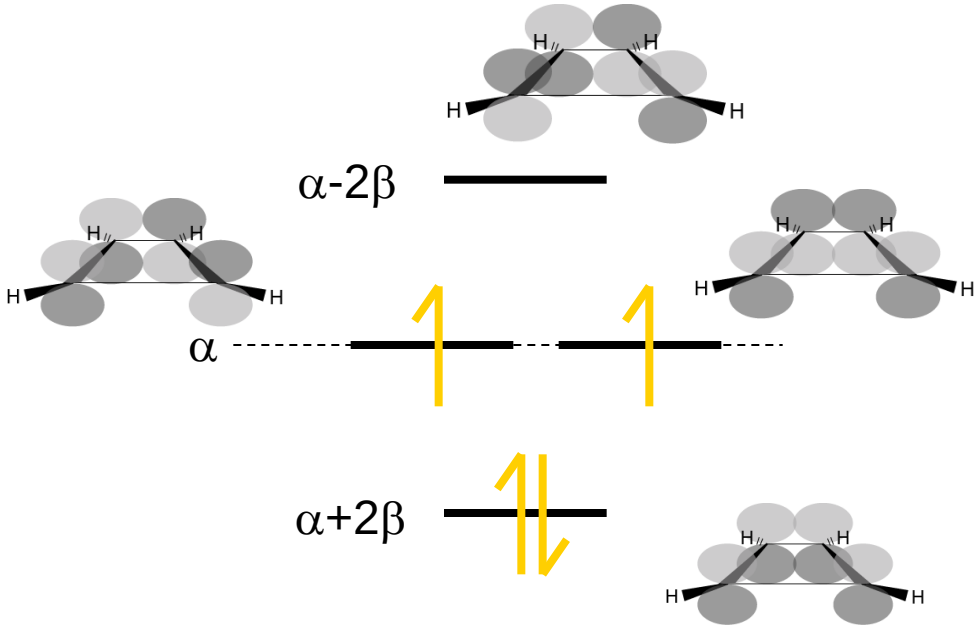
http://www.stolaf.edu/depts/chemistry/courses/toolkits/247/js/huckel/index.htm

$$E_\pi = 2\times(\alpha+2\beta)+2\times\alpha$$

$$= 4\alpha + 4\beta$$

The energy of a normal double bond is $2\alpha+2\beta$ (2 electrons in $\alpha+\beta$)

Therefore, the energy of each resonance form is $4\alpha+4\beta$



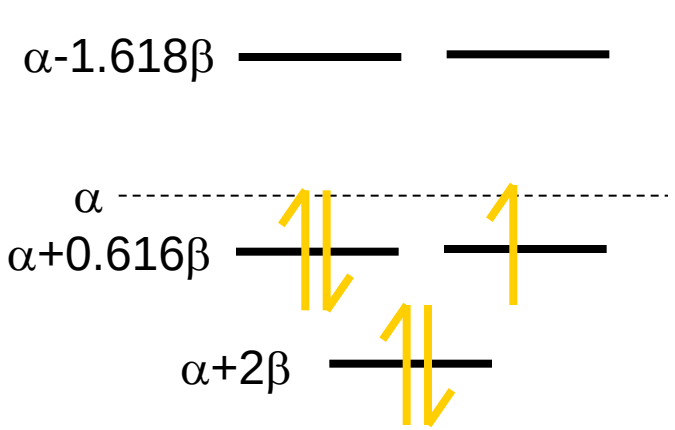
Cyclobutadiene is not resonance stabilized! *i.e.* its *resonance energy* is 0

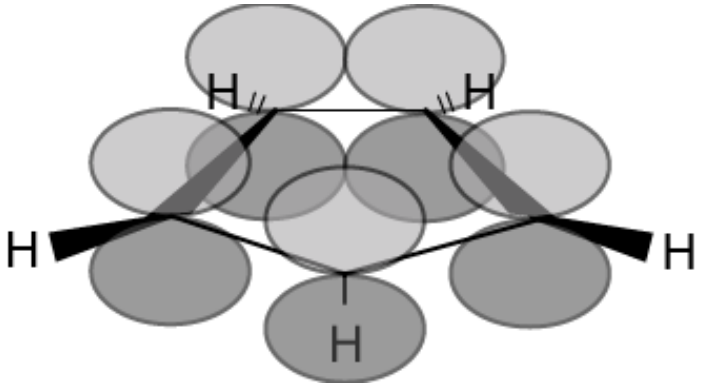
4e$^-$ system is *anti-aromatic* and *σ-strained*

σ-bonding orbitals

Cyclopentadienyl radical – C_5H_5 : سيستم راديكال سيكلو پنتا دي ان

$$\begin{vmatrix} x & 1 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 1 & x \end{vmatrix} = 0$$





Lowest orbital has no node

Second lowest has 1 node

Highest has two nodes

This radical suffers from Jahn-Teller distortion… not a true pentagon

Cyclopentadienyl anion – $C_5H_5^-$

سيستم آنيون سيكلو پنتادي ان :

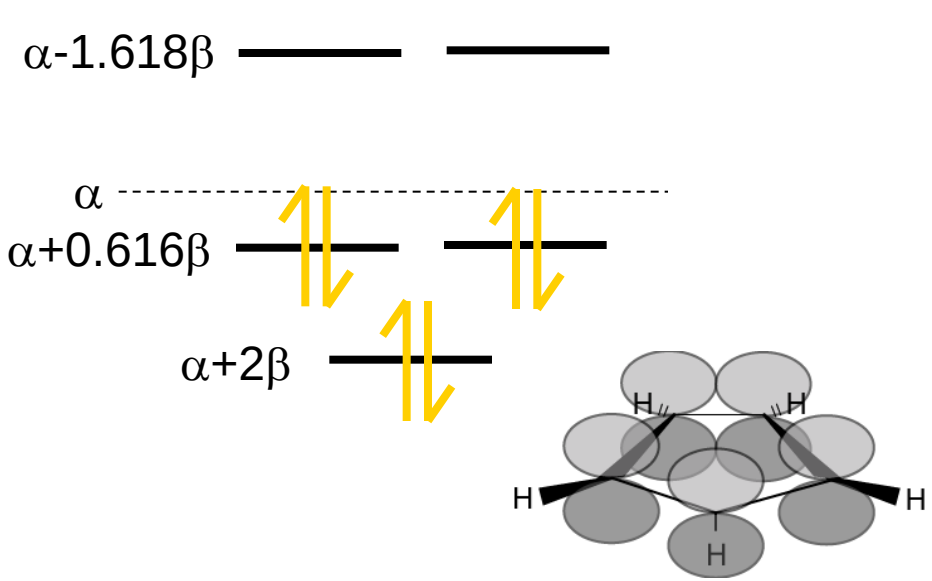
This system readily accepts an extra electron

As it does so it can no longer lower its energy by distortion

This anion is perfectly pentagonal

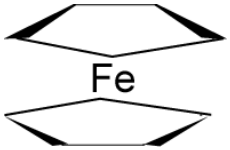
It is resonance stabilized!

$E_\pi = 6\alpha+5.232\beta$ (Compare to energy of two double bonds and a p-orbital : $6\alpha+4\beta$)



$6e^-$ system nicely aromatic

Will ligate to transition metal ions to make metallocenes e.g. Ferrocene



cp^- is a closed shell singlet

cp^+ is also stable as a triplet

Benzene – C_6H_6

بنزن:

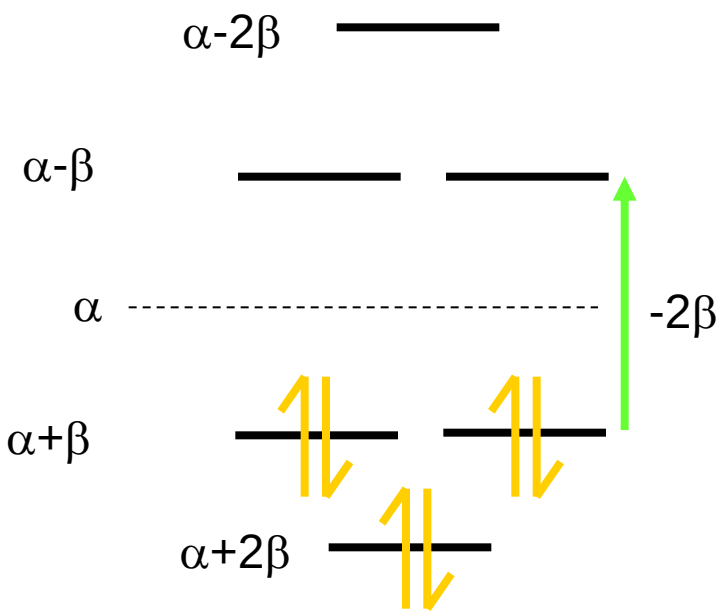
Benzene is the archetypal aromatic molecule

It has no σ-strain – it is a perfect hexagon

You may wish to compute its stability compared to the mythical beast – 1,3,5-hexatriene (it's a quiz question!)

It energy levels and orbitals are readily computed by a program on my website.

Benzene cation is Jahn-Teller distorted and is not a perfect hexagon



Benzene absorbs in UV at 260nm

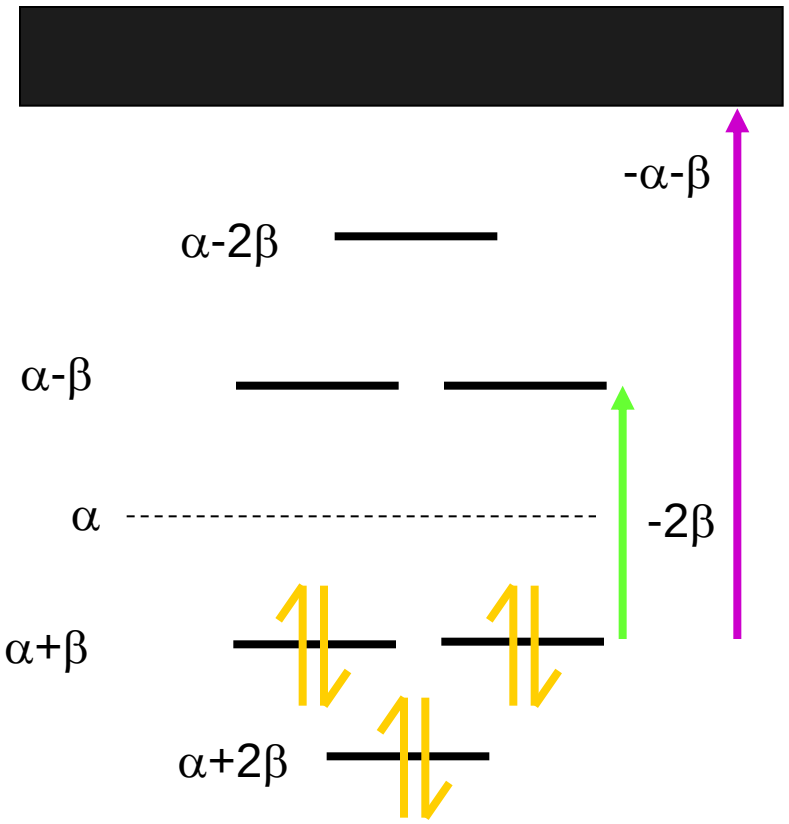
This corresponds to 460 kJ/mol

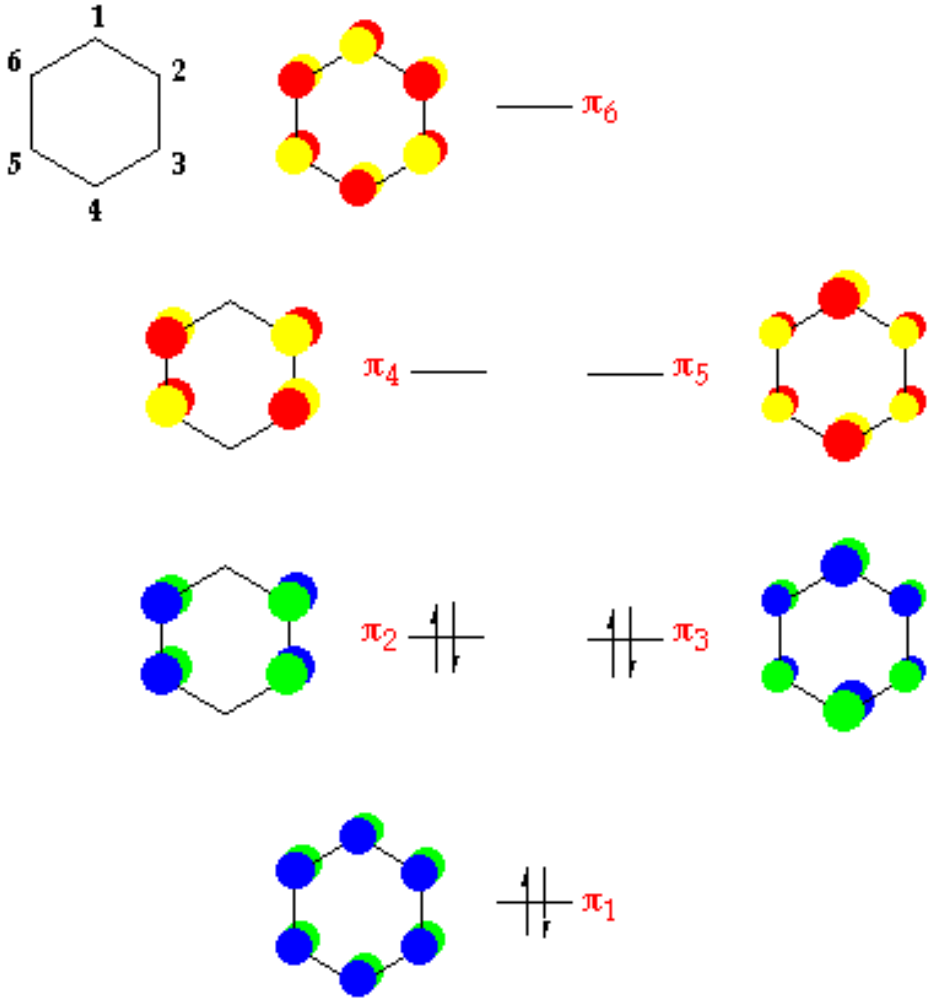
We can parametrize the β in Hückel theory by setting -2β equal to this energy!

Benzene's ionization potential is 730 kJ/mol

We can parametrize the α integral by setting this to be –α-β.

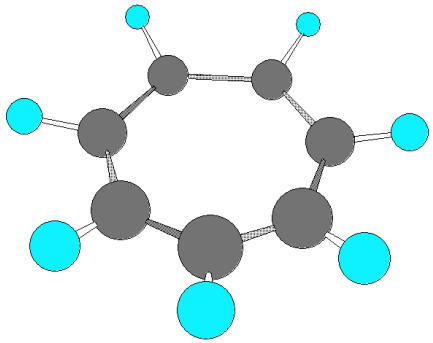
Doing this…. α = -500 kJ/mol, β = -230 kJ/mol




1
2
3
4
5
6
π6
π4
π5
π2
π3
π1

Tropyl – C_7H_7

تروپوليوم:



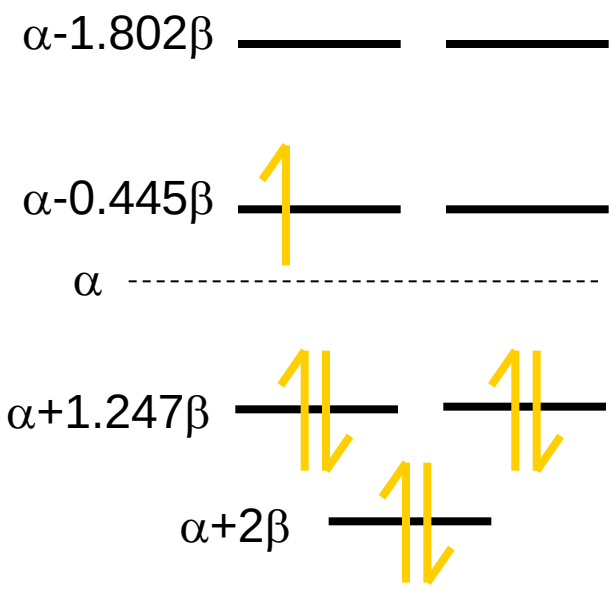
Tropyl radical is a Jahn-Teller distorted heptagon

It is easily ionized – its experimental IP is 48000cm^{-1} or 570 kJ/mol

Hückel theory predicts α-0.445β or 397kJ/mol… but there is σ-strain &c.

Tropyl anions and cations are both perfect heptagons

Tropyl cation is very stable… 6e$^-$ system!



Cyclooctatetraene – C_8H_8

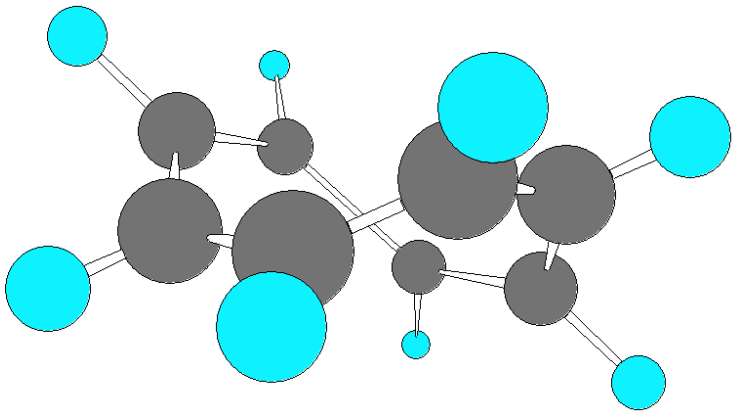
سيكلو اكتاتترا ان :

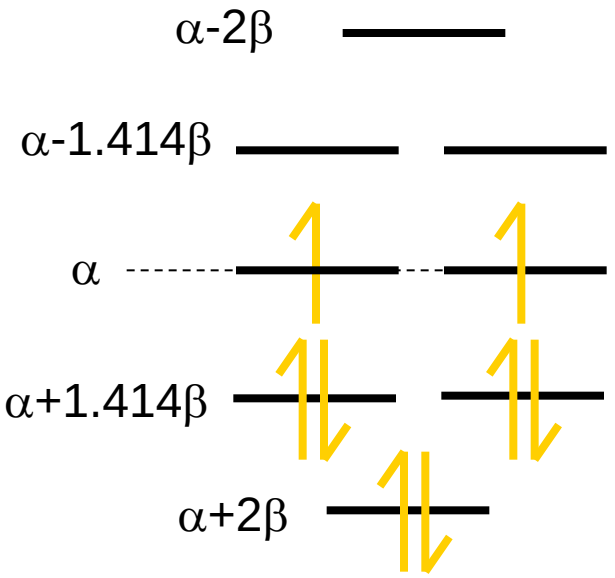
$E_\pi = 8\alpha + 9.656\beta$

But planar structure is highly strained.

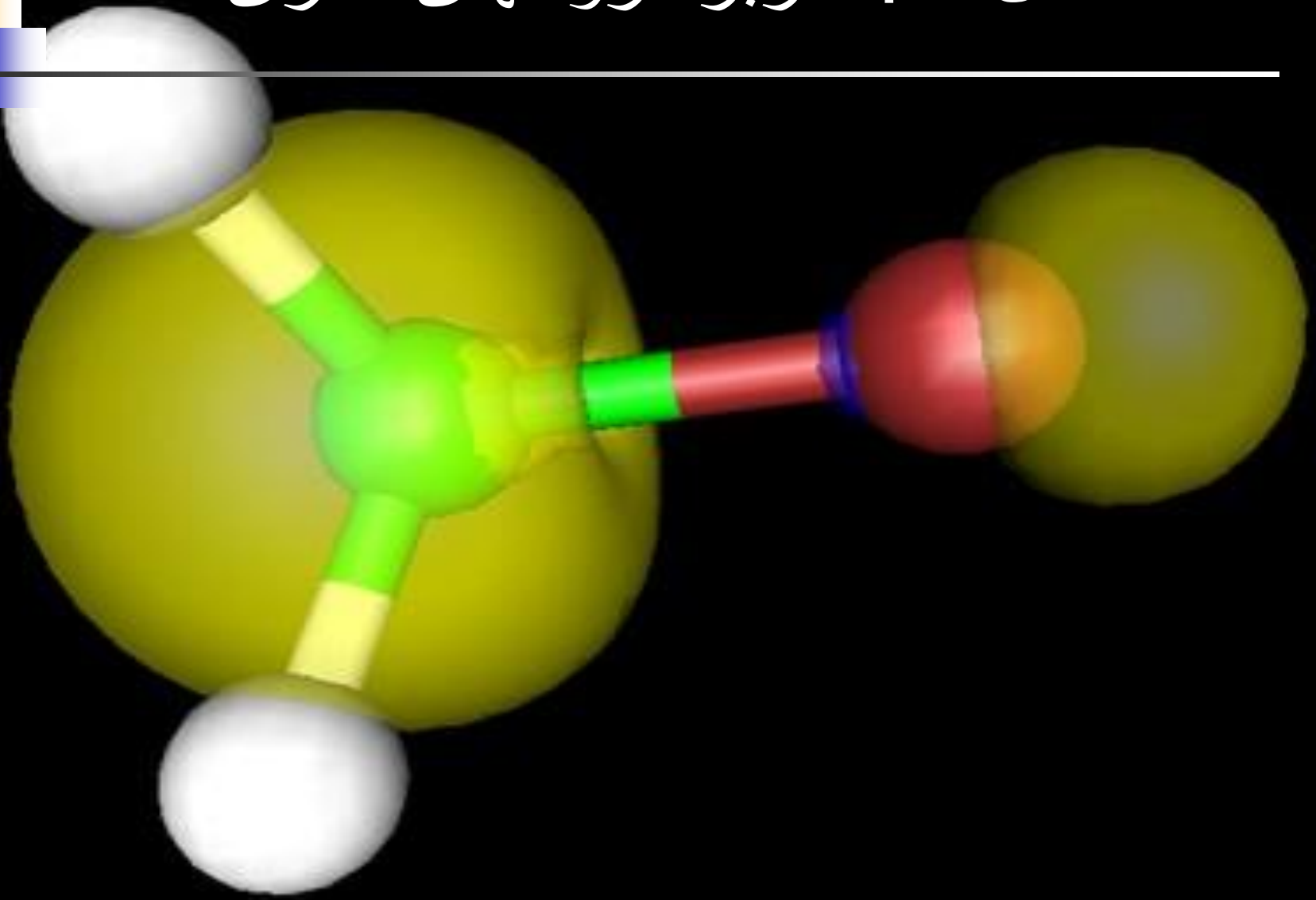
Ring puckers to relieve bond strain at the expense of slight delocalization energy

The molecule is not flat – it is not aromatic





فصل ۲ : کاربرد روشهای نظری



هدفهاي كلي :

به منظور توصیف کاربرد نگرش نظری در حل مسائل شیمی آلی و آشناتر ساختن دانشجویان با روشهای موجود ، چهار کاربرد خاص را بررسی خواهیم کرد :

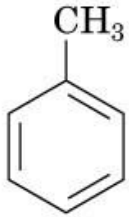
۱- خصلت آروماتیسیته

۲- جایگزینی الکتروفیلی آروماتیک

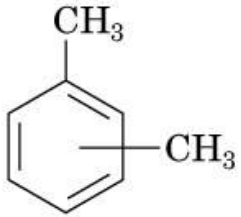
۳- جایگزینی نوکلئوفیلی آروماتیک

۴- واکنشهای پری سیکلی

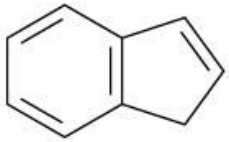
Benzene
(bp 80°C)



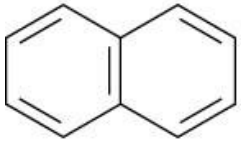
Toluene
(bp 111°C)



Xylene
(bp: ortho, 144°C;
meta, 139°C; para, 138°C)

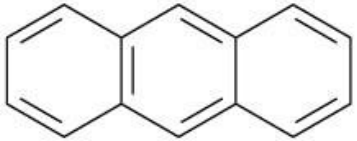


Indene
(bp 182°C)

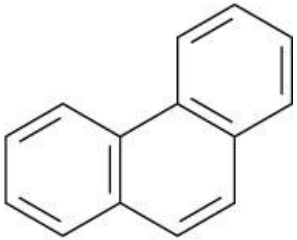


Naphthalene
(mp 80°C)

Biphenyl
(mp 71°C)



Anthracene
(mp 216°C)



Phenanthrene
(mp 101°C)

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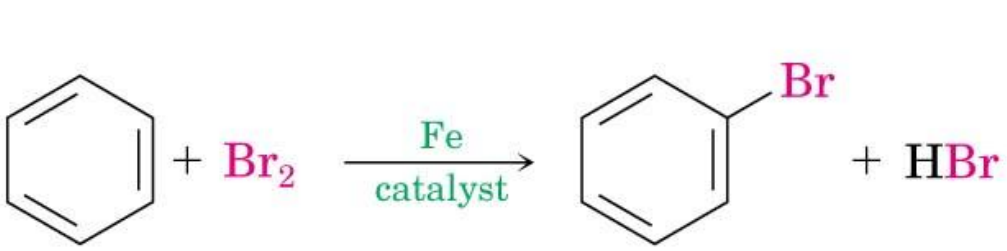

Benzene

Bromobenzene (substitution product)

(Addition product)
***NOT* formed**

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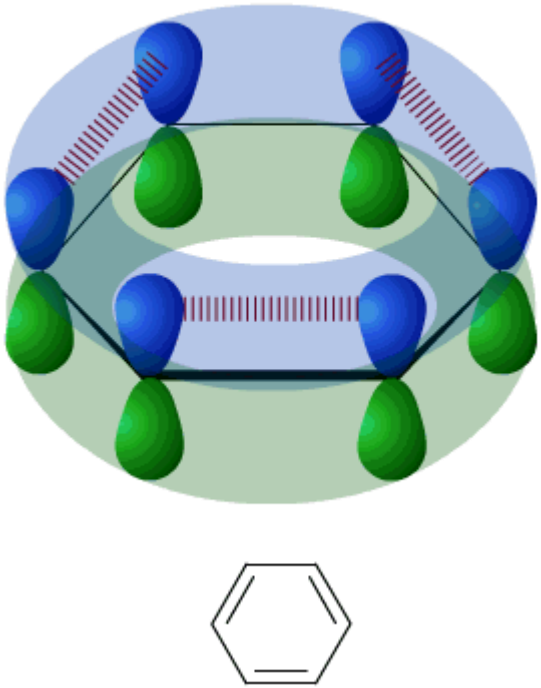
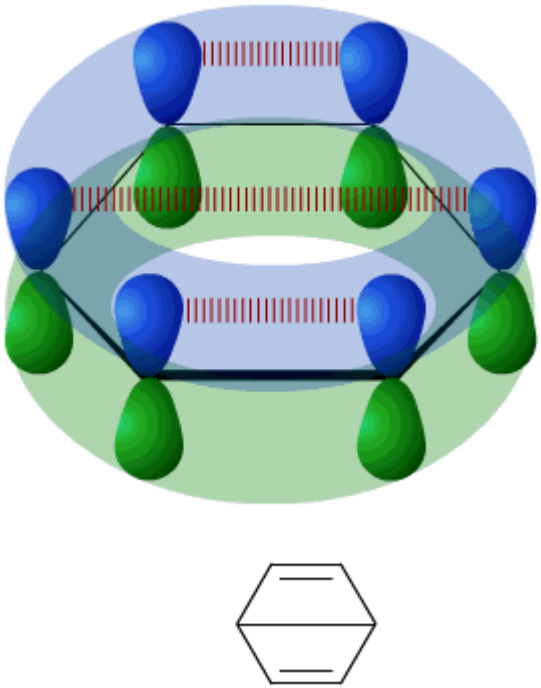
خصلت آروماتیک :

a Kekulé resonance structure



a Dewar resonance structure



Aromaticity and the $4n + 2$ Rule

قاعده هوکل:

- Huckel's rule, based on calculations – a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has ***4n+ 2*** *π electrons (n is 0,1,2,3,4)*
- For n=1: 4n+2 = 6; **benzene** is stable and the electrons are delocalized

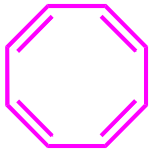
Benzene

Three double bonds;
six π electrons

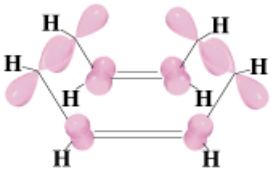
Compounds With 4n π Electrons Are Not Aromatic (May be Antiaromatic)

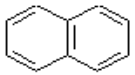
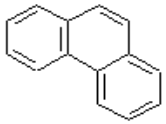
- Planar, cyclic molecules with ***4 n*** π electrons are much *less* stable than expected (anti-aromatic)
- They will distort out of plane and behave like ordinary alkenes
- 4- and 8-electron compounds are not delocalized (single and double bonds)
- Cyclobutadiene is so unstable that it dimerizes by a self-Diels-Alder reaction at low termperature
- Cyclooctatetraene has four double bonds, reacting with Br2, KMnO4, and HCl as if it were four alkenes

cyclobutadiene



cyclooctatetraene

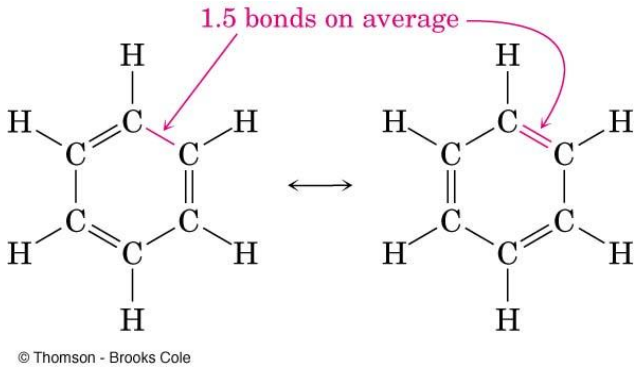


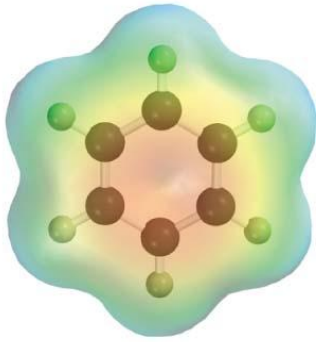
		Resonance Energy (kcal/mol)	Comments
Benzene		36	Typical Aromatic
Naphthalene		61	Less than 2 x Benzene
Phenanthrene		84	Less than 3 x Benzene
Pyridine		28	N analogue of Benzene N lone pair NOT in Ar. 6x system
Furan		16	
Thiophene		29	5 memebered ring Heterocycles
Pyrrole		22	NH lone pair part of Ar. 6x system
Cyclopentadiene		3	C analogue of Furan, Thiophene Pyrrole, but much lower Res. energy since it is not aromatic, just a diene like butadiene
Butadiene		4	Compare to Cyclopentadiene
Ethene		0	Isolated C=C, no resonance
Imidazole		22	Like Pyrrole NH lone pair IN, other N lone pair OUT of Ar. 6x system

انرژی رزونانس:

اهمیت رزونانس در یک مولکول ، معمولا نسبت به انرژی رزونانس بنزن سنجیده می شود؛ انرژی رزونانس، حاصل تفریق انرژی واقعی مولکول از انرژی پایدارترین شکل پیوندظرفیتی آن می باشد.

$$DE = E_{\pi} - E_{LOC}$$





گرمای تشکیل پلی ان خطی:

$$\Delta H_f = n(E_{C-C}) + (n+1)(E_{C=C}) + (2n+4)E_{C-H}$$

انرژی رزونانس دوار:

$$DRE = \Delta H_f^{loc} - \Delta H_f$$

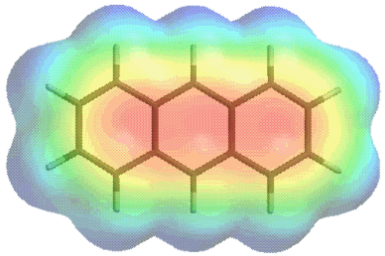
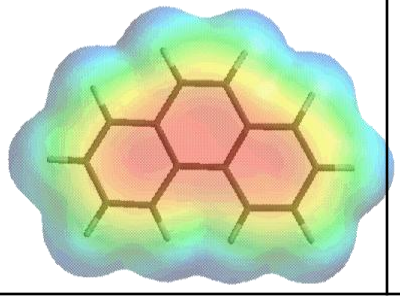
$$\Delta H_f^{loc}\left(Kcal/mol\right) = 7.435\left(no.ofC\right) - 0.605\left(no.ofH\right)$$

مولکول آروماتیک ← $DRE \rangle 0$

مولکول ضد آروماتیک ← $DRE \langle 0$

مولکول غیر آروماتیک ← $DRE = 0$

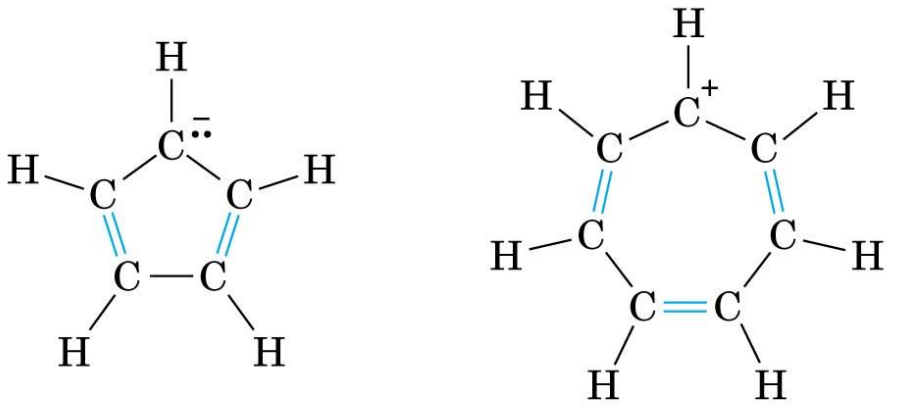
مقایسه DRE و DE جهت هیدروکربن های بنزوئیدی:

DRE		
ساختار	تجربی	نیمه تجربی
	۴۳	۴۲
	۴۹	۴۹

Aromatic Ions

هیدروکربنهای تک حلقه ای مزدوج :

- The $4n + 2$ rule applies to ions as well as neutral species
- Both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic
- The key feature of both is that they contain 6 π electrons in a ring of continuous p orbitals



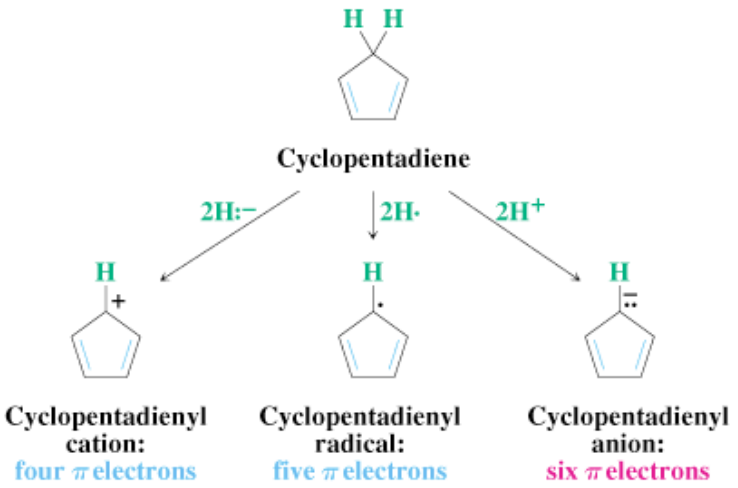
Cyclopentadienyl anion **Cycloheptatrienyl cation**

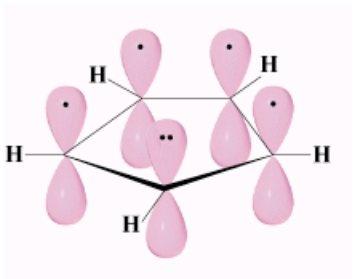
Six π electrons; aromatic ions

© Thomson - Brooks Cole

Aromaticity of the Cyclopentadienyl Anion : خصلت آروماتیسیته آنیون سیکلو پنتا دی ان

- 1,3-Cyclopentadiene contains conjugated double bonds joined by a CH2 that blocks delocalization
- Removal of H+ at the CH2 produces a cyclic 6-electron system, which is stable
- Removal of H- or H• generate nonaromatic 4 and 5 electron systems
- Relatively acidic (p*K*a = 16) because the anion is stable





جایگزینی نوکلئوفیلی آلیفاتیک :

در فصل ۴ توضیح داده خواهد شد.

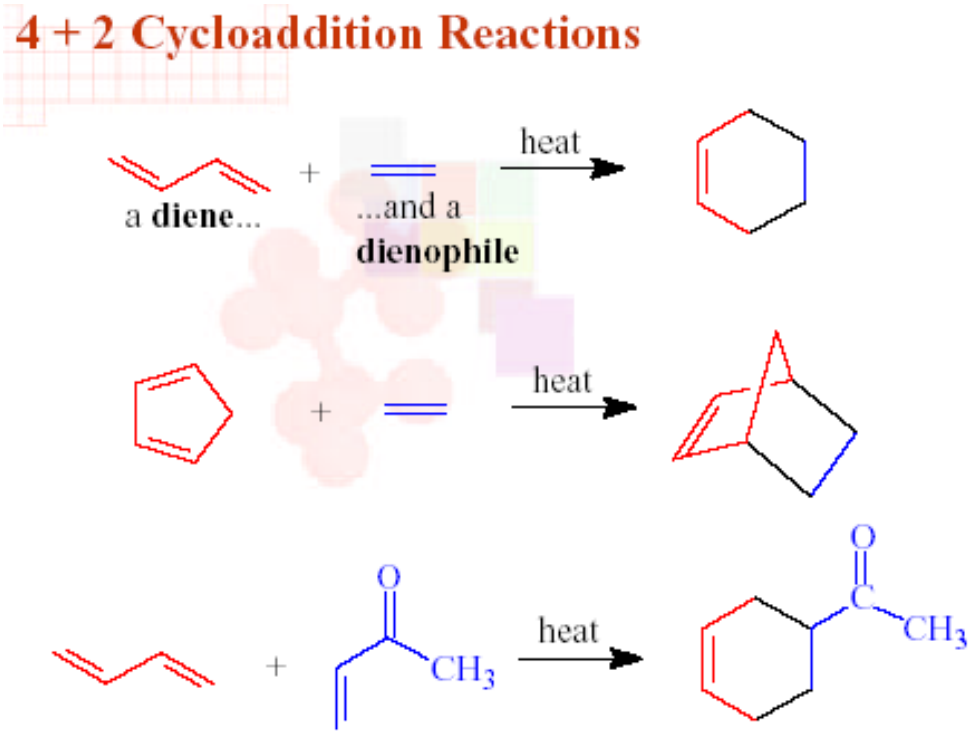
واکنشهای پری سیکلی :

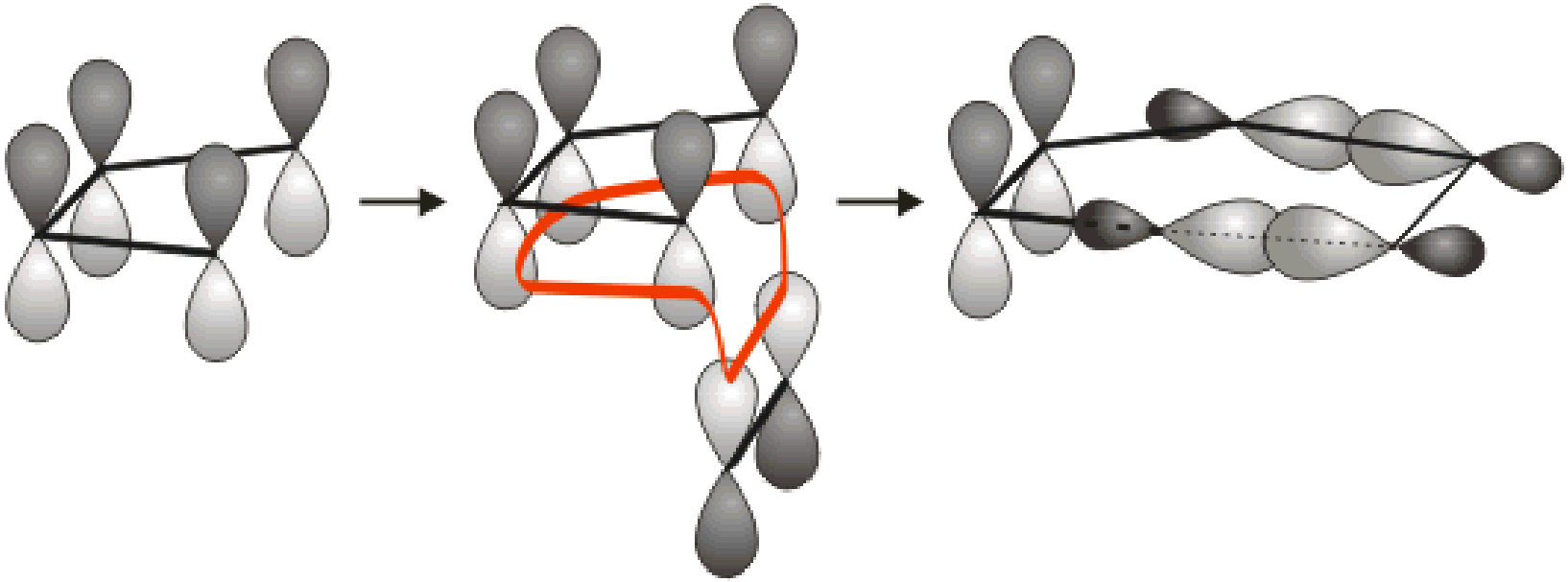
واکنش پری سیکلی، واکنشی است که در آن پیوندها به طور هماهنگ و در یک حالت گذرای حلقوی، گسسته و تشکیل می شوند .

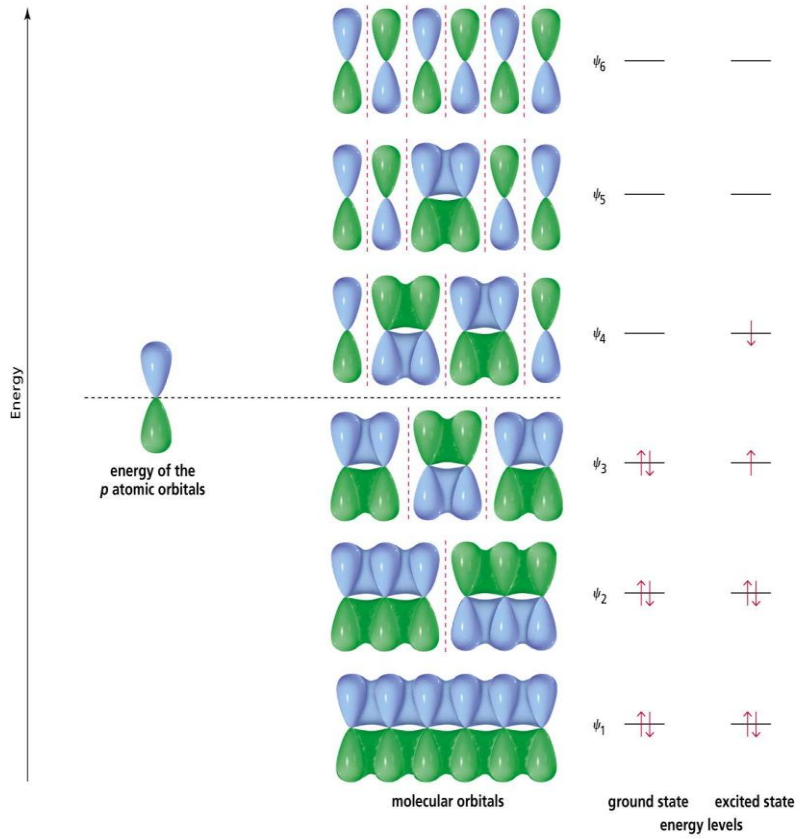
Cycloaddition	حلقه زایی
Electrocyclic Reactions	واکنشهای الکتروسیکلی
Sigmatropic Rearrangements	نوآرایی سیگما تروپی
Group Transfer Reactions	واکنشهای انتقال گروه

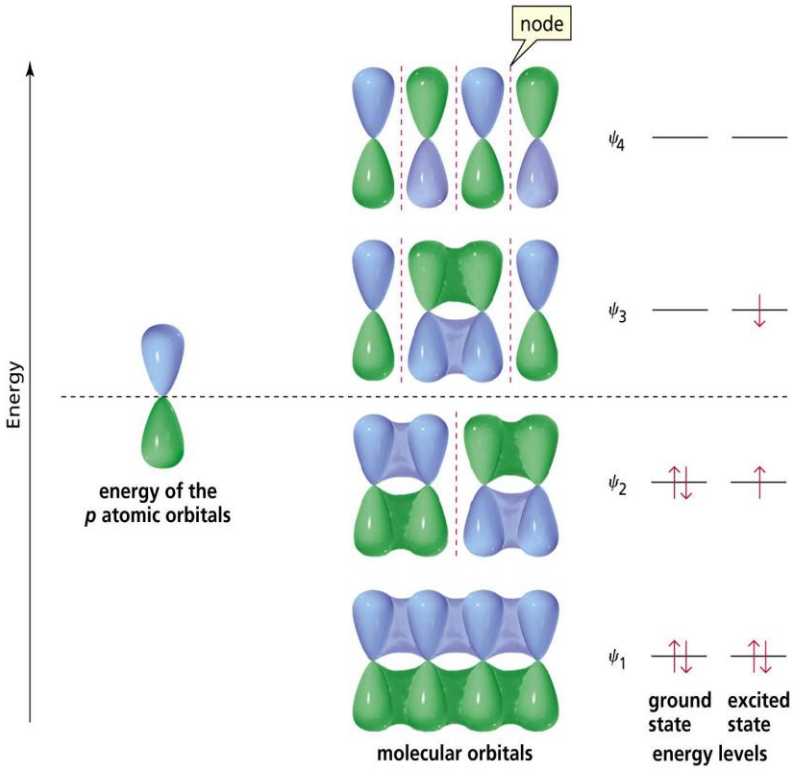
واکنشهای حلقه زایی :

دیالز- آلدر



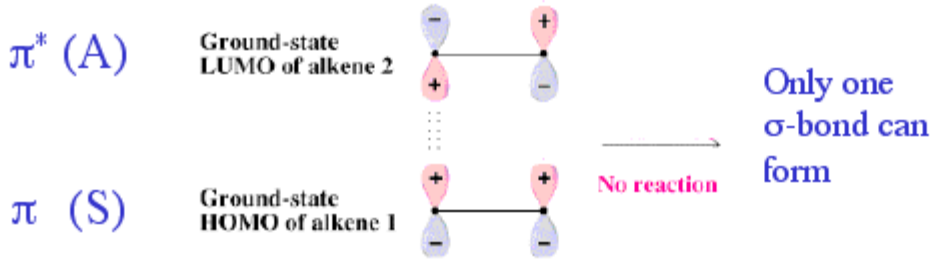



Energy
energy of the
p atomic orbitals
ψ6
ψ5
ψ4
ψ3
ψ2
ψ1
molecular orbitals
ground state
excited state
energy levels

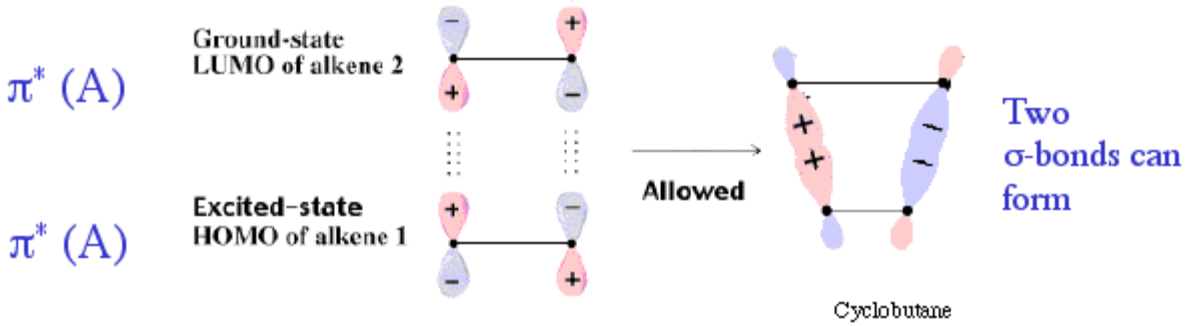

node
Energy
energy of the
p atomic orbitals
ψ4
ψ3
ψ2
ψ1
molecular orbitals
ground
state
excited
state
energy levels

[2+2] Cycloaddition reaction

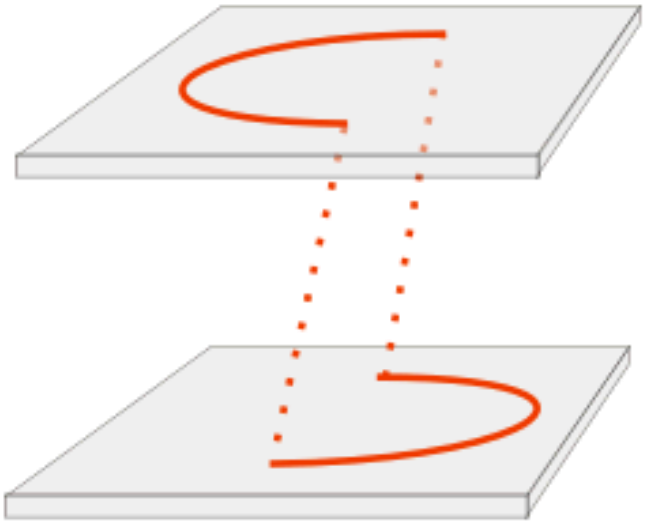
- Ground state reaction forbidden:



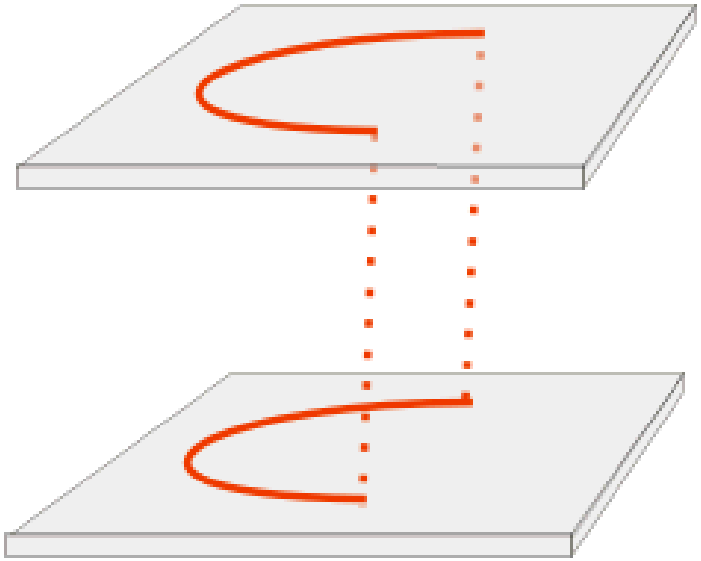
- Excited state reaction allowed:



اگزو

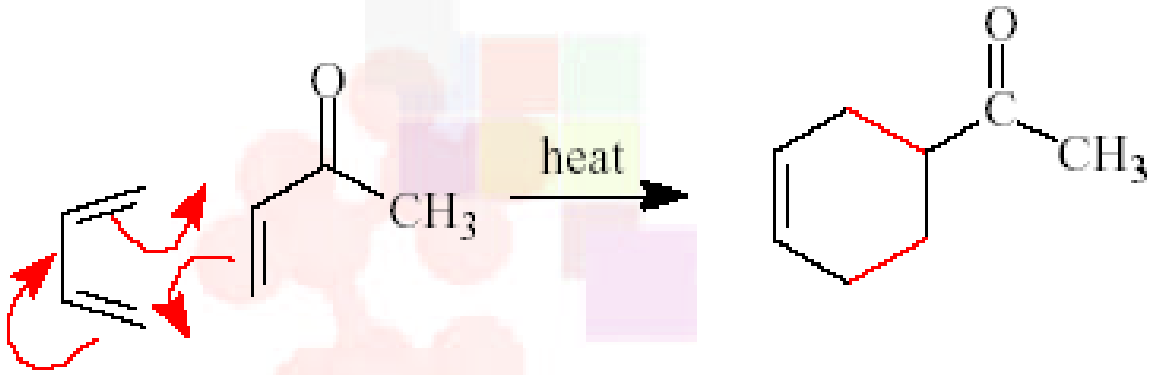


اندو



درواکنش های حلقه زایی:

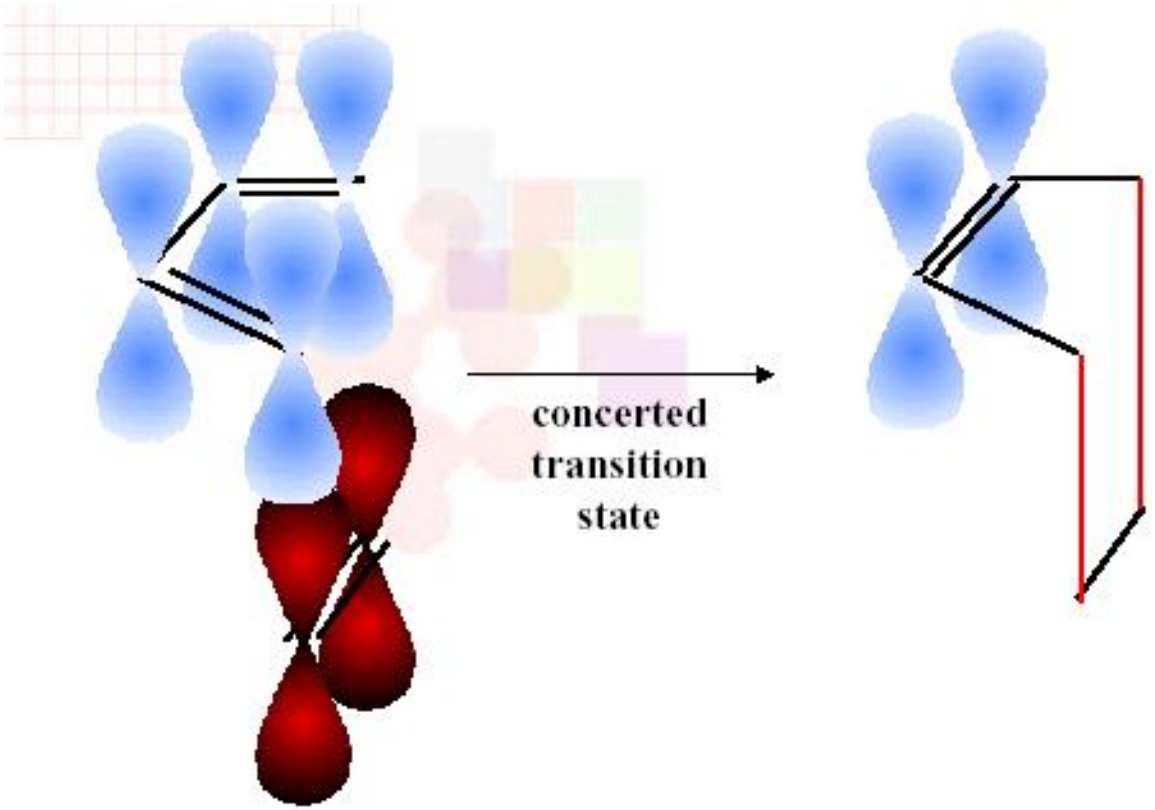
دی انهایی که شامل گروه الکترون دهنده و دی انوفیل هایی که دارای گروههای الکترون کشنده می باشند این عمل را بهتر انجام میدهند.



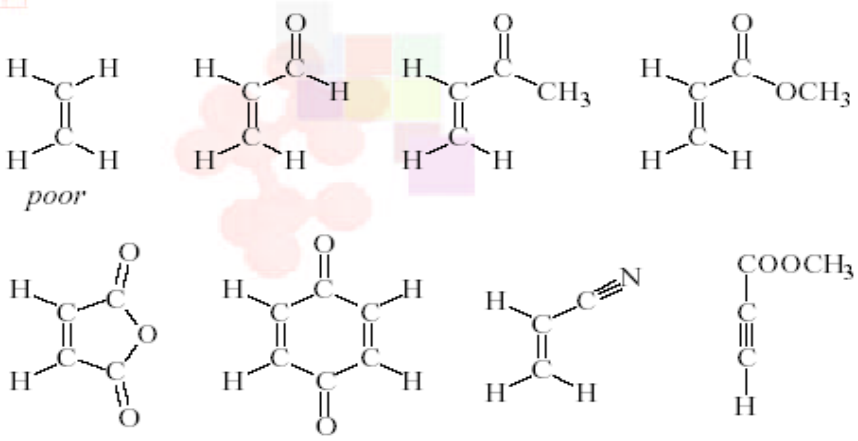
a diene **a dieneophile**

Cycloaddition reactions work best with **dienes** containing **electron donating substituents** and **dienophiles** containing **electron withdrawing substituents**.

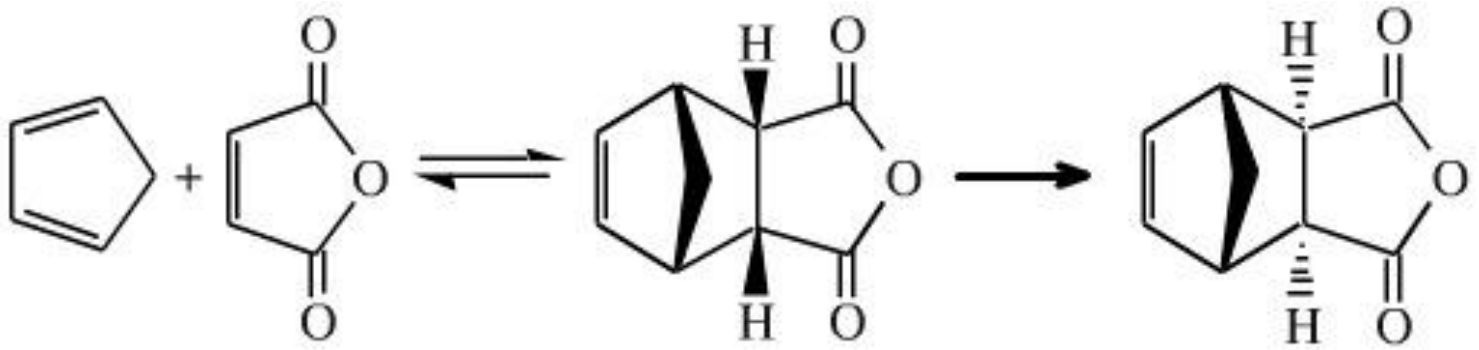
s-*cis* stereochemistry is required for a 4+2 cycloaddition reaction


concerted
transition
state

Common Dienophiles



Maleic anhydride is an electron poor dieneophile which reacts with cyclopentadiene to give an endo Diels-Alder adduct. Upon heating at 190°C, the endo conformation adduct adopts the more stable exo-adduct conformation.



1-Methoxy-1,3-butadiene reacts with acrylonitrile to give 3-methoxy-4-cyanocyclohexene rather than the 3-methoxy-5-cyanocyclohexene isomer. This "ortho" regioselectivity of this reaction can be rationalised using FMO theory.

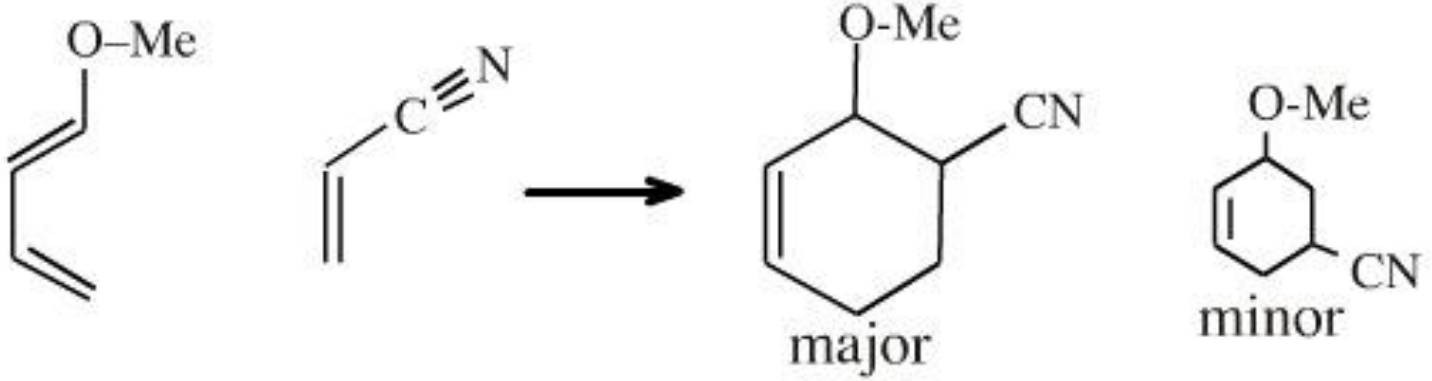
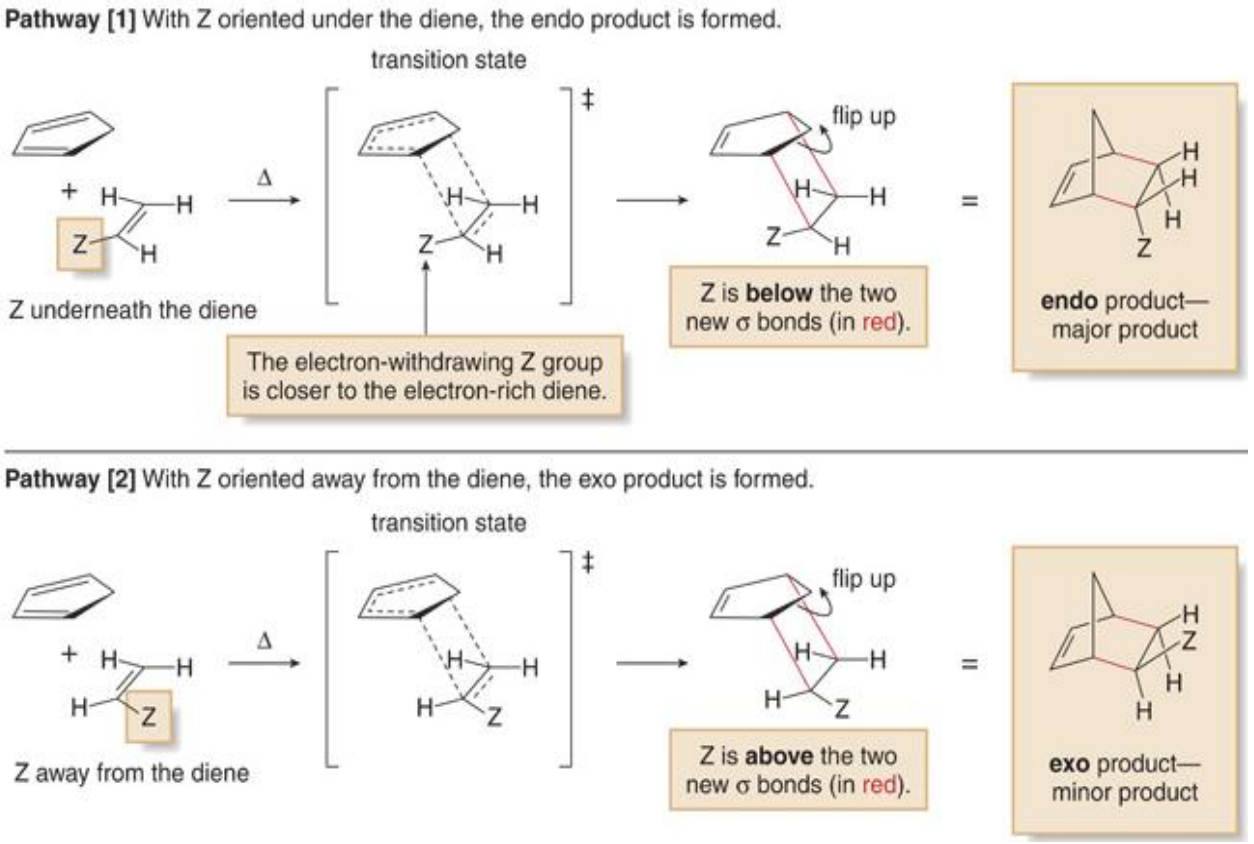
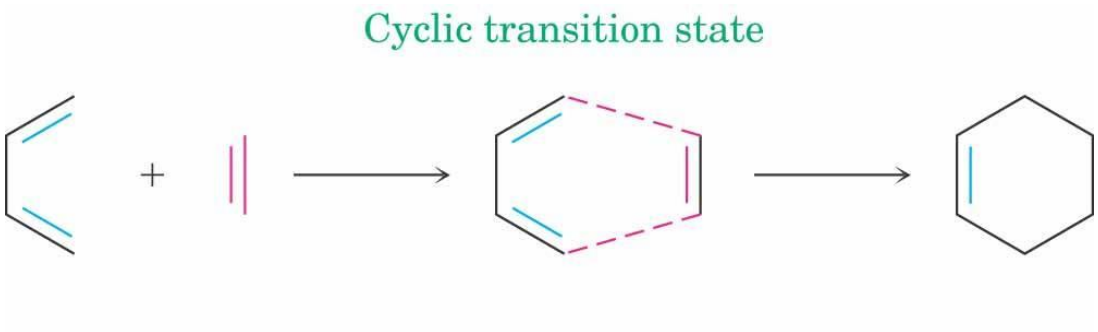
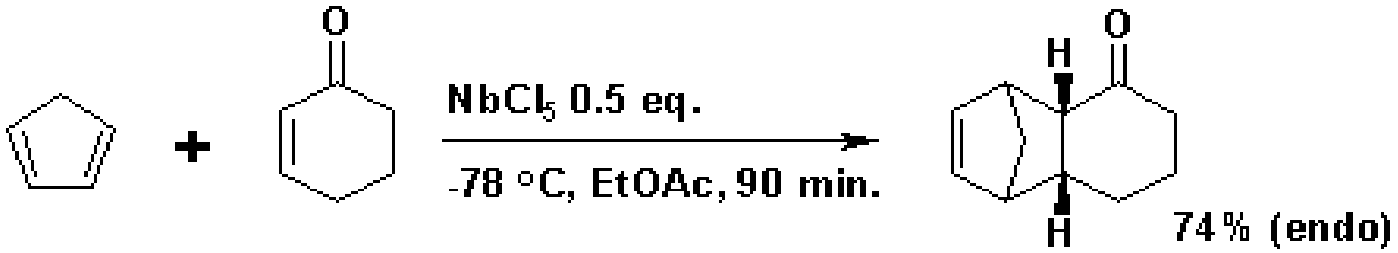


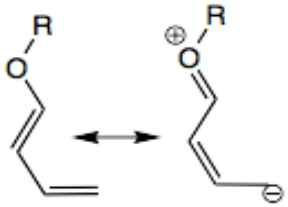
Figure 16.11
How endo and exo products are formed in the Diels–Alder reaction



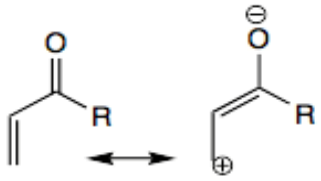
diene + dienophile



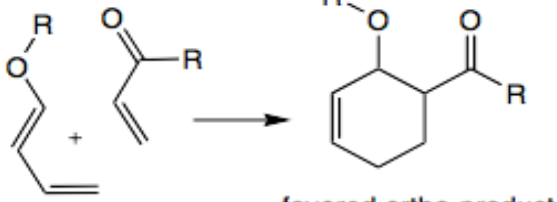




diene with ERG

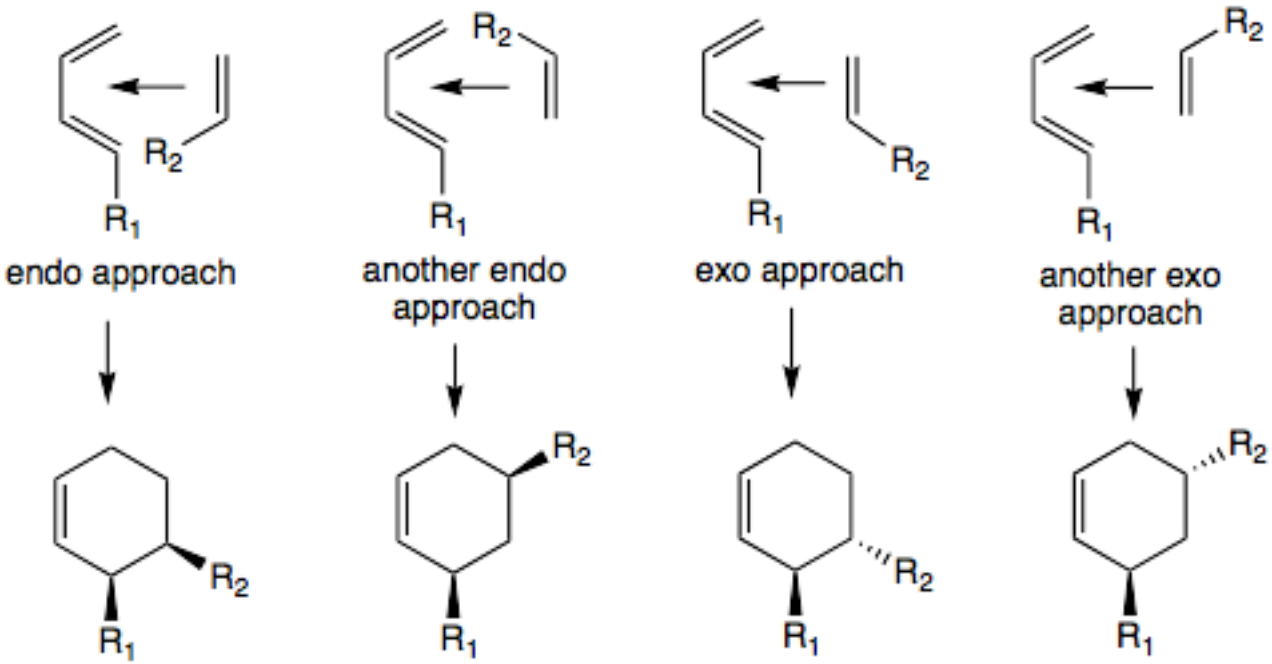


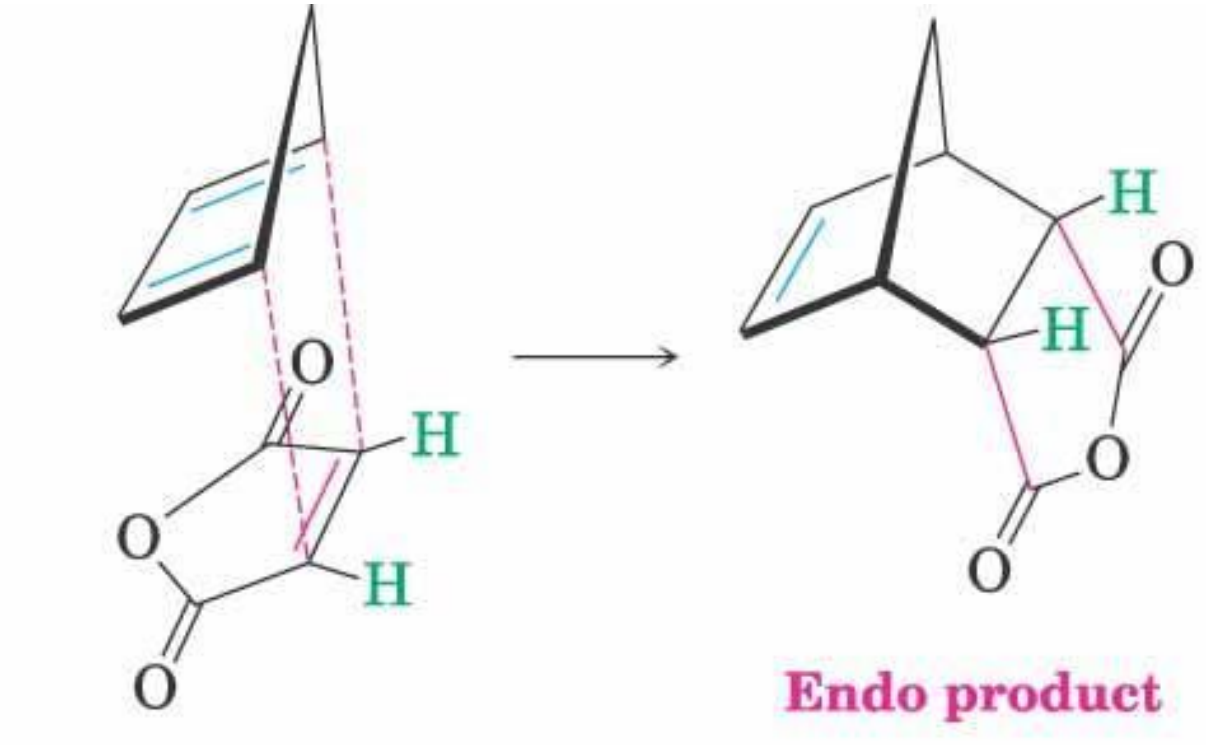
dienophile with EWG

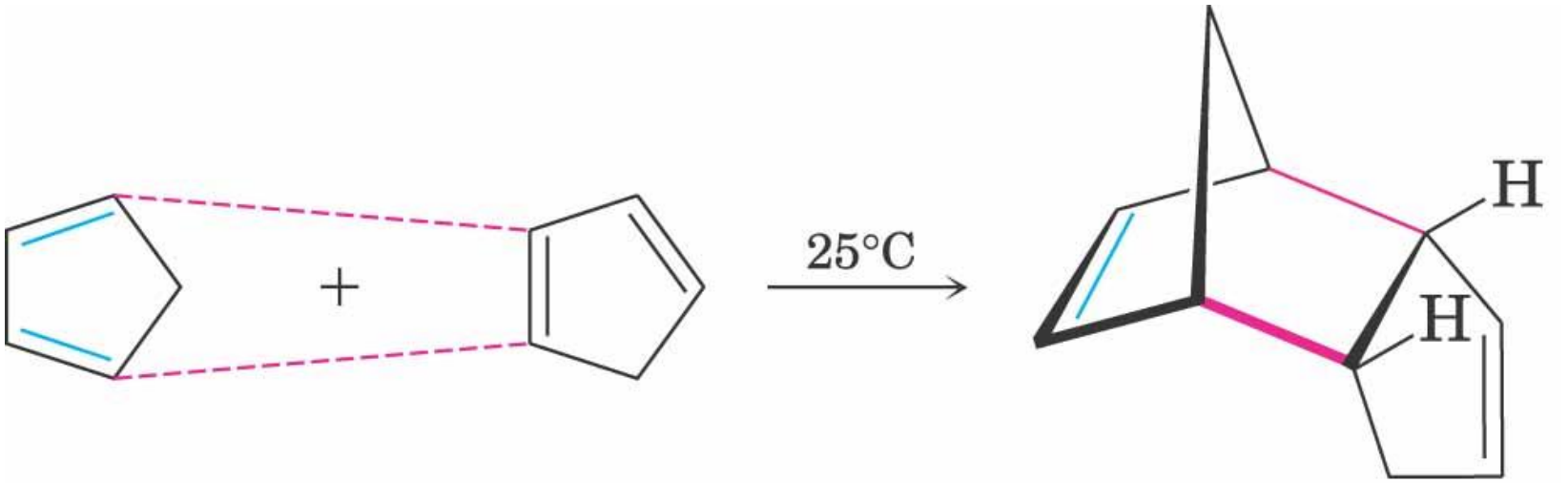


Diels-Alder reaction

favored ortho-product (meta will be minor or will not form at all)


R2
R1
endo approach
R2
R1
another endo approach
R2
R1
exo approach
R2
R1
another exo approach
R2
R1
R2
R1
R2
R1
R2
R1


O
H
O
H
O
H
H
O
O
O
Endo product

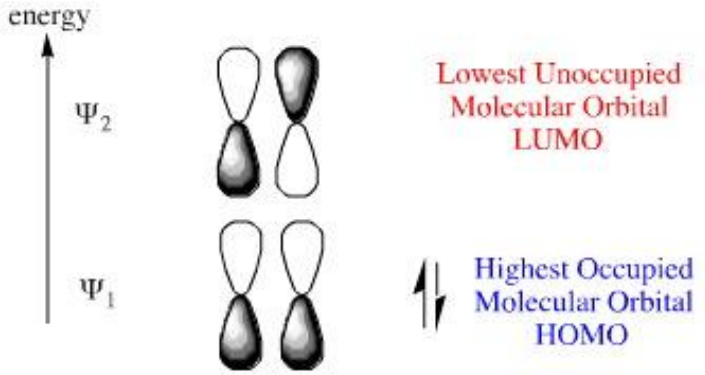


1,3-Cyclopentadiene (*s*-cis)

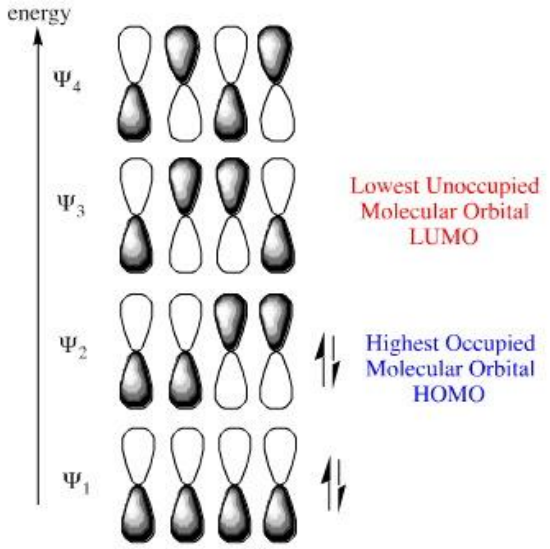
Bicyclopentadiene

©2004 Thomson - Brooks/Cole

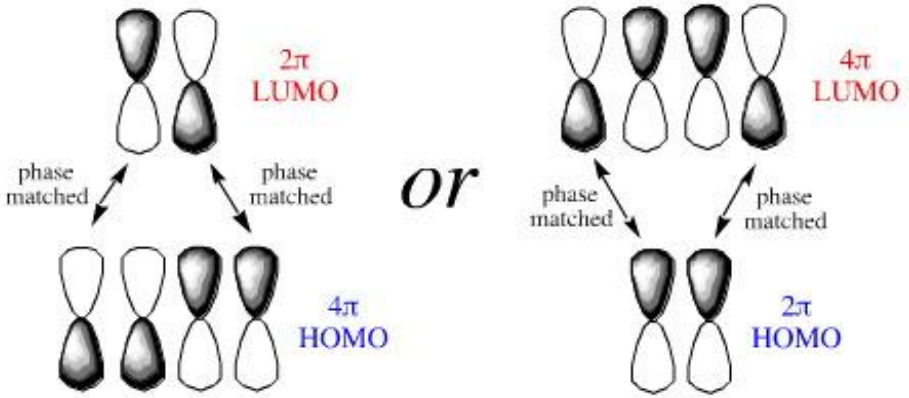
توضیح واکنش های حلقه زایی با استفاده از تئوری اوربیتالهای مولکولی مرزی:FMO

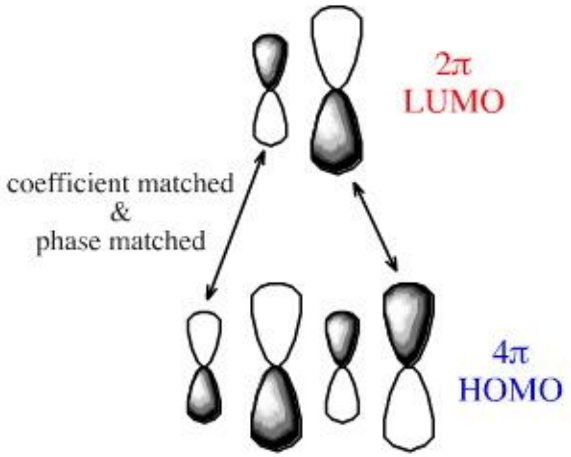


The alkene (dienophile) component has two electrons is a "single" pi-bond. FMO theory, here, identifies the HOMO and LUMO components of this system:

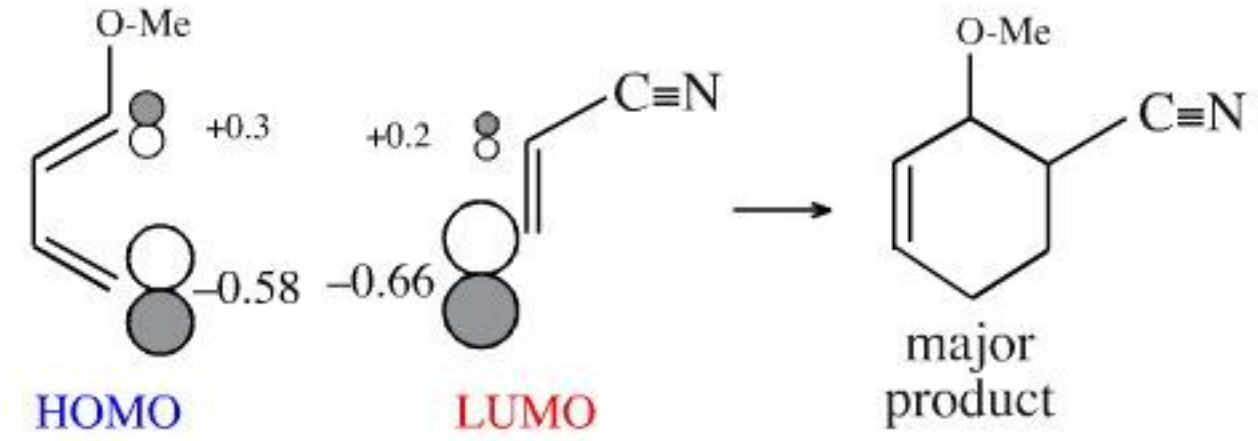


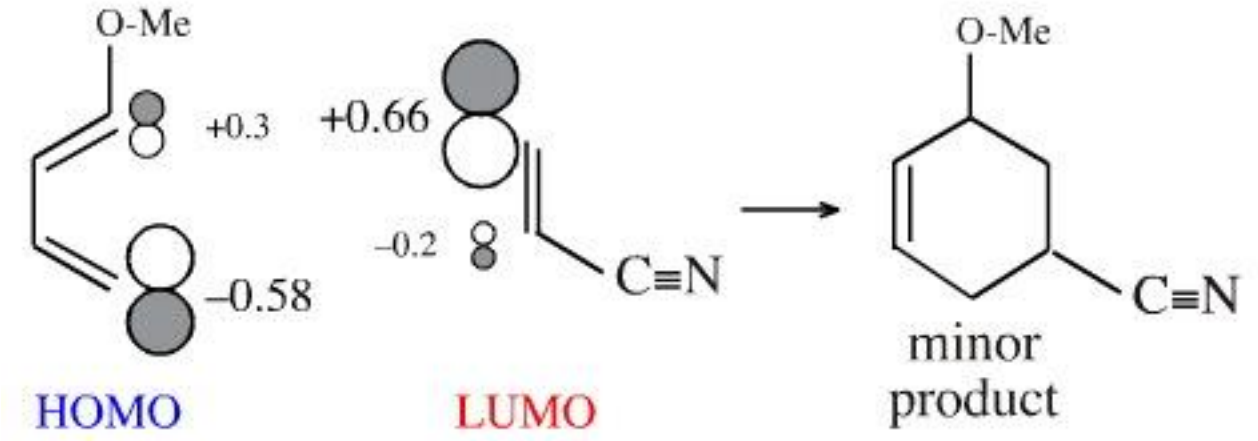
the diene which has four electrons in is conjugated pi-system can have its HOMO and LUMO identified within FMO theory


2π
LUMO
phase
matched
phase
matched
4π
HOMO
or
4π
LUMO
phase
matched
phase
matched
2π
HOMO

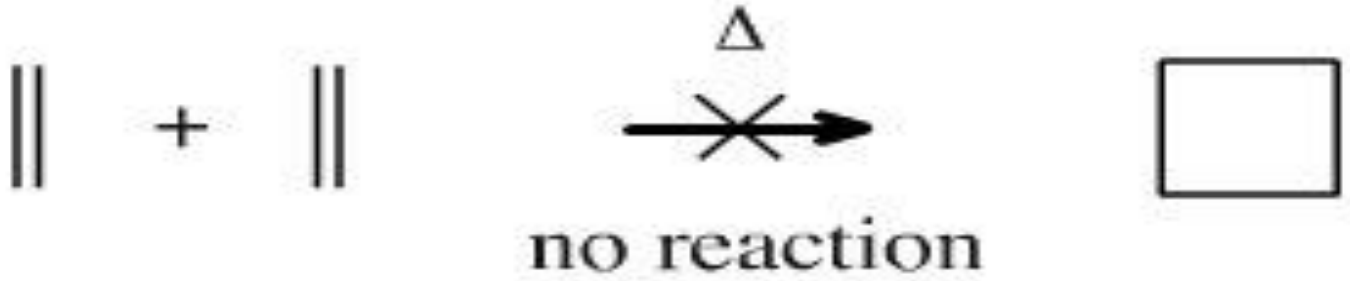

2π
LUMO
coefficient matched
&
phase matched
4π
HOMO

توضیح استرئوشیمی واکنش بر اساس برهم کنش HOMO-LUMO

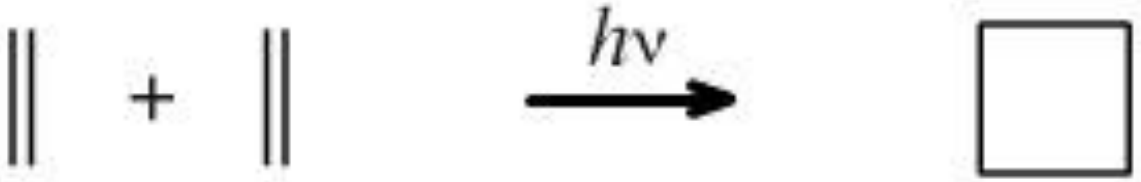




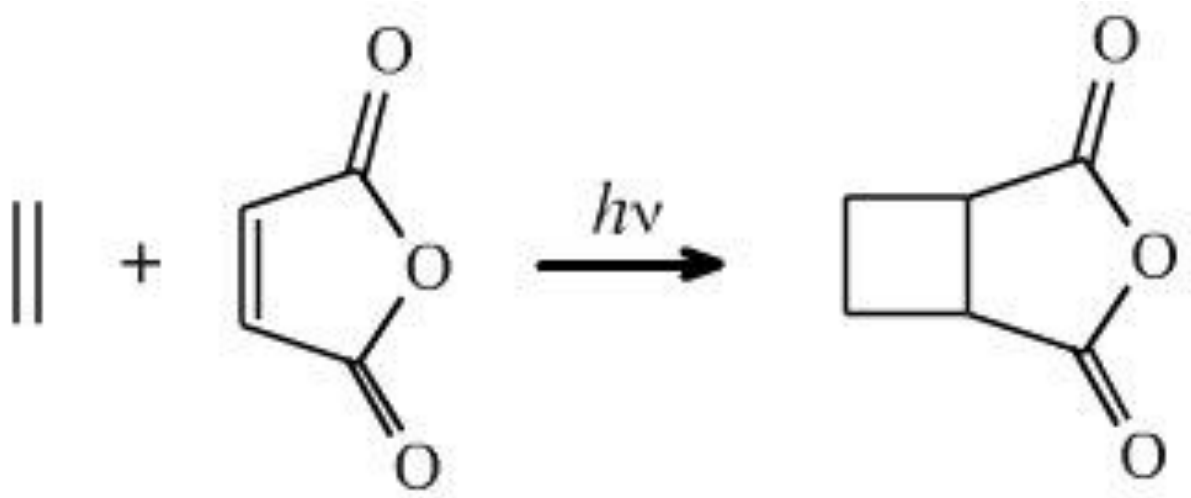
Using the FMO logic discussed above, some pi/pi interactions are FMO symmetry forbidden and do not result in cycloaddition. Consider dimerisation of ethene to cyclobutane.
This reaction does not occur in either the forward or reverse directions under thermal conditions:



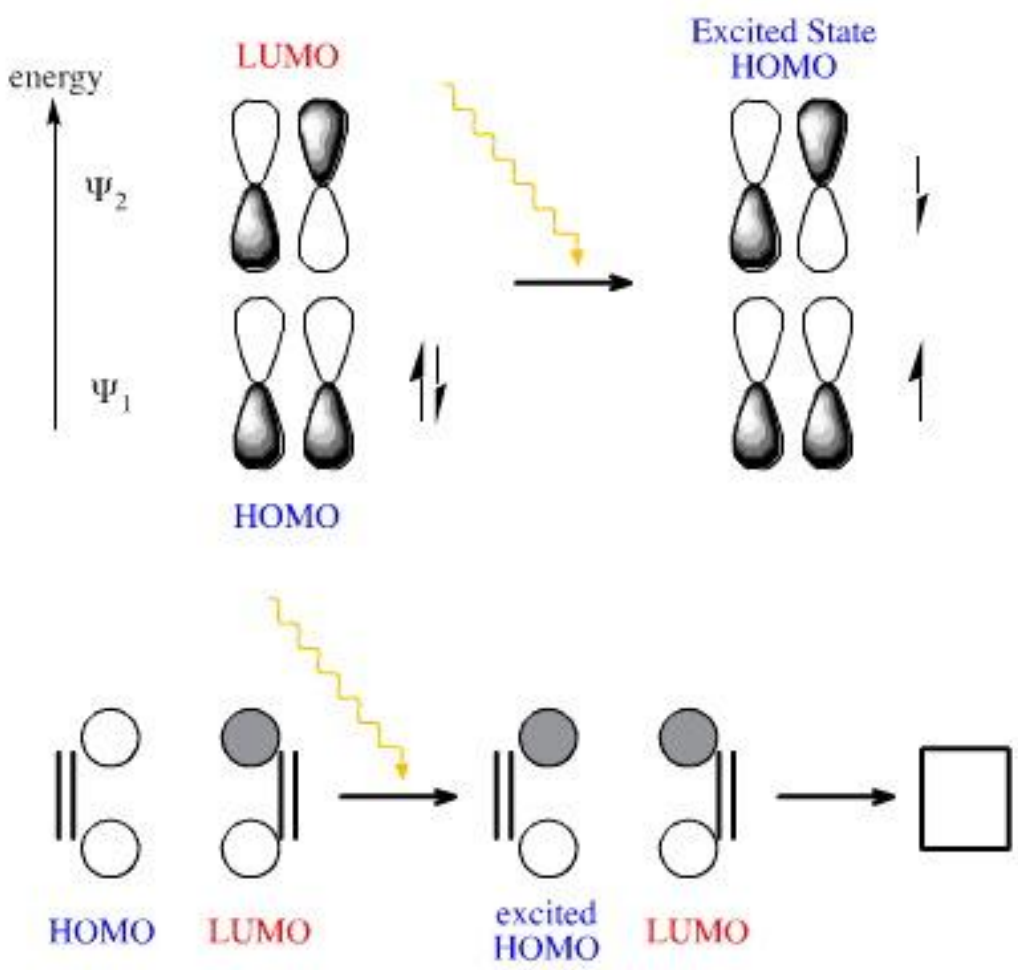
But... the [2+2] cycloaddition reaction *does* occur under photochemical conditions:



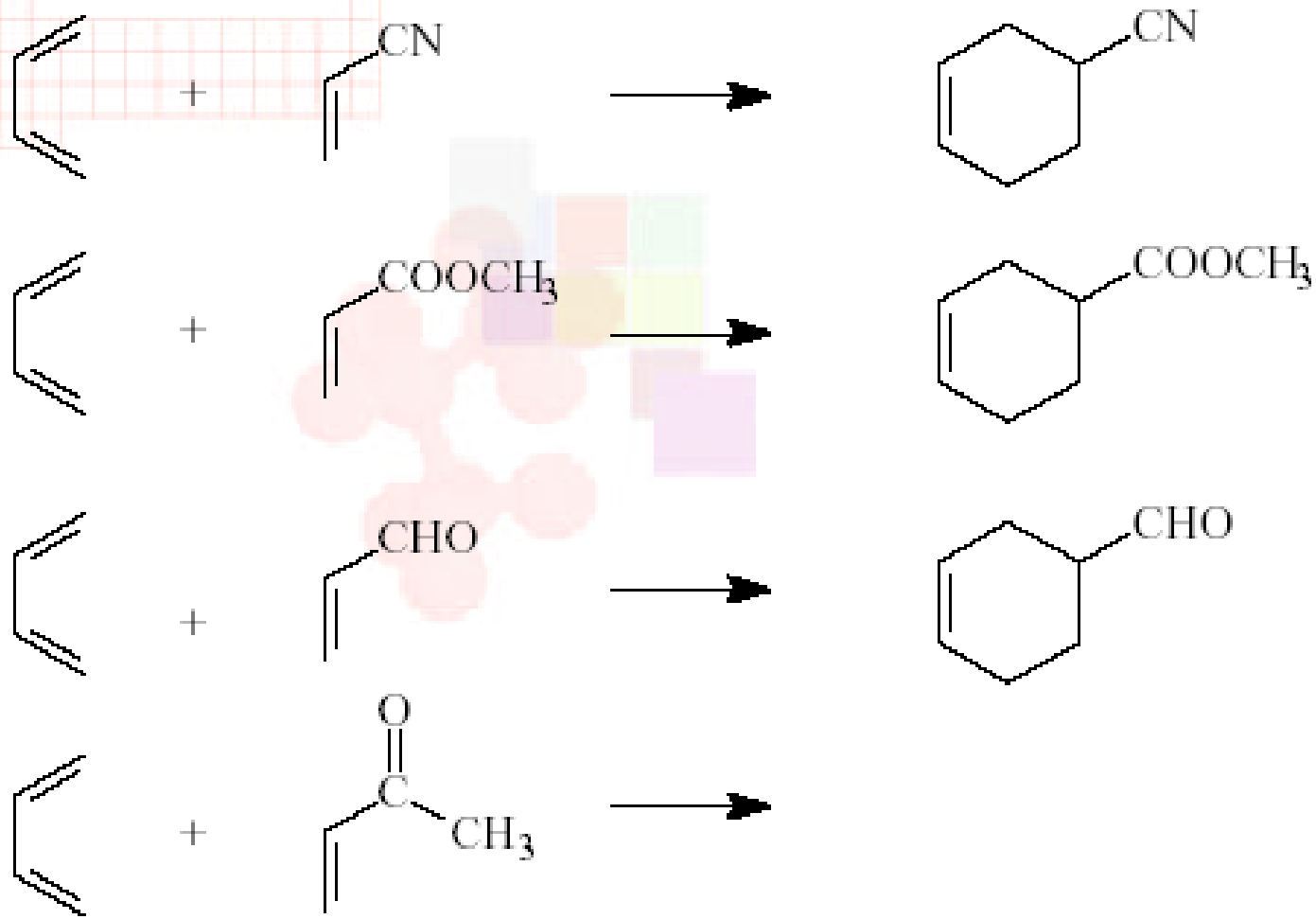
Ethene can [2+2] cycloadd to maleic anhydride to give the cyclobutane diacid anhydride:

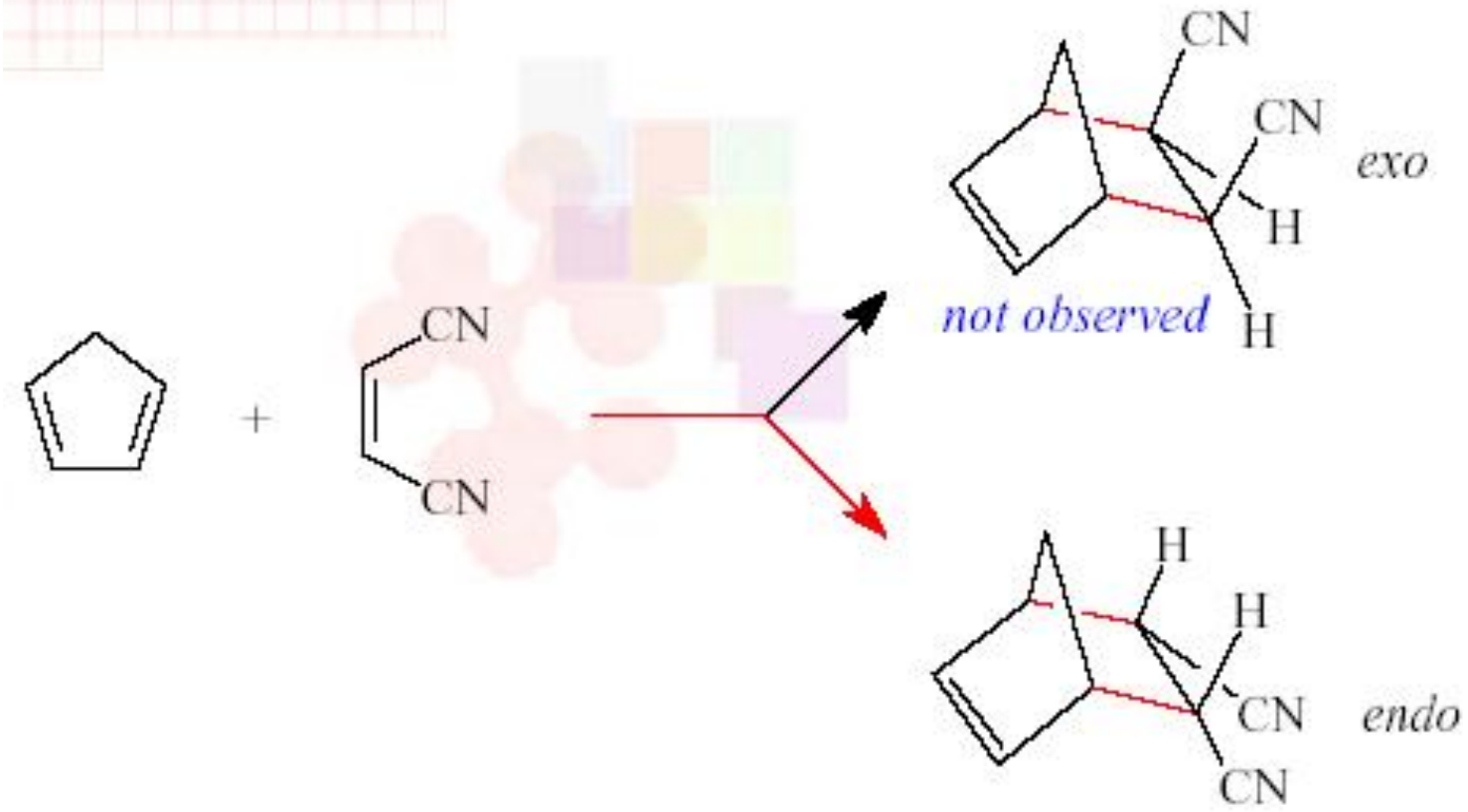


UV light, –65°C, 44 hours, 77% yield.

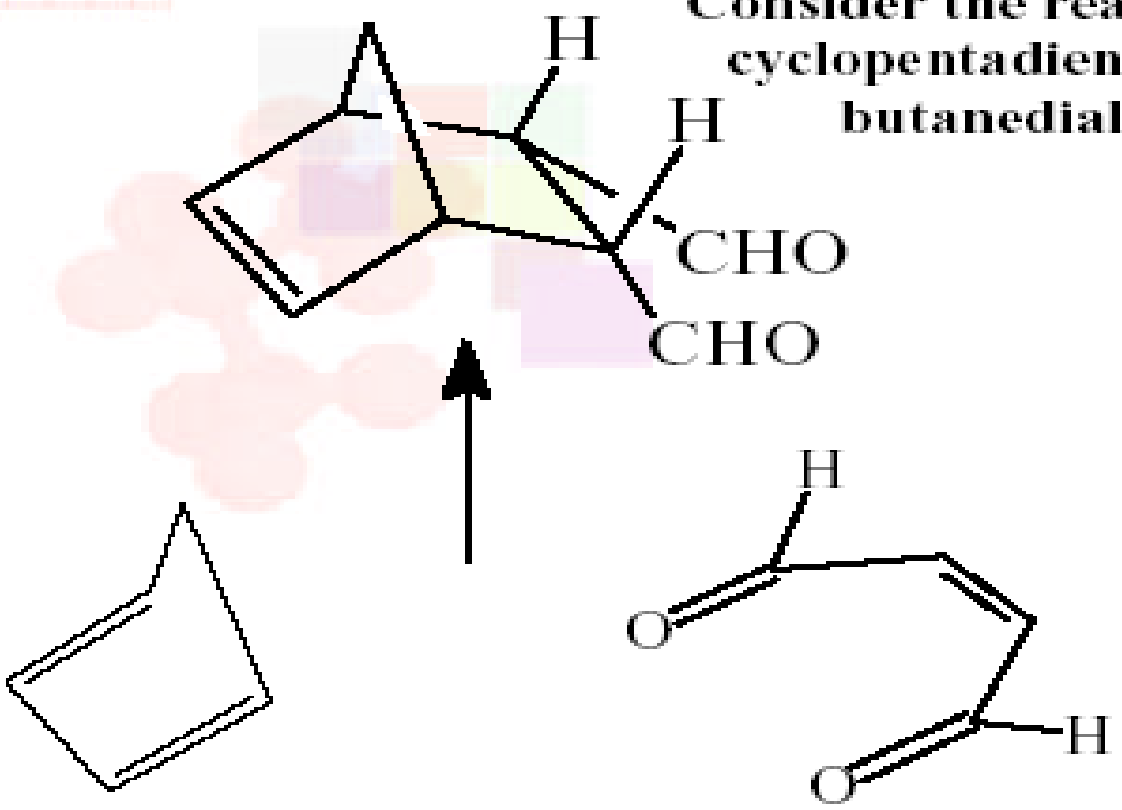


[2+2], [4+4] and [6+6] cycloadditions are thermally disallowed, but photochemical examples are known.

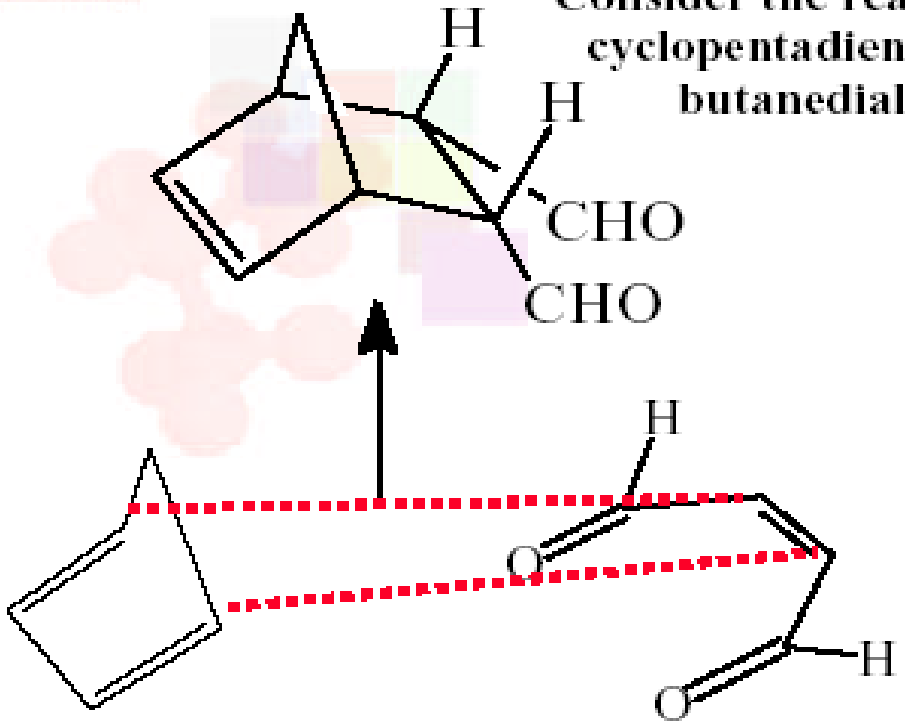

CN
COOCH3
CHO
O
C
CH3
CN
COOCH3
CHO

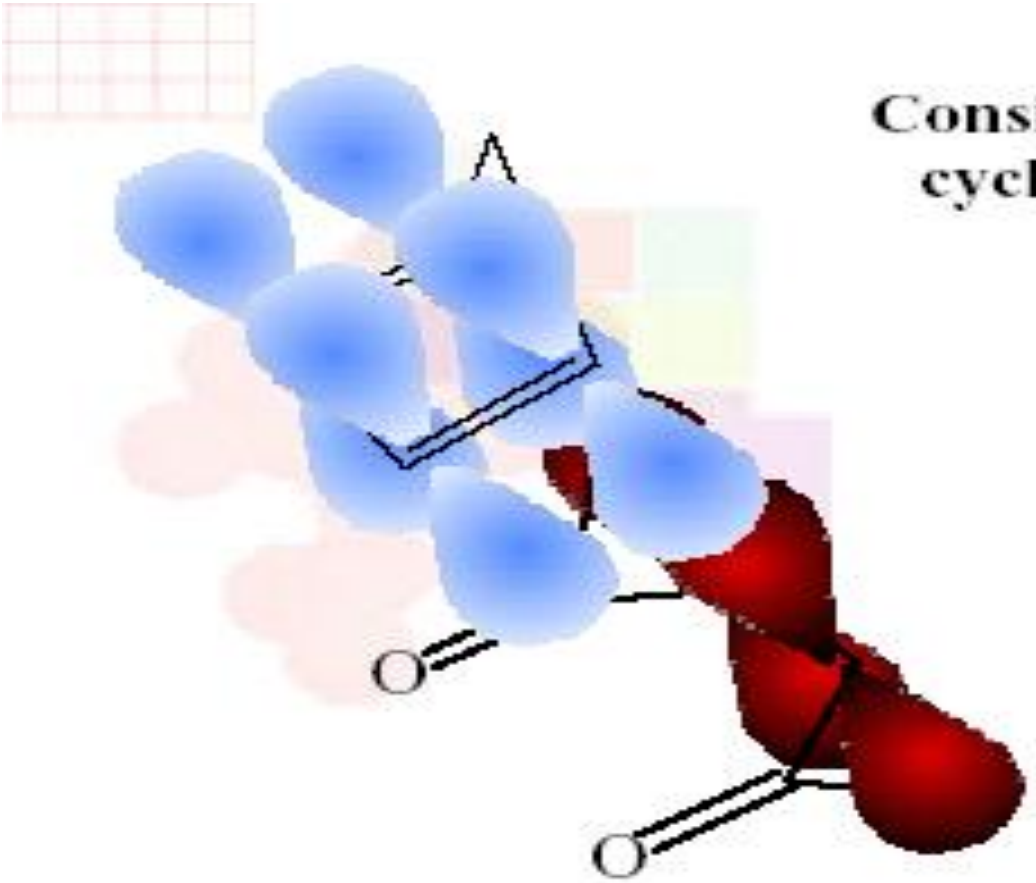

CN
CN
CN
CN
exo
H
H
not observed
H
H
CN
CN
endo

Consider the reaction of cyclopentadiene with butanedial...

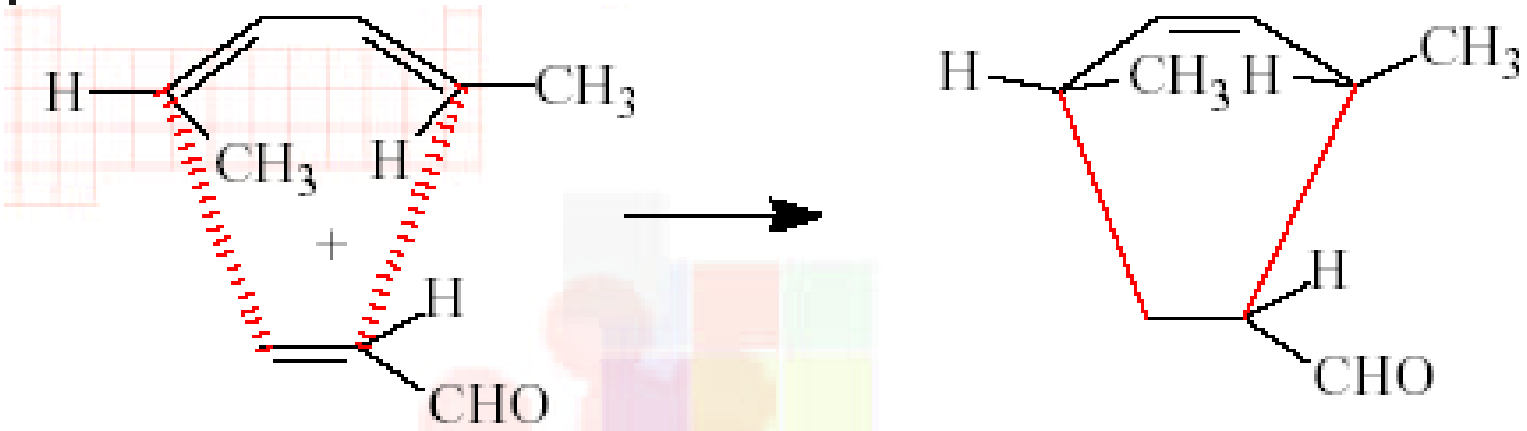


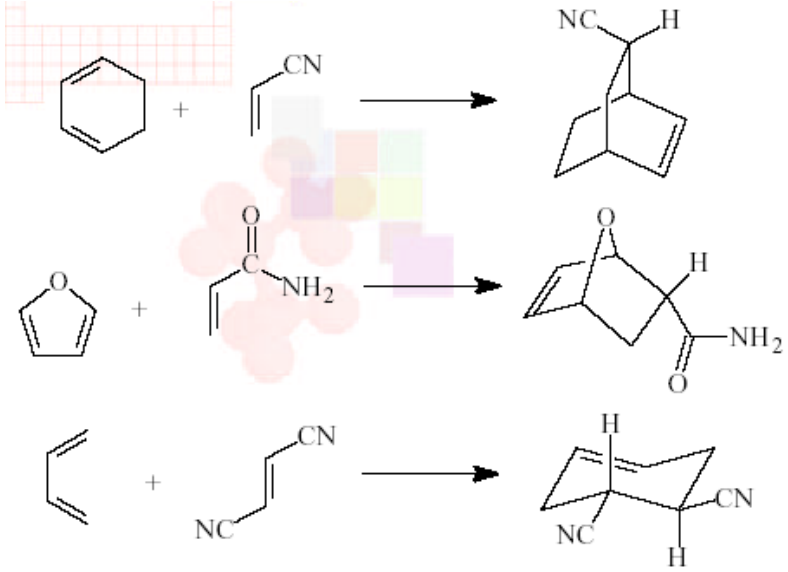
Consider the reaction of cyclopentadiene with butanedial...





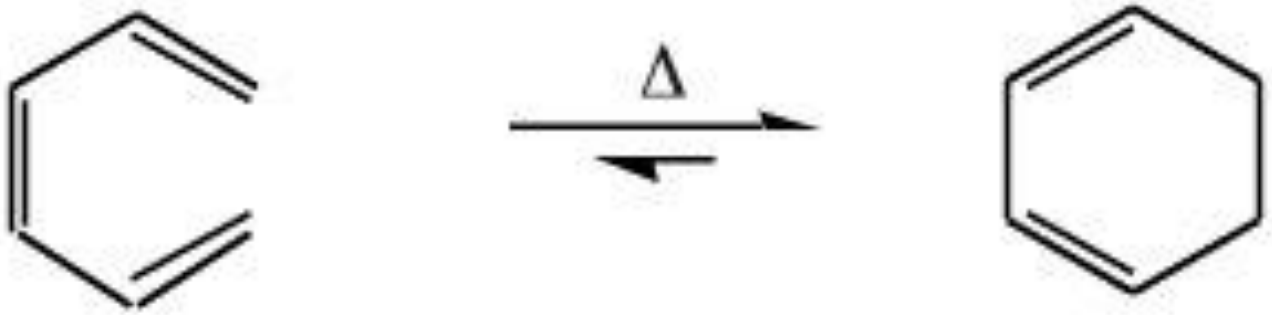
Consider the reaction of cyclopentadiene with butanedial...


H
CH3
CH3
H
+
H
CHO
H
CH3
H
CH3
H
CHO


+
CN
NC
H
O
+
O
C
NH2
O
H
NH2
O
+
CN
NC
H
CN
NC
H

Electrocyclic reactions : واکنشهای الکتروسیکلی

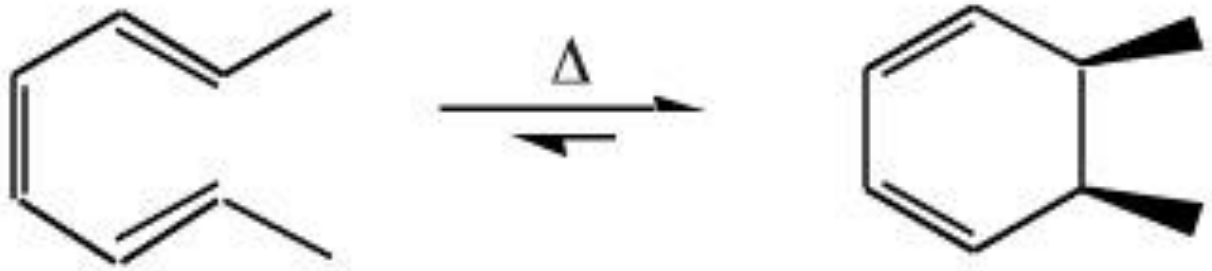
واکنشهای الکتروسیکلی دارای مرحله تک مولکولی بوده که در این مرحله پیوندهای پای به سیگما تبدیل شده و حلقه زایی میشود .



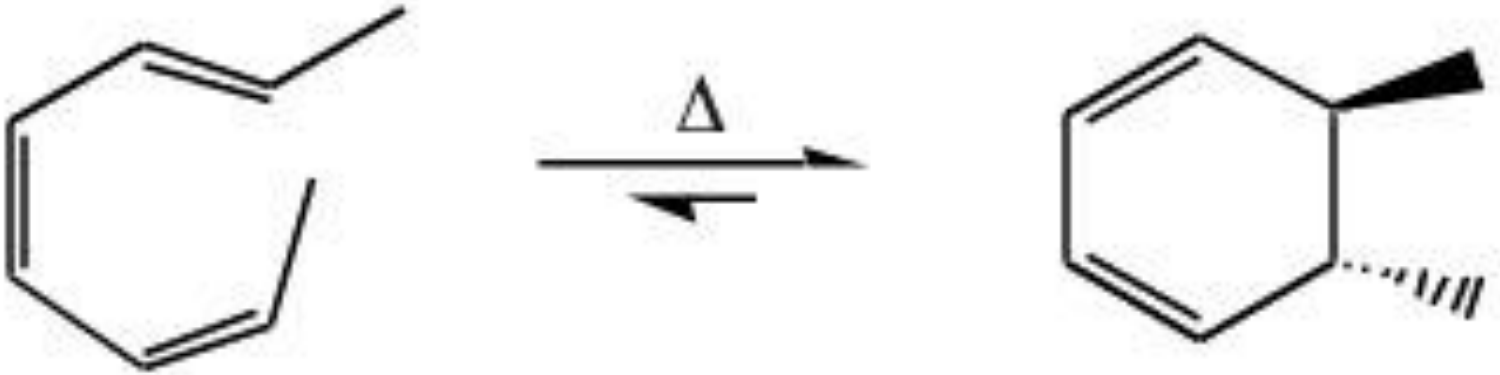
Note that the 3-alkene must be *cis* for the reaction to occur.

The reverse, or *retroelectrocyclic*, reaction can also occur. This is seen with the ring opening of cyclobutene to 1,3-butadiene:

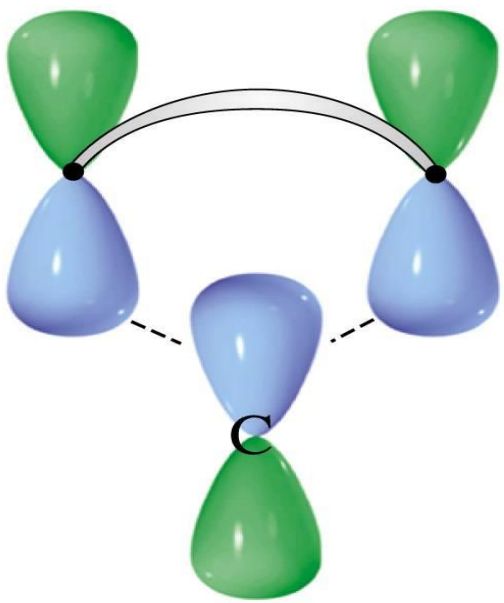
Electrocyclic reactions, like all pericyclic processes, exhibit great stereoselectivity. Consider two 1,3,5-hexatriene systems embedded into longer hydrocarbon chains.
***trans-cis-trans*-2,4,6-Octatriene will ring close to give a *cis* ring:**



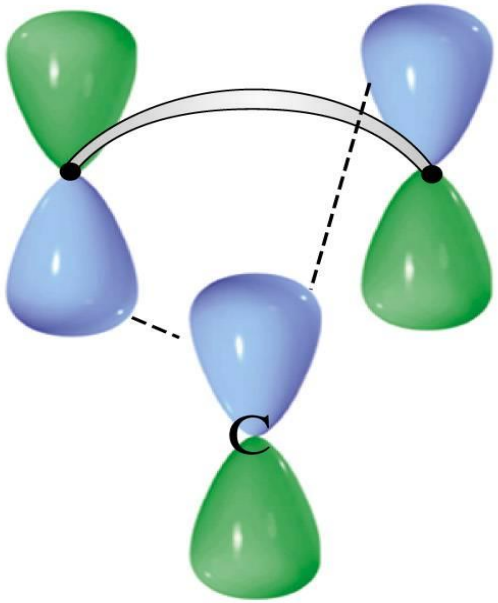
trans-cis-cis-2,4,6-Octatriene will ring close to give a trans ring



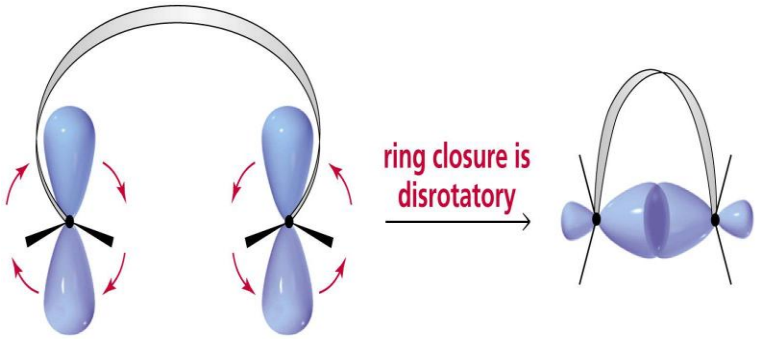
carbon migrating with one of its lobes interacting

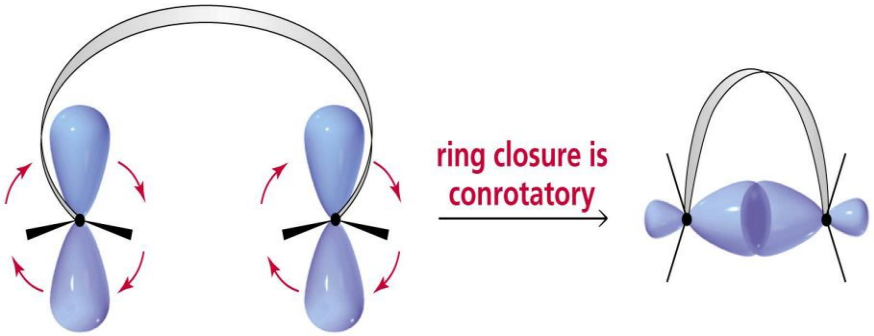


suprafacial rearrangement



antarafacial rearrangement


ring closure is
disrotatory

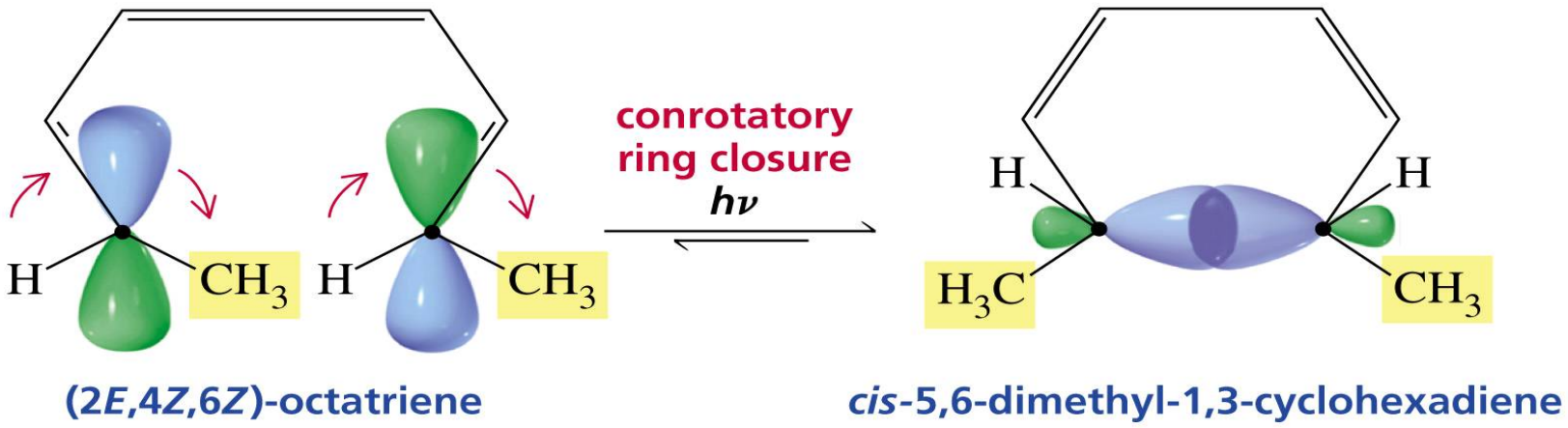

ring closure is
conrotatory

disrotatory
ring closure
HOMO is symmetric

conrotatory
ring closure
HOMO is asymmetric

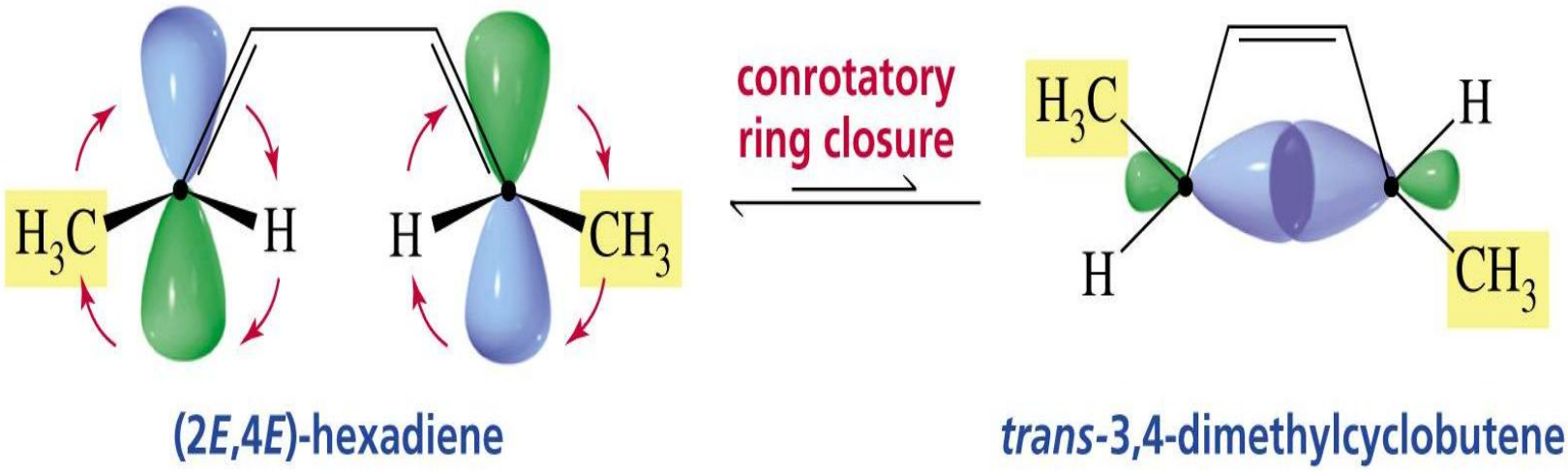
(2*E*,4*Z*,6*Z*)-octatriene

trans-5,6-dimethyl-1,3-cyclohexadiene



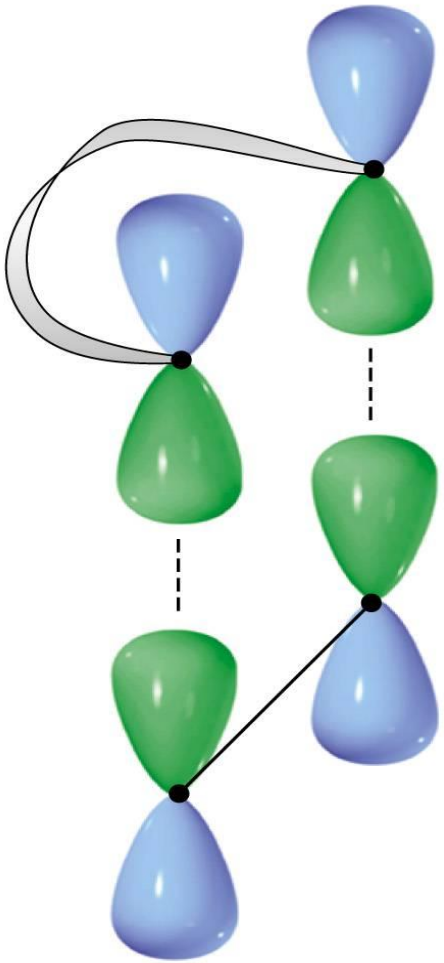
(2*E*,4*Z*,6*Z*)-octatriene

cis-5,6-dimethyl-1,3-cyclohexadiene

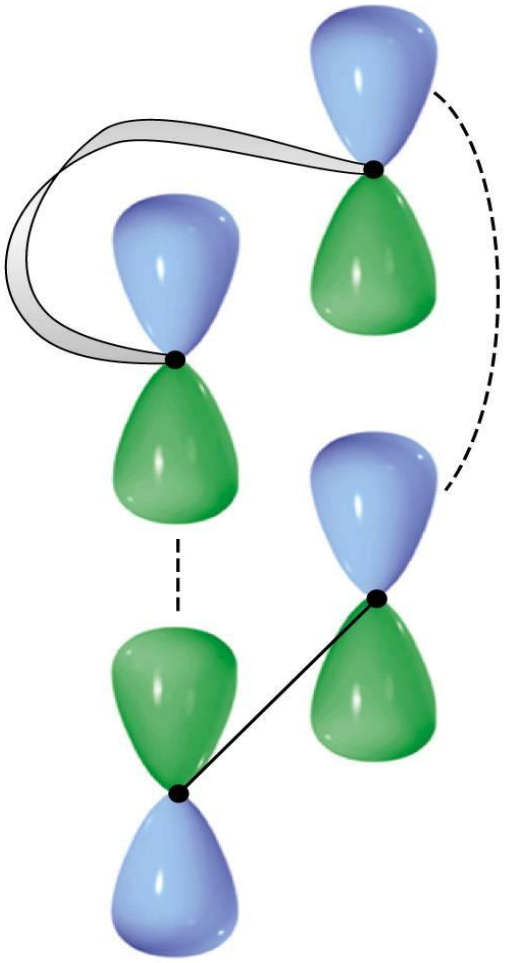


(2*E*,4*E*)-hexadiene

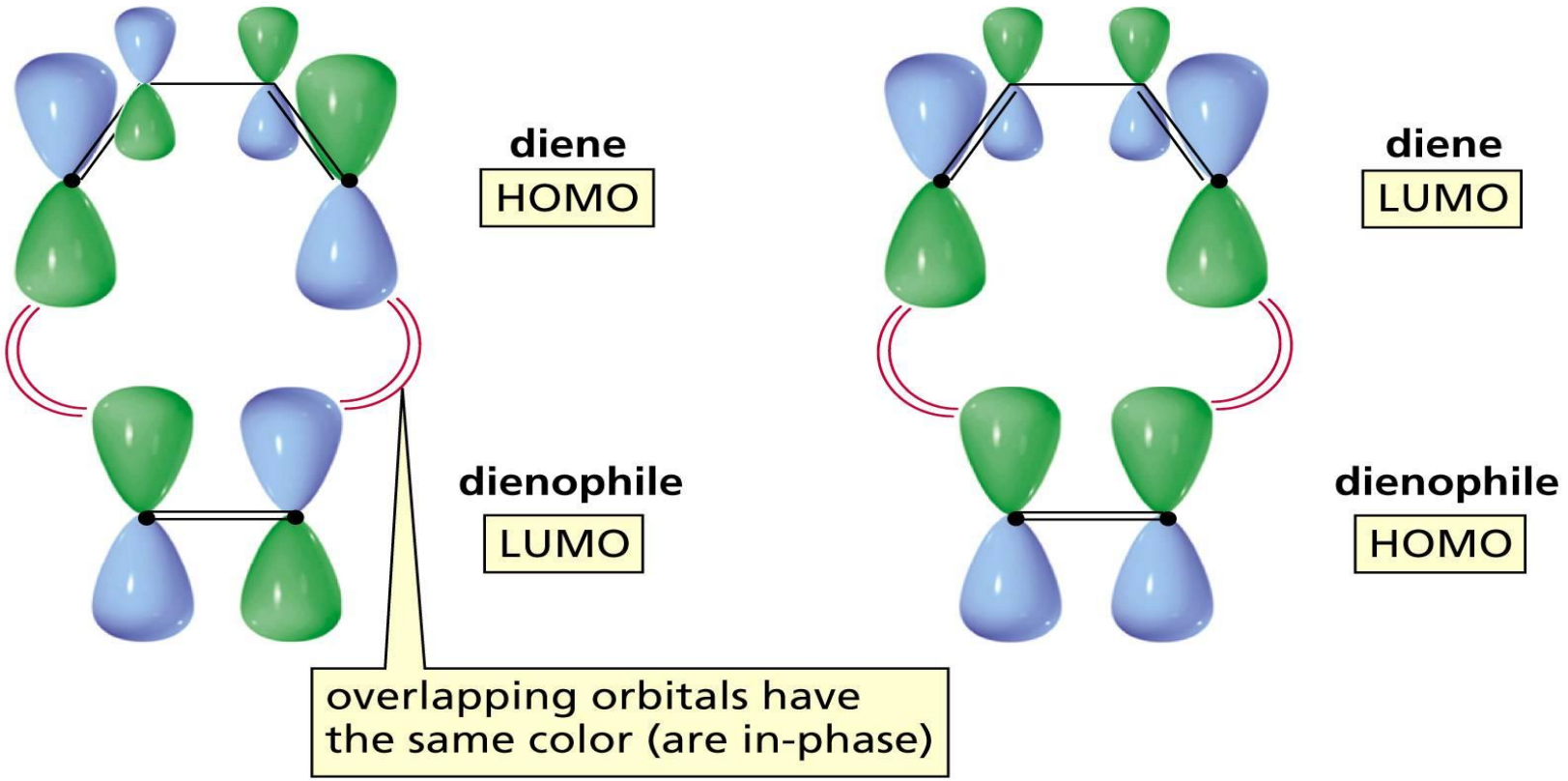
trans-3,4-dimethylcyclobutene

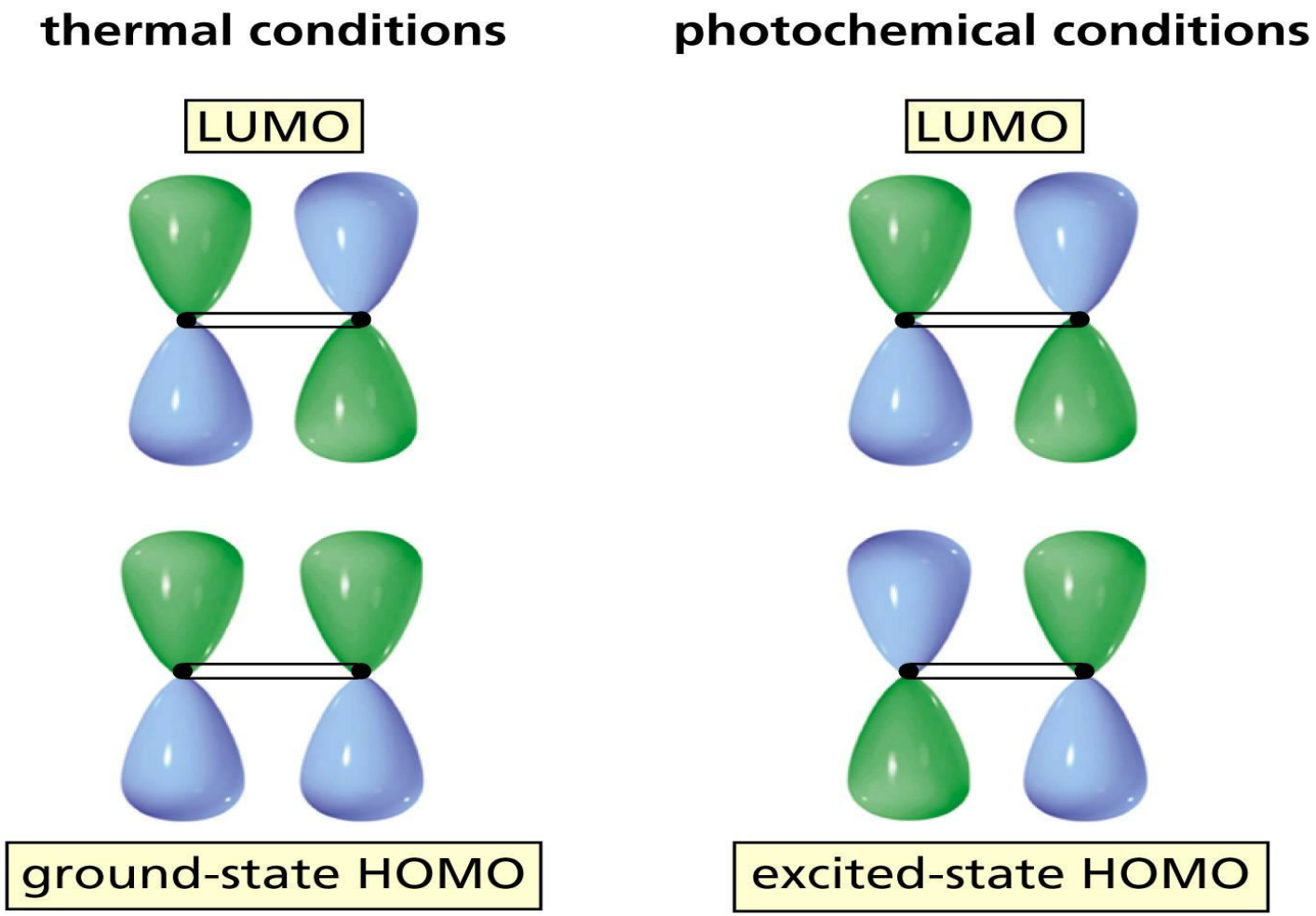


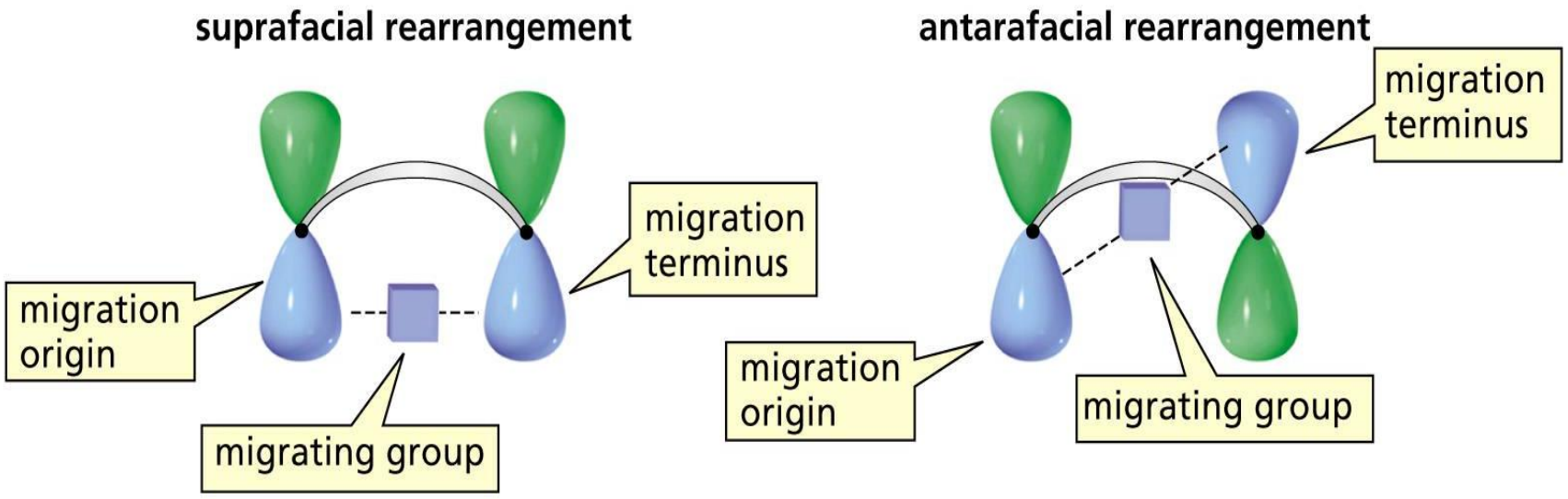
suprafacial
bond formation



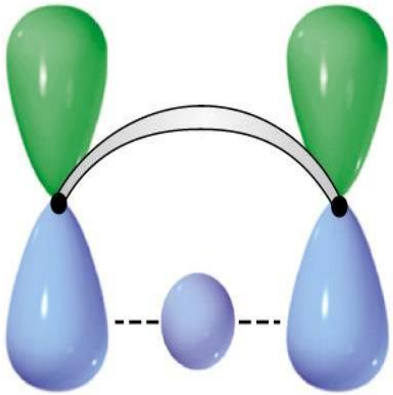
antarafacial
bond formation


diene
HOMO
dienophile
LUMO
overlapping orbitals have
the same color (are in-phase)
diene
LUMO
dienophile
HOMO

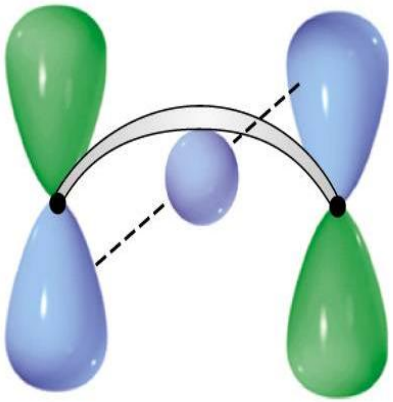

thermal conditions
photochemical conditions
LUMO
LUMO
ground-state HOMO
excited-state HOMO


suprafacial rearrangement
migration terminus
migration origin
migrating group
antarafacial rearrangement
migration terminus
migration origin
migrating group

migration of hydrogen

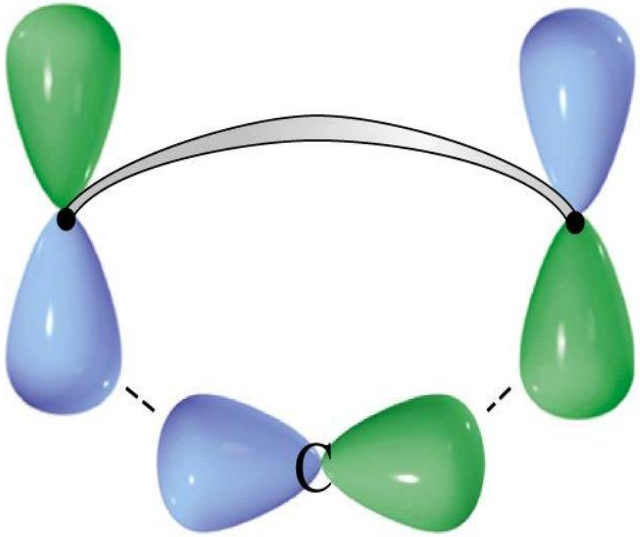


suprafacial rearrangement

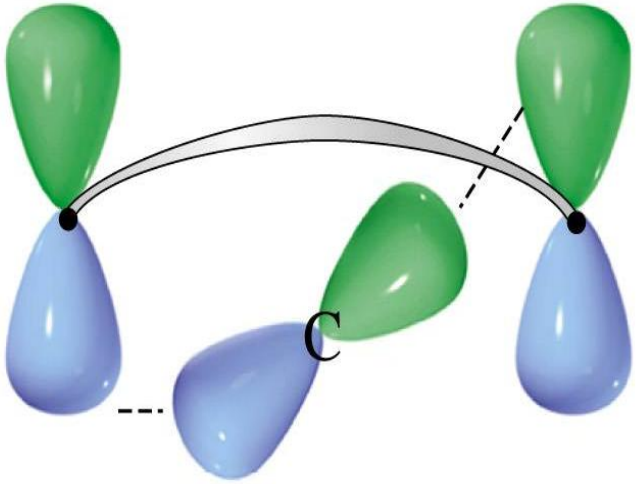


antarafacial rearrangement

carbon migrating with both of its lobes interacting

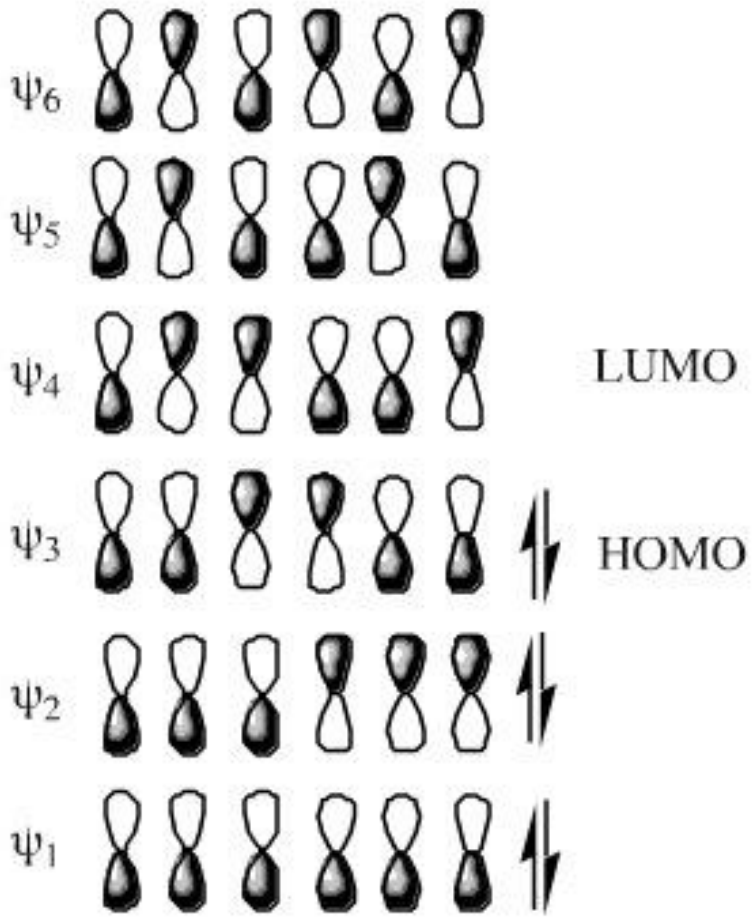


suprafacial rearrangement

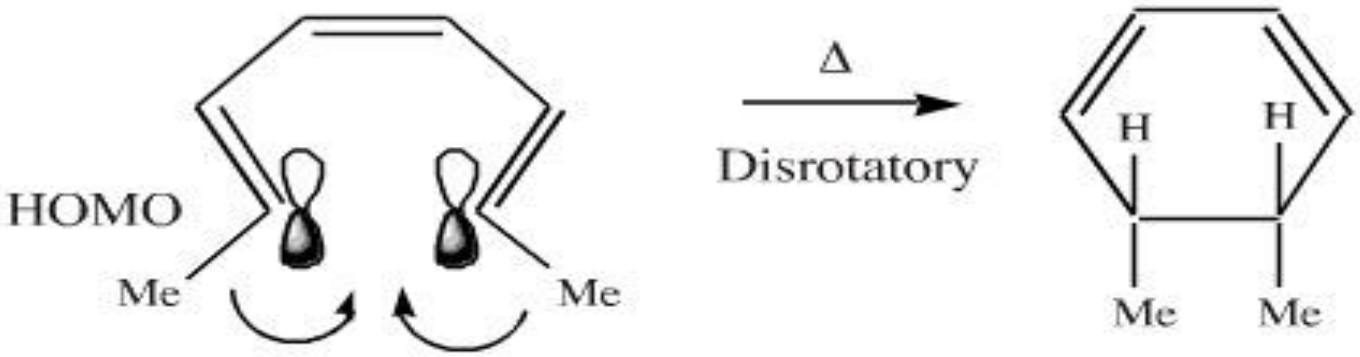


antarafacial rearrangement

As with cycloaddition, this selectivity can be explained by examining the FMOs, specifically the HOMO:

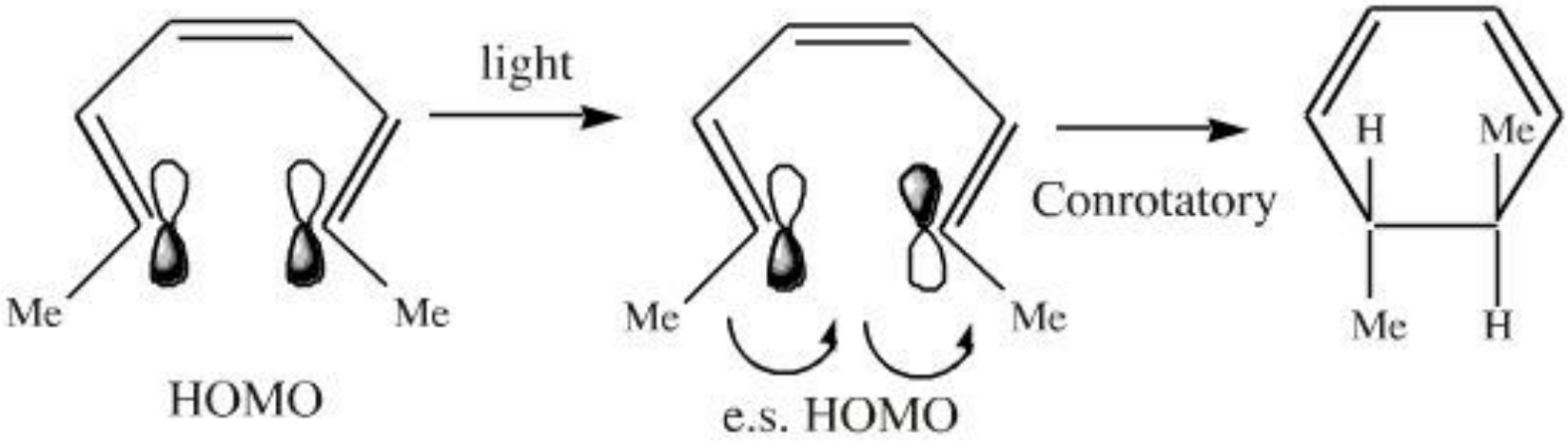


If the termini of the HOMO is superimposed upon the triene system, it can be seen that the end groups must rotate in a disrotatory manner to form the bond:

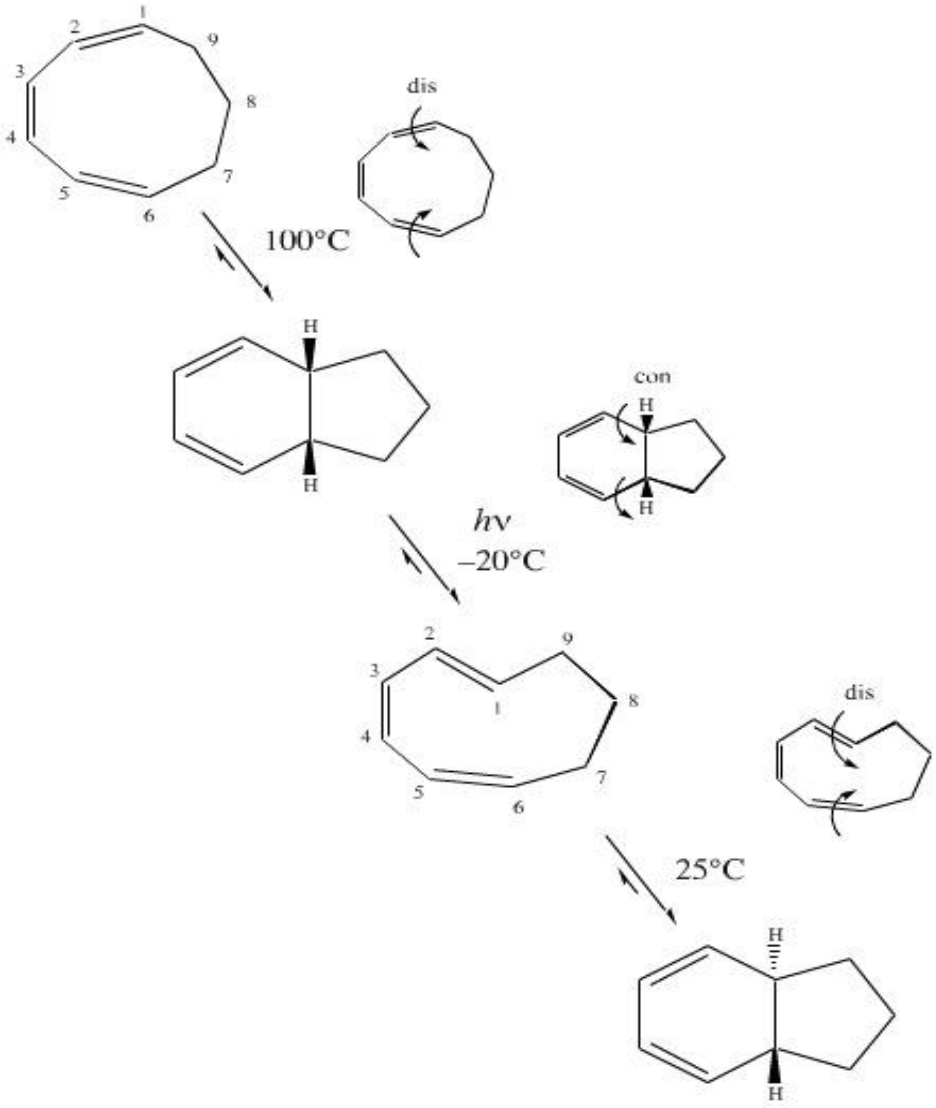


However, electrocyclic reactions can also occur photochemically. When photoactivated, an electron moves from the HOMO to the next orbital, the LUMO. (Now this orbital contains an electron it is no longer unoccupied,it is either a SOMO or an excited state HOMO).

The photoexcited system will ring close in an opposite manner to the thermal system and the groups conrotate to form the sigma bond.



This thermal and photo selectivity can be exploited in the reaction sequence below in which 1,3,5-cyclononatriene is converted into bicyclic systems with first *cis* and then *trans* ring junctions.
The initial 1,3,5-cyclononatriene is all *cis*. This is thermally ring closed in a disrotatory manner and then photo-ring opened at -20°C in a conrotatory manner. The 1,3,5-cyclononatriene now has two *cis* and one *trans* double bonds, however, the nine membered ring is able to accommodate the strain of a *trans* alkene. Thermal ring closure gives the *trans*-ring junction.

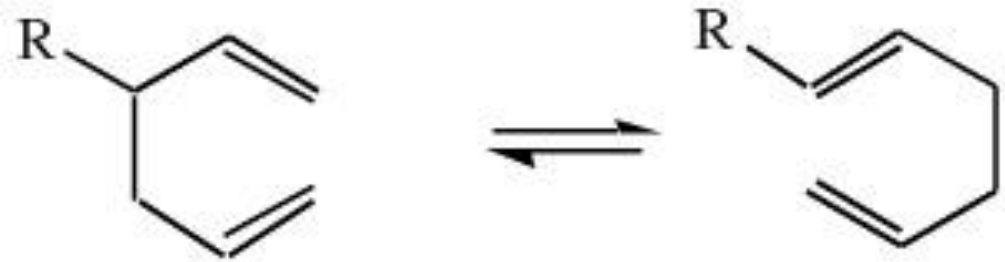


نوآرایی های سیگما تروپی : Sigmatropic Rearrangements

واکنشهای سیگما تروپی نیز مشابه واکنشهای الکتروسیکلی تک مولکولی هستند در این نوآرایی پیوند سیگما به موقعیت جدیدی در سیستم منتقل می شود .

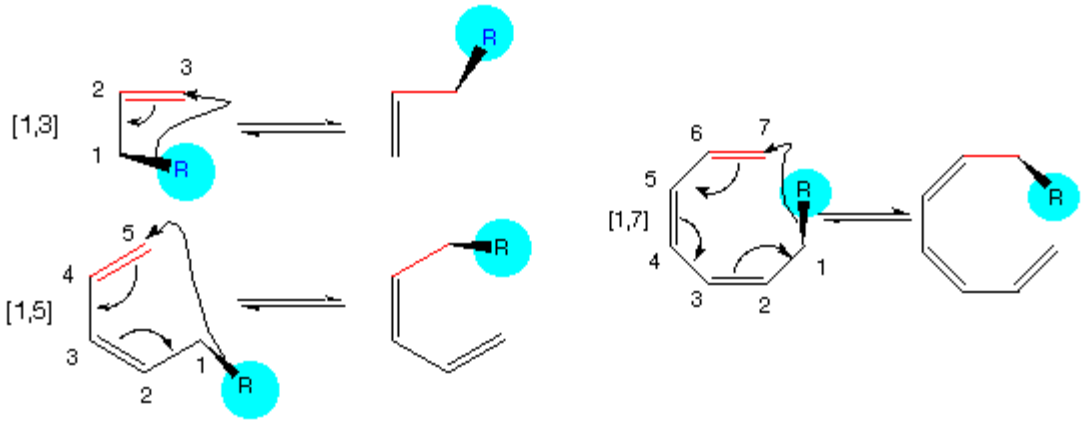
The [1,5] shift of hydrogen in a 1,3-pentadiene system:

The [3,3] Cope rearrangement:



Sigmatropic rearrangements

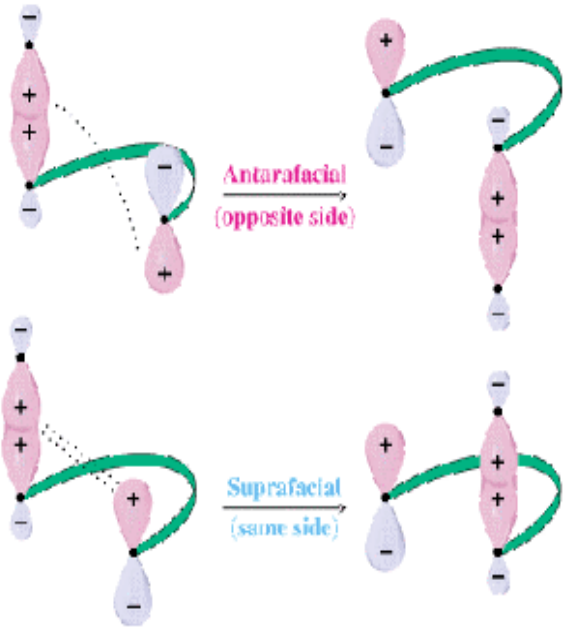
- Reaction governed by the symmetry of the LUMO of the pi-system
- Suprafacial and antarafacial migrations



Sigmatropic rearrangements

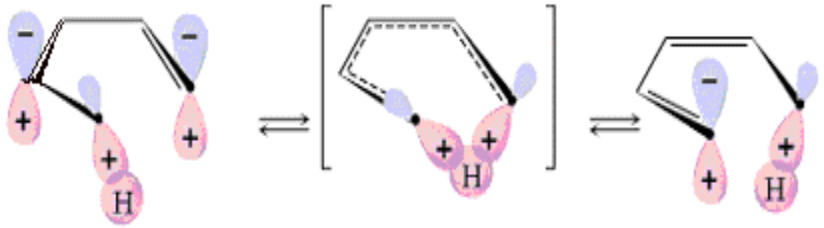
If LUMO antisymmetrical, antarafacial migration (top to bottom)

If LUMO symmetrical, suprafacial migration (top to top)



[1,5] Sigmatropic

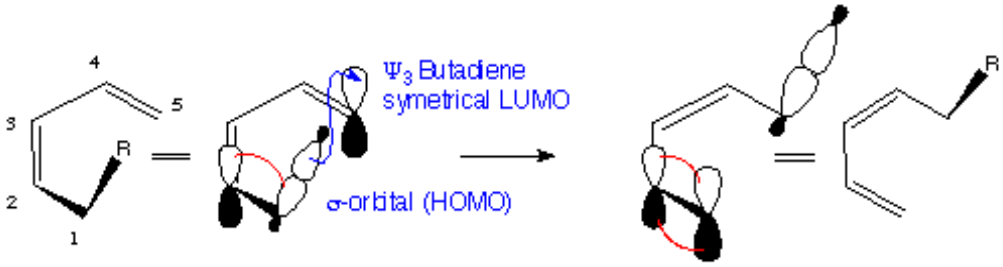
LUMO, Ψ_3 (odd)
symmetrical,
suprafacial
migration (top to
top)



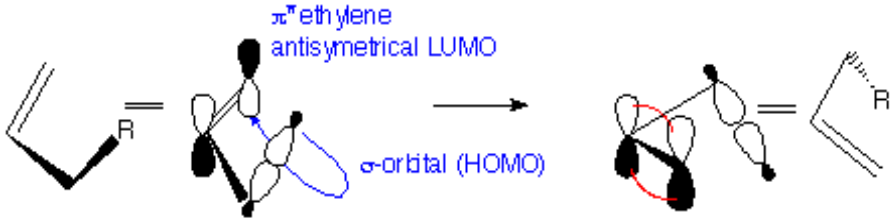
Transition state

[1,5] and [1,3] sigmatropic rearrangements

LUMO symmetrical, suprafacial migration (top to top)

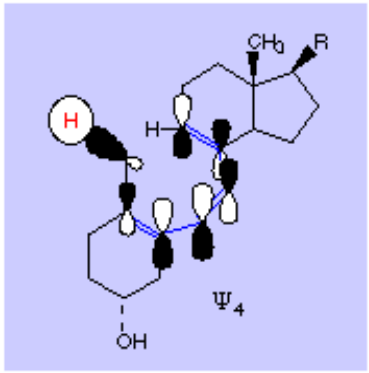


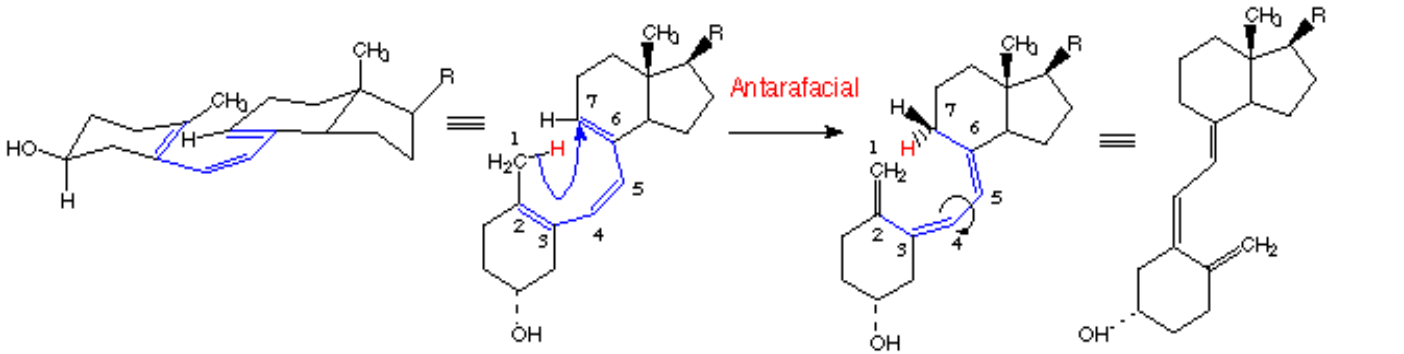
If LUMO antisymmetrical, antarafacial migration (top to bottom)



Cholecalciferol/ergocalciferol

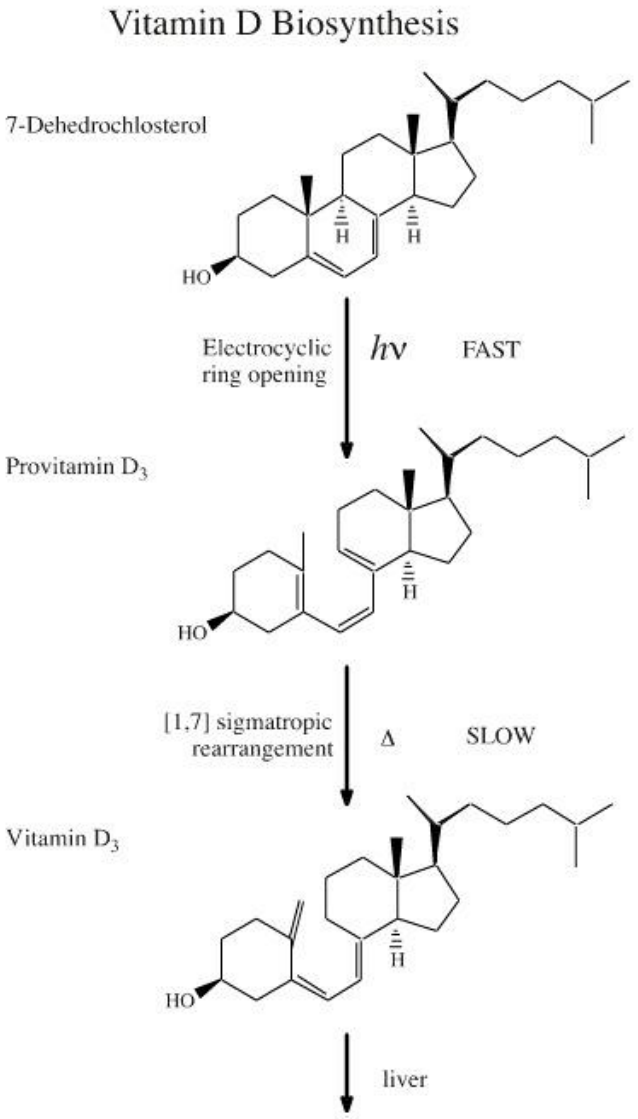
- Final step is a [1,7] sigmatropic migration
  - LUMO of hexatriene is Ψ_4
  - Antisymmetric— antarafacial migration of hydrogen



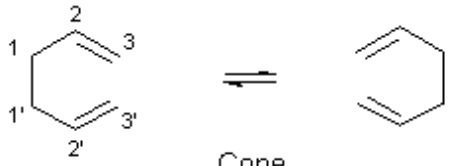


Cholecalciferol /ergocalciferol

The biosynthesis of vitamin D has photochemical step, and the reaction takes place in skin cells.
A 1,3-cyclohexadiene system associated with the b ring of a steroid undergoes a photoactivated, retroelectrocyclisation to give 1,3,5-hexatriene system.
The thermal reaction is not allowed because it would be necessary for form a six membered ring with a *trans*-alkene, a sterically impossible structure.
1,3,5-hexatriene system then undergoes a thermal [1,7] sigmatropic rearrangement to give vitamin D3. This is further processed in the liver.



نوآرایی کوپ :

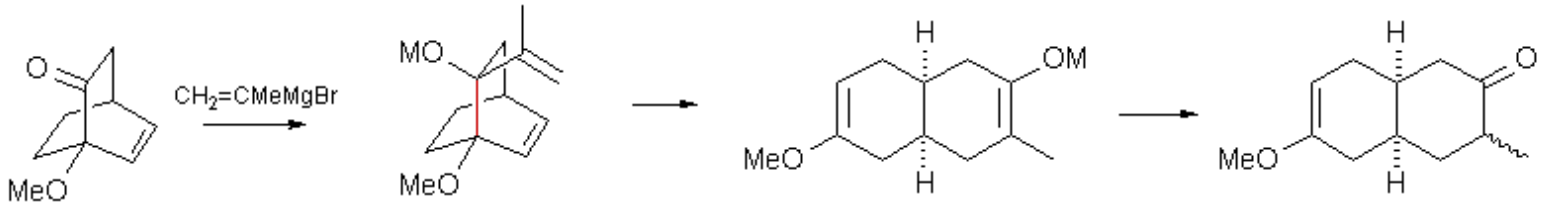


Cope

The Cope Rearrangement for most systems requires temperatures in the neighborhood of 250 °C, and the equilibrium constant tends to be fairly evenly balanced, so synthetic applications are infrequent. The rates for systems bearing a hydroxy group (oxy-Cope) can be greatly accelerated by conversion to an alkoxide (anionic oxy-Cope), and such reactions have found more extensive applications in synthesis.

The Anionic Oxy-Cope

Evans, Golob *J. Am. Chem. Soc.* **1975**, *97*, 4765; *J. Am. Chem. Soc.* **1972**, *94*, 4780.

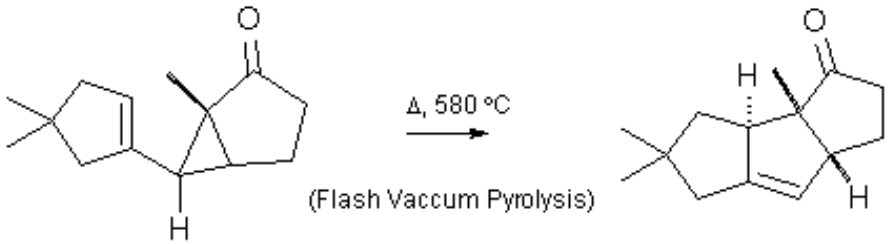


M	**Temp. °C**
H	250
Li, MgBr	no reaction at 66 °C
K	66
K (18-crown-6)	25

1,3-sigmatropic rearrangement

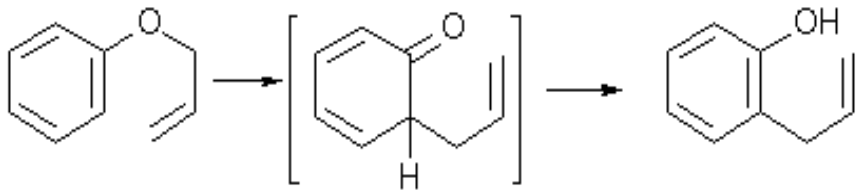
Vinyl cyclopropane rearrangement

Synthesis of Hirsutene: Hudlicky, T.; Kutchan, T. M.; Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6351.



The suprafacial [1,3]-sigmatropic rearrangement is an orbital symmetry forbidden process, and thus typically has high activation barriers and potentially proceeds through radical or zwitterionic intermediates. Such rearrangements can, however be performed in special circumstances where ring strain lowers the activation barrier, for example in vinyl cyclopropanes.

نوآرایی کلایزن :



Aromatic Claisen

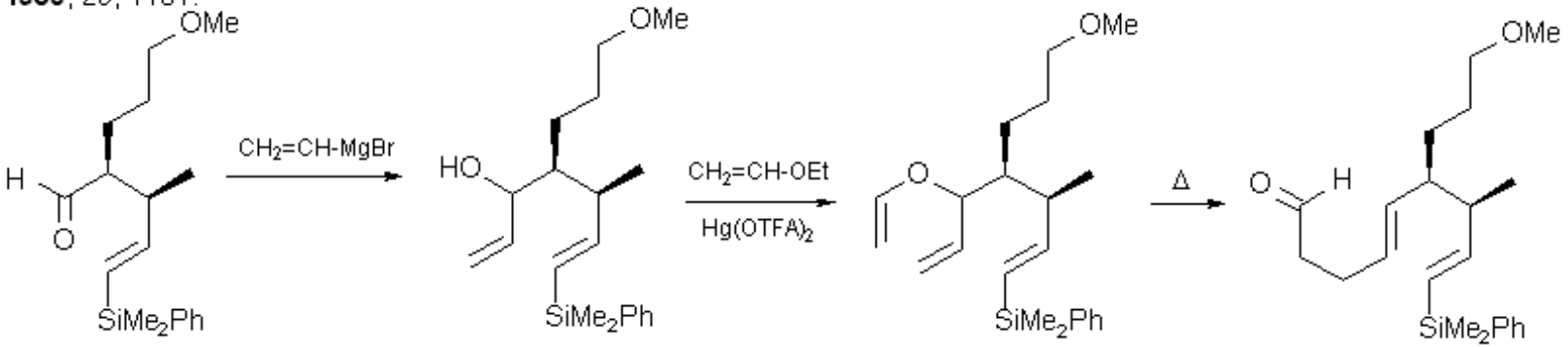
Aliphatic Claisen

The Aldehyde-Claisen Process

85-01

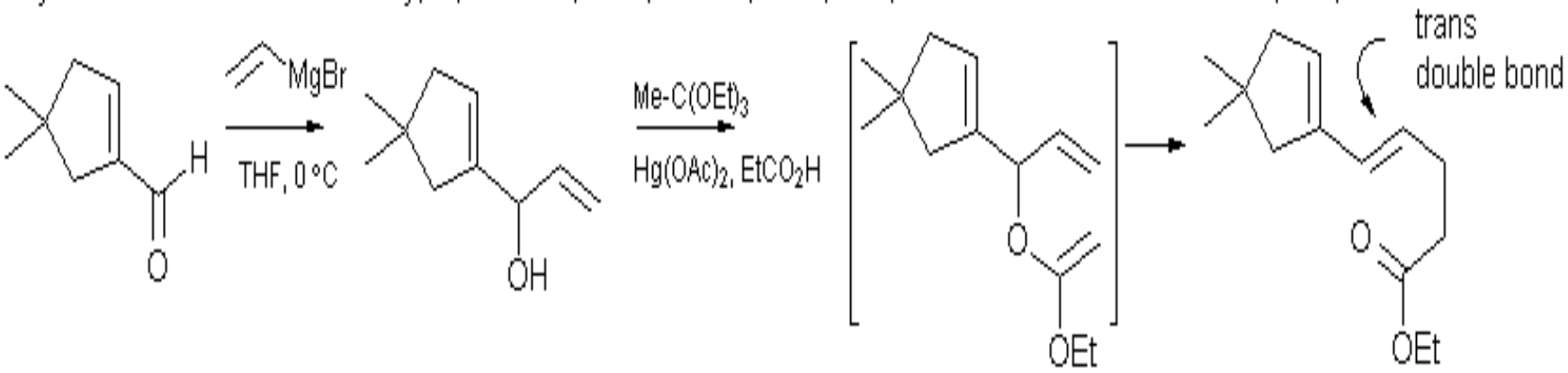
4-Carbon chain extension

Synthesis of Dihydrocompactin: Burke, S. D., Saunders, J. O.; Oplinger, J. A.; Murtiashaw, C.W. *Tetrahedron Lett.*, **1985**, *26*, 1131.



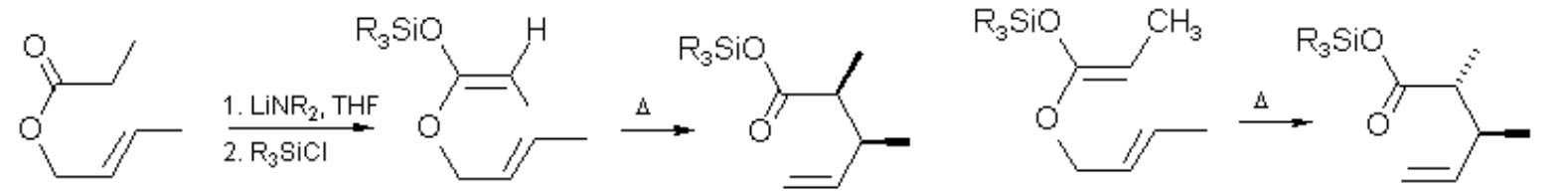
4-Carbon chain extension using aldehyde Claisen Rearrangement

Synthesis of Hirsutene: Hudlicky, T.; Kutchan, T. M.; Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6351.



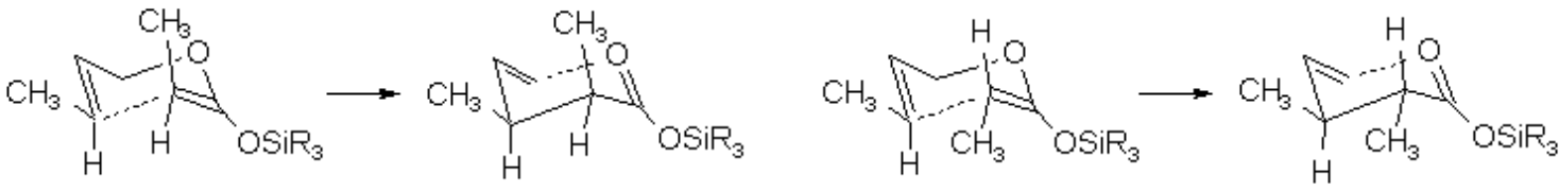
Stereochemistry of Claisen: erythro-threo Selectivity

Stereospecific for interconversion of cis/trans double bonds and sp^3 bonds (Ireland).

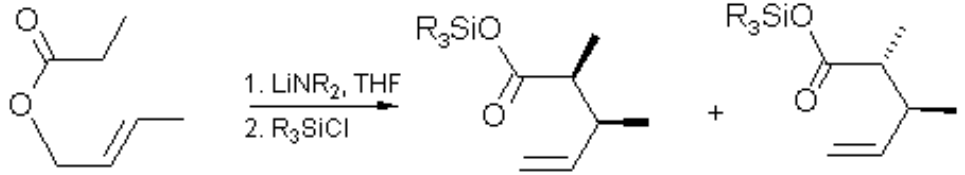


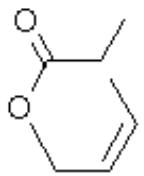
Kinetic Enolate

Thermodynamic Enolate (THF/HMPA)



Observed Stereochemistry: Ireland, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 2868



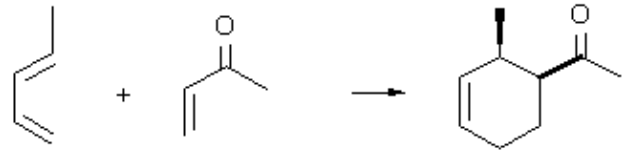


THF	87 / 13
THF / HMPA	19 / 81
THF	11 / 89
THF / HMPA	86 / 14

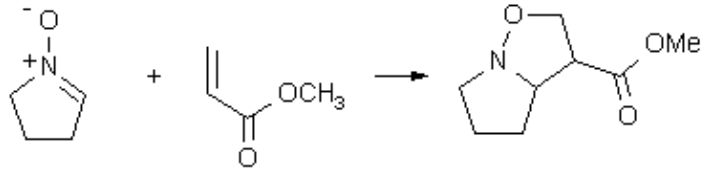
Switching the crotyl alcohol stereochemistry switches the major isomer formed

Cycloadditions

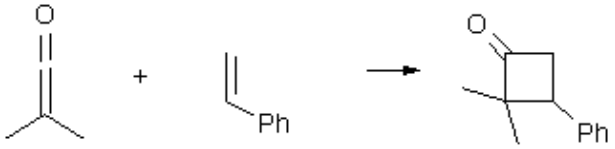
2π + 4π Cycloadditions - Diels-Alder Reaction



1,3-Dipolar Cycloaddition



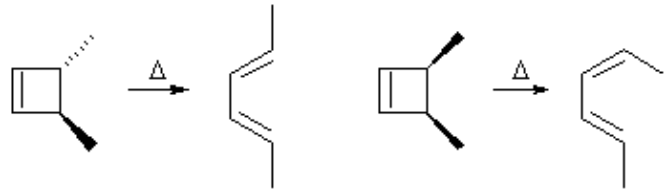
2π + 2π Cycloadditions



Electrocyclic Reactions

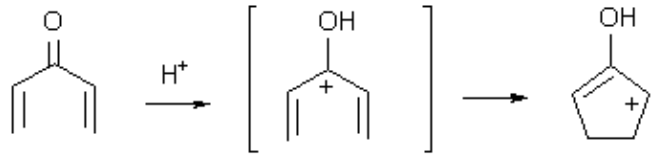
Reich
Chem 547

Cyclobutene - butadiene



Hexatriene - cyclohexadiene

Nazarov cyclization

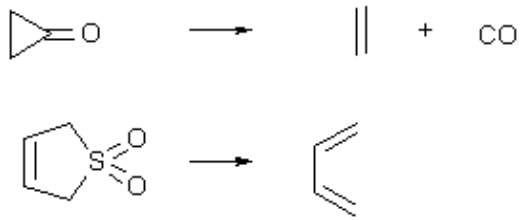


Sigmatropic Rearrangements

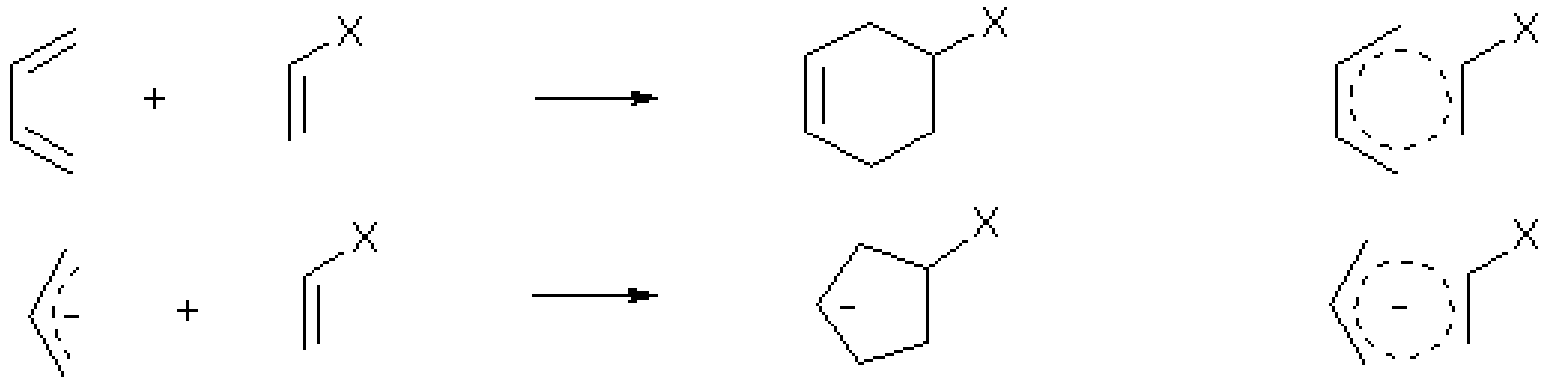
Claisen [3,3] Sigmatropic

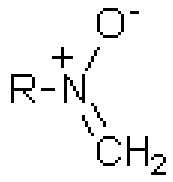
[2,3] Sigmatropic

Chelotropic Reactions

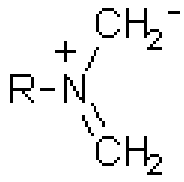


2π + 4π Cycloadditions - Aromatic Transition States



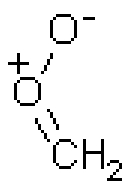


Nitrone



Azomethine Ylide

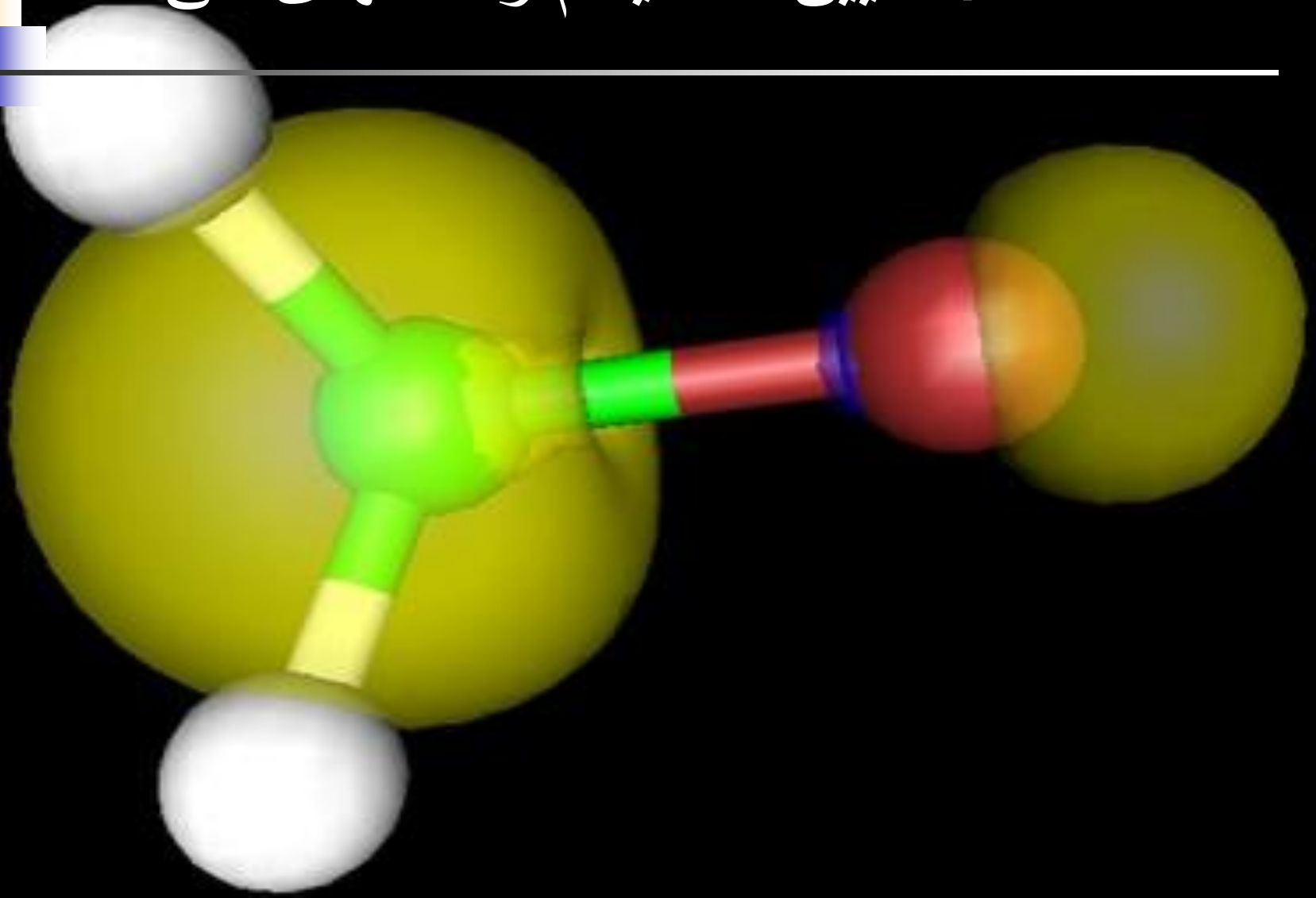
Ozone



Carbonyl Oxide

Nitrile Oxide

فصل ۳: تعیین مکانیسم واکنشهای آلی



هدفهای کلی :

مطالعه مکانیسم واکنشها در بطن شیمی جای دارد بنابراین دانشجویان باید برای توصیف مکانیسم واکنش های آلی ،تبدیل مولکولهای اولیه به محصول و موقعیت تمام اتمها بر حسب تابعی از زمان بدانند.این امر میسر نمیشود مگر با دانستن سینتیک وترمودینامیک شیمیایی .

پیشنهاد یک مکانیسم قابل قبول :

۱- هیچ تجمعی بدون ضرورت صورت نمیگیرد.

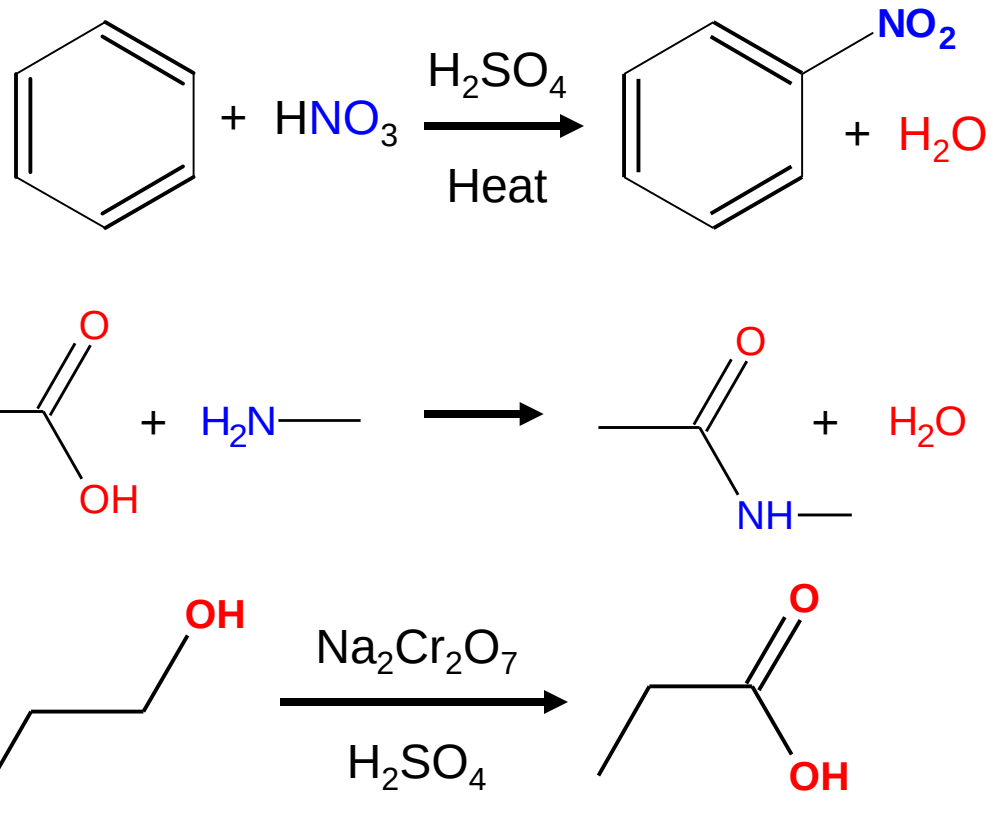
۲- در هر مکانیسم چند مرحله ای، هر یک از مراحل منفرد باید تک مولکولی یا دو مولکولی باشد.

۳- هر مرحله باید از لحاظ انرژیتیکی امکان پذیر باشد.

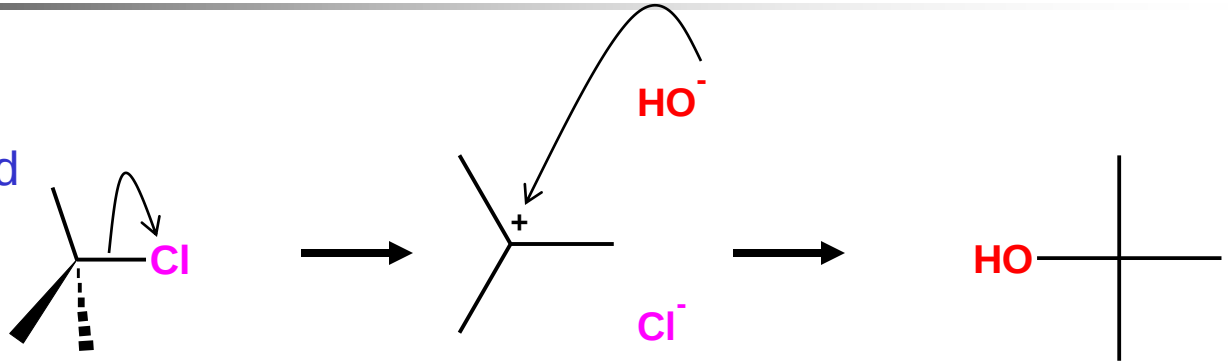
۴- هر مرحله باید از لحاظ شیمیایی قابل قبول باشد.

طبقه بندی واکنشها :

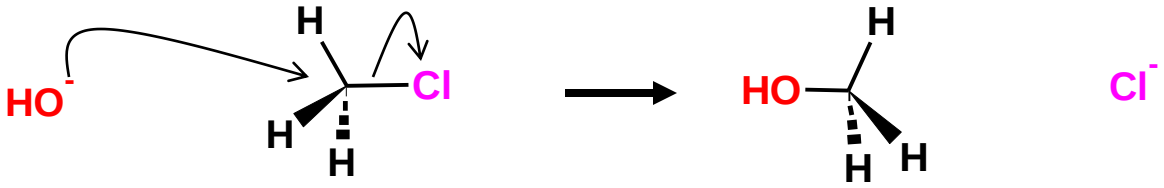
- Functional classification
  - Acid-catalyzed, Electrophilic
  - Base-catalyzed, Nucleophilic
  - Oxidation-Reduction
  - Free-radical
  - Etc.



- Mechanism-based
  - Sn1



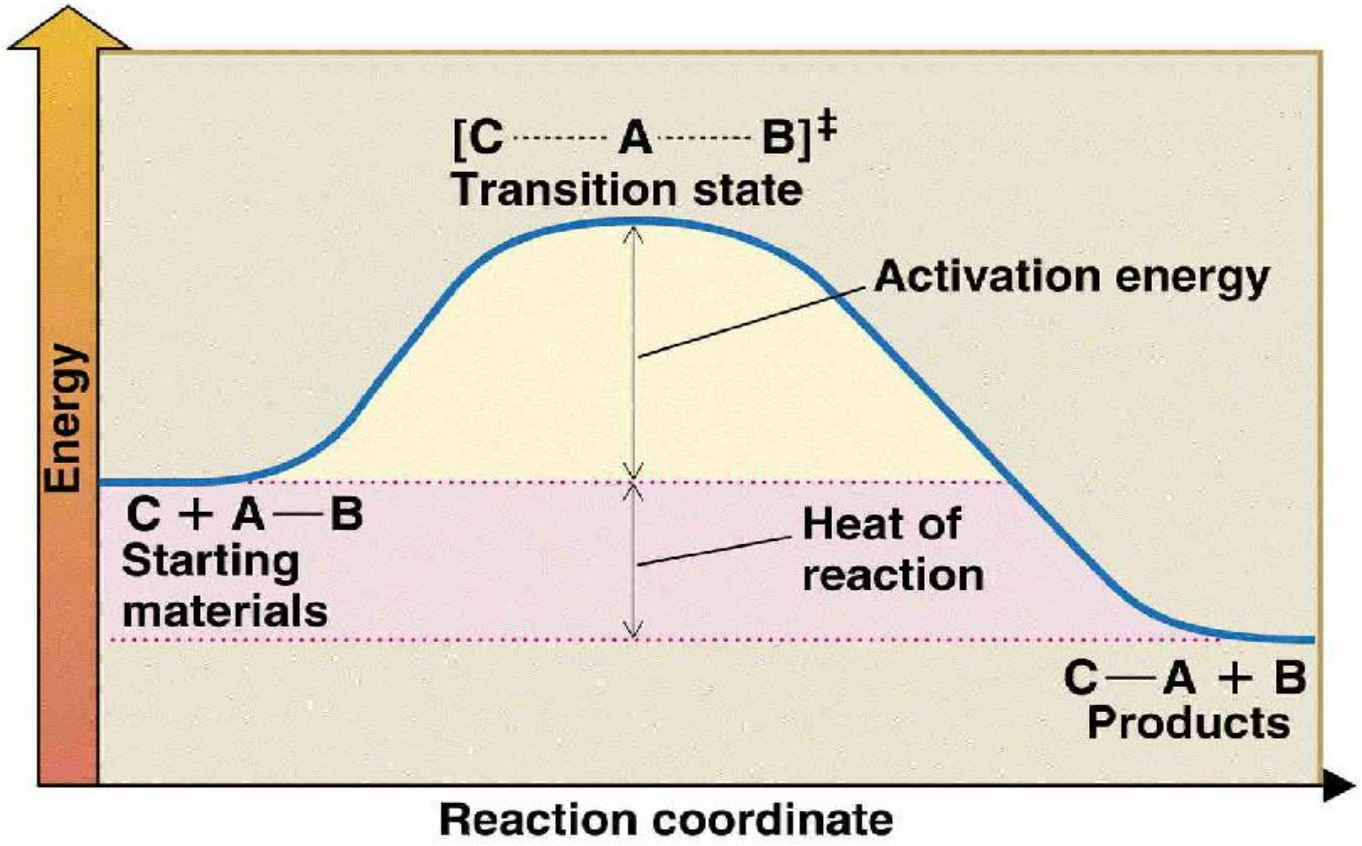
  - Sn2



  - E1
  - E2
  - etc.
  - Most informative classification patterns, but
    - Reaction mechanisms often unknown
    - Mechanisms cannot be directly observed, can only be proposed and supported with exp. evidence

مطالعه محصولات :

برای درک مکانیسم یک واکنش باید ماهیت دقیق واکنش را بدانیم .به این خاطر ساختمان مواد اولیه باید کاملا مشخص باشد و ساختمان دقیق محصولات نیز باید تعیین گردد.



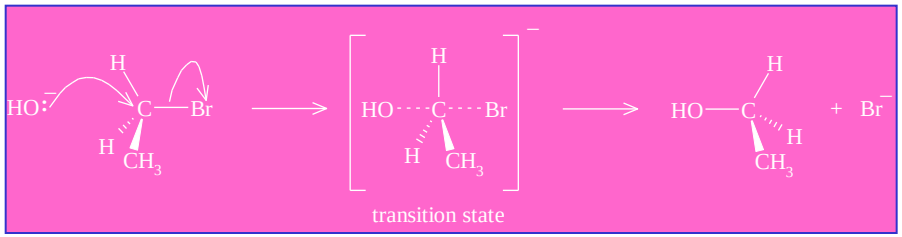
این مطالعه ساختار محصولات از دو طریق امکان پذیر است :

۱- شیمی فضایی

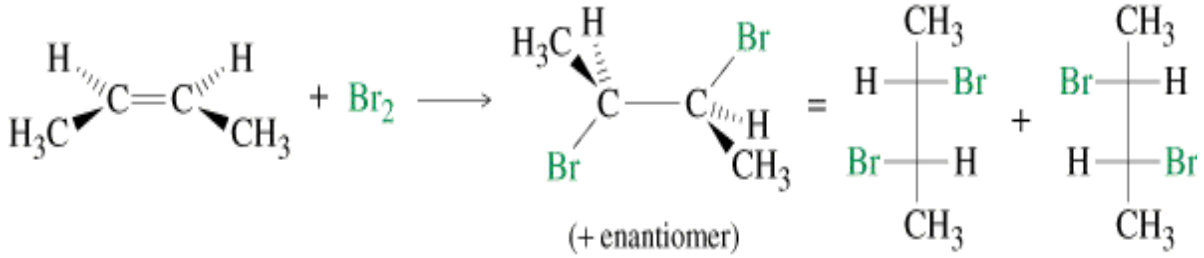
۲- نشاندارکردن ایزوتوپی

شیمی فضایی :

دارای مرکز کایرال : در تعیین ساختمان دقیق محصولات، به اطلاعات فضاشیمیایی ویژه ای نیاز است که از اتمهای کربن نا متقارن بدست می آید .



بدون مرکز کایرال : حتی موقعی که مواد اولیه فعال نوری نیشتند، هر کجا که محصولات احتمالا شیمی فضایی خاصی را نشان می دهند بررسی باید صورت گیرد .



نشاندار کردن ایزوتوپی :

استفاده از ایزوتوپها روشی ظریف ولی بسیار موثر برای بدست آوردن اطلاعات خاص درباره پیوندهایی است که در یک واکنش شرکت میکنند.توضیحات این قسمت داده خواهد شد .

سینتیک :

به زبان ساده سرعت تغییر غلظت یکی از مواد شرکت کننده در واکنش ، سرعت واکنش نامیده میشود .

- $aA + bB \rightarrow cC + dD$
- Rate can be expressed by any reactant or product.

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

- Understand each term in the above equation.

متداول ترین موارد سینتیکی :

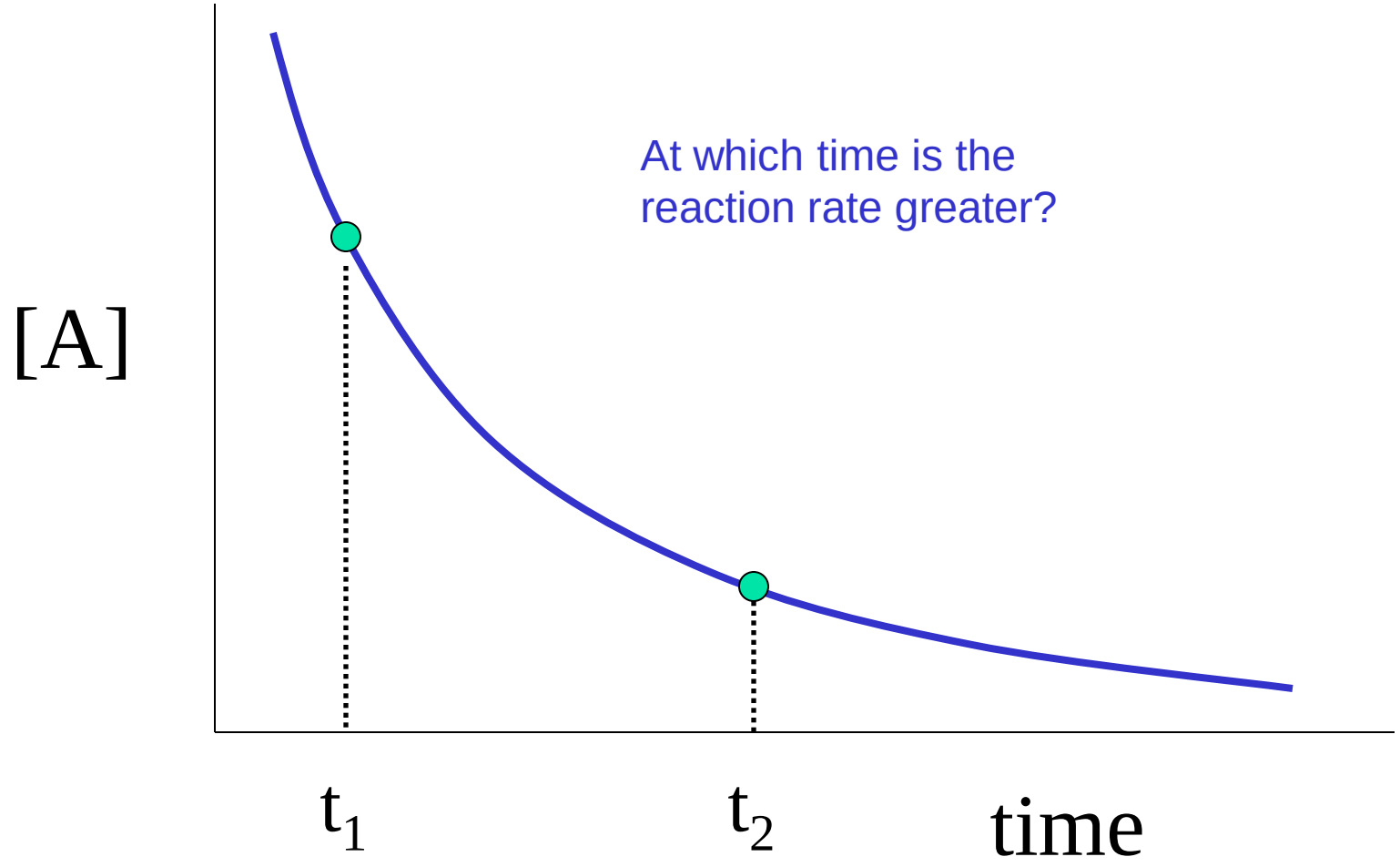
A → product

- Zero-order reaction — درجه صفر
- First-order reaction — درجه یک
- Second-order reaction — درجه دو

مفاهیم مکانیسمی :

۱- سینتیک یک واکنش با سینتیک آهسته ترین مرحله مقدماتی در مکانسیم (مرحله تعیین کننده سرعت) یکسان خواهد بود .
۲- درجه سینتیکی هر مرحله مقدماتی با مولکولاریته آن مرحله یکسان است .

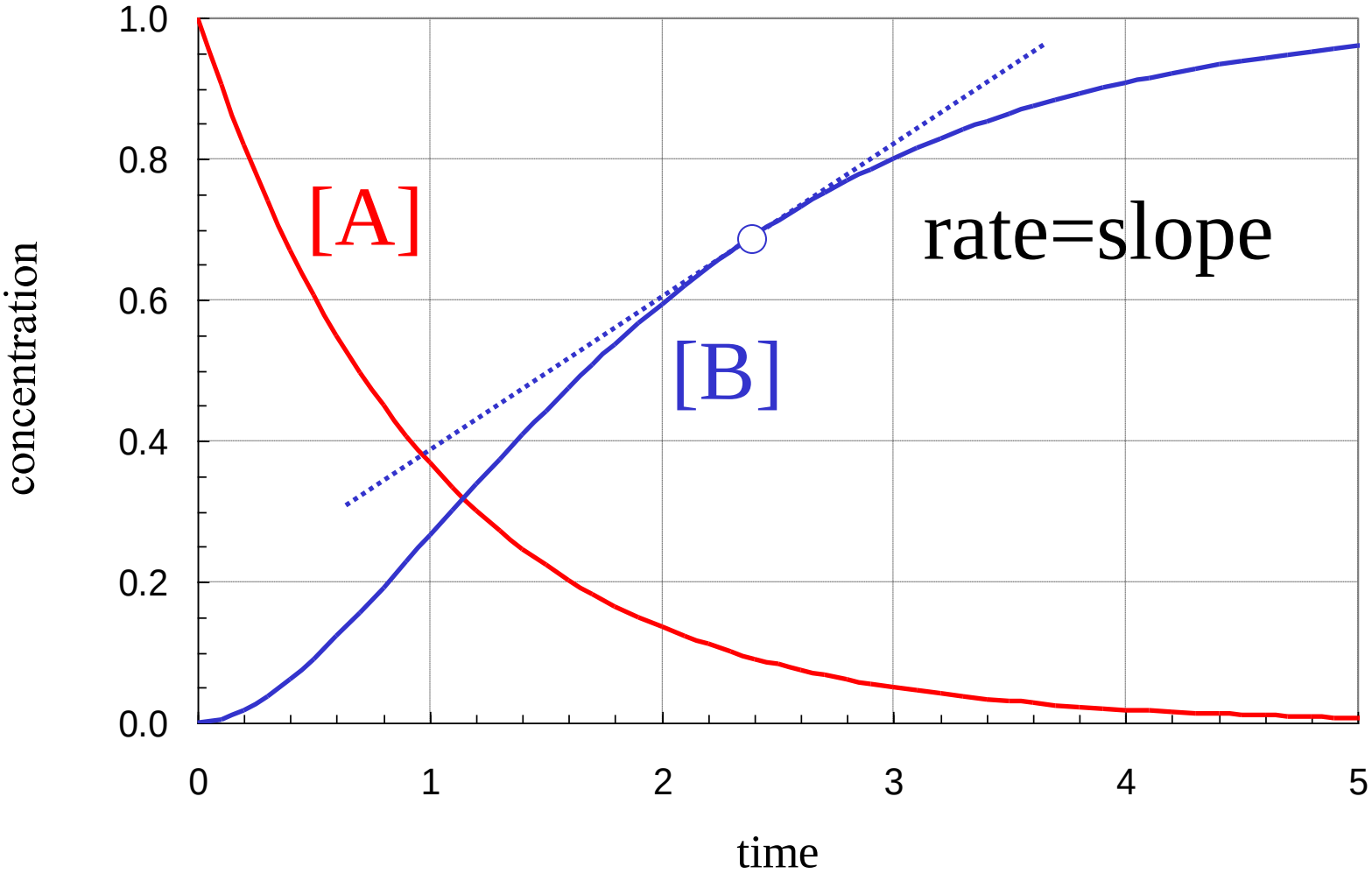
سرعت واکنش :



$$R = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma} \ldots$$

- k = rate constant
- α = order with respect to A
- β = order with respect to B
- γ = order with respect to B
- etc.

Reaction Kinetics: A→B



سینیتیک درجه ۱ :

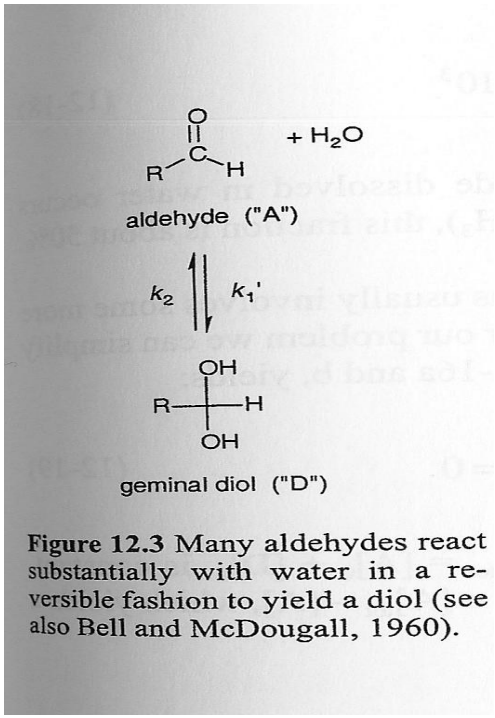


Figure 12.3 Many aldehydes react substantially with water in a reversible fashion to yield a diol (see also Bell and McDougall, 1960).

$$rate = -\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]$$

$$\ln[A] = -kt + \ln[A]_0$$

$$t_{1/2} = \ln 2/k = 0.693/k$$

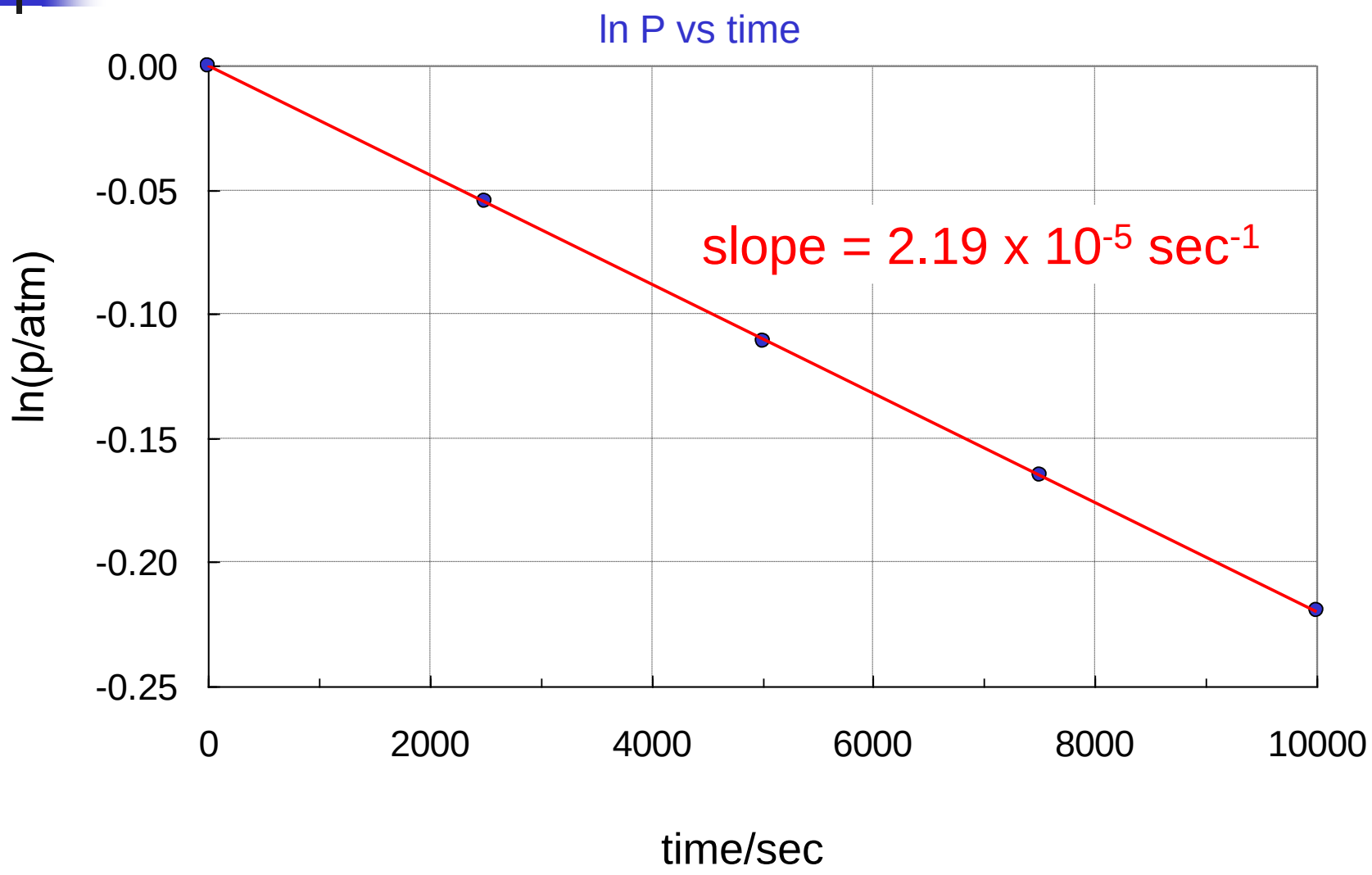
Unit of k: 1/s

SO_2Cl Example

- The reaction $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ gives the following experimental data:

Time (s)	Pressure SO_2Cl_2 (atm)
0	1.000
2,500	0.947
5,000	0.895
7,500	0.848
10,000	0.803

SO_2Cl Example



سینیتیک درجه ۲ (نوع اول) :

$$2A \xrightarrow{k} P$$

$$R = -k_{eff}[A]^2 \quad \text{or} \quad \frac{d[A]}{dt} = -k_{eff}[A]^2$$

$$\frac{d[A]}{[A]^2} = -k_{eff}\,dt \quad \text{or} \quad \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -\int_0^t k_{eff}\,dt$$

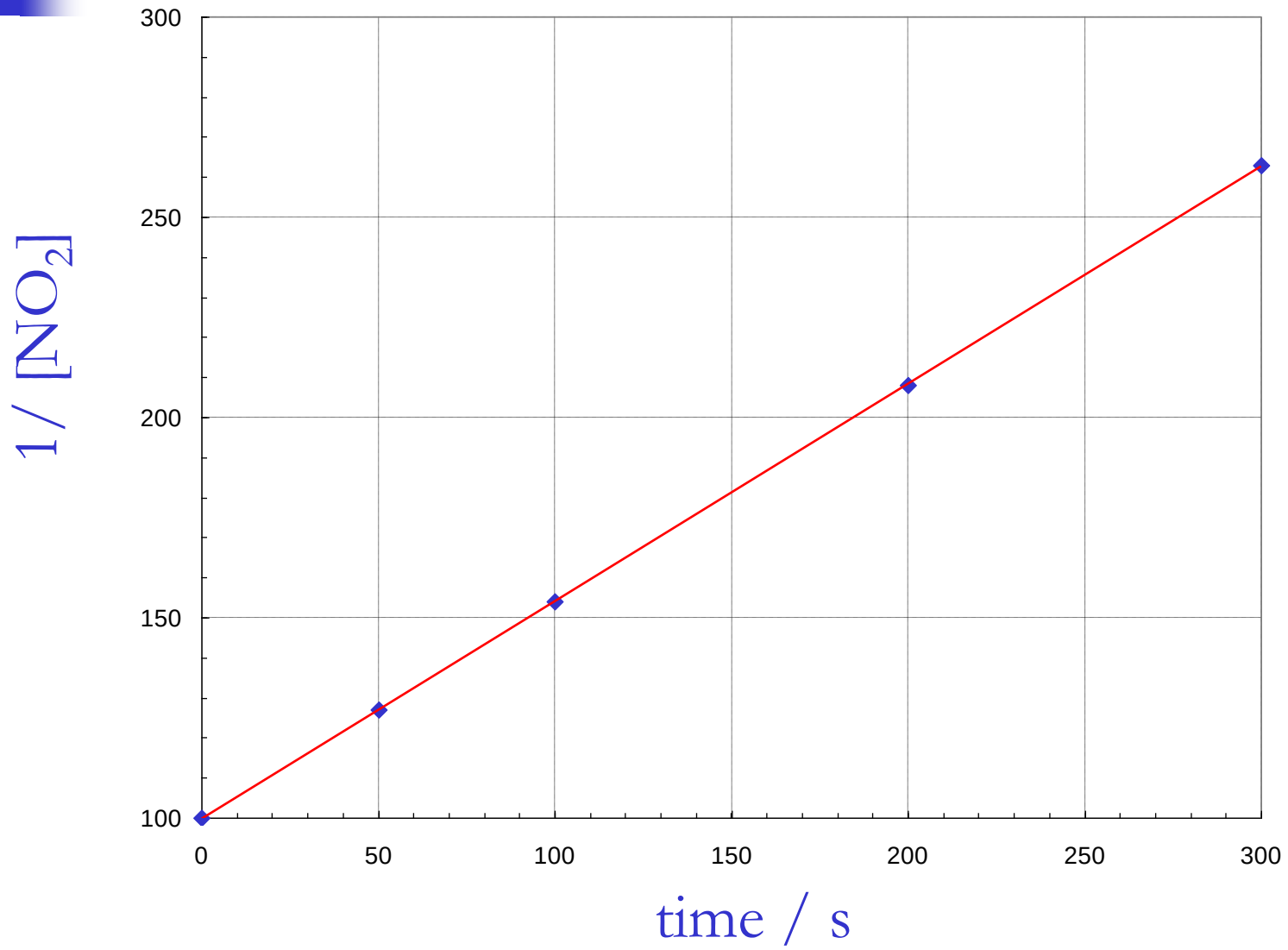
$$-\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = -k_{eff}t \quad \text{or} \quad \boxed{\frac{1}{[A]} = \frac{1}{[A]_0} + k_{eff}t}$$

NO_2 Example

The following data were obtained for the gas-phase decomposition of $NO_2(g)$ at 300°C.

Time (s)	$[NO_2]$	ln $[NO_2]$	$1/[NO_2]$
0	0.01000	-4.610	100
50	0.00787	-4.845	127
100	0.00649	-5.038	154
200	0.00481	-5.337	208
300	0.00380	-5.573	263

Second Order Plot



سینیتیک درجه ۲ (نوع دوم) :

$$A + B \xrightarrow{k} P$$

$$R = -k[A][B] \quad \text{where} \quad [A]_0 - [A] = [B]_0 - [B]$$

$$R = -k[A](\Delta + [A]) \quad \text{where} \quad \Delta = [B]_0 - [A]_0$$

$$\frac{d[A]}{[A](\Delta + [A])} = -k dt \quad \text{or} \quad \int_{[A]_0}^{[A]} \frac{d[A]}{[A](\Delta + [A])} = -\int_0^t k dt$$

$$\boxed{\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = kt}$$

تئوری آرنیوس :

A $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ B

$$K = \frac{k_1}{k_{-1}} \qquad \left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$$

van't Hoff's Equation

$$\left(\frac{\partial \ln k_1}{\partial T}\right) - \left(\frac{\partial \ln k_{-1}}{\partial T}\right) = \frac{\Delta H}{RT^2}$$

$$\left(\frac{\partial \ln k_1}{\partial T}\right) = \frac{E_1}{RT^2} \qquad \left(\frac{\partial \ln k_{-1}}{\partial T}\right) = \frac{E_{-1}}{RT^2} \qquad E_1 - E_{-1} = \Delta H$$

معادله آرنیوس:

$$\ln k = \ln A - \frac{E_A}{RT}$$

- With E the apparent activation energy in kJ mol^{-1}
  A the frequency factor
- Plot of ln k vs. 1/T gives a slope of $-E_A/R$
  which allows the calculation of the activation energy
- A rule of thumb: the rate doubles for 10 K rise in temperature

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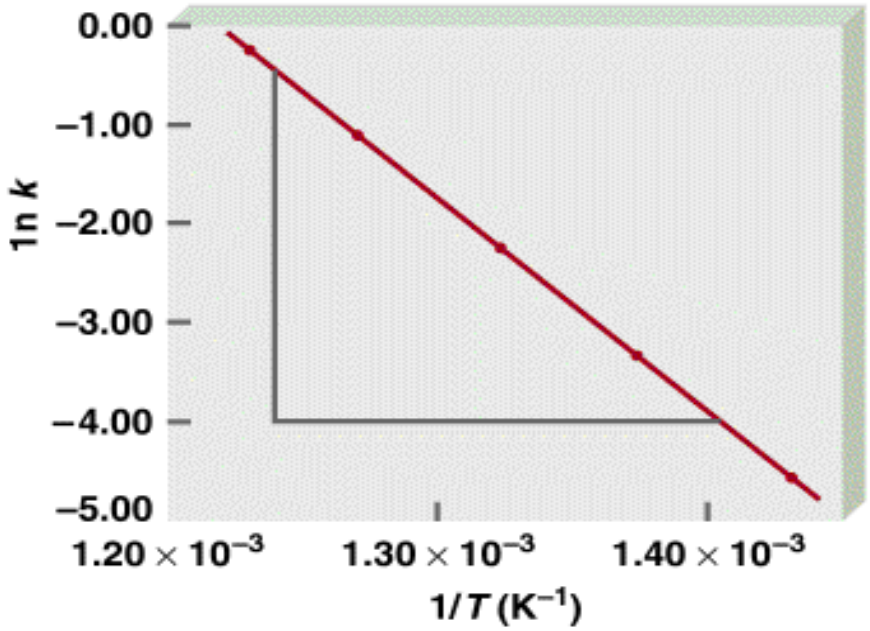
ln *k* Versus 1/*T*



k ($1/M^{\frac{1}{2}} \cdot s$)	T (K)
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810

نظریه برخورد :

- According to the simple collision theory, the preexponential factor is dependent on $T^{1/2}$

$$A = N_A \sigma \sqrt{\frac{8k}{\pi \mu}} \sqrt{T}$$

- with N_A Avogadro's number, σ cross section, μ reduced mass, k Boltzmann's constant

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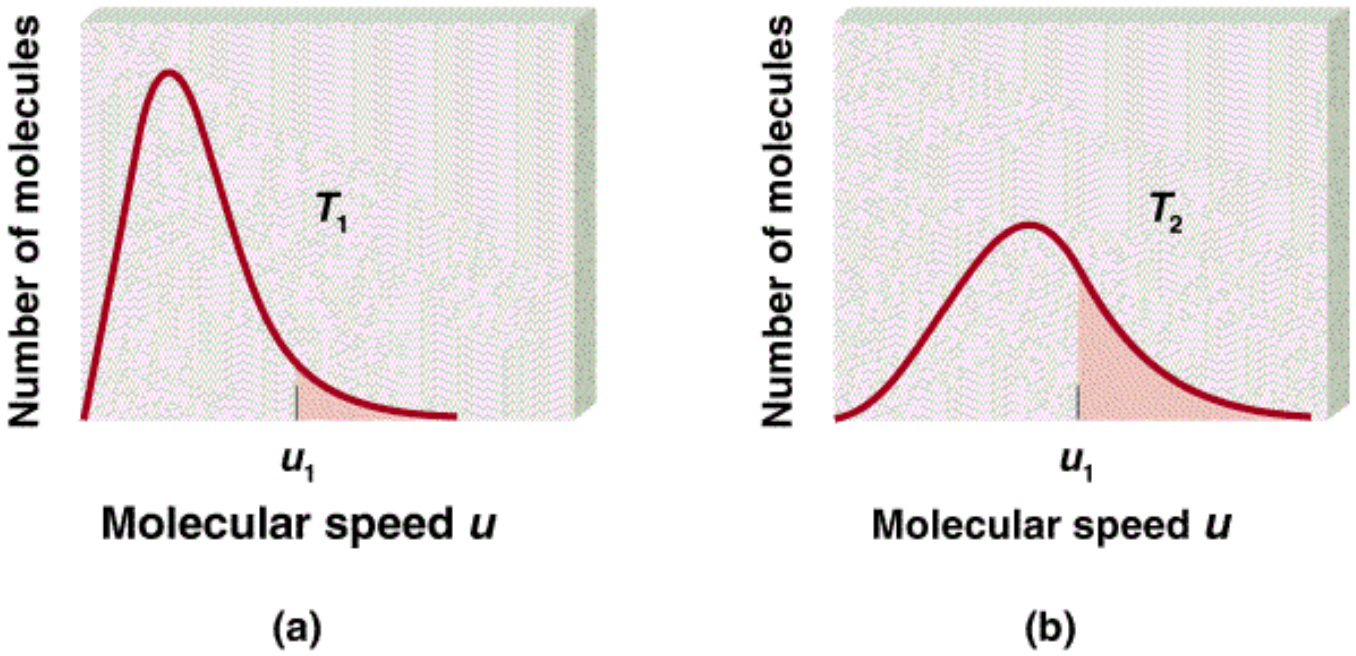
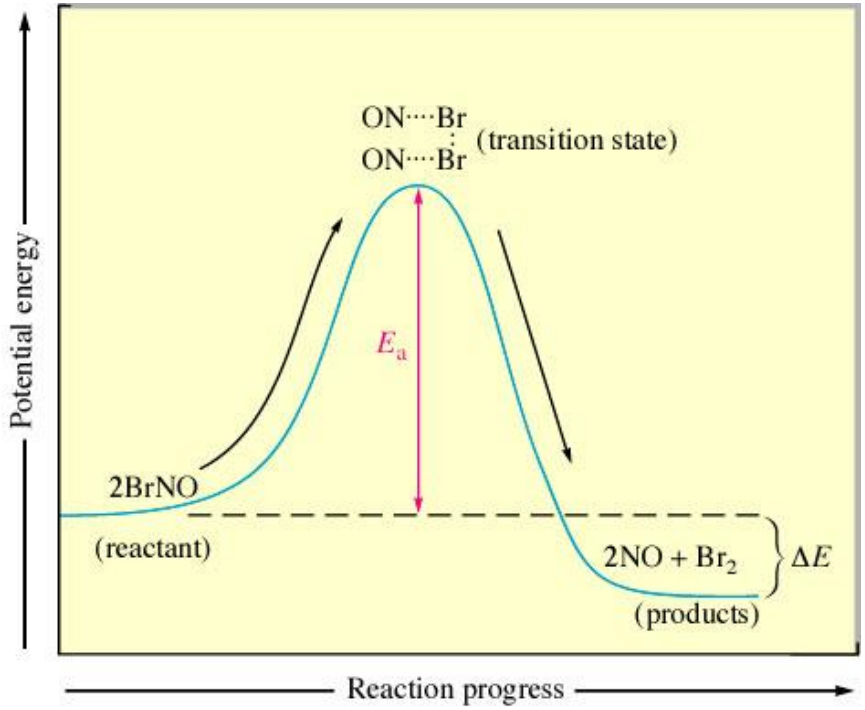
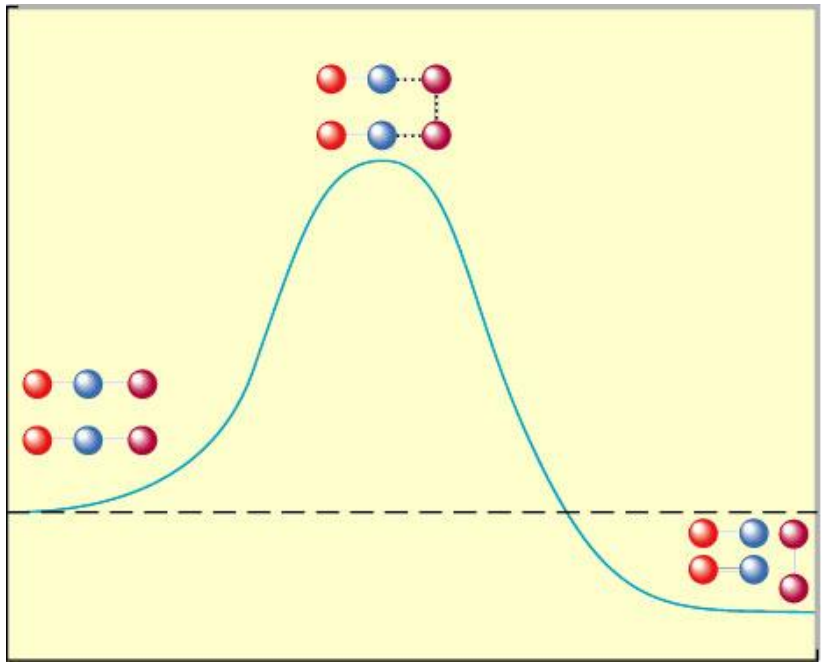
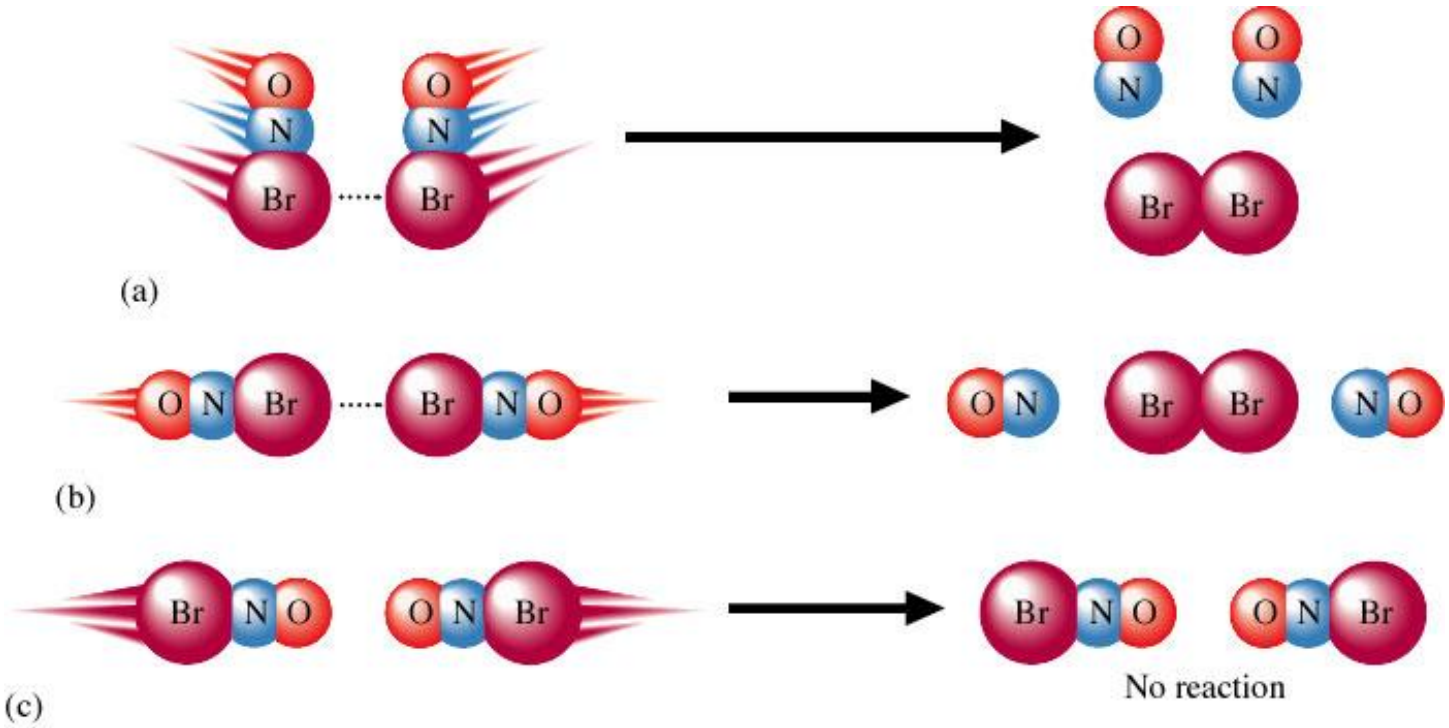
Maxwell Speed Distribution Curves at Two Different Temperatures




ON···Br
ON···Br
(transition state)
E_a
2BrNO
(reactant)
2NO + Br_2
ΔE
(products)
Potential energy
Reaction progress




O
N
Br
Br
O
N
O
N
Br
Br
(a)
O N Br
Br N O
O N
Br
Br
N O
(b)
Br N O
O N Br
Br N O
O N Br
No reaction
(c)

نظریه کمپلکس فعال :

$$A + BC \longrightarrow A \cdots B \cdots C \longrightarrow AB + C$$

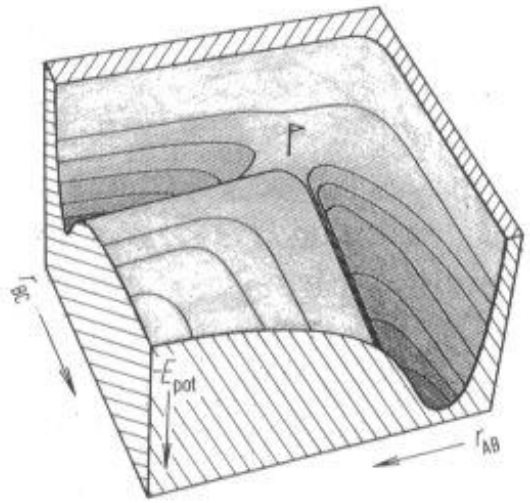
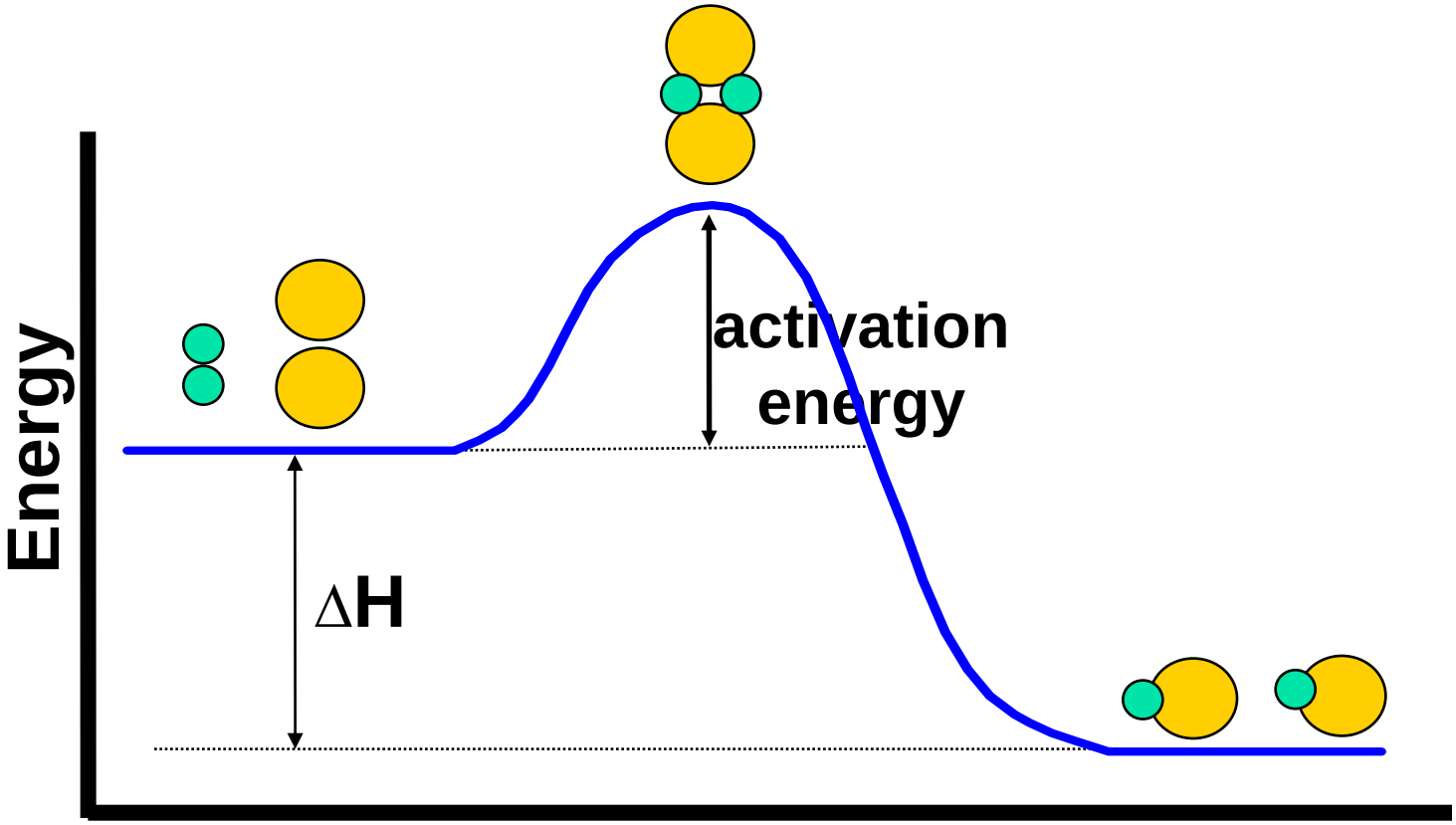


Abb. 6.4-12. Fläche der potentiellen Energie für das System $A + BC \rightleftharpoons AB + C$.


Energy
activation
energy
ΔH

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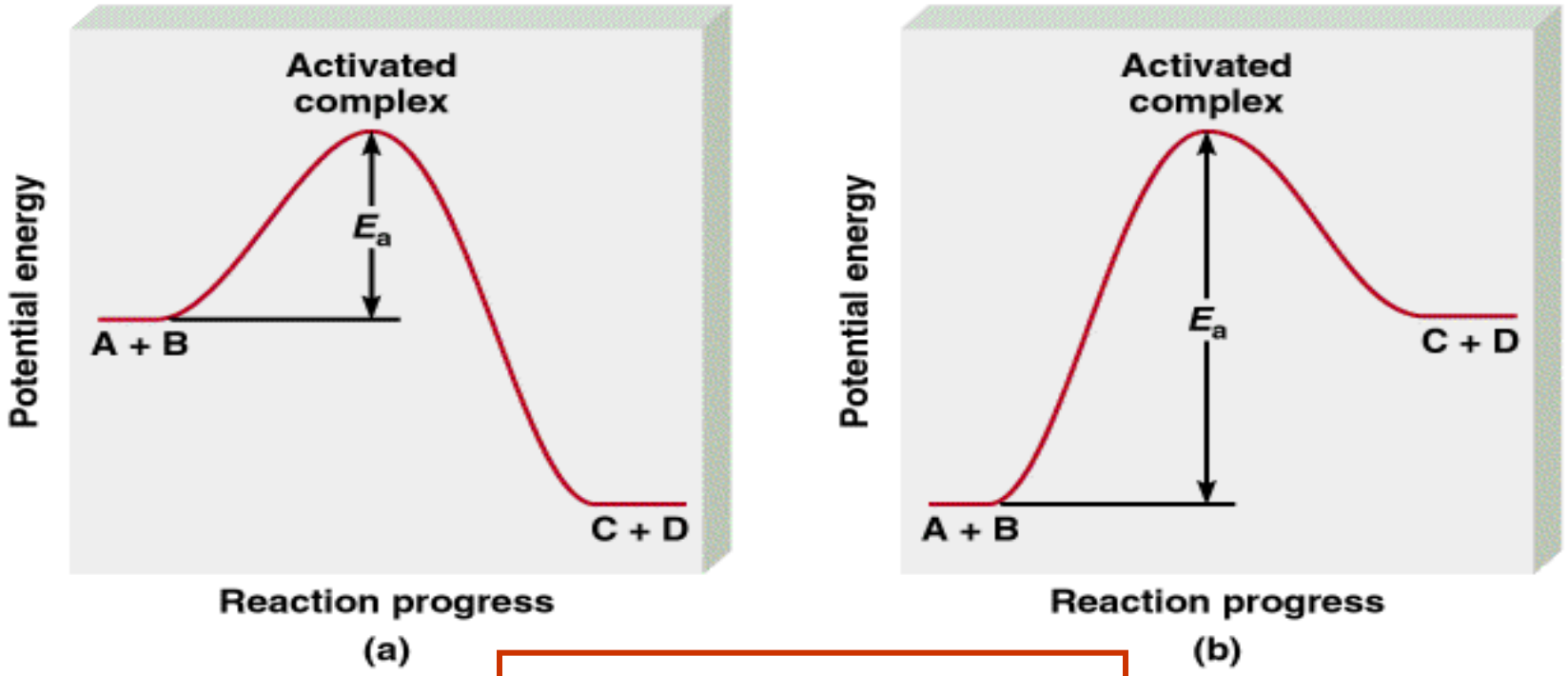
Potential Energy Profiles for Exothermic and Endothermic Reactions



Activated Complex

نتایج نظریه کمپلکس فعال :

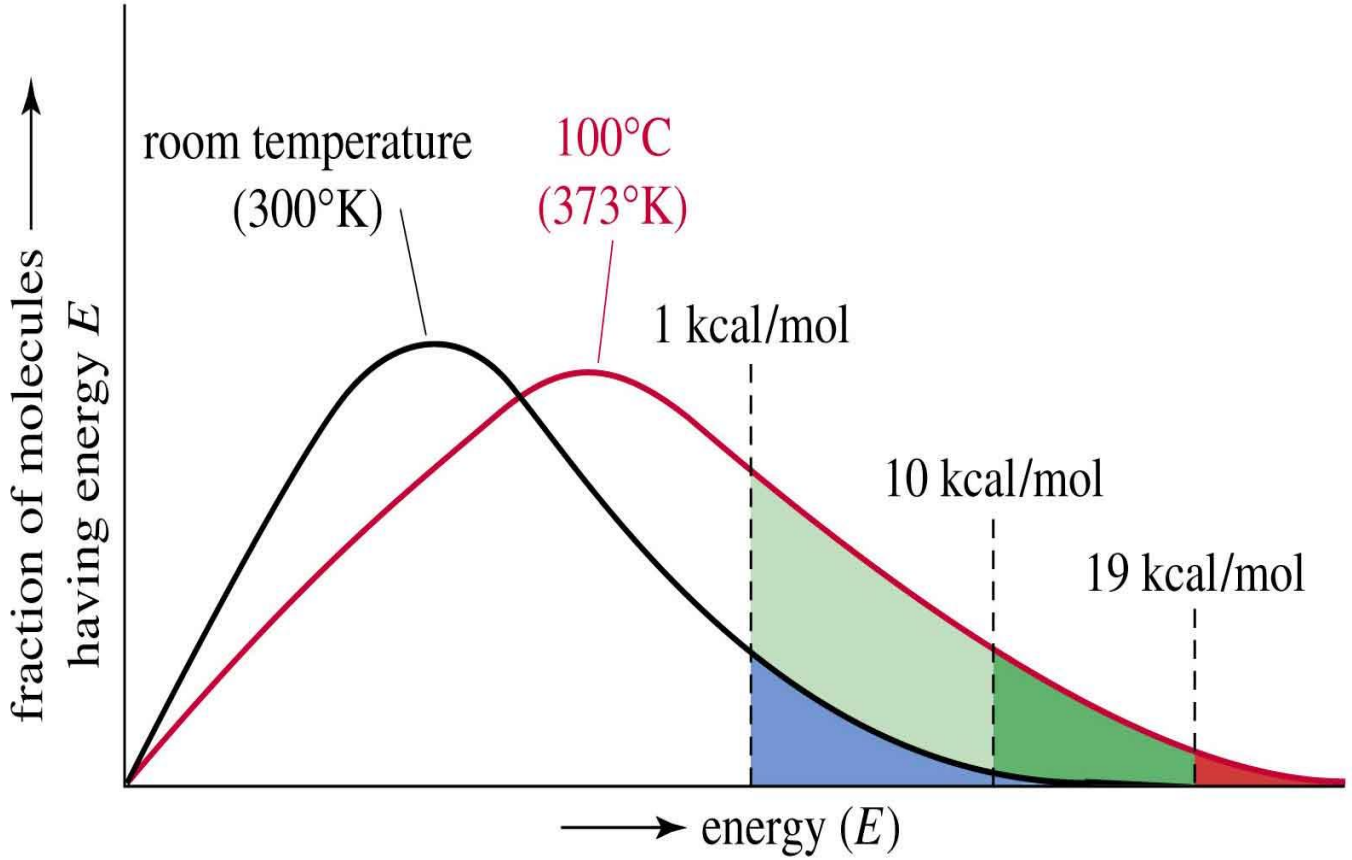
- Rate constant (based on number of moles)

$$k_n = \frac{kT}{h} K^{\neq}$$

- Function of T
- From the equilibrium constant for the activated complex, a standard free enthalpy of activation can be calculated

$$\Delta G^{\circ\neq} = -RT \ln K^{\neq}$$

انرژی فعالسازی :



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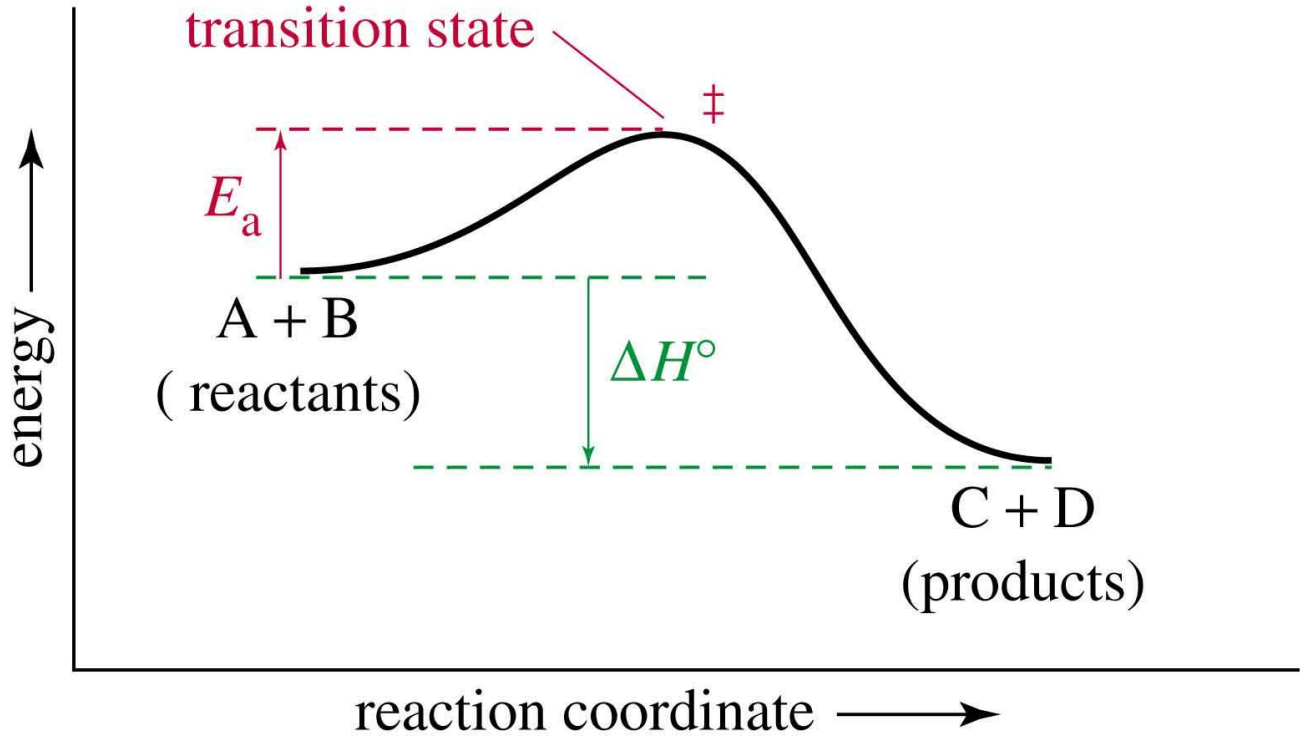
واکنش یک مرحله ای :



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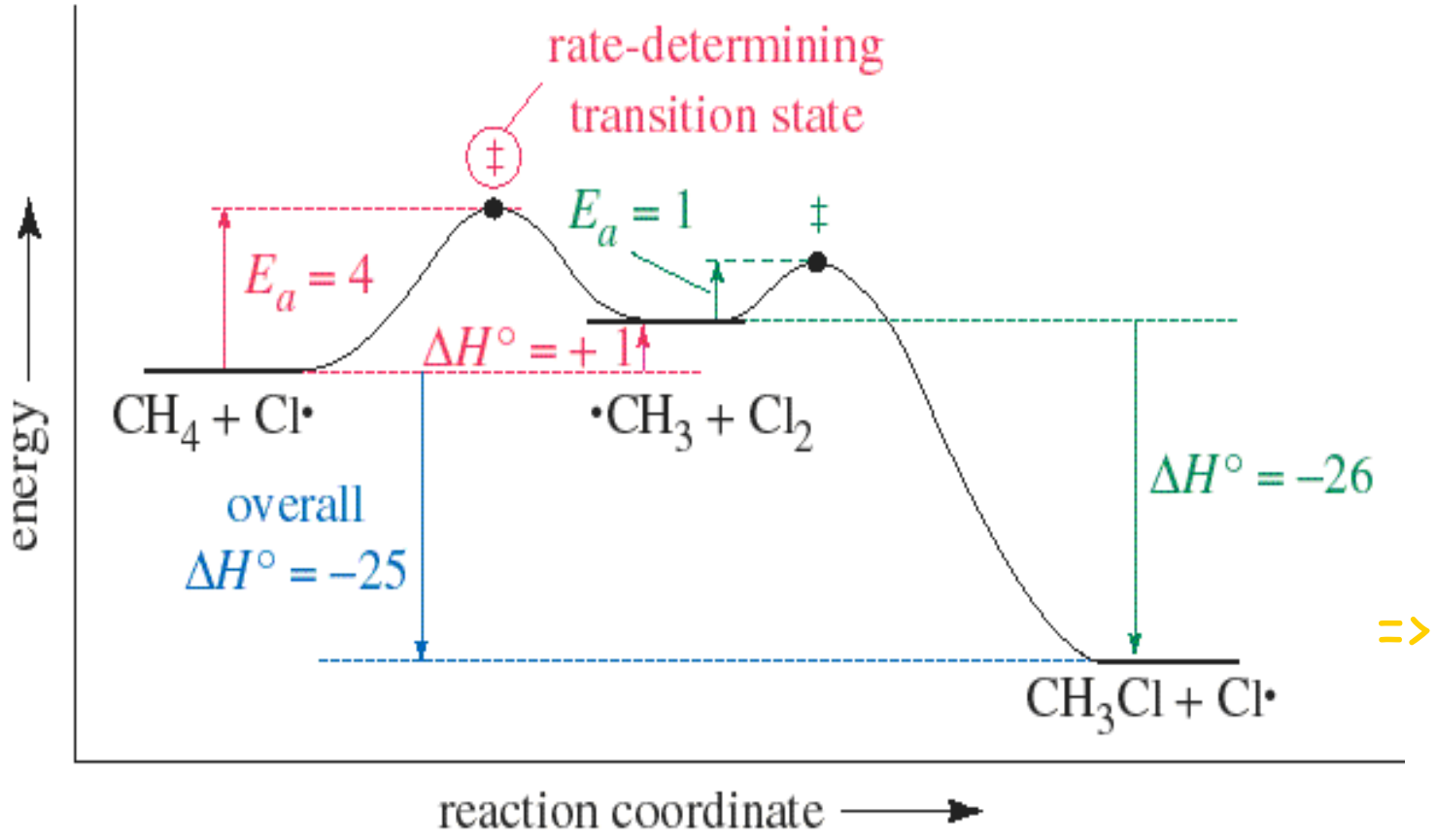
واکنش دو مرحله ای :



=>

تقریب حالت پایا :

Generic: $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ overall: $A + B + D \rightarrow P$

$$C + D \xrightarrow{k_2} P$$

$$\text{Rate} = k_2[C][D]$$

Steady state assumption: $d[C]/dt = 0$

$$\therefore\ k_1[A][B] = k_{-1}[C] + k_2[C][D]$$

$$[C] = \frac{k_1[A][B]}{k_{-1} + k_2[D]}$$

$$\therefore\ \text{Rate} = \frac{k_1 k_2[A][B][D]}{k_{-1} + k_2[D]}$$ generic rate law

$$\text{Rate} = \frac{k_1 k_2 [\text{A}][\text{B}][\text{D}]}{k_{-1} + k_2[\text{D}]}$$

if $k_{-1} >> k_2[\text{D}]$ (*i.e.*, 1st step rapid equilibrium, 2nd step slow)

$$\text{then Rate} = \frac{k_1 k_2 [\text{A}][\text{B}][\text{D}]}{k_{-1}}$$

if $k_2[\text{D}] >> k_{-1}$ (*i.e.*, 1st step slow, 2nd step fast)

$$\text{then Rate} = k_1[\text{A}][\text{B}]$$

مثال :

e.g., $H_2C{=}CH_2 + HBr \rightarrow CH_3CH_2Br$

1. $H_2C{=}CH_2 + HBr \xrightarrow{k_1} CH_3CH_2^+ + Br^-$ slow

   $CH_3CH_2^+ + Br^- \xrightarrow{k_2} CH_3CH_2Br$ fast

   Rate = $k_1[C_2H_4][HBr]$

2. $H_2C{=}CH_2 + HBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2C(\overset{HBr}{\cdots}){=}CH_2$ rapid equilibrium

   $H_2C(\overset{HBr}{\cdots}){=}CH_2 + HBr \xrightarrow{k_2} CH_3CH_2Br + HBr$ slow

   Rate = $k_2[C_2H_4 \cdot HBr][HBr]$

steady state: $k_1[C_2H_4][HBr] = k_{-1}[C_2H_4 \cdot HBr] + k_2[C_2H_4 \cdot HBr][HBr]$

$$[C_2H_4 \cdot HBr] = \frac{k_1[C_2H_4][HBr]}{k_{-1} + k_2[HBr]}$$

$$\text{Rate} = \frac{k_1 k_2[C_2H_4][HBr]^2}{k_{-1} + k_2[HBr]}$$

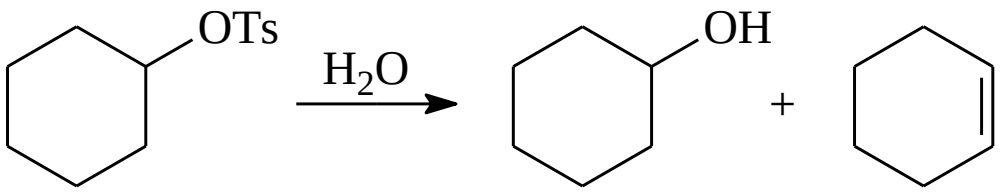
with $k_{-1} >> k_2[HBr]$

$$\text{Rate} = \frac{k_1 k_2[C_2H_4][HBr]^2}{k_{-1}}$$

or Rate = $k_2 K_1[C_2H_4][HBr]^2$

equilibrium constant for step 1

مثال :

e.g., 

(S_N1 & E1)

$$ROTs \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + TsO^-$$

k_1 small (RLS)
k_{-1}, k_2, k_3 large

$$R^+ + H_2O \xrightarrow{k_2} ROH + H^+$$

$$R^+ \xrightarrow{k_3} R + H^+$$

From RLS, overall: Rate = k_1[ROTs]

But to get the relative rates of each product formation, we need to multiply this by the fractional rate of each:

$$\text{fraction of ROH} = \frac{k_2[R^+][H_2O]}{k_2[R^+][H_2O] + k_3[R^+]} = \frac{k_2[H_2O]}{k_2[H_2O] + k_3}$$

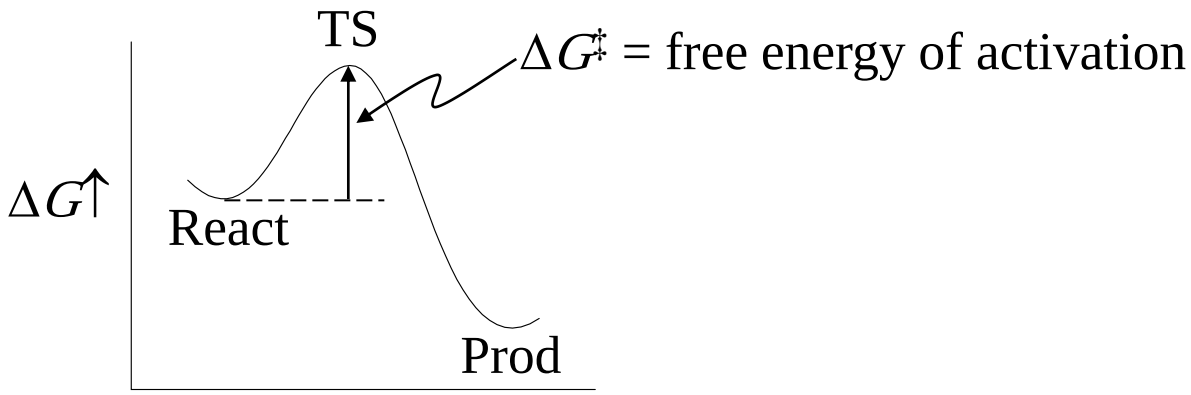
$$\text{fraction of R} = \frac{k_3[R^+]}{k_2[R^+][H_2O] + k_3[R^+]} = \frac{k_3}{k_2[H_2O] + k_3}$$

Thus:

$$\frac{d[ROH]}{dt} = \frac{k_1 k_2[ROTs][H_2O]}{k_2[H_2O] + k_3}$$

$$\frac{d[R]}{dt} = \frac{k_1 k_3[ROTs]}{k_2[H_2O] + k_3}$$

نظریه حالت گذار :



$$\text{React} \overset{K^{\ddagger}}{\rightleftharpoons} \text{TS} \xrightarrow{k^{\ddagger}} \text{Prod}$$

$k^{\ddagger}$ = rate constant for decay of TS (statistical thermodynamics)

$$= \frac{\kappa k T}{h}$$

κ = transmission coefficient (=1)
k = Boltzmann's constant
h = Planck's constant

$= 6 \times 10^{12}\ s^{-1}$ at 25ºC

Rate = $k^{\ddagger}$[TS]

Rate = $k^{\ddagger}$[TS]

steady state: Rate = $k^{\ddagger}K^{\ddagger}$[React]

with $\Delta G^{\ddagger} = -RT \ln K^{\ddagger}$ or $K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$

then $\text{Rate} = \underbrace{k^{\ddagger}e^{-\Delta G^{\ddagger}/RT}}_{k_r}$[React]

$$k_r = k^{\ddagger}e^{-\Delta G^{\ddagger}/RT}$$

$$= k^{\ddagger}\left(e^{-\Delta H^{\ddagger}/RT}\right)\left(e^{\Delta S^{\ddagger}/R}\right)$$

$$\frac{k_r}{T} = \frac{\kappa k}{h}\left(e^{-\Delta H^{\ddagger}/RT}\right)\left(e^{\Delta S^{\ddagger}/R}\right)$$

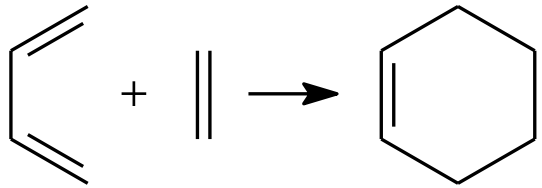
$$\ln\frac{k_r}{T} = \underbrace{\frac{-\Delta H^{\ddagger}}{R}}_{\text{slope}} \cdot \frac{1}{T} + \underbrace{\left(\frac{\Delta S^{\ddagger}}{R} + \ln\frac{\kappa k}{h}\right)}_{\text{intercept}}$$

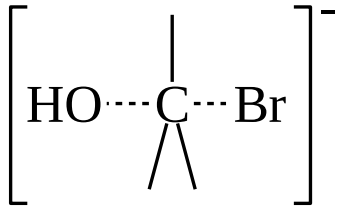
Plot $\ln\frac{k_r}{T}$ vs $\frac{1}{T}$

slope: $\Delta H^{\ddagger}$ reflects increase in energy in React $\rightarrow$ TS

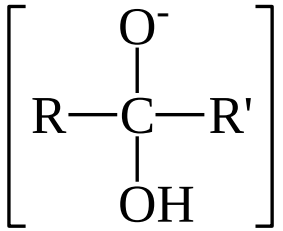
intercept: $\Delta S^{\ddagger}$ reflects loss ($\Delta S^{\ddagger} < 0$) or gain ($\Delta S^{\ddagger} > 0$) of degrees of freedom in React $\rightarrow$ TS

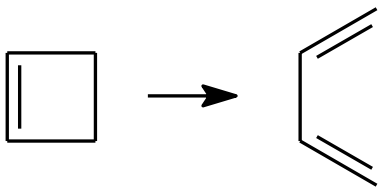
مثال :

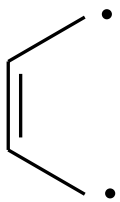
	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$OH^- + RBr \longrightarrow ROH$	large	< 0
$H_2O + RBr \longrightarrow ROH$	large	> 0
$OH^- + RCO_2R' \longrightarrow RCO_2^-$	smaller	< 0
	small	< 0
$t\text{Bu—O—O—}t\text{Bu} \longrightarrow t\text{Bu—O}\bullet$	large	> 0



$RBr \longrightarrow R^+ + Br^-$



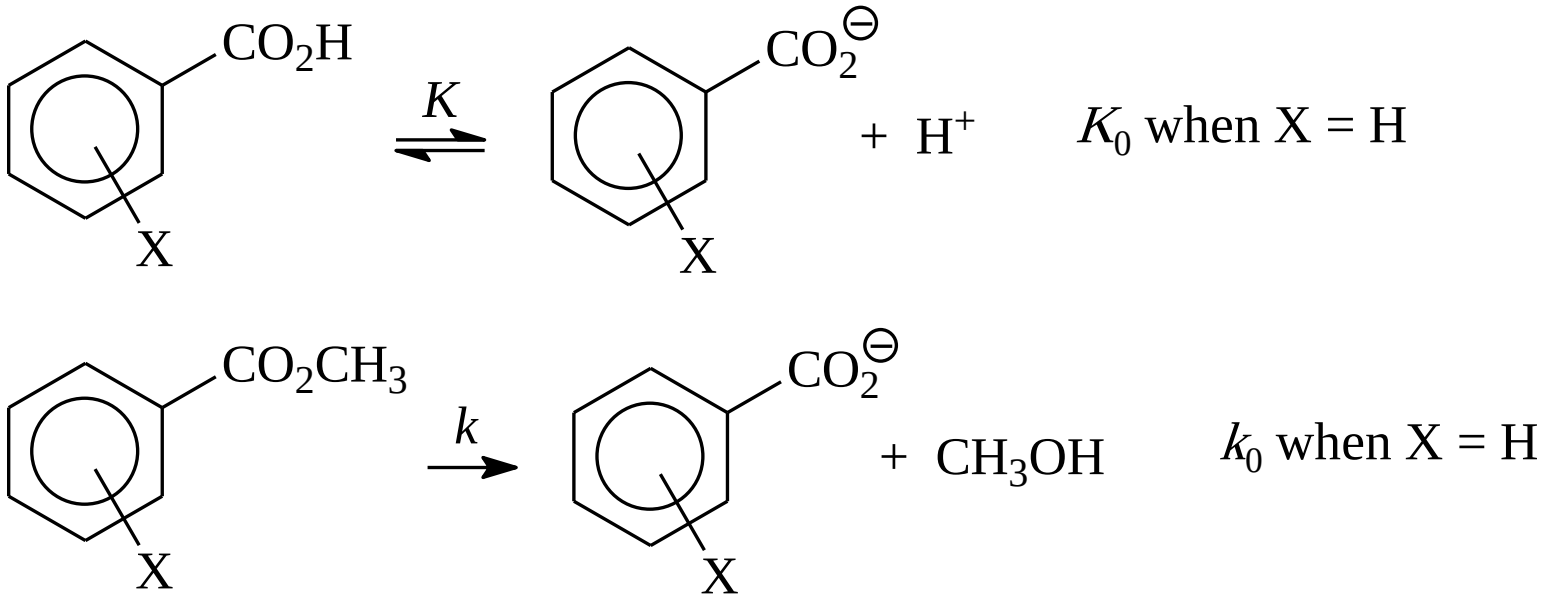


if via  then $\Delta S^{\ddagger} > 0$

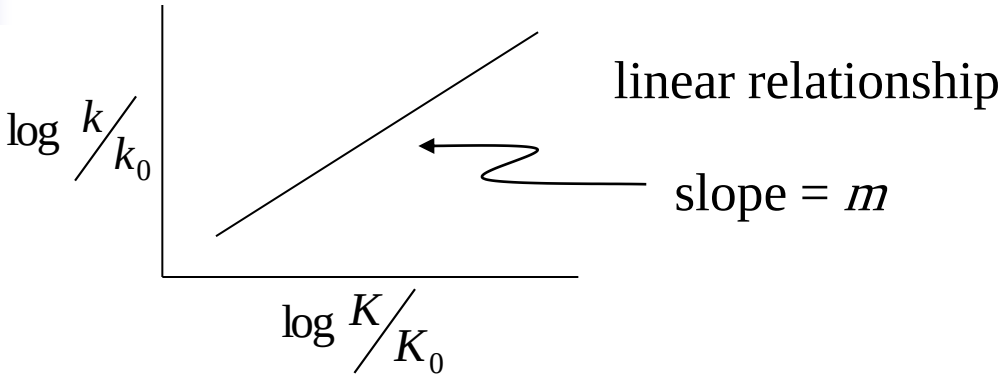
if via then $\Delta S^{\ddagger} \sim 0$

معادله هامت :

For example, compare an equilibrium and a reaction of benzoic acid derivatives:



Vary X and plot log k/k_0 vs log K/K_0 :



$$\log \frac{k}{k_0} = m \log \frac{K}{K_0}$$

from $k = k^{\ddagger} e^{-\Delta G^{\ddagger}/RT}$ and $K = e^{-\Delta G/RT}$

$$\left(\frac{-\Delta G^{\ddagger}}{RT}\right) - \left(\frac{-\Delta G_0^{\ddagger}}{RT}\right) = m\left[\left(\frac{-\Delta G}{RT}\right) - \left(\frac{-\Delta G_0}{RT}\right)\right]$$

or $\Delta\Delta G^{\ddagger} = m\Delta\Delta G$

i.e., (change in free energy of activation with change in substituents) $\propto$ (change in free energy of ionization with change in substituents)

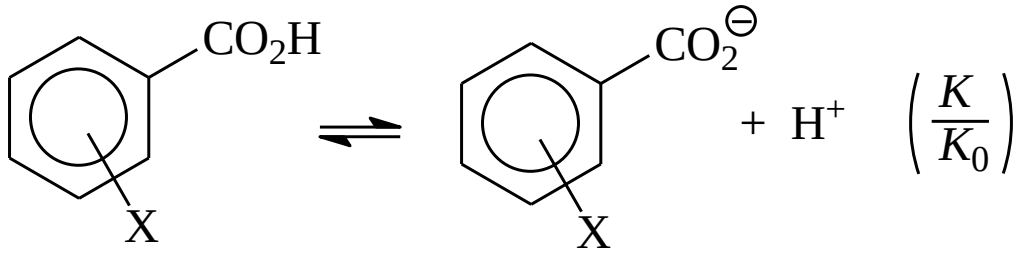
Hammett: $\log \frac{K}{K_0} = \sigma\rho$ (equilibrium data)

$\log \frac{k}{k_0} = \sigma\rho$ (kinetic data)

σ: reflects substituent effects

ρ: reflects reaction mechanism, sensitivity to σ

definition: ρ = 1 for



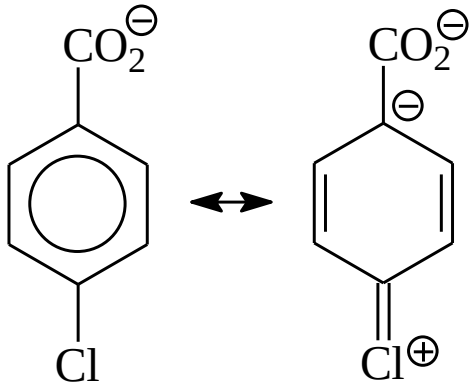
Strategy: 1. calculate σ for various X groups in above reaction

2. use these σ values to calculate ρ values for other reactions

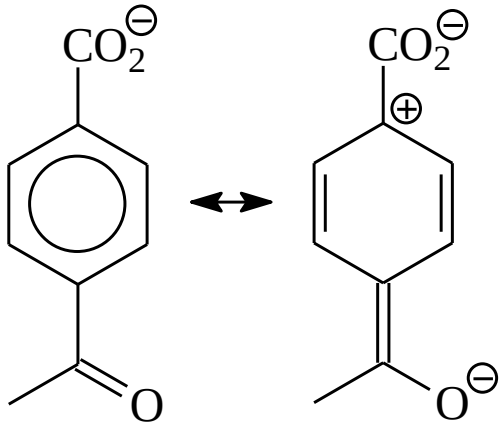
اثرهای رزونانس و میدان :

1. resonance and field effects

Resonance effects (only effective when X is *ortho* or *para*):

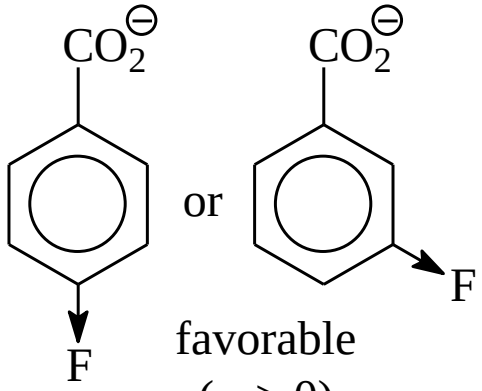


unfavorable
($\sigma < 0$)

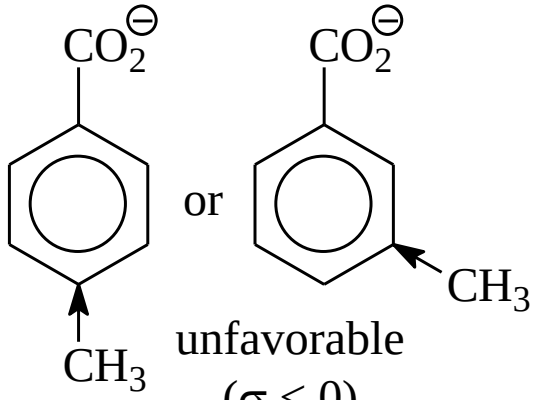


favorable
($\sigma > 0$)

Field effects (any position):



favorable
($\sigma > 0$)



unfavorable
($\sigma < 0$)

اثرهای فضایی :

2. σ_m and σ_p values (σ_o not used because of steric effects)

		σ_m	σ_p
e.g.,	$H_3C-\overset{\overset{O}{\|\|}}{C}-$	0.36 favorable field effect	0.47 favorable resonance and field effects
	HO—	0.13 favorable field	-0.38 unfavorable resonance (outweighs field effect)
	CH_3—	-0.06 unfavorable field	-0.14 unfavorable field
	F—	0.34 favorable field	0.15 favorable field outweighs unfavorable resonance

Shortcoming: relative extents of field and resonance effects are not constant, vary with type of reaction (*i.e.*, when resonance is involved, one sees a "normal" mixture of resonance and field effects; otherwise not). Instead…

3. σ^+ and σ^- values (for *para* substituents only)

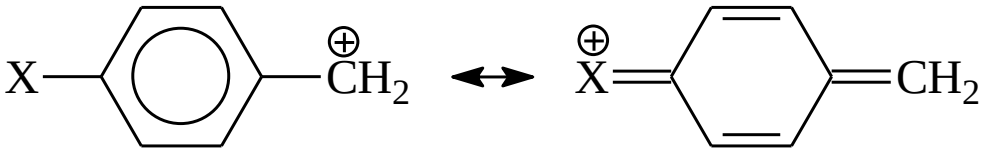
σ^+: degree of resonance interaction between an electron donor group and a cationic reaction center

σ^-: degree of resonance interaction between an electron acceptor group and an anionic reaction center

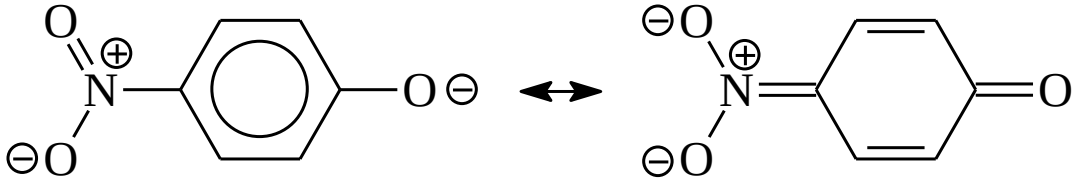
e.g.,

σ^+: Br = 0.15 ↑ worse
Cl = 0.11 ↕
F = -0.07 ↓ better

at



σ^-: NO_2 = 1.23
CH_3CO = 0.82

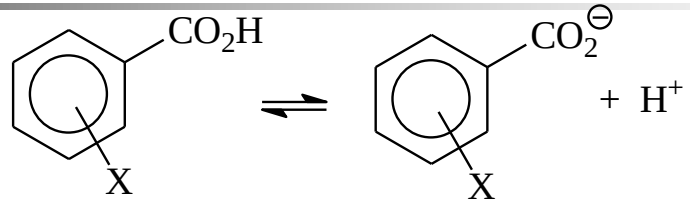


(There are other modifications on σ values, but these will suffice for us.)

II. Hammet σρ Relationships

C. ρ values: information about reaction mechanisms

For the equilibrium:



definition: ρ = 1

$$\log \frac{K}{K_0} = \sigma \cdot 1$$

i.e., for electron donor groups, σ < 0
for electron acceptor groups, σ > 0

For other reactions:

1. for $\log \frac{K}{K_0} = \sigma\rho$

ρ > 0 for equilibria favored by electron acceptors
ρ < 0 for equilibria favored by electron donors

2. for $\log \frac{k}{k_0} = \sigma\rho$

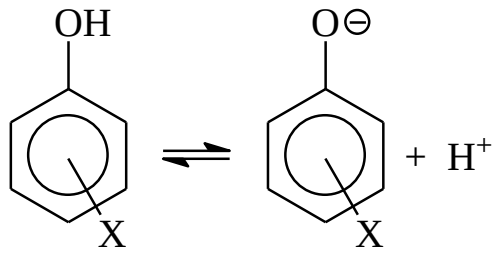
ρ > 0 for TS favored by electron acceptors
ρ < 0 for TS favored by electron donors

i.e., **ρ > 0** indicates **negative** charge development in TS
ρ < 0 indicates **positive** charge development in TS
and larger ρ indicates greater sensitivity to substituents,
i.e., a larger buildup or closer proximity of charge in TS

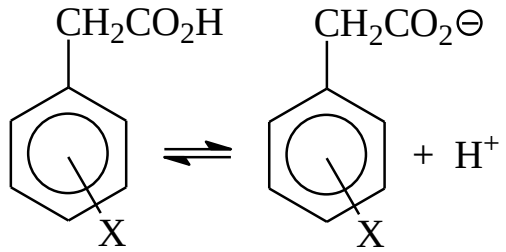
II. Hammet σρ Relationships

C. ρ values

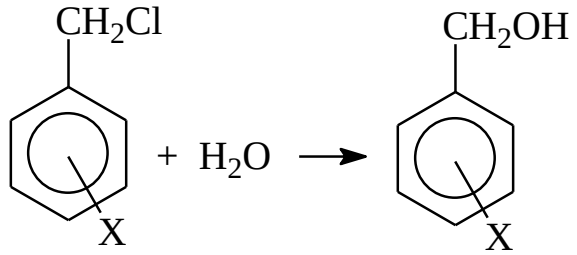
Examples:



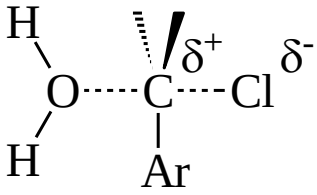
ρ = 2.26 more sensitive to substituent effects



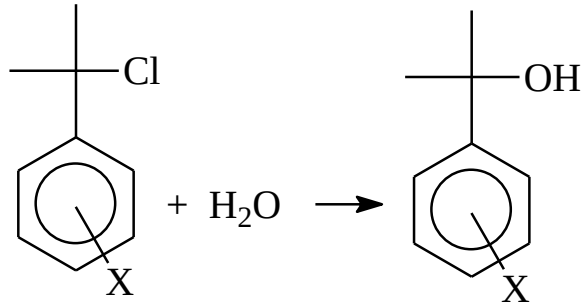
ρ = 0.56 less sensitive



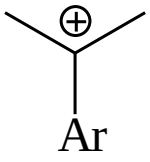
ρ = -1.31



partial charge buildup (S_N2-like)



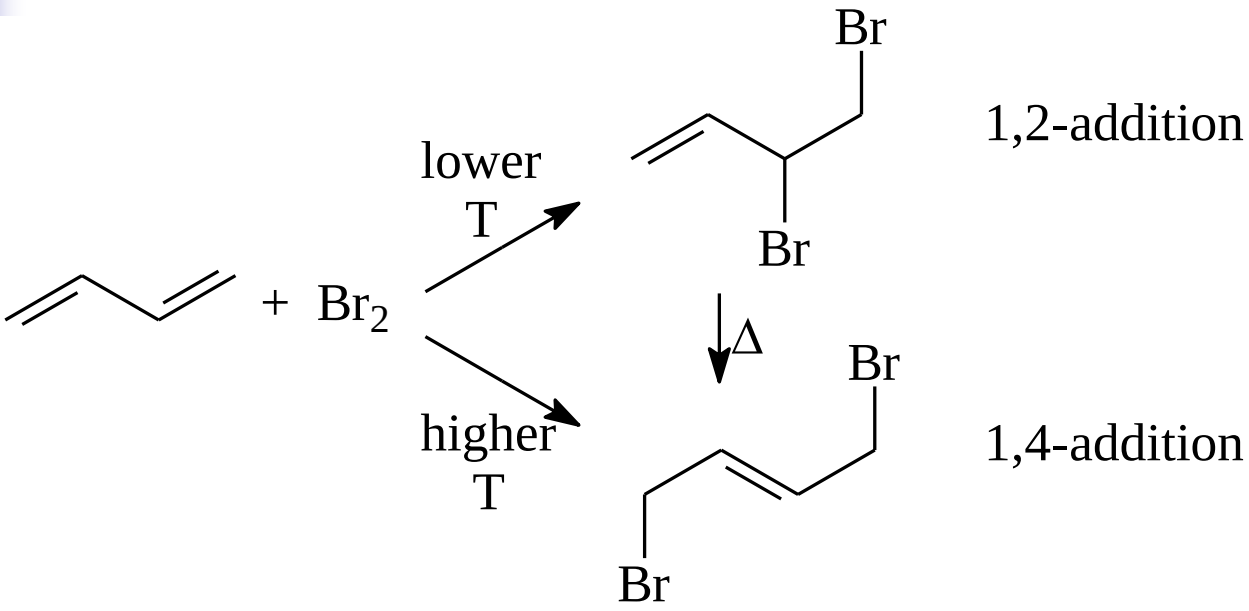
ρ = -4.48

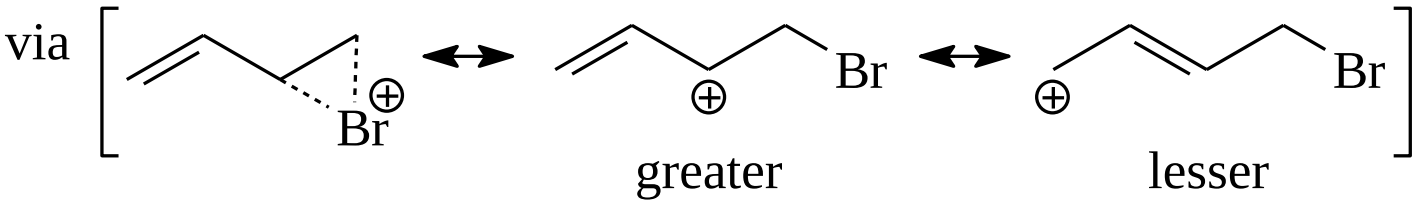


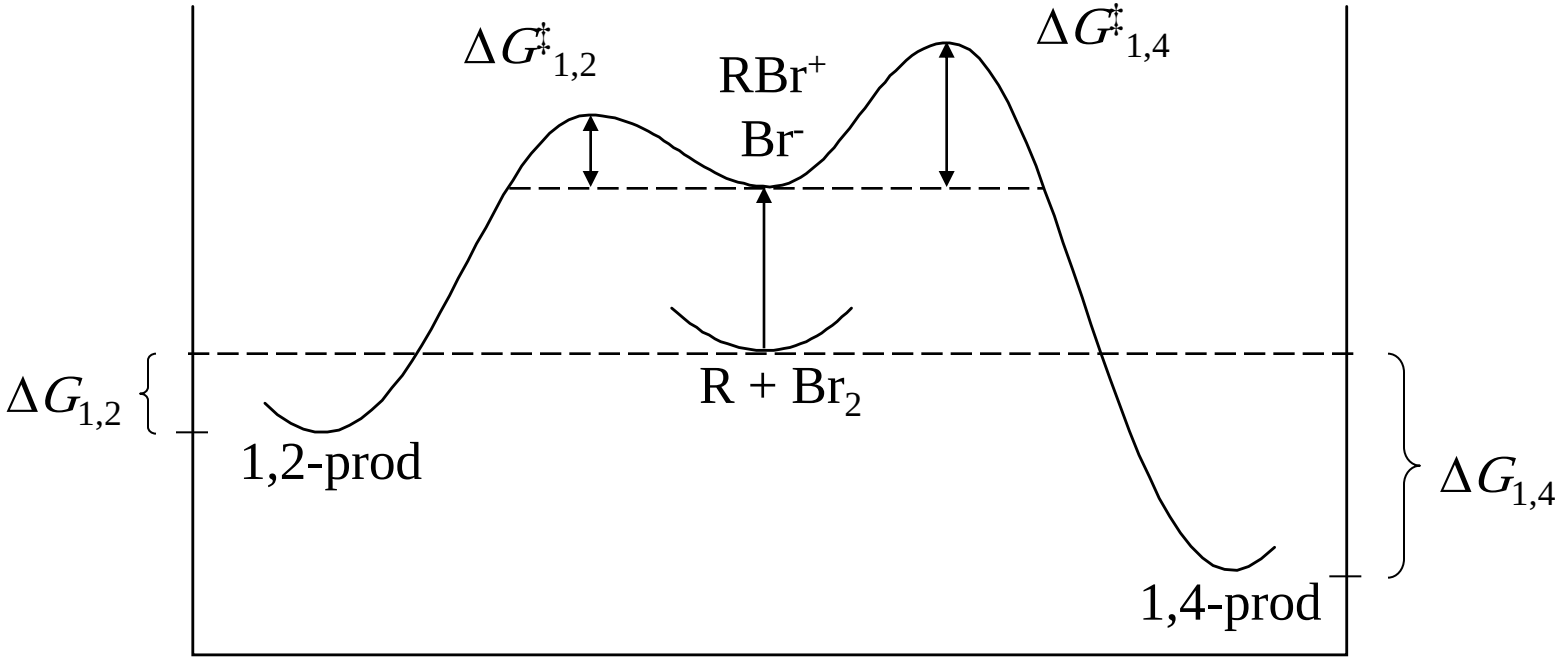
+ Cl^-

greater charge buildup (S_N1-like)

کنترل سینیتیکی و ترمودینامیکی :

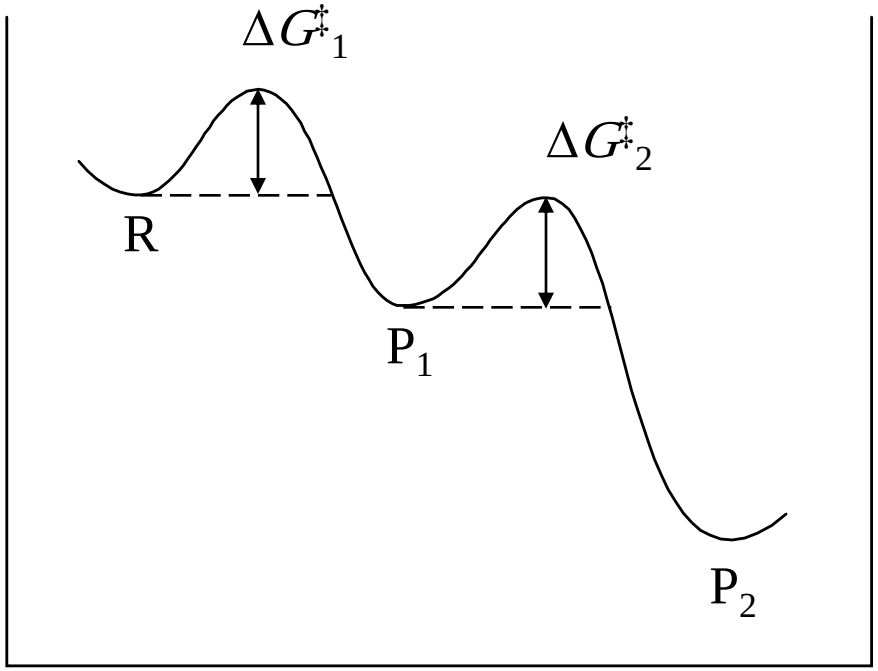






At low T, reaction is governed by $\Delta G^{\ddagger}$: **kinetic control** (*k*)
At higher T, reaction is governed by ΔG: **thermodynamic control** (*K*)

In general:

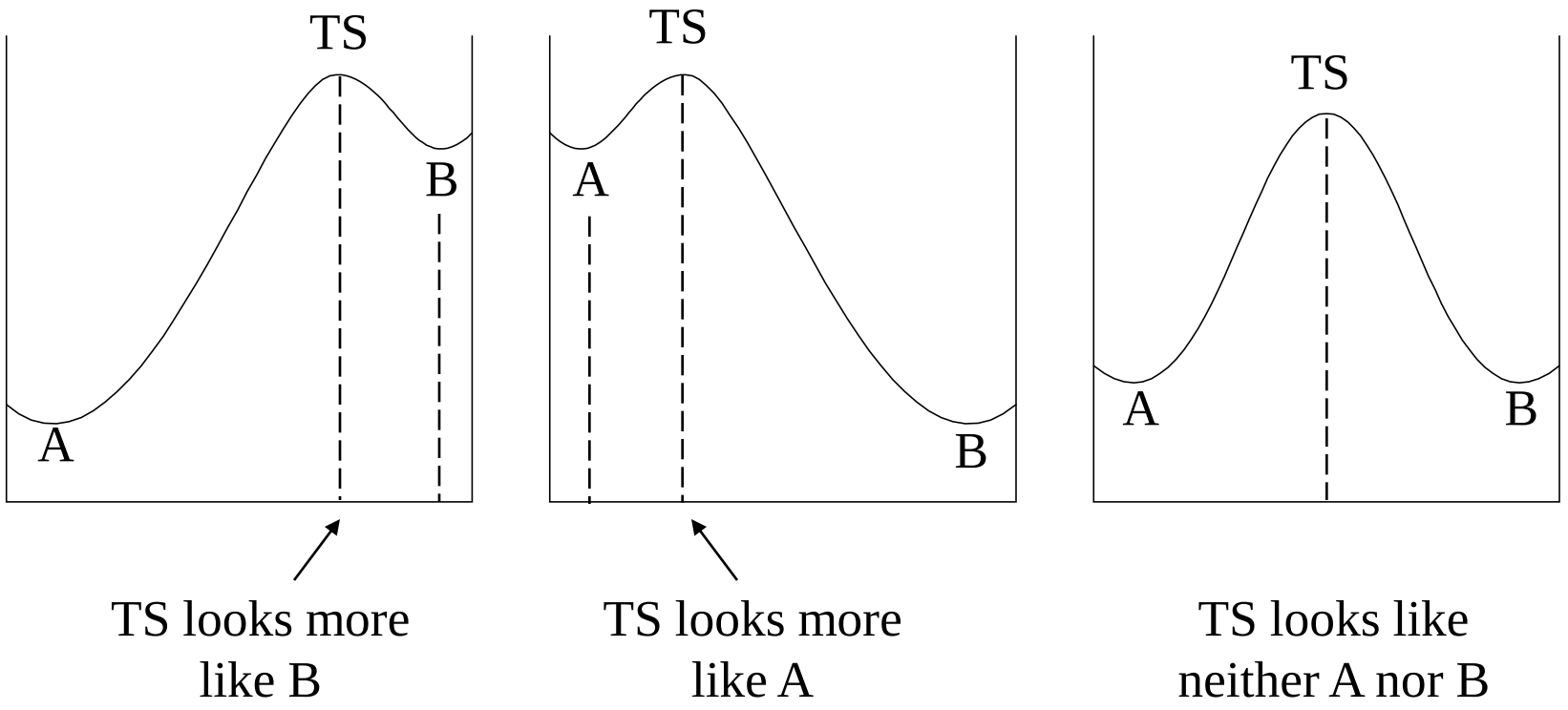


If $\Delta G^{\ddagger}_1 < \Delta G^{\ddagger}_2$
- kinetic control at low T
- thermodynamic control at higher T

If $\Delta G^{\ddagger}_1 > \Delta G^{\ddagger}_2$
- thermodynamic control at any T

اصل هاموند :

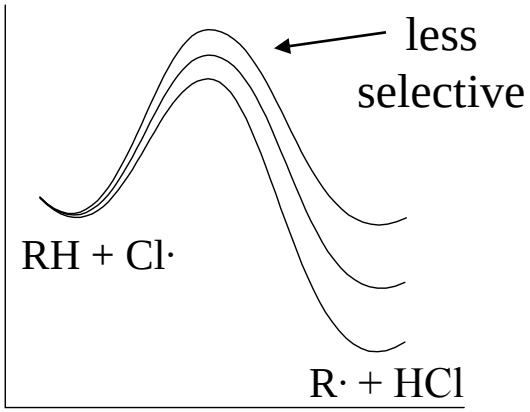
If two adjacent states along a reaction path have similar energies, they will have similar structures.

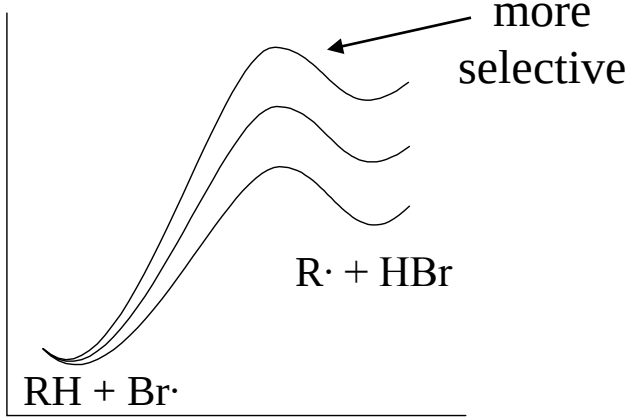


e.g., $RH + X_2 \rightarrow RX + HX$

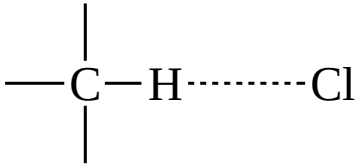
selectivity:	Cl_2	Br_2
1º	1	1
2º	4	80
3º	5	1600

RLS: $RH + X\cdot \rightarrow R\cdot + HX$

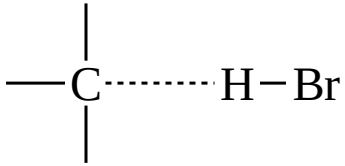




TS looks more like reactants:

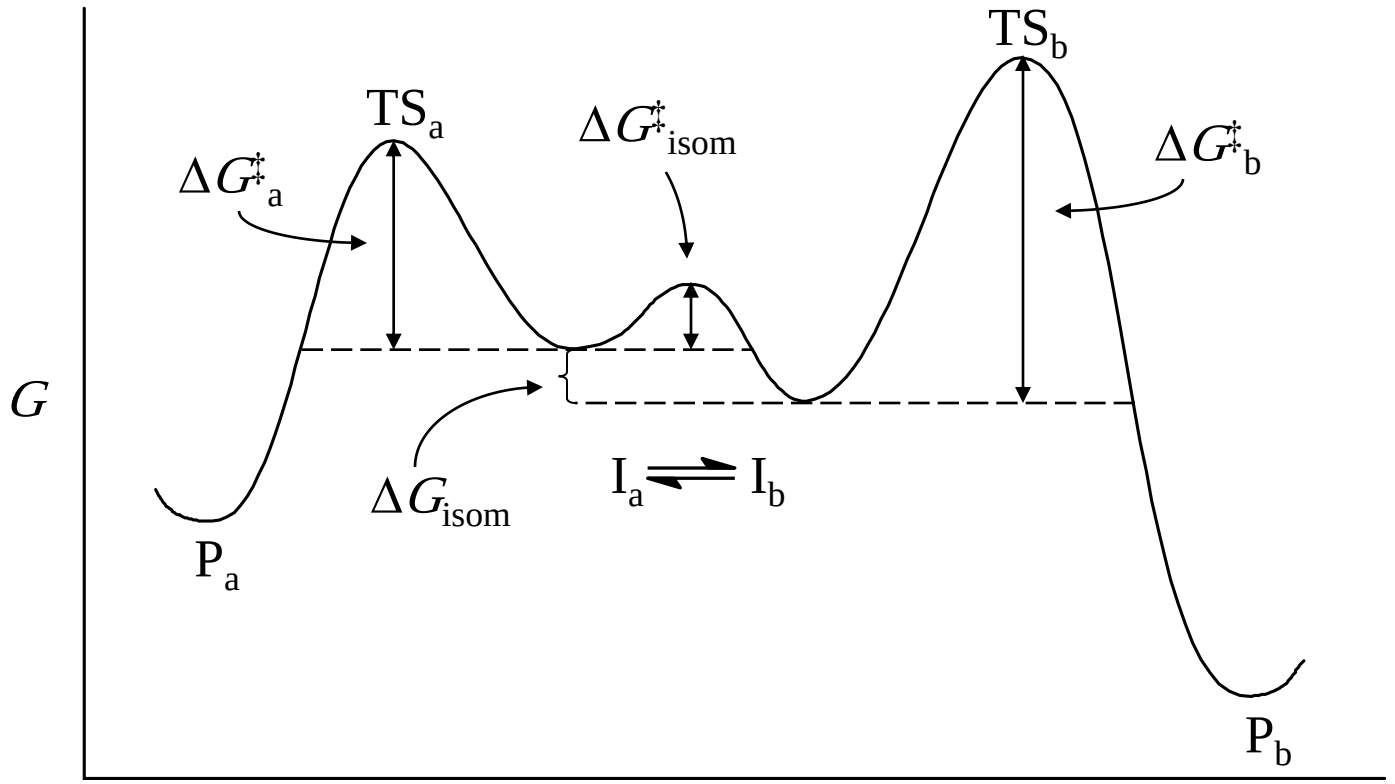


TS looks more like products:



اصل کورتین- هامت :

The population ratio of two equilibrating intermediates cannot be inferred from the product population ratio.



P_a/P_b ratio is determined by $\Delta G^{\ddagger}_a$, $\Delta G^{\ddagger}_b$ (kinetic)

$$[P_a]/[P_b] = \frac{k_a[I_a]}{k_b[I_b]} = \frac{k_a}{k_b K_{isom}}$$

$$= \frac{e^{-\Delta G_a^{\ddagger}/RT}}{e^{-\Delta G_b^{\ddagger}/RT} e^{-\Delta G_{isom}/RT}}$$

$$= e^{(\Delta G_b^{\ddagger} - \Delta G_a^{\ddagger} + \Delta G_{isom})/RT}$$

but $\Delta G_b^{\ddagger} - \Delta G_a^{\ddagger} + \Delta G_{isom}$

$$= (G_b^{\ddagger} - G_b) - (G_a^{\ddagger} - G_a) + (G_b - G_a)$$

$$= G_b^{\ddagger} - G_a^{\ddagger}$$

$$\therefore [P_a]/[P_b] = e^{G_b^{\ddagger} - G_a^{\ddagger}/RT}$$

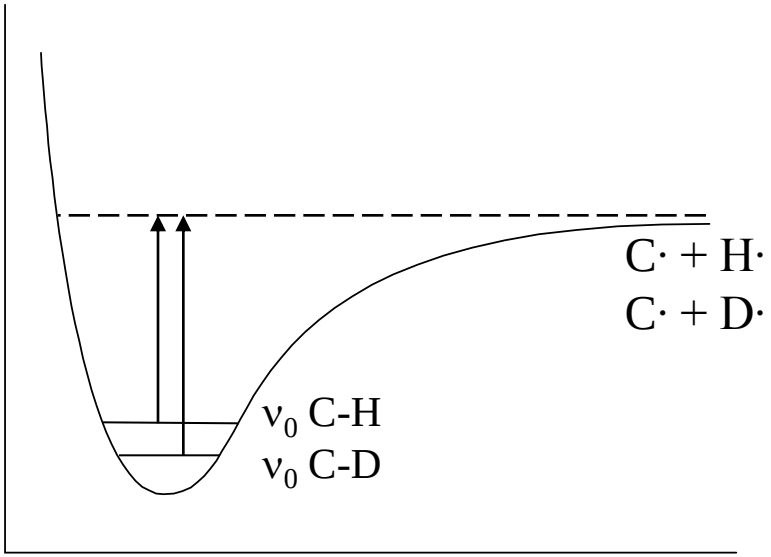
i.e., not $\propto \Delta G_{isom}$

not $\propto K_{isom}$

اثرهای سینیتیکی ایزوتوپها :

اثرات اولیه :

- when C-H (C-D) bond breaks in RLS



$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \cong \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$\Delta G^{\ddagger}_{C-H} < \Delta G^{\ddagger}_{C-D}$$

$$\therefore \frac{k_H}{k_D} > 1 \quad (\max \sim 7)$$

k_H/k_D	Indicates:
~7 (theor max)	strong bonding to H by both partners

$$AH + B \longrightarrow A + BH \qquad TS: A\cdots H\cdots B$$

>~2	significant C-H bond breaking in TS
~1	slightly or nearly completely broken in TS

$$A{-}H\cdots\cdots B$$

or

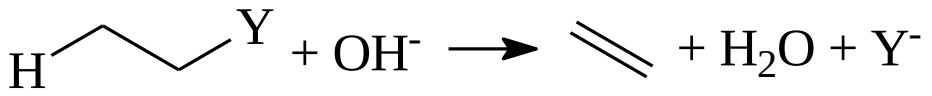
$$A\cdots\cdots H{-}B$$

i.e., TS looks much like reactant or product

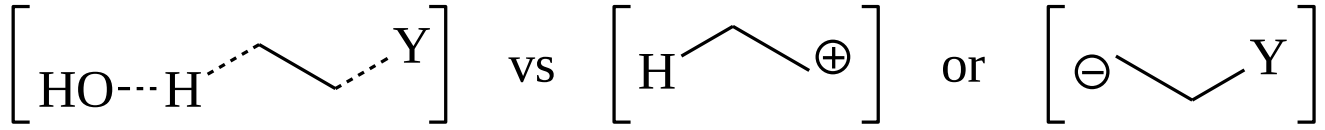
e.g., $RCH_3 + Br_2 \longrightarrow RCH_2Br + HBr$ $\quad k_H/k_D \approx 4\text{-}5$

$\therefore$ $RCH_3 + Br\bullet \longrightarrow RCH_2\bullet + HBr$ $\quad$ is RLS

TS: $\left[RCH_2 \cdots H \cdots Br\right]$

e.g.,  $k_H/k_D \approx 4\text{-}5$

$\therefore$ E2 (instead of E1 or $E1_{cb}$ where $k_H/k_D \sim 1$)

TS: 

E2 $\quad$ E1 $\quad$ $E1_{cb}$

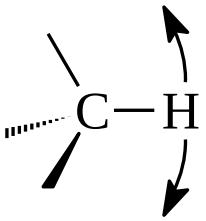
اثرات ثانویه ایزوتوپی :

When isotopic substitution is at a bond **not** broken in TS.

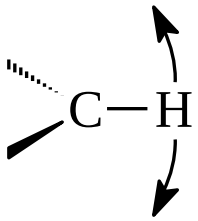
$k_H/k_D \sim 0.7\text{-}1.5$ > 1 = **normal** isotope effect

< 1 = **inverse** isotope effect

1. H on C undergoing rehybridization (α carbon)



bend
~1350 cm^{-1}

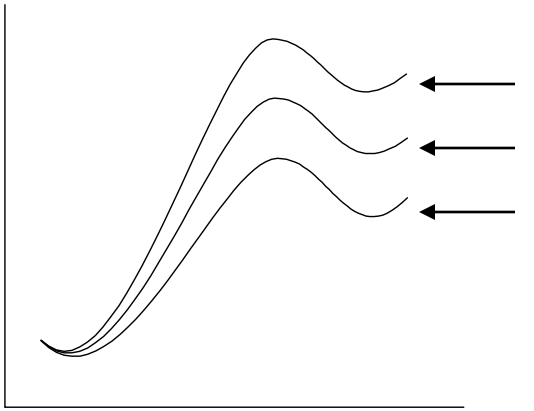


oop bend
~ 800 cm^{-1}
(lower E)

ΔE(C-H) > ΔE(C-D)
(because $r_{C\text{-}H} > r_{C\text{-}D}$)

1. H on C undergoing rehybridization

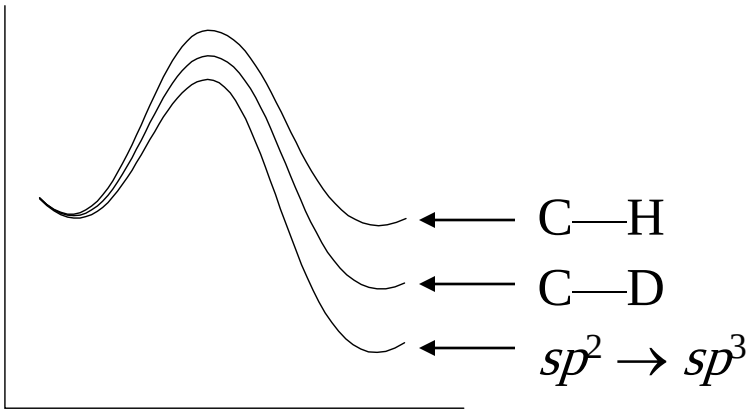
$sp^3 \rightarrow sp^2$



lowering of energy
greater for C-H

$\therefore\ k_H/k_D > 1$

$sp^2 \rightarrow sp^3$

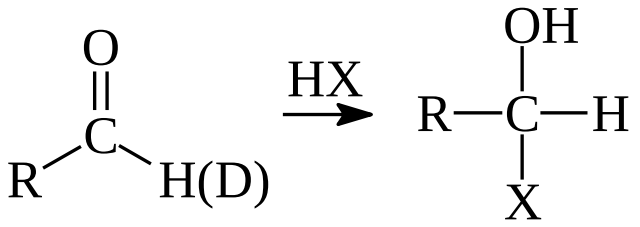


raising of energy
greater for C-H

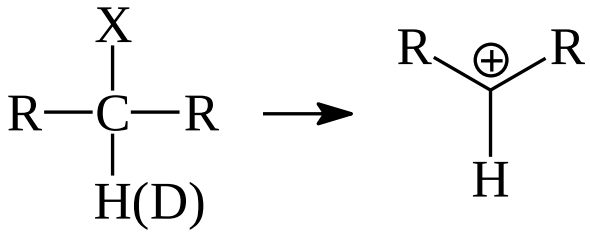
$\therefore\ k_H/k_D < 1$

1. H on C undergoing rehybridization

e.g.,



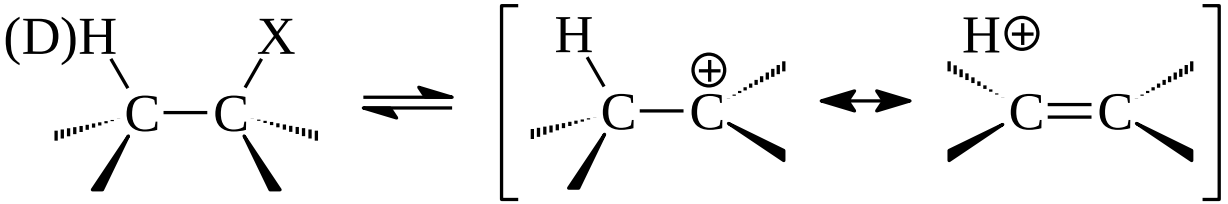
$k_H/k_D \sim 0.7$



$k_H/k_D \sim 1.3$

2. H on β carbon: hyperconjugation

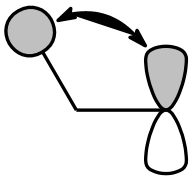
VB:



$k_H/k_D > 1$ (1.1 ~ 1.4)

C-H bond weaker, ∴ greater contribution

MO:



$HOMO_{C\text{-}H} > HOMO_{C\text{-}D}$

اثرات حلال :

قطبیت :

1. polarity

$\propto$ dielectric constant, *f*(dipole, polarizability)

polar protic:	H_2O, ROH, RCO_2H
polar aprotic:	acetone, acetonitrile, HMPA, DMF, DMSO
nonpolar:	hexane, benzene, CCl_4, Et_2O, THF

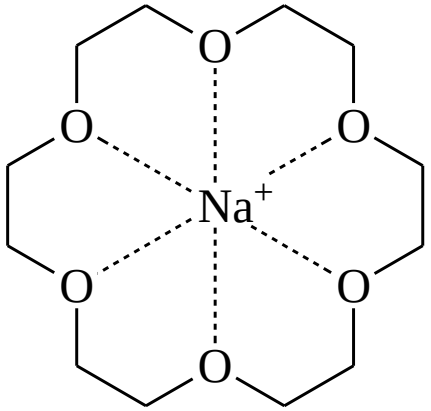
Reaction type	Favored by
$A-B \longrightarrow A^{\delta+}\cdots B^{\delta-} \longrightarrow A^+ + B^-$	polar
$A^+ + B^- \longrightarrow A^{\delta+}\cdots B^{\delta-} \longrightarrow A-B$	nonpolar
$A + B \longrightarrow A\cdots B \longrightarrow A-B$	either

خصلت نوکلئوفیلیسیته :

2. nucleophilicity of Nu^-

e.g., OH^- (from NaOH)

Solvent	Nucleophilicity	
H_2O	low	large solvation energy
DMSO	high	lower solvation energy
C_6H_6 + 18-crown-6	highest	



very strong complex with Na^+ leaves OH^- “naked”

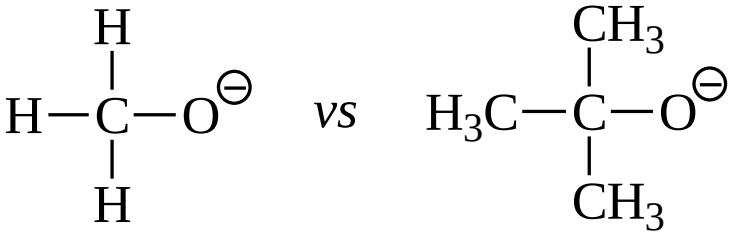
مقایسه فاز حلال و گازی :

1. acidities

Acid	$\Delta H^{o}_{diss}(aq)$	$\Delta H^{o}_{diss}(g)$
H_2O	21.4	391
MeOH	21.1	379
EtOH	21.7	376
*i*PrOH	23.2	374
*t*BuOH	26	373

all are larger in gas phase due to lack of solvation

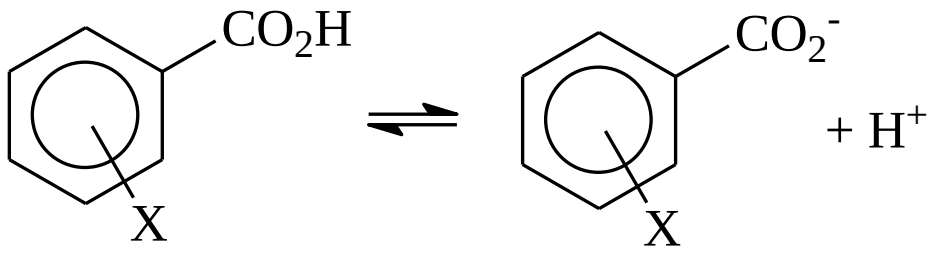
weakest — strongest!



- CH_3 more polarizable than H (more overlap between OMO on O^- and UMO on CH_3
  - main effect in gas phase
- *t*BuO^- more difficult to solvate than CH_3O^-
  - main effect in solution

اثرات الکترونی :

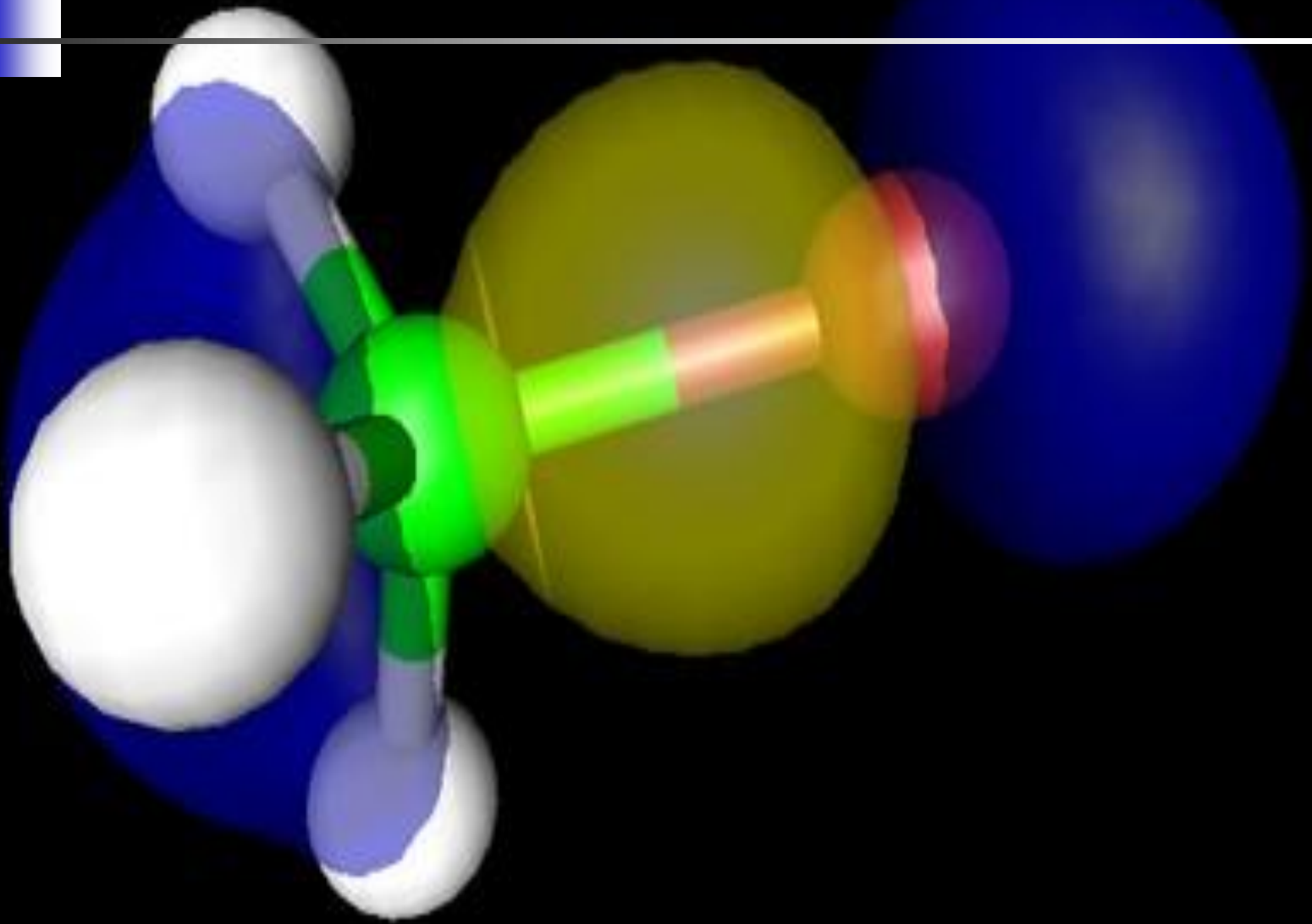
2. electronic effects



X	$\Delta\Delta H_a(aq)$	$\Delta\Delta H_a(g)$
m-Me	0.11	0.5
m-Cl	-0.50	-8.0
p-Cl	-0.28	-6.7
m-NO_2	-0.98	-16

In solution, $ArCO_2^-$ is stabilized by solvation. In the gas phase the relative effects of the substituents are magnified.

فصل ۴ : کربوکاتیون‌ها



هدف های کلی :

کربوکاتیونها واسطه های آلی عمومی هستند که به روشهای مختلف تهیه میگردند.بسیاری از اصول اساسی حاکم بر برهم کنش های درون مولکولی وبین مولکولی از مطالعه کربوکاتیونها نتیجه میشود بنابراین در این فصل دانشجویان با ماهیت کربوکاتیون ، عوامل پایداری وواکنشهای آن آشنا میشوند.

مقدمه :

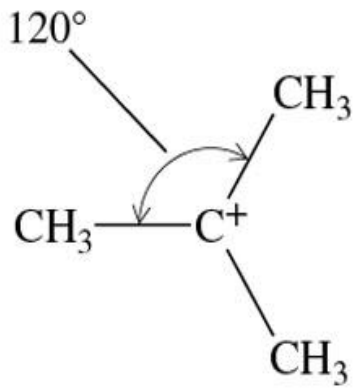
کربوکاتیونها واسطه های آلی عمومی هستند که در آنها کربن دارای بار مثبت می باشد این ذرات می توانند به روشهای مختلف ایجاد گردند :

۱- واکنشهای جیگزینی وحذفی

۲- جایگزینی الکتروفیلی آروماتیک

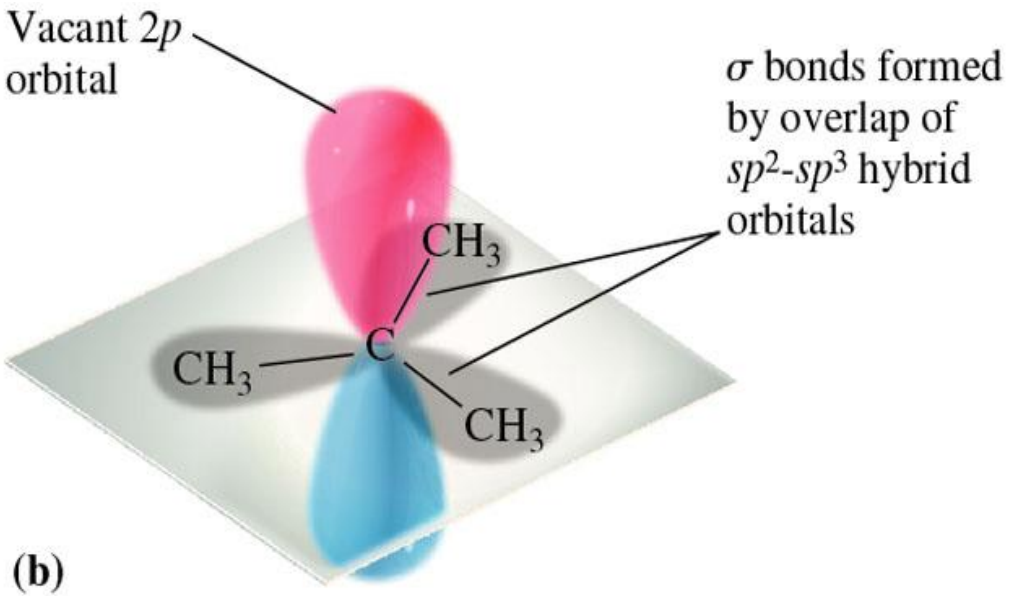
۳- افزایش الکتروفیلی به آلکنها

ساختمان :



tert-Butyl cation

(a)



(b)

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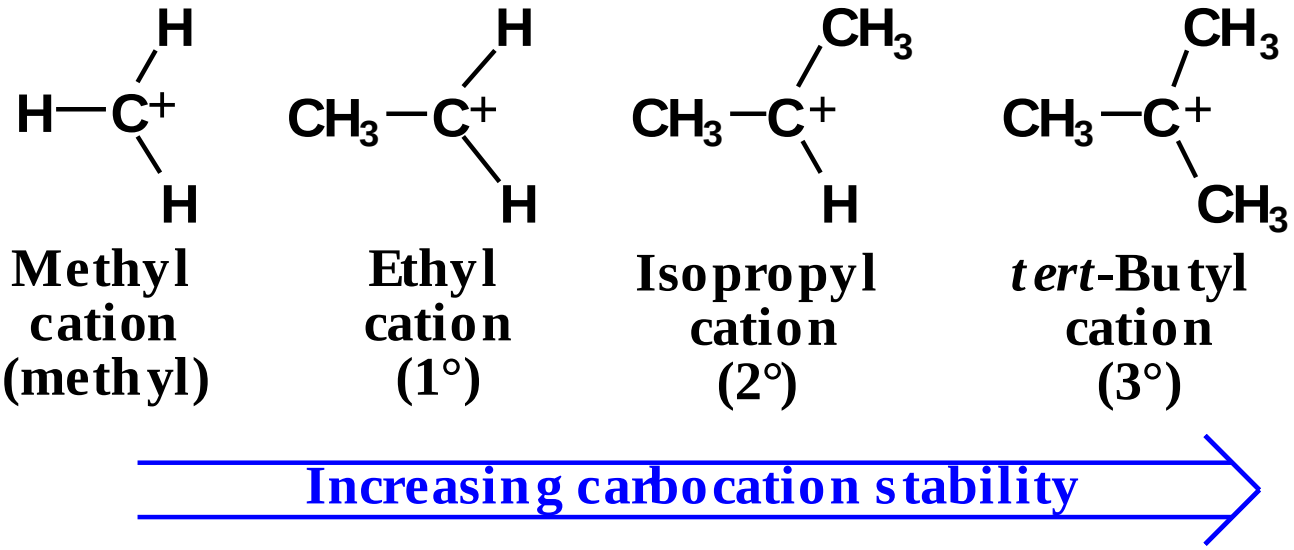
Carbocation Stability

پایداری کربوکاتیون :

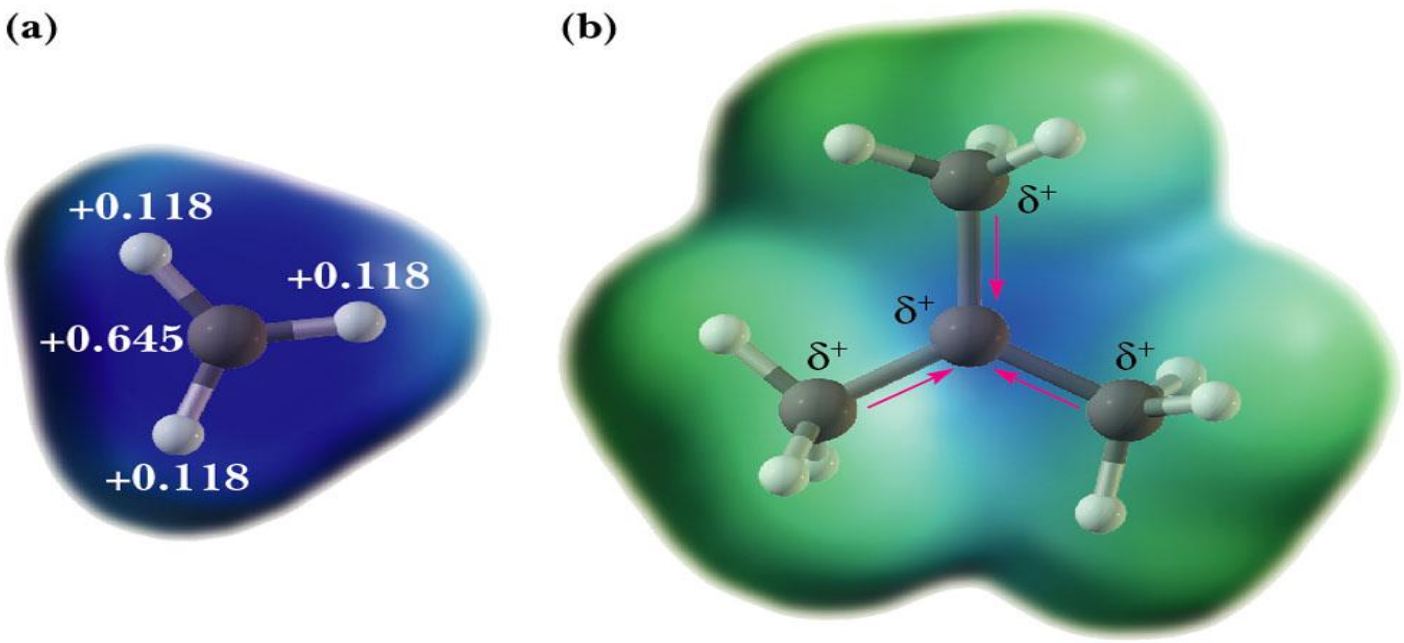
اثر حلال :



حلال نقش مهمی در تسهیل عمل یونش دارد و این بخاطر خاصیت دو قطبی برخی از حلال ها است که یونها را پایدار تر می کند.

اثرهای الکترونی :

کربوکاتیونها کمبود الکترون دارند بنابراین هر تغییری در ساختمان که باعث افزایش دانسیته الکترونی در مرکز بار مثبت گردد، کربوکاتیون را پایدار می کند .



اثر القایی :

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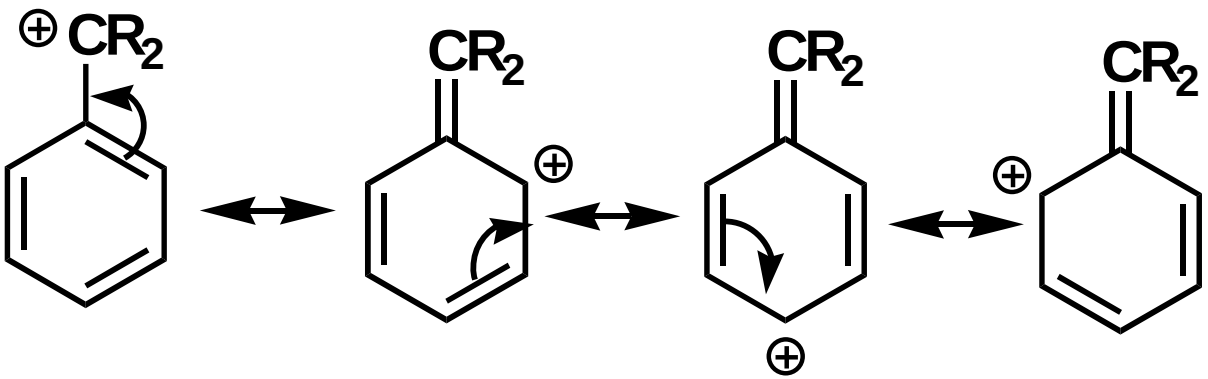
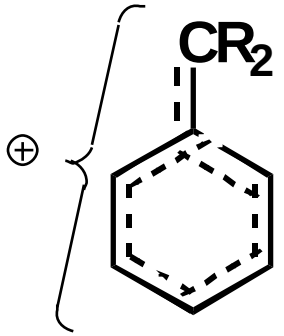


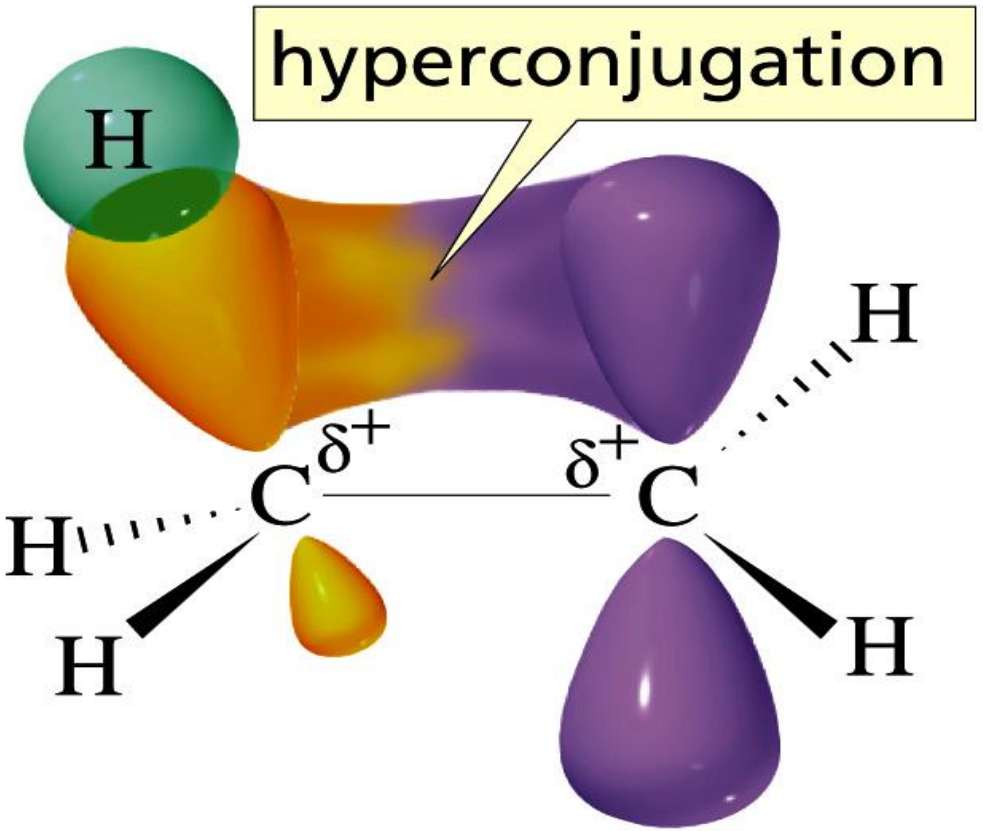
or hybrid



Hyperconjugation

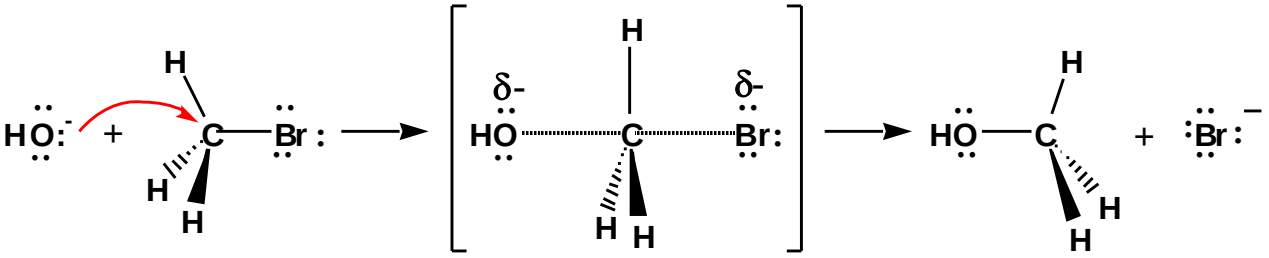
هایپرکانجوگه شدن :

یکی از روشهای پایداری کربوکاتیون :



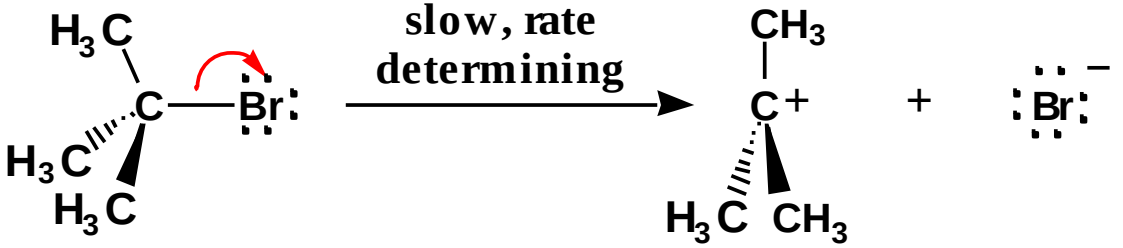
جایگزینی نوکلئوفیلی آلیفاتیک : Nucleophilic aliphatic Substitution

Mechanism - SN2

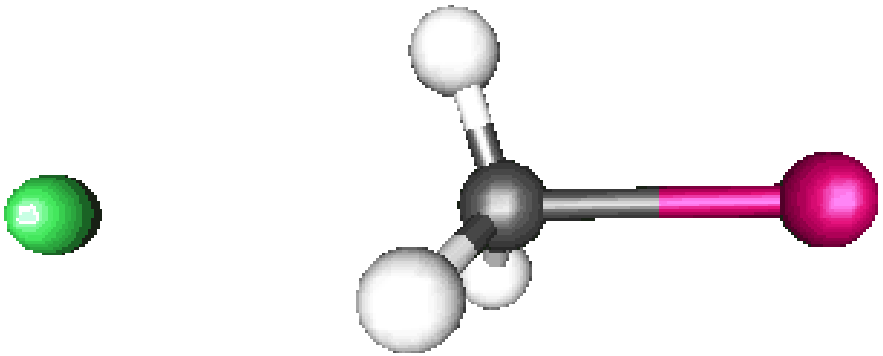


Transition state with simultaneous bond breaking and bond forming

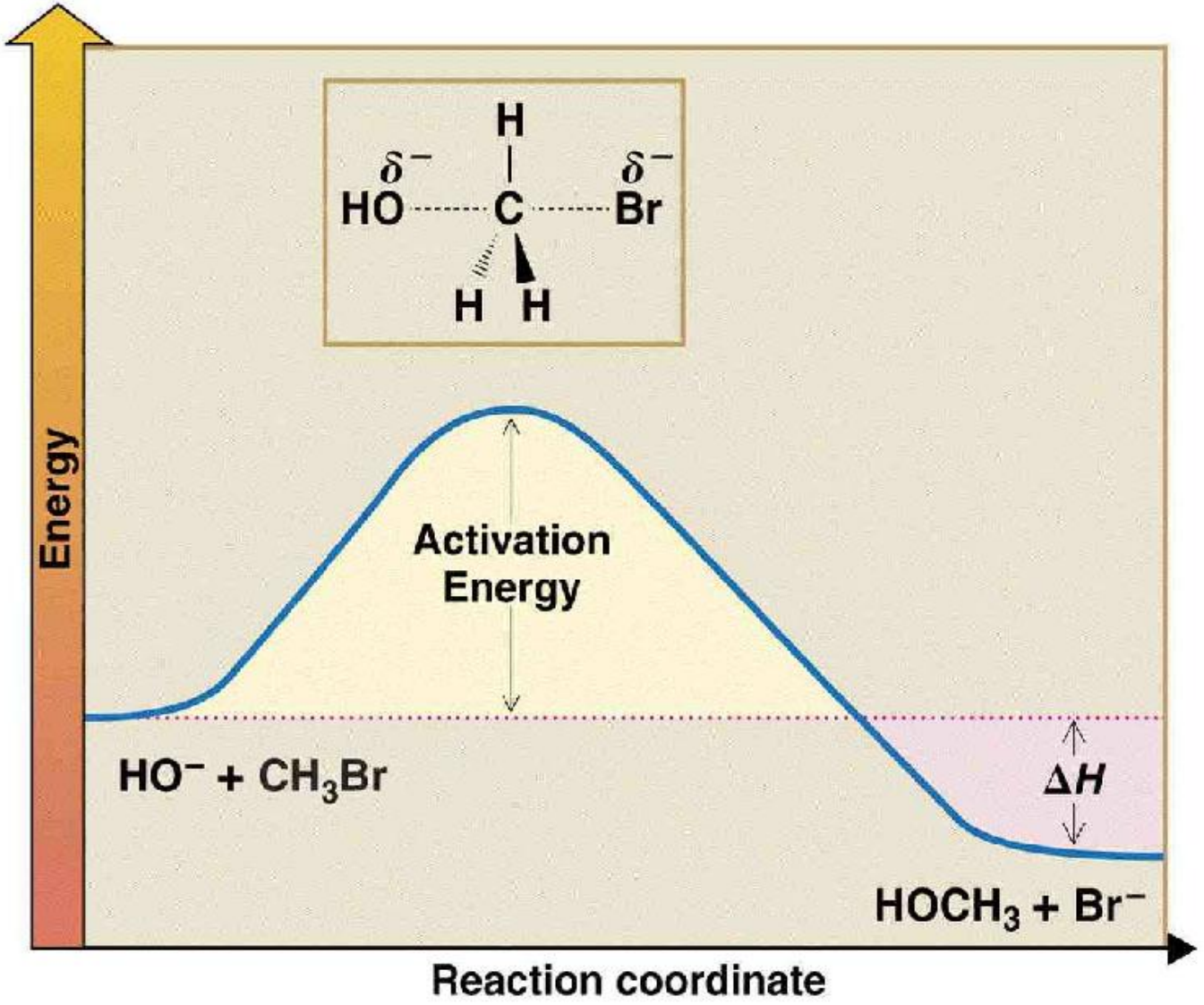
Mechanism - S_N1



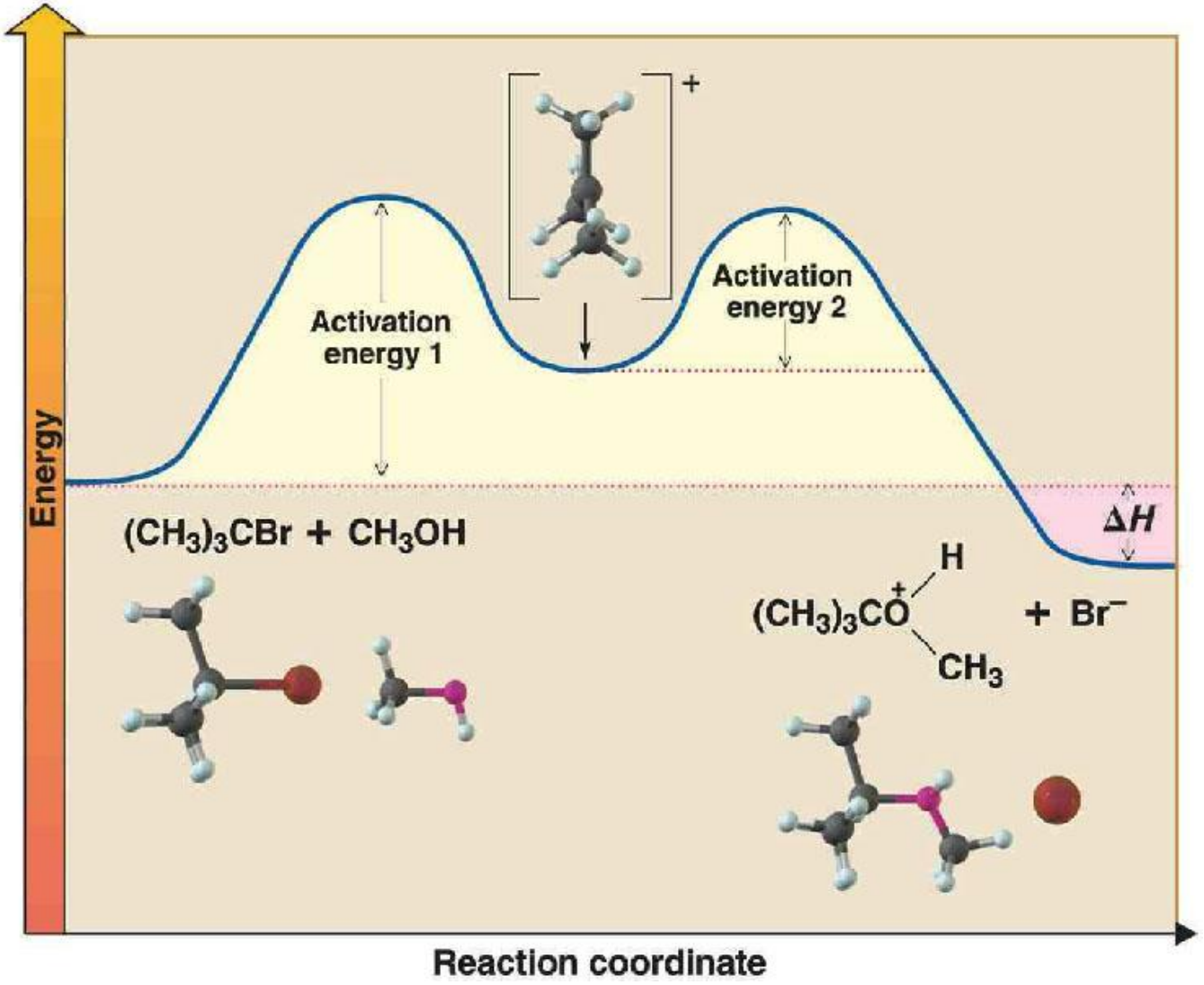
A carbocation intermediate; its shape is trigonal planar



Mechanism - SN2

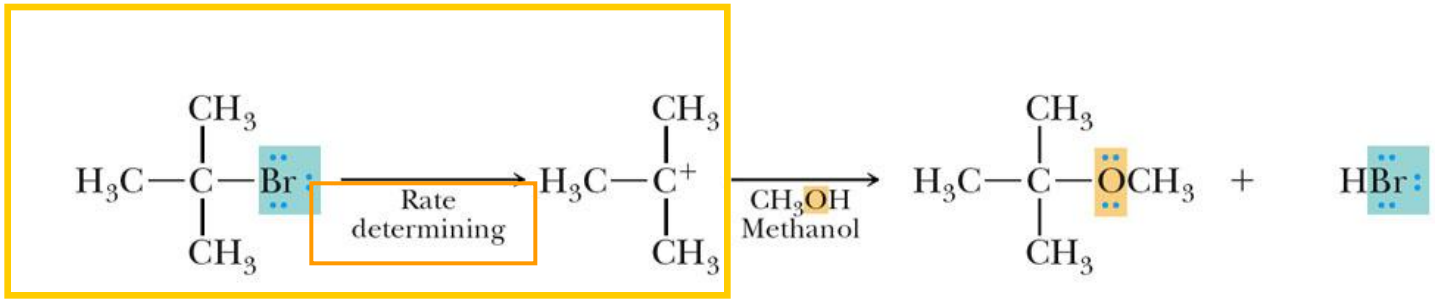


Mechanism - SN1



سینتیک واکنش های S_N1 و S_N2

S_N1



2-Bromo-2-methylpropane
(*tert*-Butyl bromide)

2-Methoxy-2-methylpropane

$$\text{Rate} = -\frac{d[(CH_3)_3CBr]}{dt} = k[(CH_3)_3CBr]$$

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S_N2

$$CH_3Br: + Na^+ :\ddot{O}H^- \longrightarrow CH_3\ddot{O}H + Na^+ :\ddot{Br}:^-$$

Bromomethane Methanol

$$\text{Rate} = -\frac{d[CH_3Br]}{dt} = k[CH_3Br][OH^-]$$

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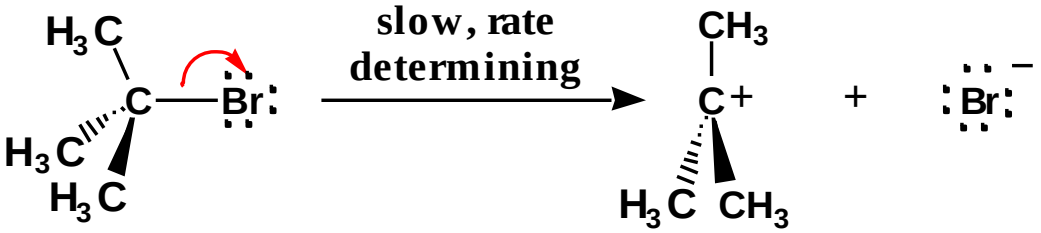
Nucleophilicity

: نوکلئوفیلیسیته

Effectiveness	Nucleophile
Good	Br^-, I^-
	CH_3S^-, RS^-
	HO^-, CH_3O^-, RO^-
	CN^-, N_3^-
Moderate	Cl^-, F^-
	CH_3COO^-, $RCOO^-$
	CH_3SH, RSH, R_2S
	NH_3, RNH_2, R_2NH, R_3N
Poor	H_2O
	CH_3OH, ROH
	CH_3COOH, $RCOOH$

گروه آلکیل :

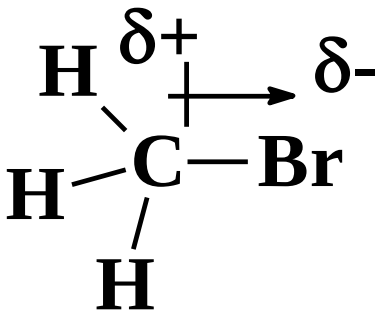
هر تغییر ساختمانی که باعث پایداری کربوکاتیون گردد ، حالت گذرایی را که به ماده واسطه منجر میگرددنیز پایدار خواهد ساخت و در نتیجه باعث سهولت یونش خواهد شد .



A carbocation intermediate;
its shape is trigonal planar

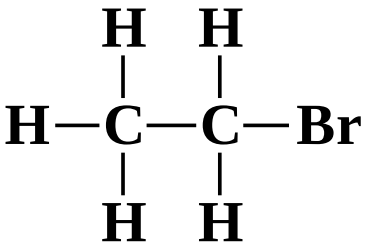
گروه ترک کننده :

افزایش توانایی گروه ترک کننده در پذیرش بار منفی آنرا گروه ترک کننده بهتری خواهد کرد وسرعت واکنش زیاد می شود.



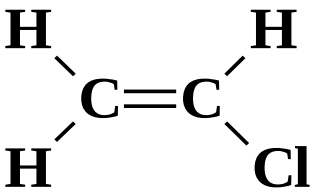
طبقه بندی هالیدها :

آلکیل هالیدها



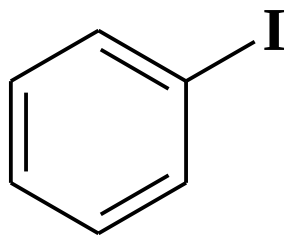
alkyl halide

وینیل هالیدها



vinyl halide

آریل هالیدها

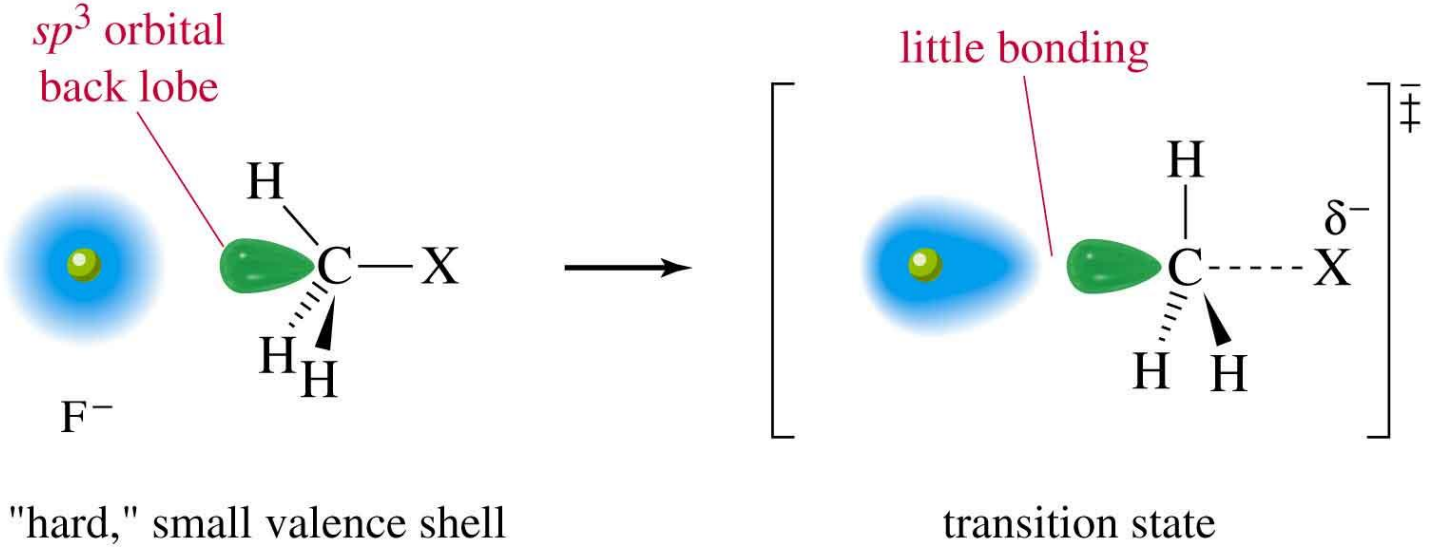


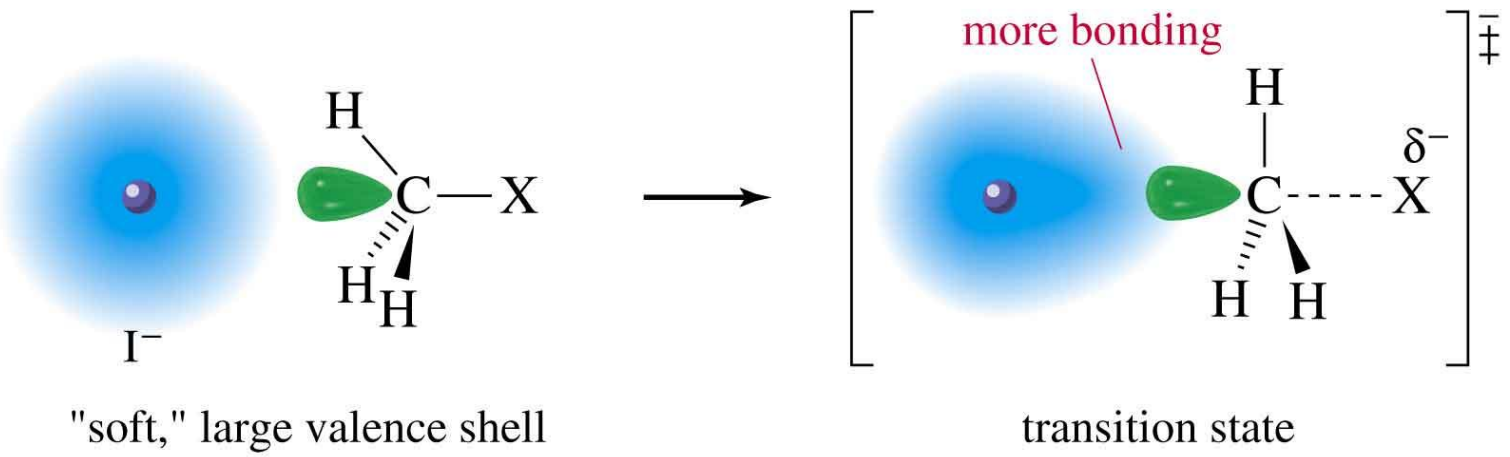
aryl halide

=>

Polarizability Effect

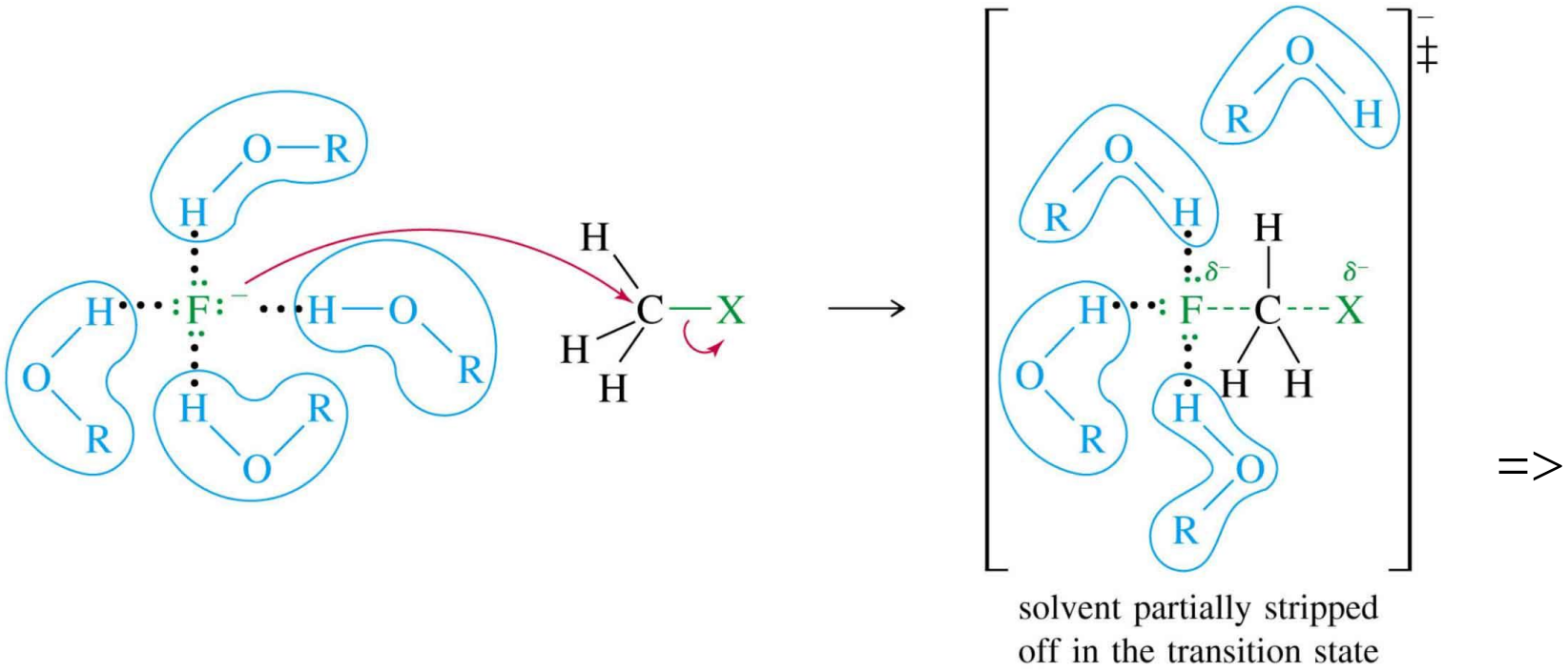
اثرات قطبش پذیری:





اثرات حلال :

حلال قطبی پروتوندار



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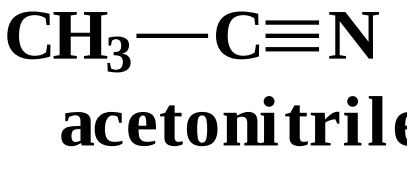
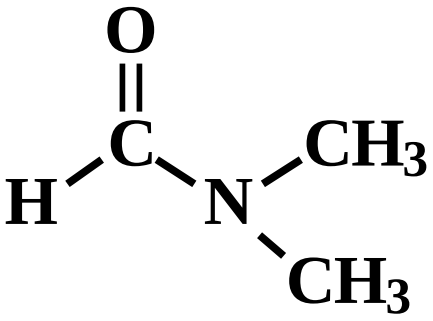
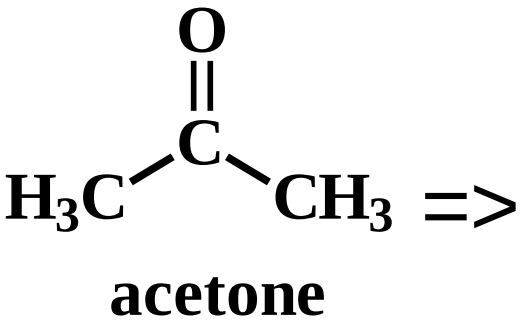
حلال های قطبی بدون پروتون :



acetonitrile



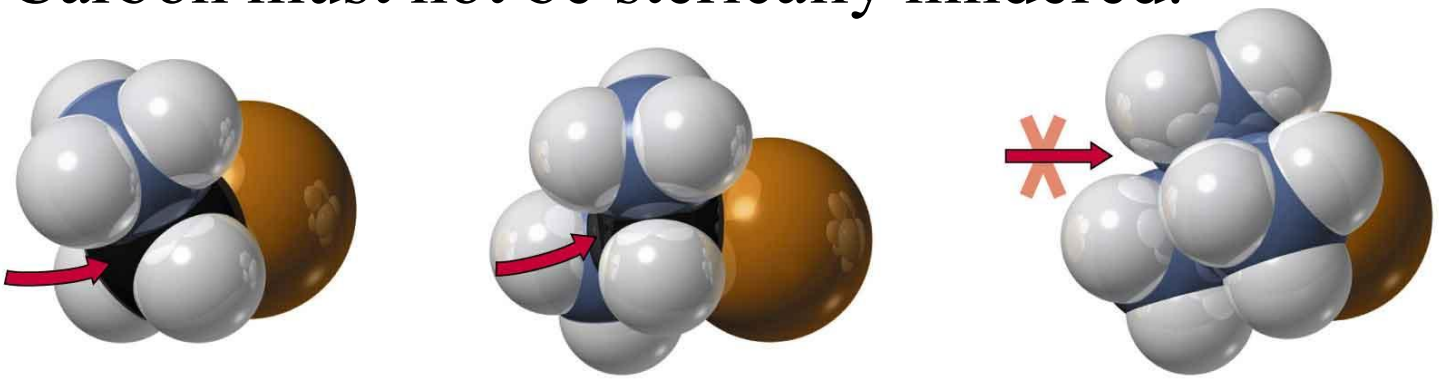
dimethylformamide
(DMF)



acetone

S_N2: Reactivity of Substrate ساختار:

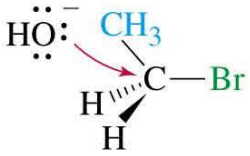
- ✓ Carbon must be partially positive.
- ✓Must have a good leaving group
- ✓Carbon must not be sterically hindered.

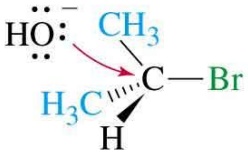


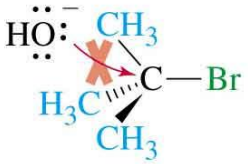
ethyl bromide (1°)
attack is easy

isopropyl bromide (2°)
attack is possible

t-butyl bromide (3°)
attack is impossible





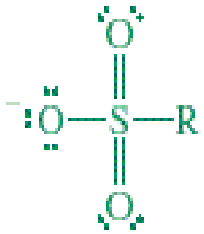
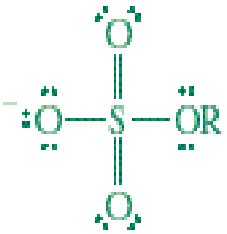
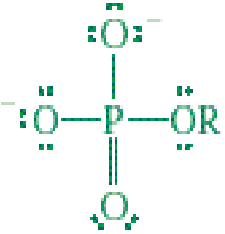
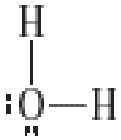
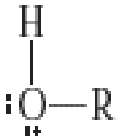
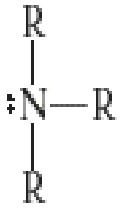
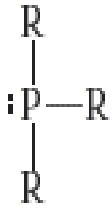


=>

Leaving Group Ability

گروه ترک کننده :

TABLE 6-4 Weak Bases that Are Common Leaving Groups

Ions:	$^{-}:\ddot{\underset{\cdot\cdot}{Cl}}:$	$^{-}:\ddot{\underset{\cdot\cdot}{Br}}:$	$^{-}:\ddot{\underset{\cdot\cdot}{I}}:$			
	halides			sulfonate	sulfate	phosphate
Neutral molecules:						
	water	alcohols	amines	phosphines		

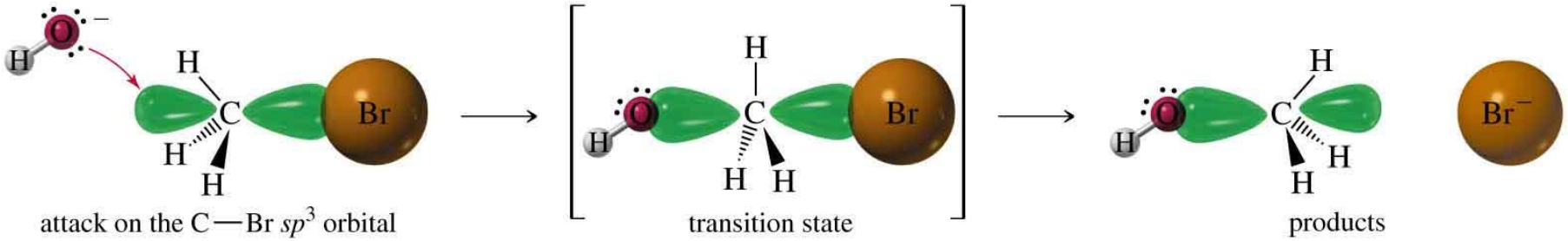
سرعت نسبی واکنش SN2

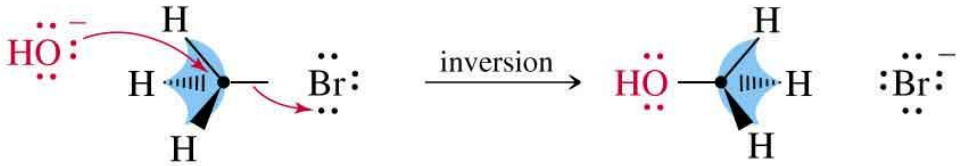
- Relative rates for S_N2:

$$CH_3X > 1° > 2° >> 3°$$

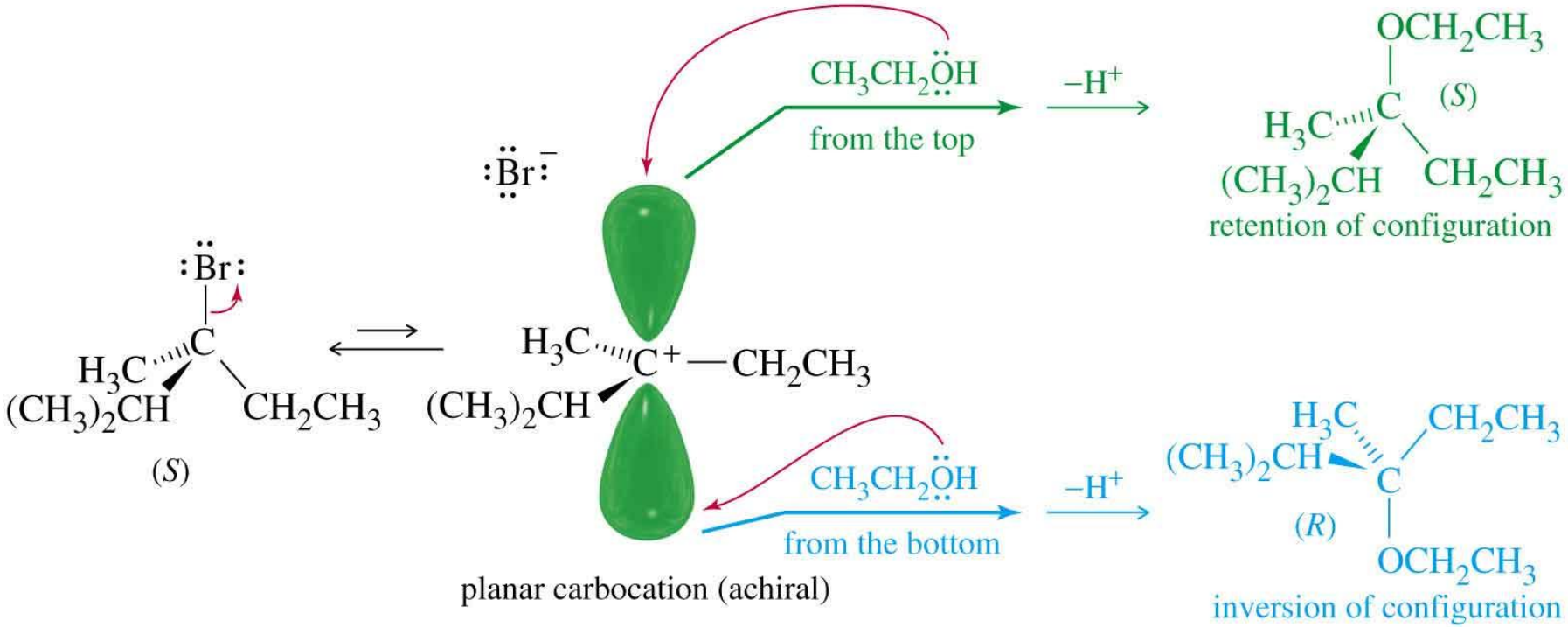
S_N2 شیمی فضایی

Walden inversion





شیمی فضایی S_N1



=>

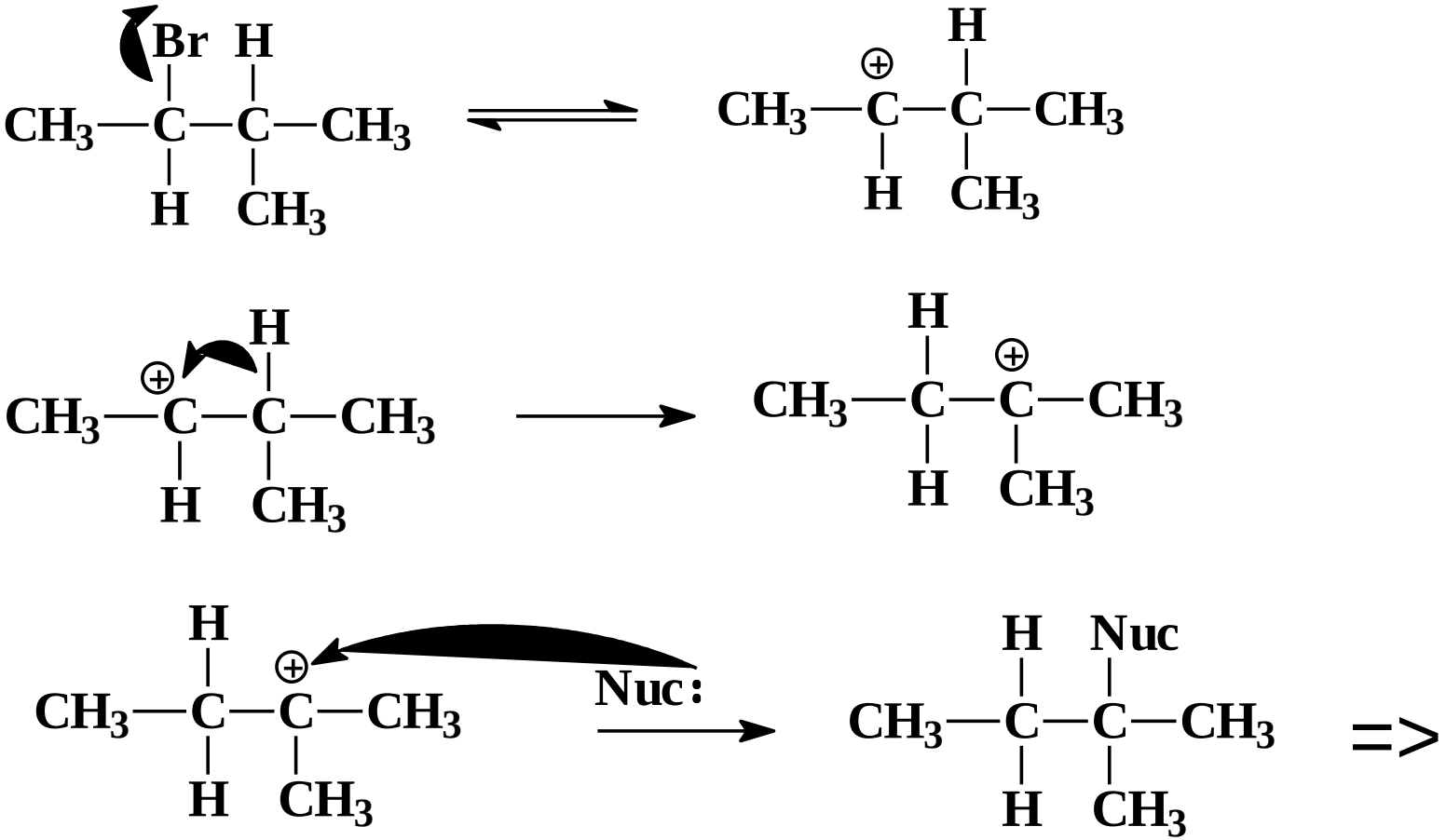
نوآرایی کربوکاتیون :

- Carbocations can rearrange to form a more stable carbocation.

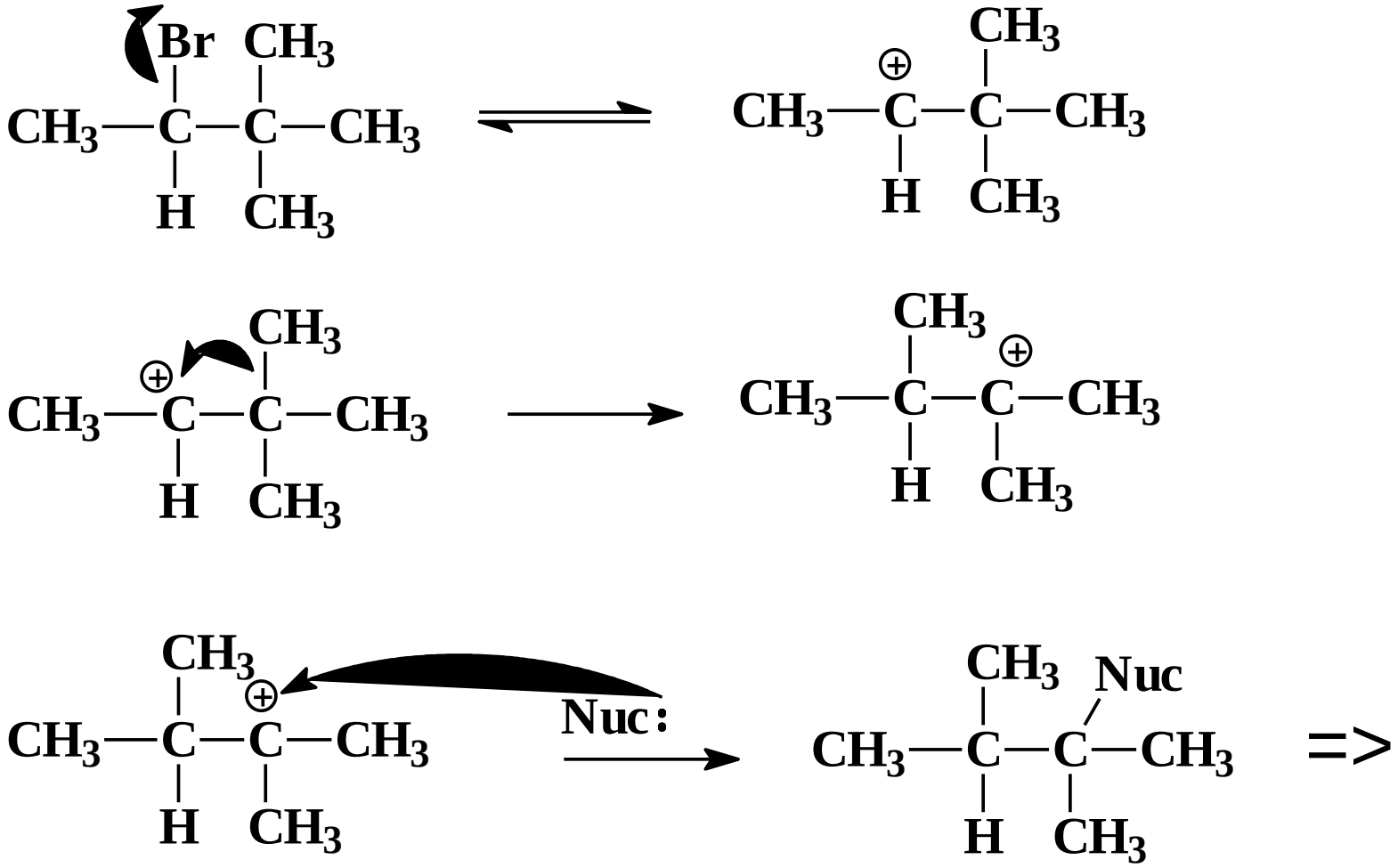
•Hydride shift: H^- on adjacent carbon bonds with C^+.

•Methyl shift: CH_3^- moves from adjacent carbon
if no H's are available.

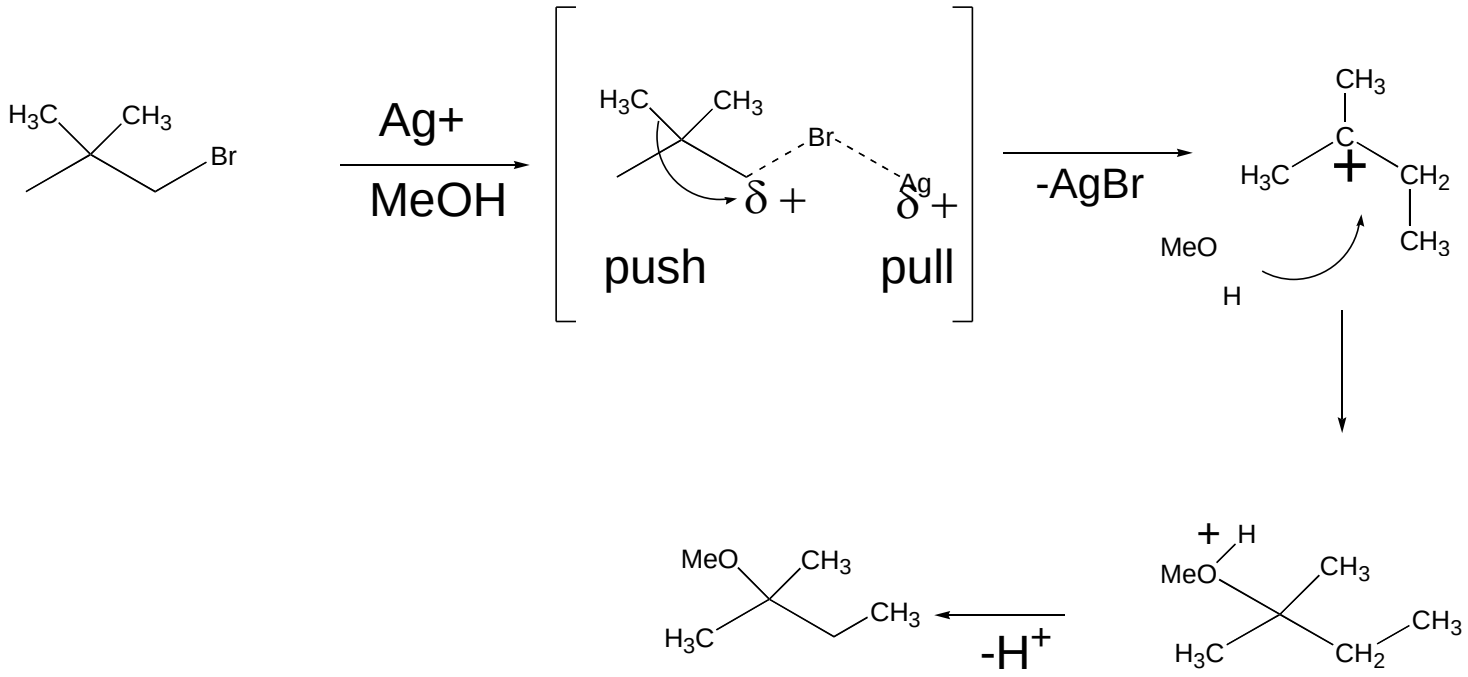
هیدروژن شیفت :



متيل شيفت :


Br
CH3
CH3—C—C—CH3
H
CH3
CH3
CH3—C—C—CH3
H
CH3
CH3
CH3—C—C—CH3
H
CH3
CH3
CH3—C—C—CH3
H
CH3
Nuc:
CH3
CH3—C—C—CH3
H
CH3
Nuc
CH3—C—C—CH3
H
CH3
=>

مثال :


H3C
CH3
Br
Ag+
MeOH
H3C
CH3
Br
Ag
δ +
δ+
push
pull
-AgBr
CH3
C
H3C
+
CH2
CH3
MeO
H
+ H
MeO
CH3
CH3
H3C
CH2
MeO
CH3
CH3
H3C
-H+

S_N2 or S_N1?

- Primary or methyl

•Strong nucleophile

•Polar aprotic solvent

•Rate = *k*[halide][Nuc]

•Inversion at chiral carbon

•No rearrangements

- Tertiary

•Weak nucleophile (may also be solvent)

•Polar protic solvent, Ag+

•Rate = *k*[halide]

•Racemization of optically active compound

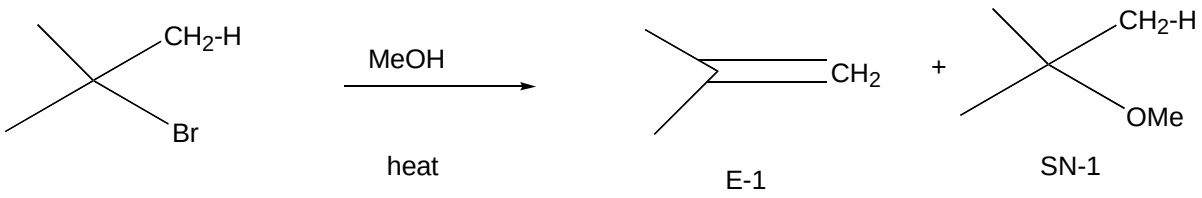
➢Rearranged products

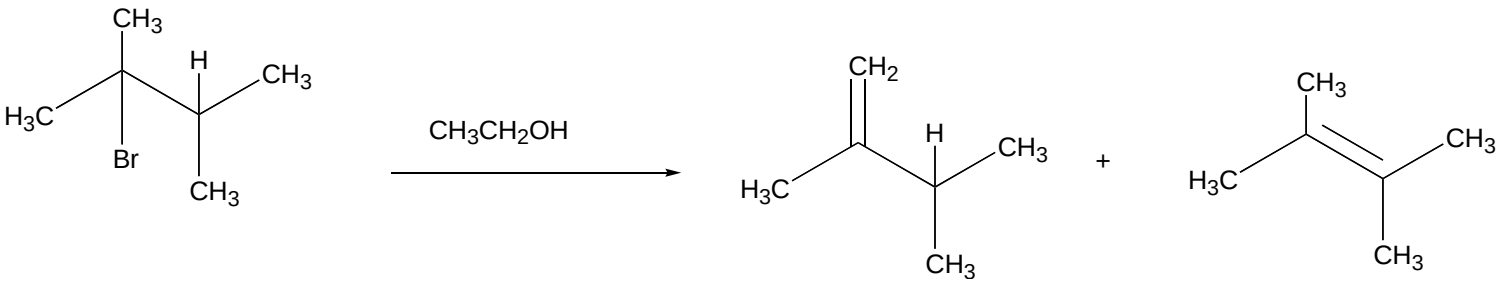
واکنشE1

- حذف یک مولکولی
  - دو گروه از دست می دهد
  - نوکلئوفیل مانند باز عمل میکند

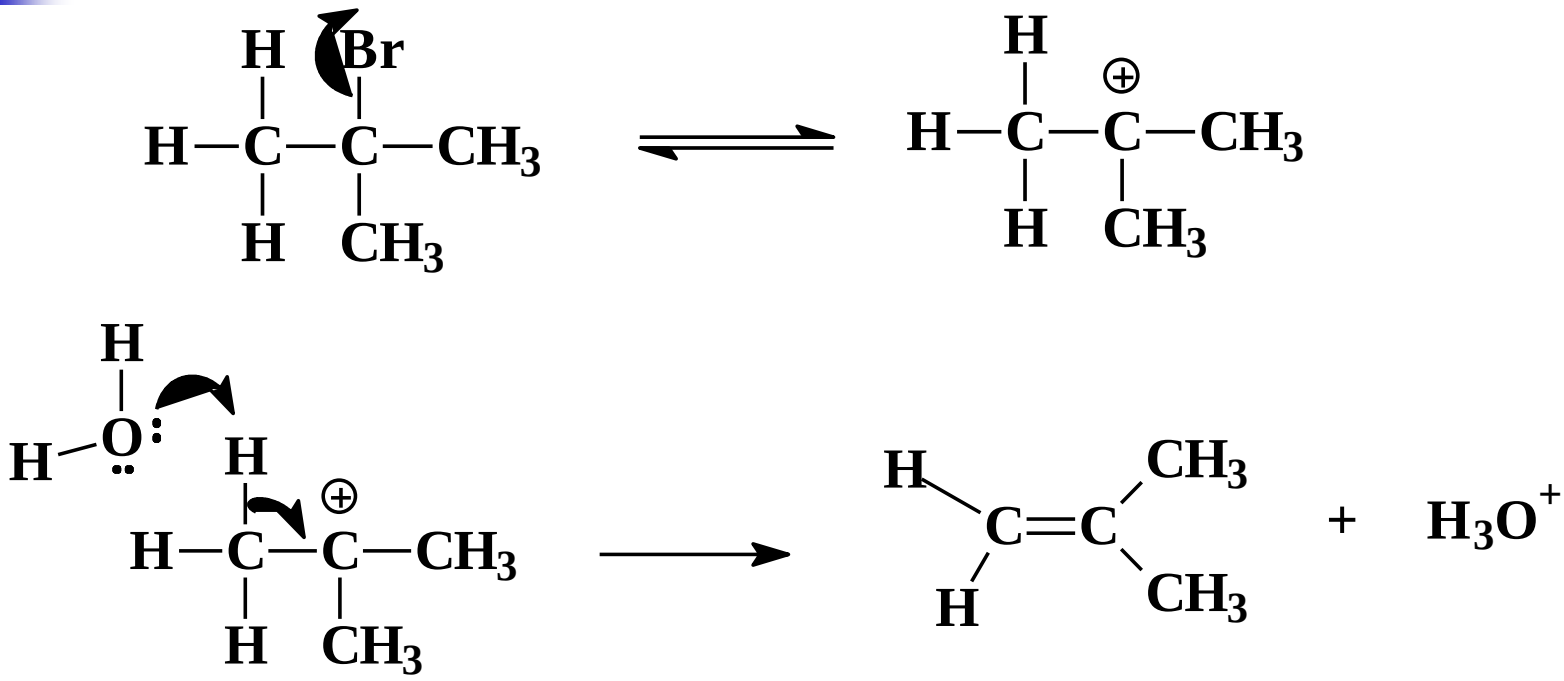
❖مانند SN1 محصول مخلوط میدهد .

مثال :


CH2-H
Br
MeOH
heat
CH2
E-1
+
CH2-H
OMe
SN-1


CH3
H
CH3
H3C
Br
CH3
CH3CH2OH
CH2
H
CH3
H3C
CH3
+
CH3
CH3
H3C
CH3

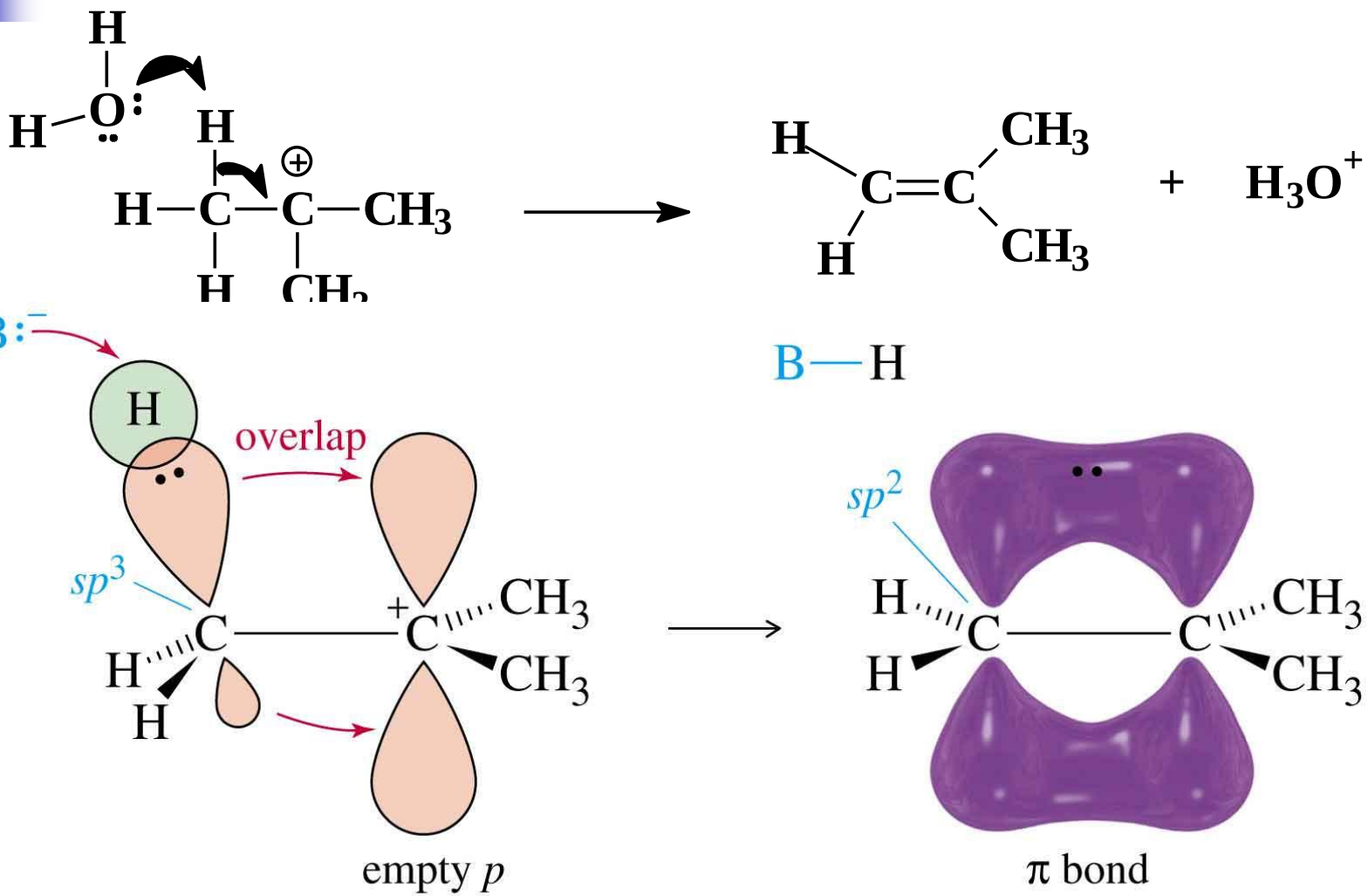
مکانیسم E1



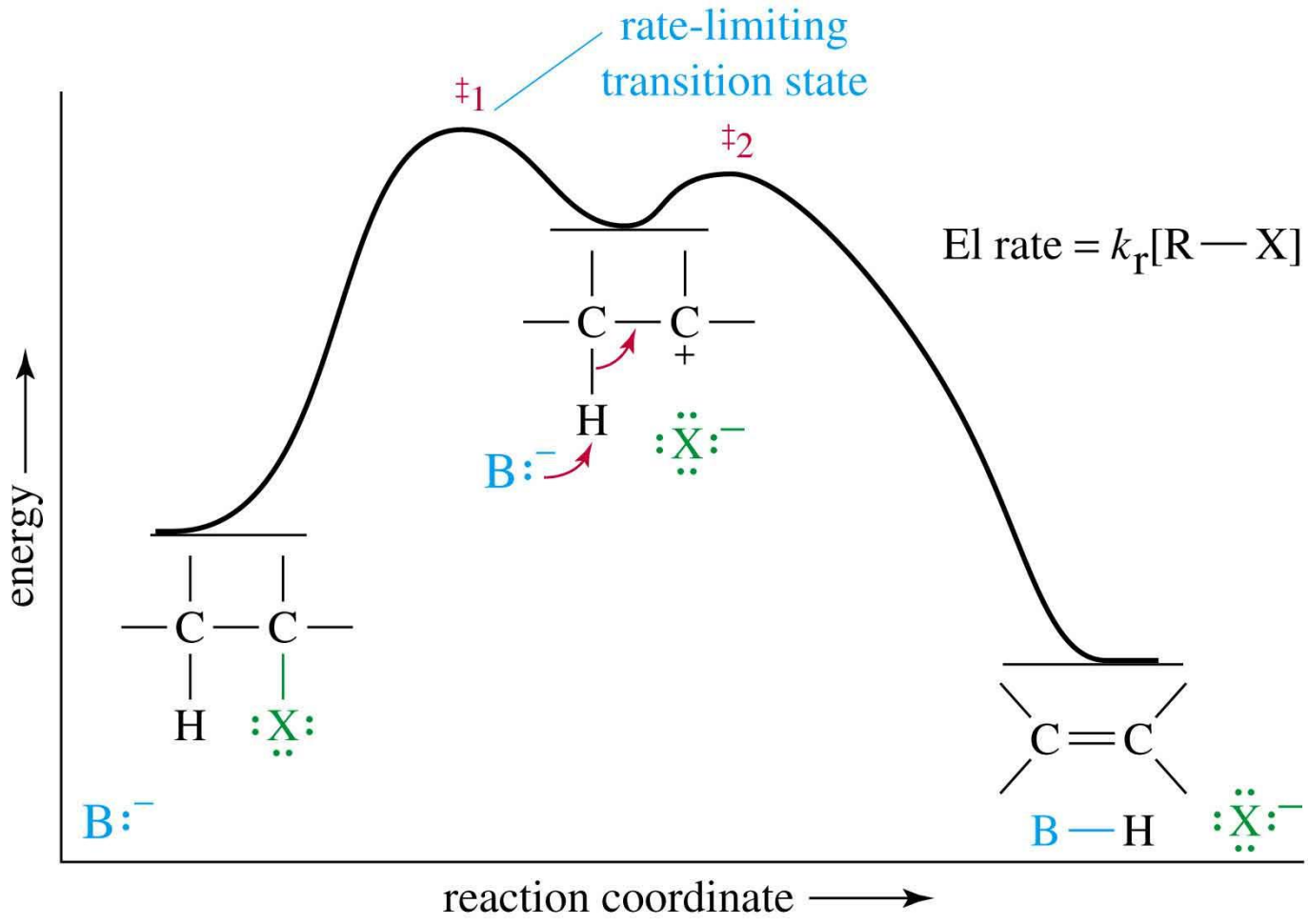
- Halide ion leaves, forming carbocation.

•Base removes H^+ from adjacent carbon.

✓Pi bond forms.


B:⁻
H
overlap
sp³
H
H
C
+
C
CH₃
CH₃
empty p
B—H
sp²
H
H
C
C
CH₃
CH₃
π bond

=>

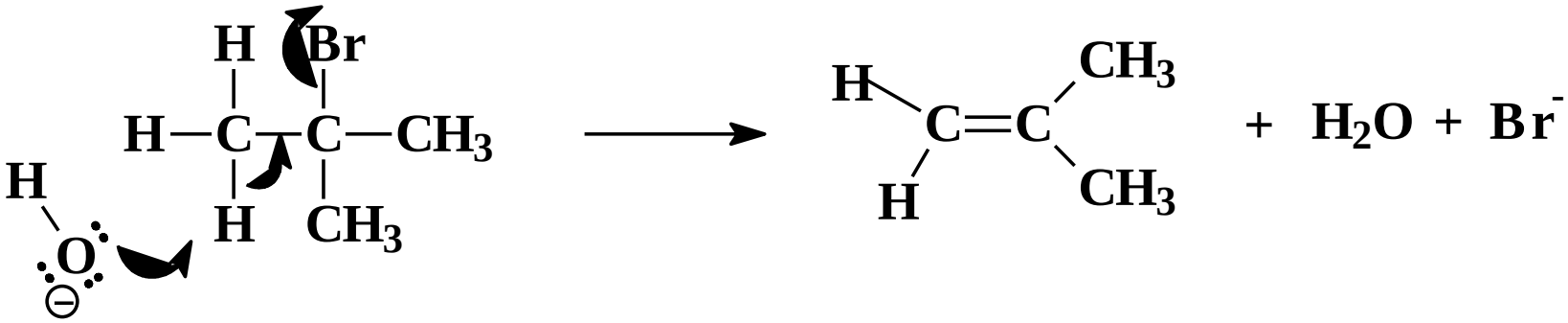


- Note: first step is same as S_N1

واکنش E2

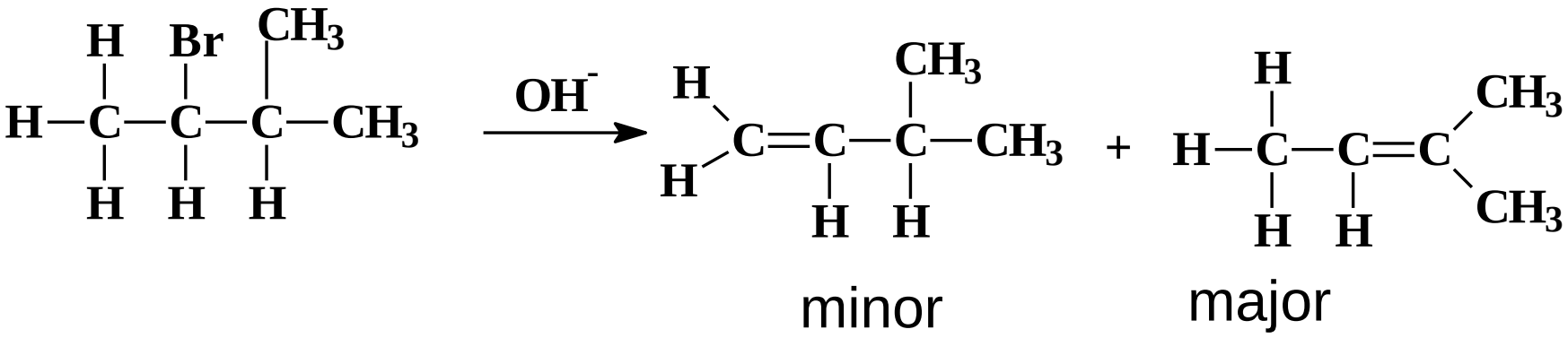
- حذف دو مولکولی
- نیازمند به یک باز قوی
- حذف گروه هالید وجذب پروتون همزمان صورت میگیرد

مکانیسم E2



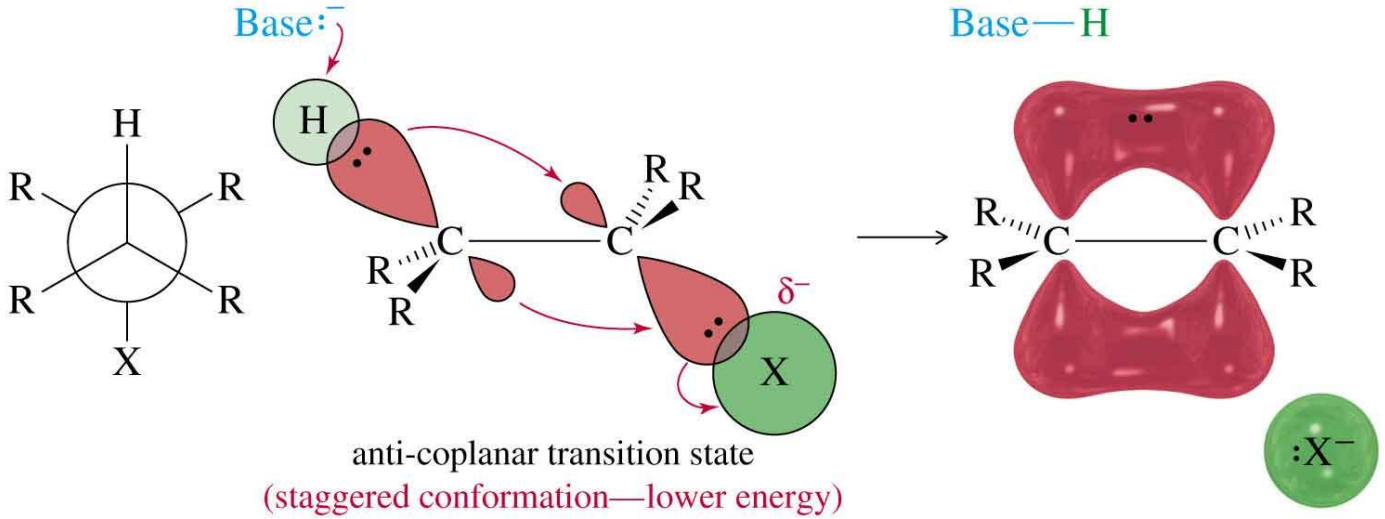
قاعده زایتسف :

- If more than one elimination product is possible, the most-substituted alkene is the major product (most stable).
- $R_2C=CR_2 > R_2C=CHR > RHC=CHR > H_2C=CHR$
  tetra > tri > di > mono

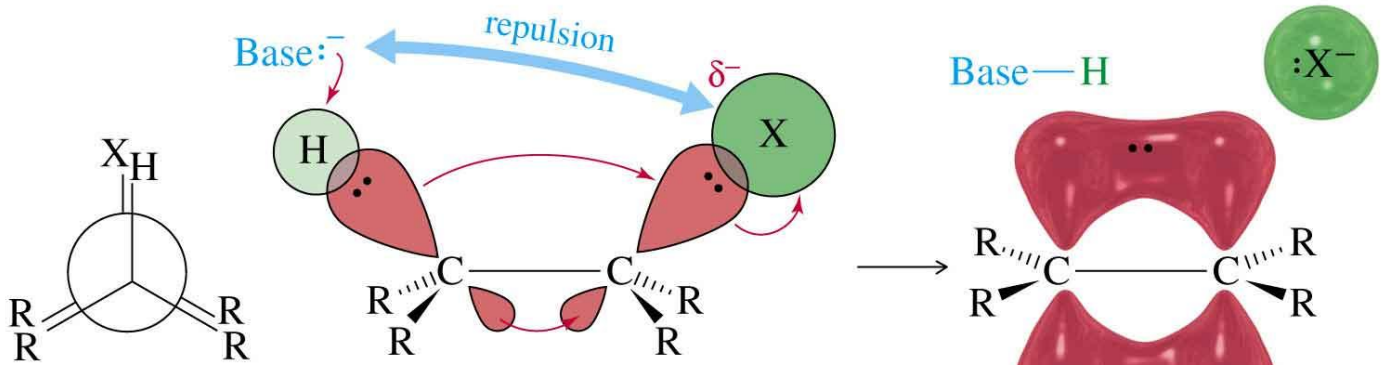


minor major

شیمی فضایی E2



anti-coplanar transition state
(staggered conformation—lower energy)



syn-coplanar transition state
(eclipsed conformation—higher energy)

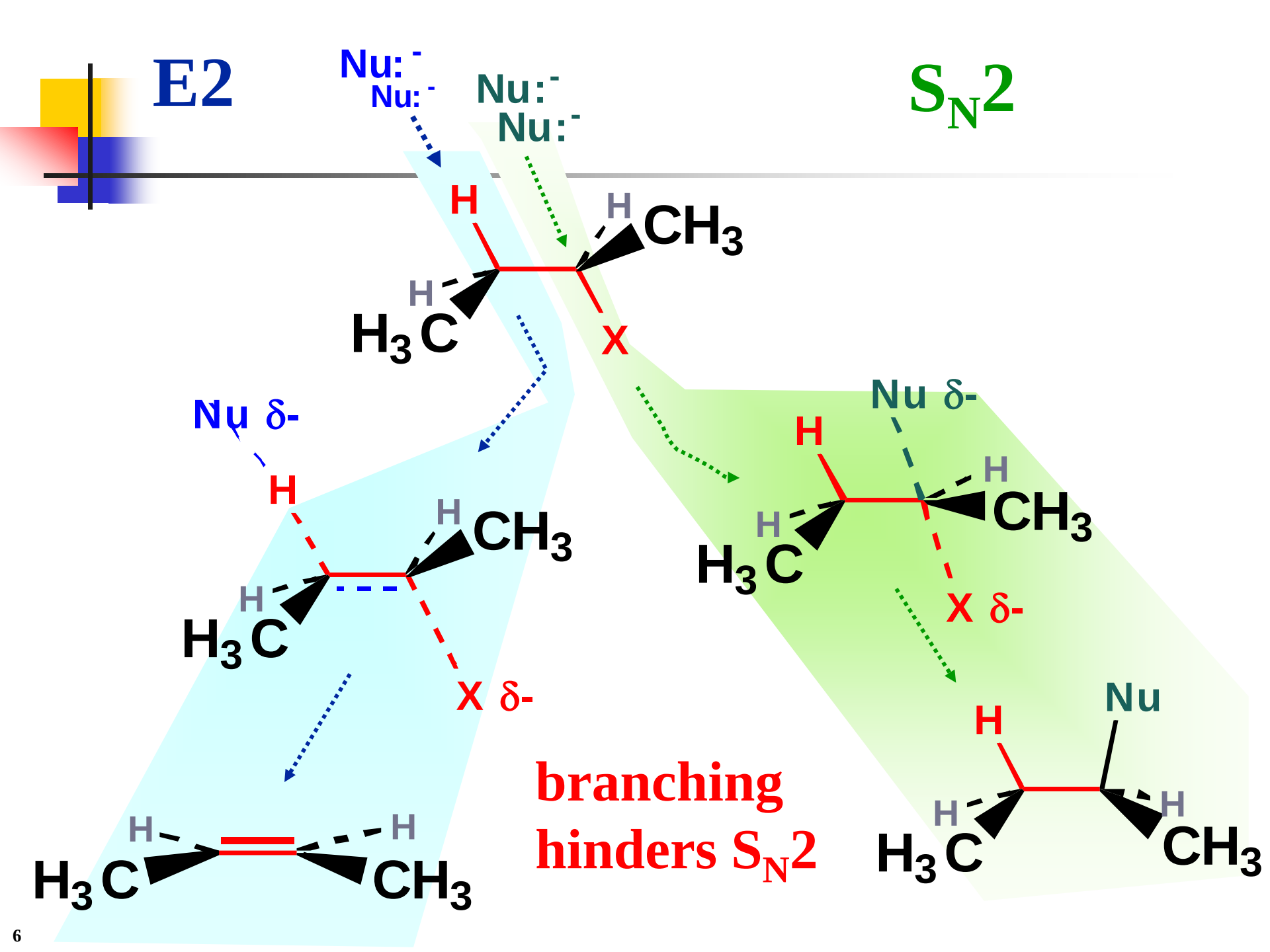
E1 or E2?

- Tertiary > Secondary
- Weak base
- Good ionizing solvent

- Rate = *k*[halide]
- Saytzeff product
- No required geometry

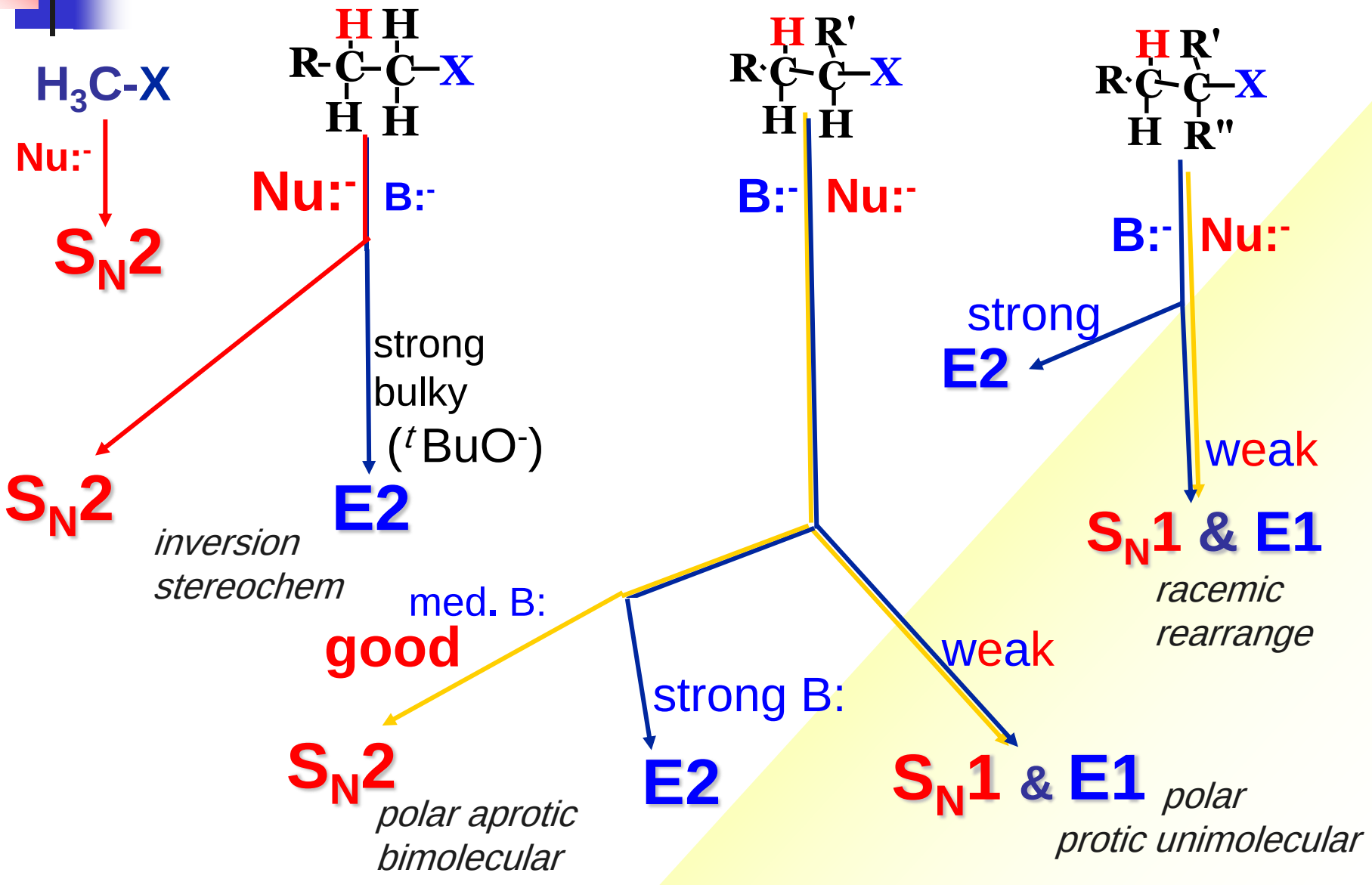
- Rearranged products

- Tertiary > Secondary
- Strong base required
- Solvent polarity not important
- Rate = *k*[halide][base]
- Saytzeff product
- Coplanar leaving groups (usually anti)
- No rearrangements

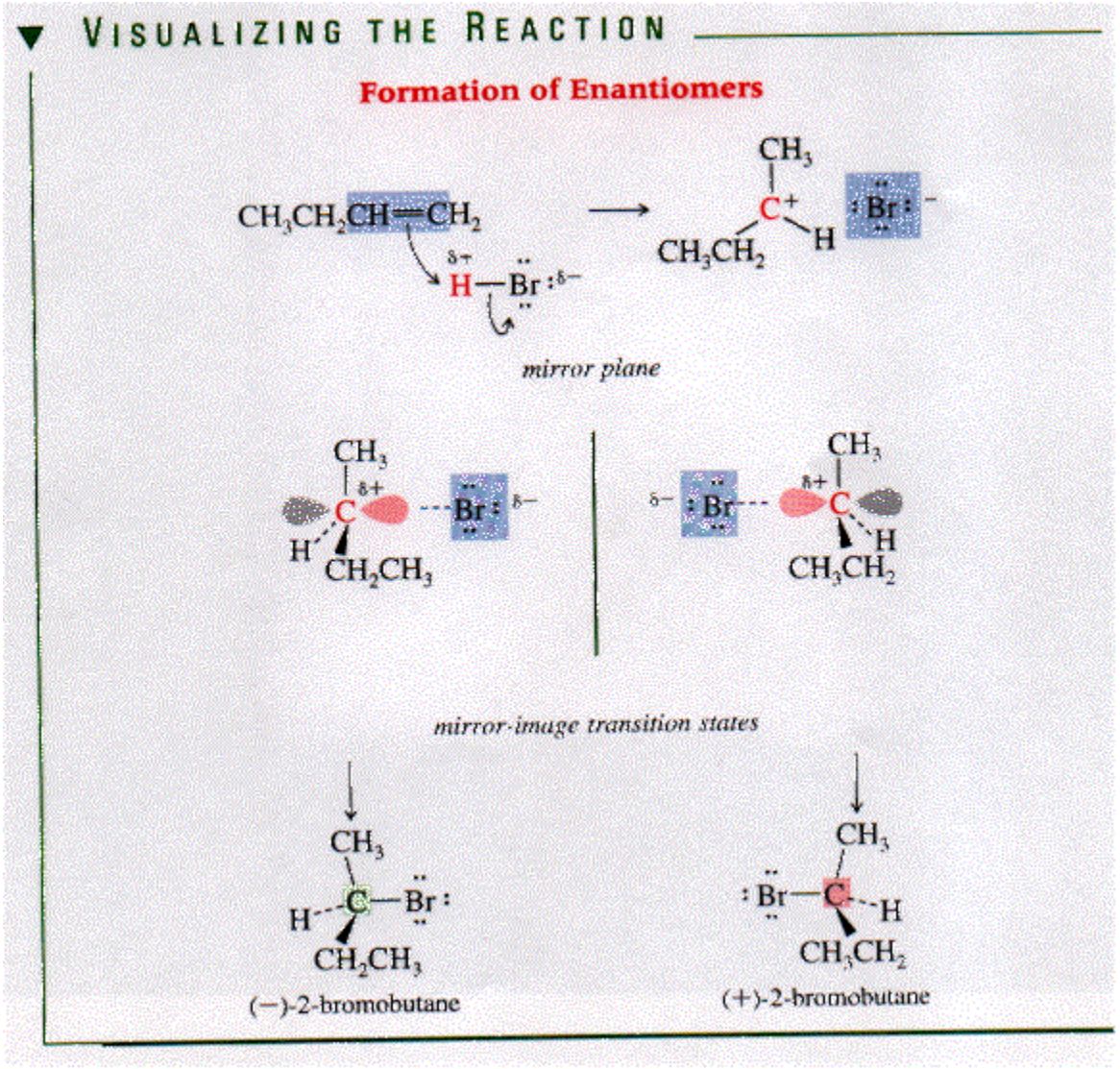

E2
Nu:-
Nu:-
Nu:-
Nu:-
SN2
H
H
CH3
H
H3C
X
Nu δ-
H
H
CH3
H
H3C
X δ-
Nu δ-
H
H
CH3
H
H3C
X δ-
Nu
H
H
CH3
H
H3C
H
H
CH3
H3C
branching
hinders SN2

Substitution & Elimination

جایگزینی در مقابل حذف :

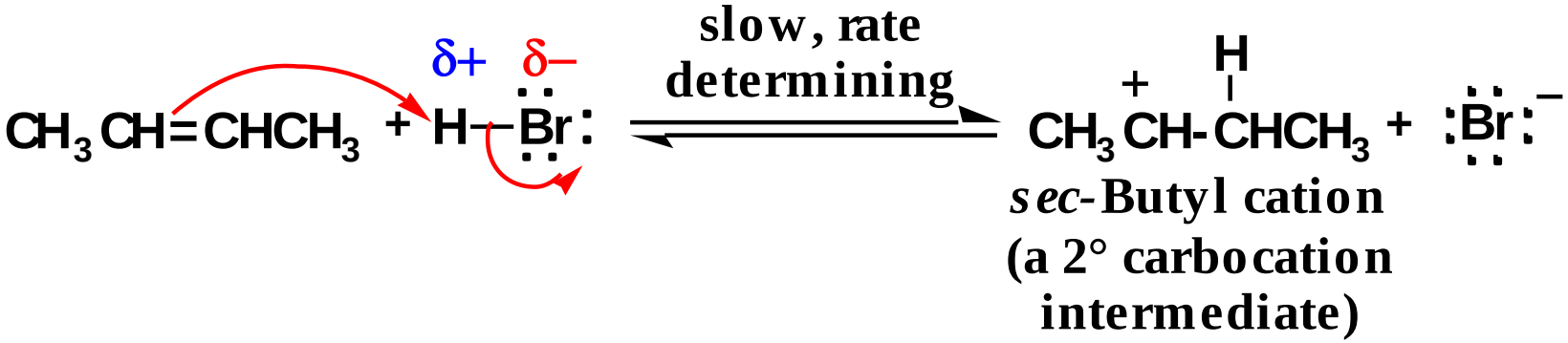


افزایش الکتروفیلی به آلکنها :

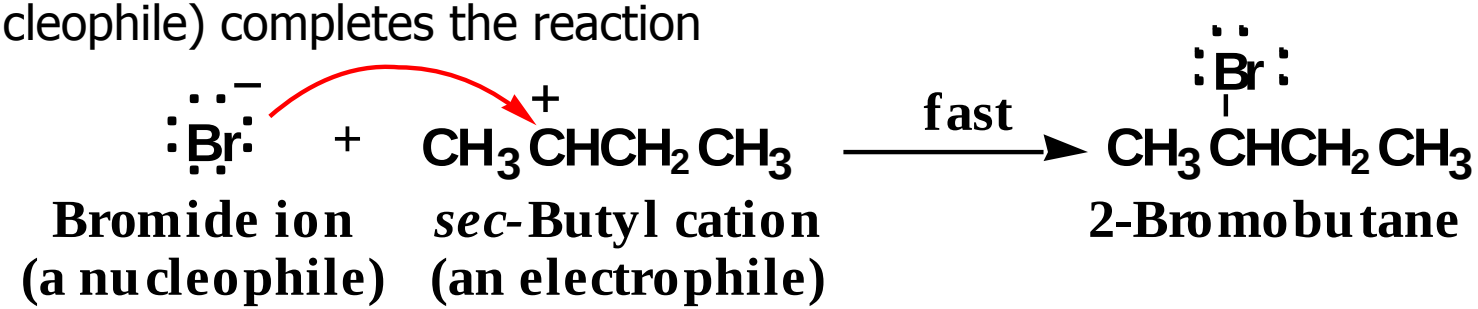


HBr + 2-Butene

- ***A two-step mechanism***
  - Step 1: proton transfer from HBr to the alkene gives a carbocation intermediate

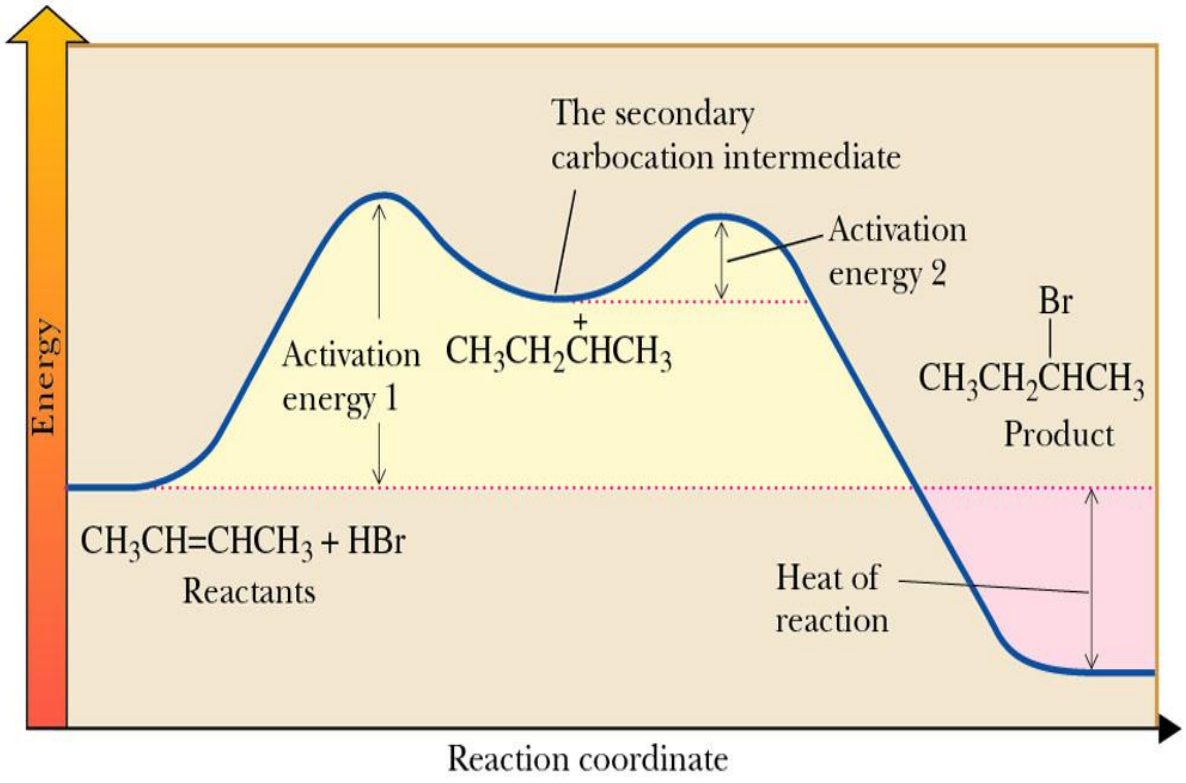


  - Step 2: reaction of the *sec*-butyl cation (an electrophile) with bromide ion (a nucleophile) completes the reaction



HBr + 2-Butene

- *An energy diagram for the two-step addition of HBr to 2-butene the reaction is exergonic*



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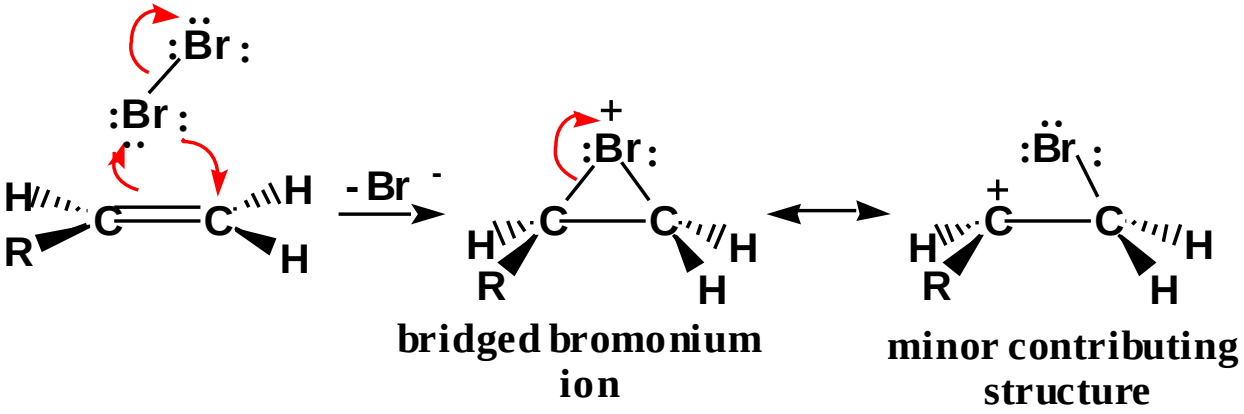
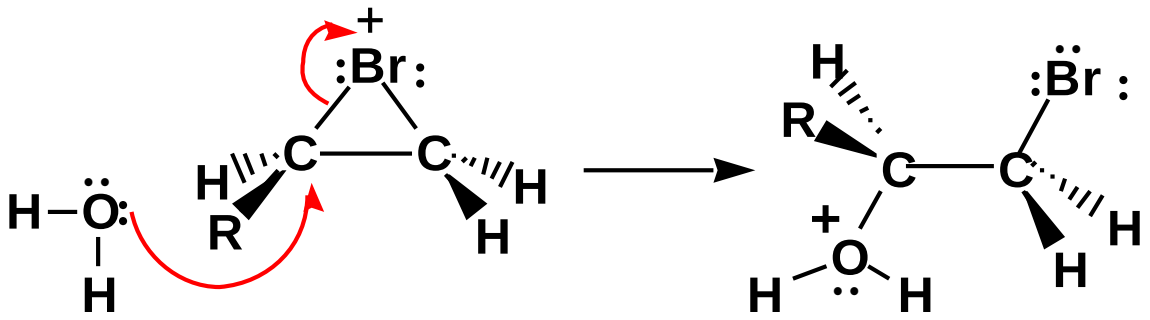
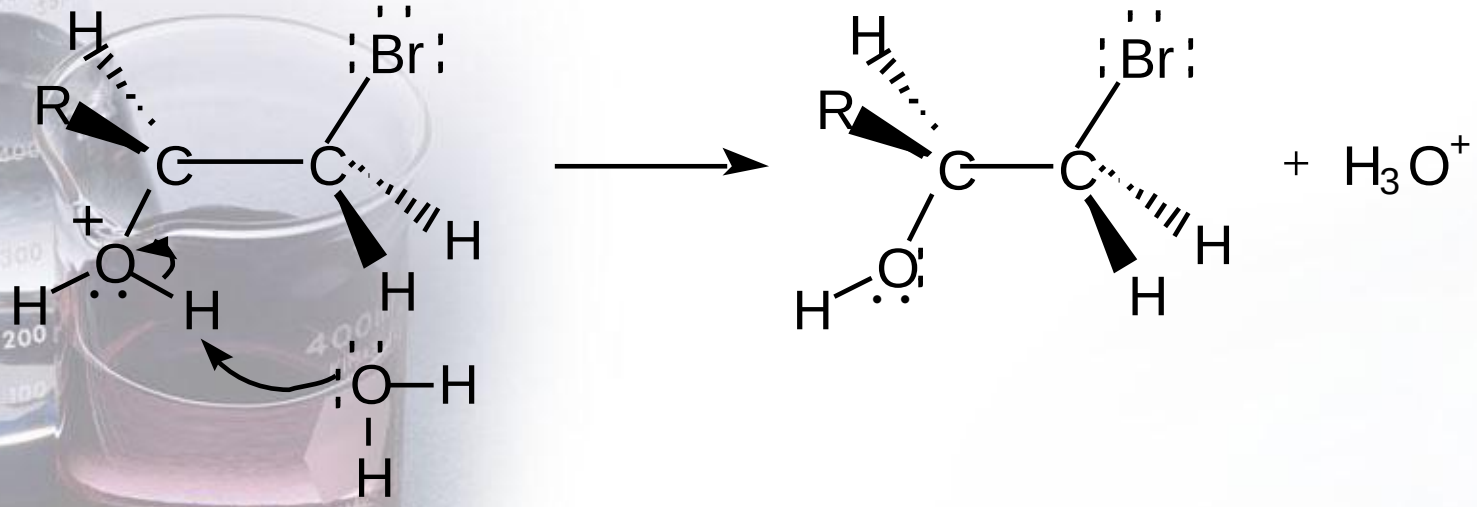
- Step 1: formation of a bridged halonium ion intermediate

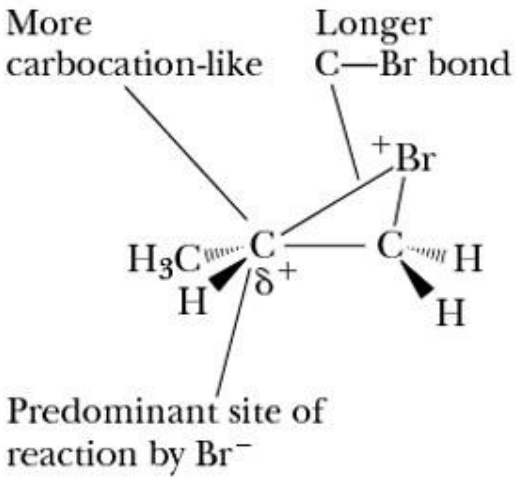


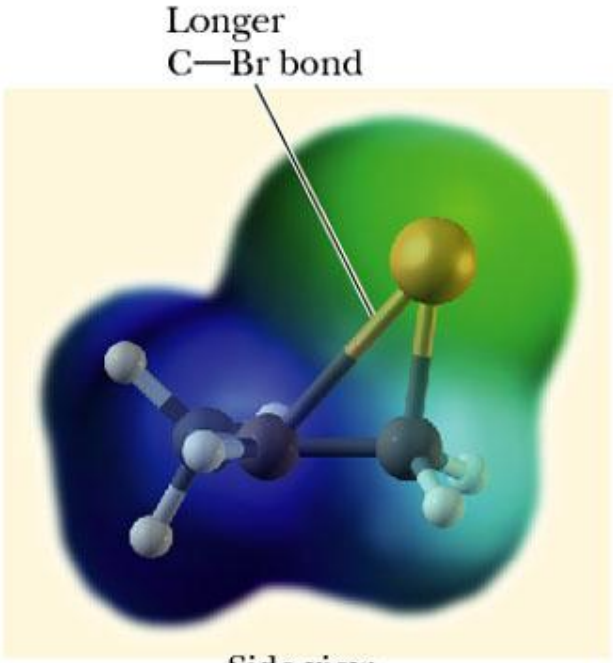
- Step 2: attack of H_2O on the more substituted carbon opens the three-membered ring



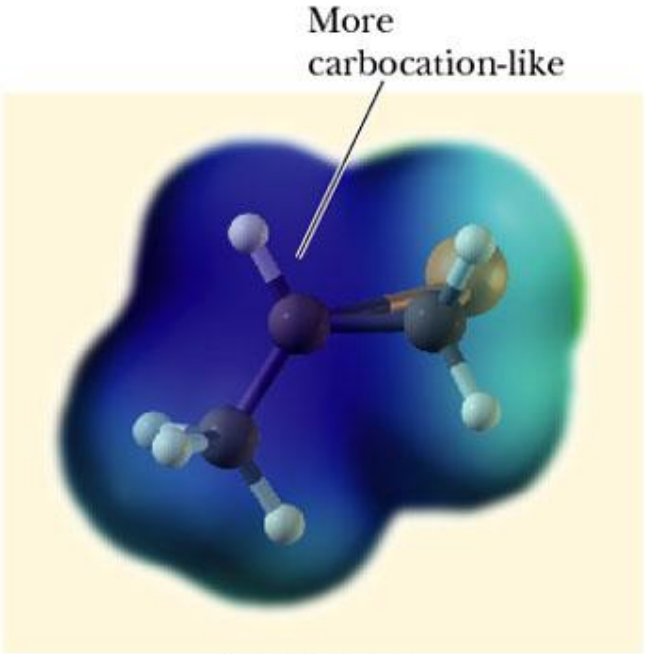
- ***Step 3: proton transfer to H_2O completes the reaction***







Side view



Bottom view

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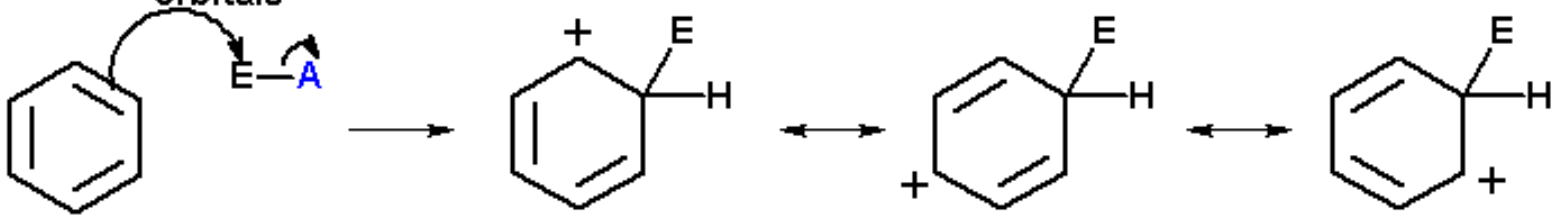
جایگزینی الکتروفیلی آروماتیک :

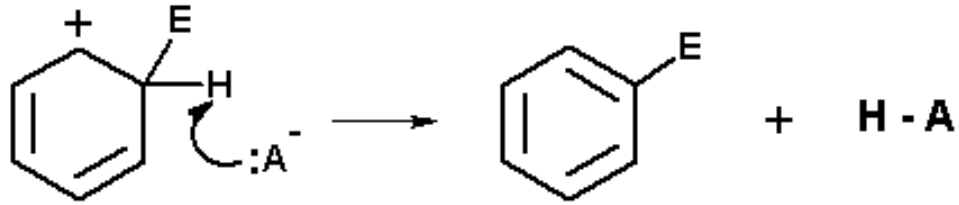
Step 1 - Electrophile (E-A) takes two Pi electrons from the ring to form a sigma bond to one carbon atom of the ring - sp^3 hybridized.

The remaing 4 Pi electrons are now delocalized through the remaining five sp^2 orbitals

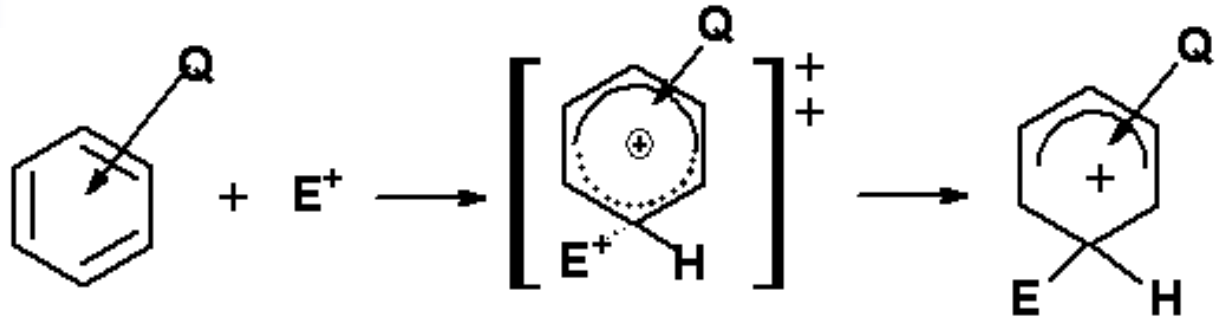


Arrhenium Ion (Sigma Complex)
(Delocalized Nonaromatic Cyclohexadienyl Carbocation)

Step 2 - The proton is removed by the Base - $:A^-$ (Anion derived from the electrophile)



کمپلکس Π



Transition State

Arrhenium Ion
(Sigma Complex)

Arrhenium Ion - A delocalized Carbocation with several resonance structures

Q - Initial group substituted on Aromatic ring

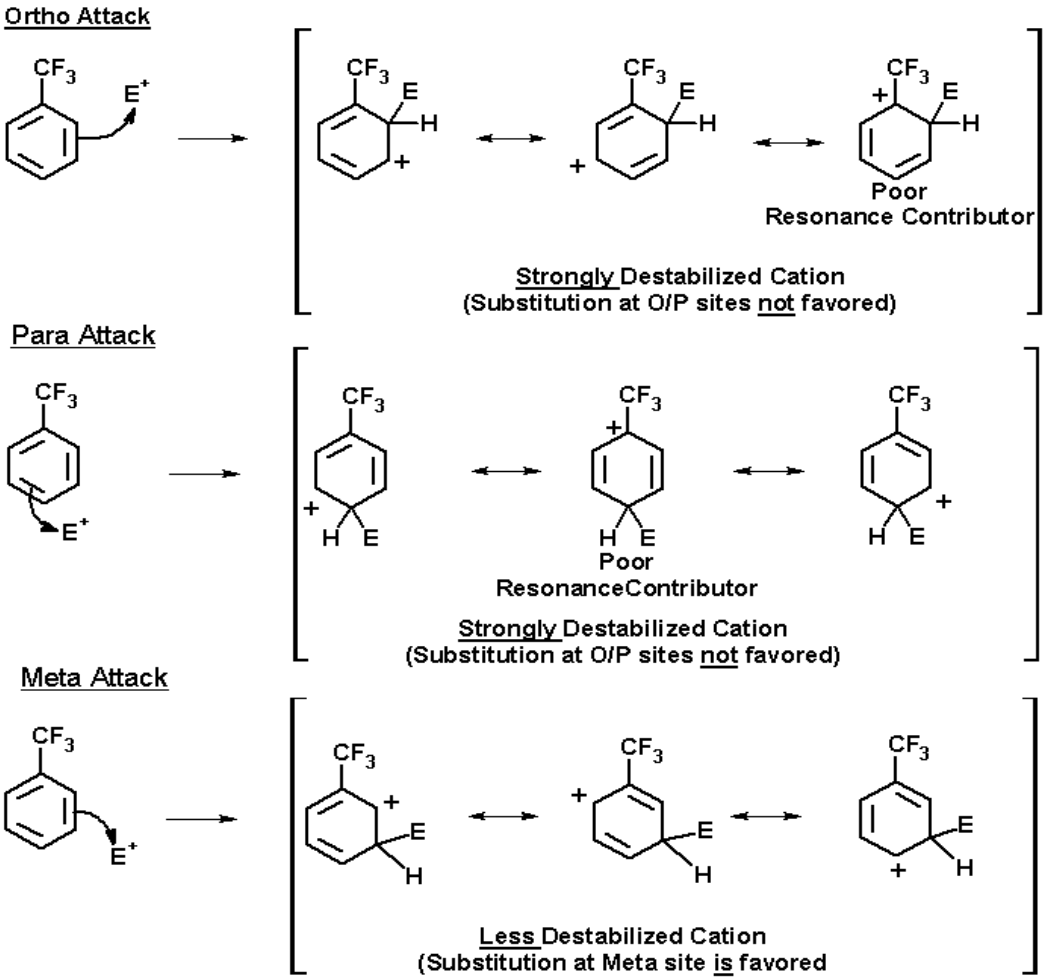
a. Q as Activator - Donates electrons to ring
b. Q as Deactivator - Withdraws electrons from ring

E - Electrophile as second group added to ring

a. If Q is Activator, E substitution is Ortho/Para favored.

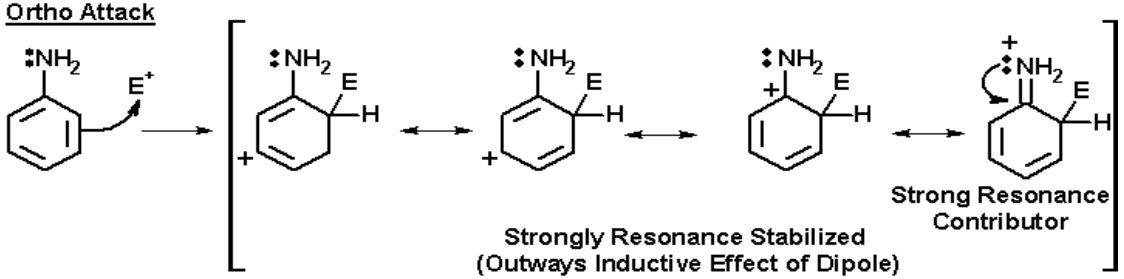
Groups that Withdraw Electrons by Induction

(CF_3, $-NR_2$, OR, X (F, Cl, Br, I), COR, CN, NO2, HSO_3^-) are Deactivating and are Meta Directing



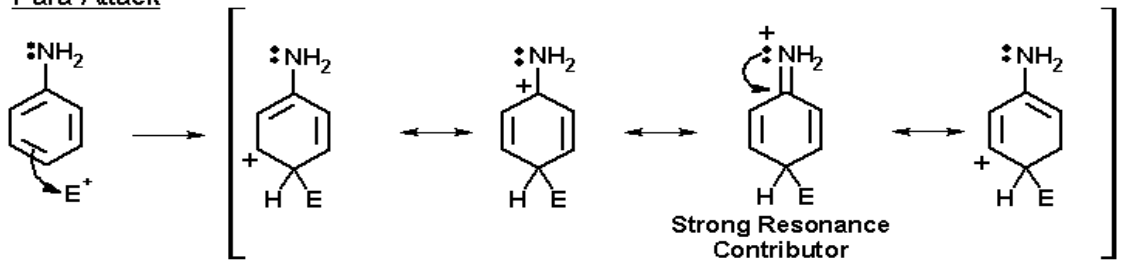
Groups that Donate Electrons by Resonance are Activating and are Ortho/Para Directing

Ortho Attack



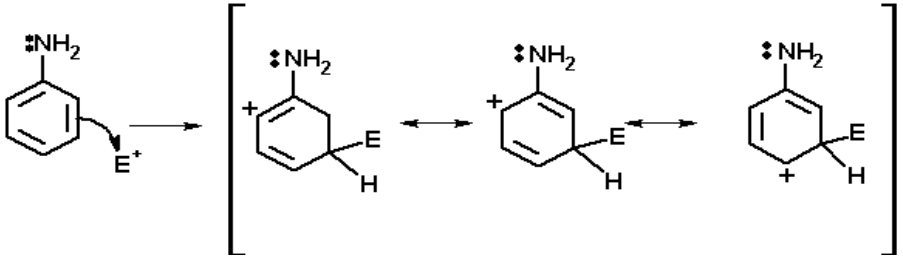
Strongly Resonance Stabilized
(Outways Inductive Effect of Dipole)
Ortho / Para Substitution Favored

Para Attack

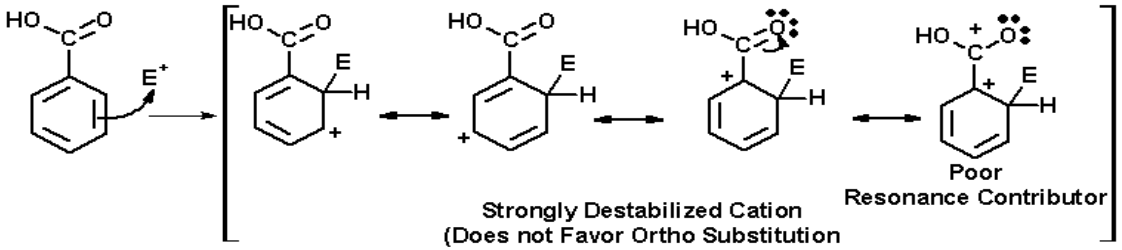


Strongly Resonance Stabilized
(Outways Inductive Effect of Dipole)
Ortho / Para Substitution Favored

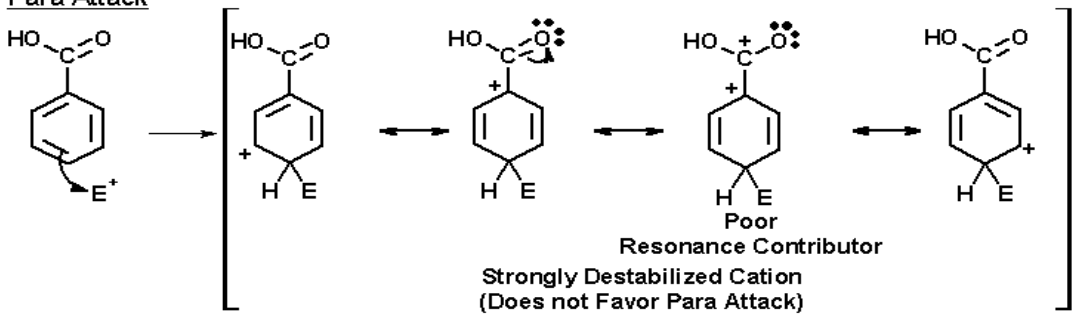
Meta Attack



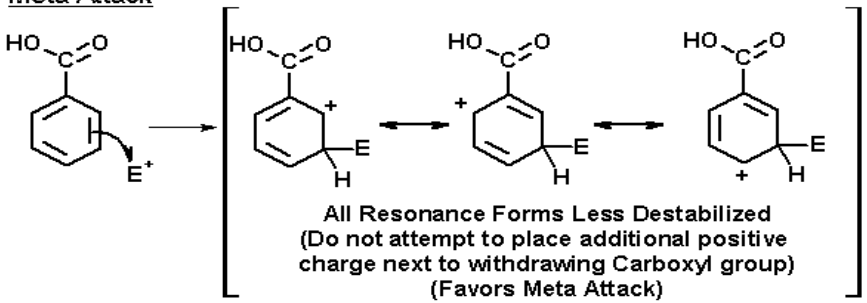
Groups that Withdraw Electrons by Resonance are Deactivating and are Meta Directing



Para Attack



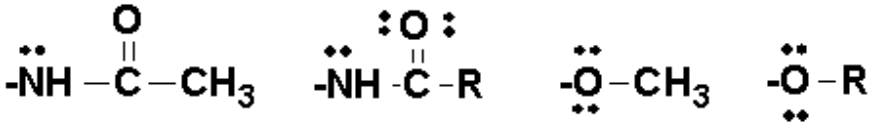
Meta Attack



Ortho & Para Directors

Strongly Activating

Moderately Activating

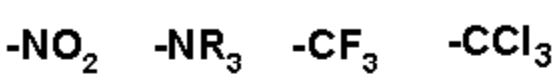


Weakly Activating

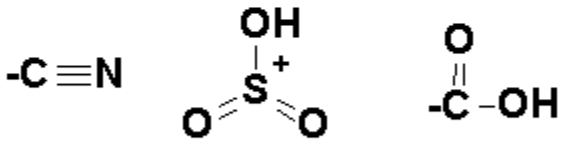
Weakly Deactivating

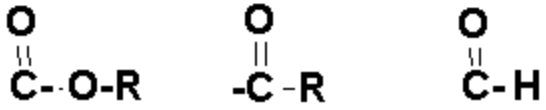
Meta Directors

Strongly Deactivating

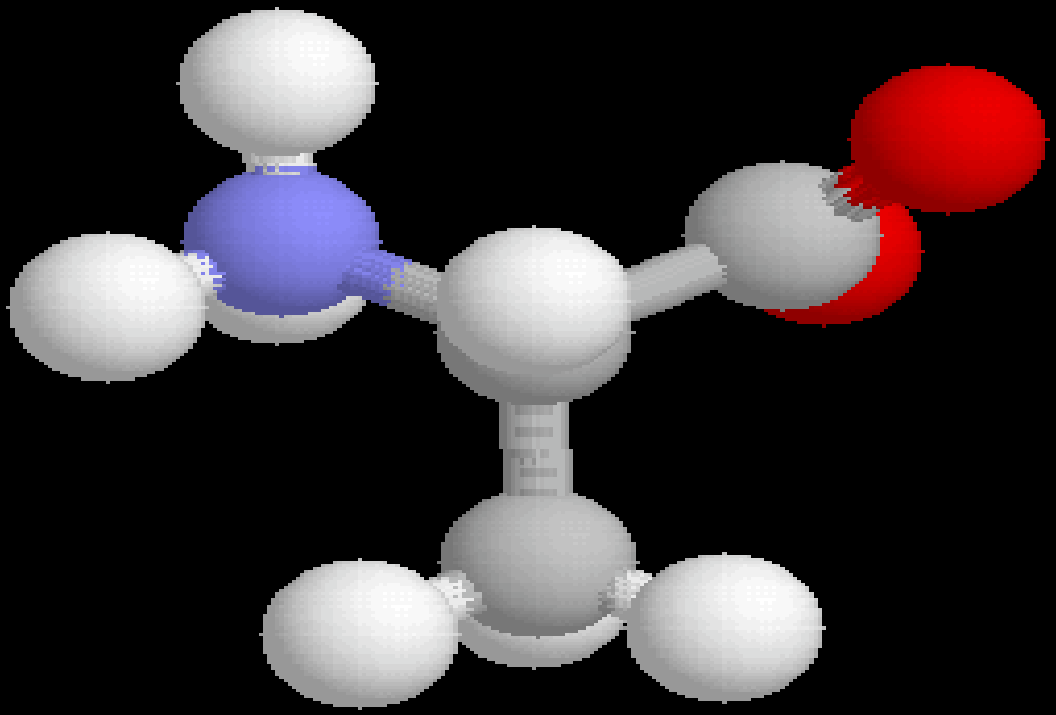


Moderately Deactivating





فصل ۵:کربانیونها

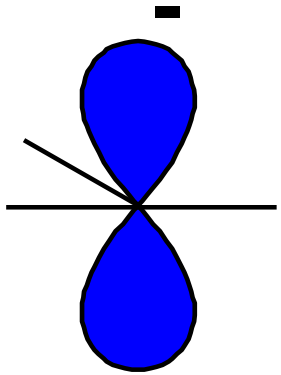


هدفهای کلی :

کربانیون ها از واسطه های مهم در شیمی آلی هستند در این فصل دانشجویان شرکت احتمالی واسطه های کربانیونی را در جایگزینی نوکلئوفیلی ، جایگزینی الکتروفیلی آلیفاتیک و مکانیسم های خاص آنها فراخواهند گرفت.

کربانیونها :

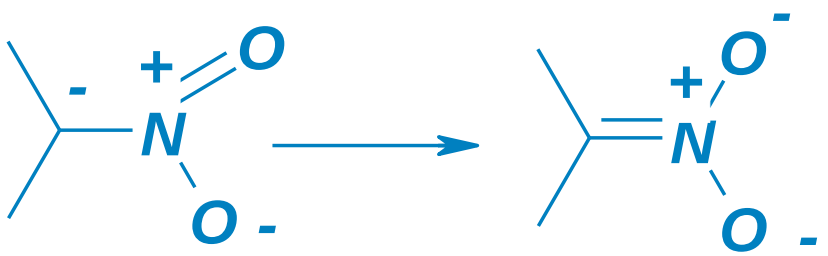
کربانیونها واسطه هایی هستند که در آنها کربن دارای بار منفی است .



عوامل موثر در پایداری :

۱- درصد خصلت s در پیوند:
هرچه درصد s افزایش یابد الکترونگاتیویته پیوند افزایش یافته وخصلت اسیدی زیاد میشود.

۲- مزدوج شدن :
بار منفی بر روی کربن یک کربانیون می تواند به نحو موثری نامستقر باشد و بوسیله مزدوج شدن پایدار گردد.



۳- اثر القایی :

واضح است که استخلافهای الکترون کشنده باعث میشود تا یک کربن با غنای الکترونی پایدار گردد.

ترکیب	سرعت نسبی
CF3H	1
CF3(CF2)5CF2H	6
(CF3)2CFH	100000
(CF3)3CH	1000000000

۴- اثر حلال :

حلال قطبی پروتوندار باعث پایداری بیشتر کربانیون میشود.

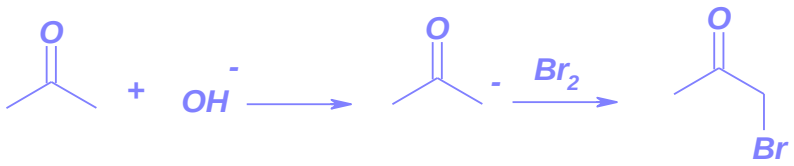
جایگزینی الکتروفیلی آلیفاتیک:

جایگزینی الکتروفیلی درجه ۱ مکانیسم: S_E1

$$R-X \xleftrightarrow{slow} R^- + X^+$$

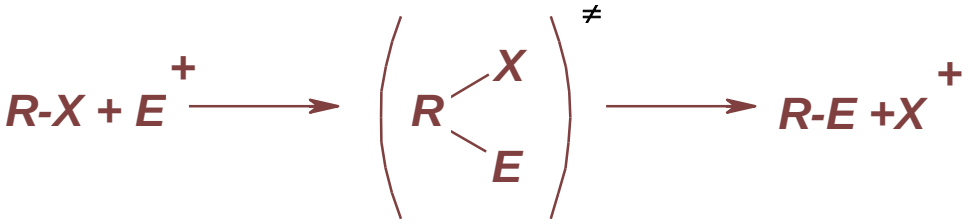
$$R^- \xrightarrow{E^+} R-E$$

مثال :

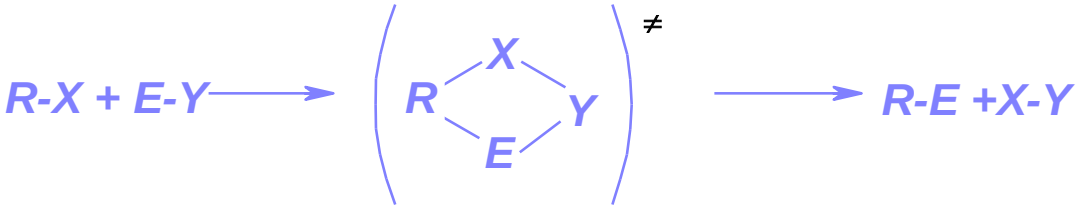


واکنش های جایگزینی الکتروفیلی از طریق مکانیسم هماهنگ دو مولکولی :

الف : مکانیسم دو مرکزی S_E2

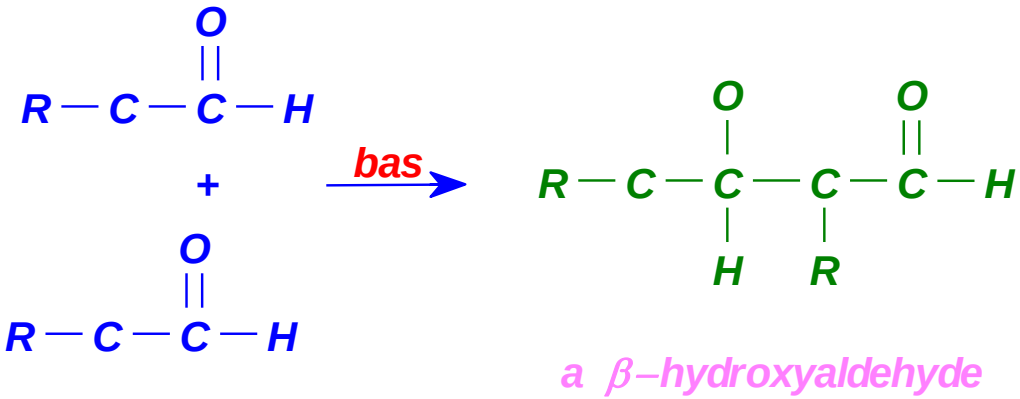


ب : مکانیسم چهر مرکزی S_Ei



Aldol condensation

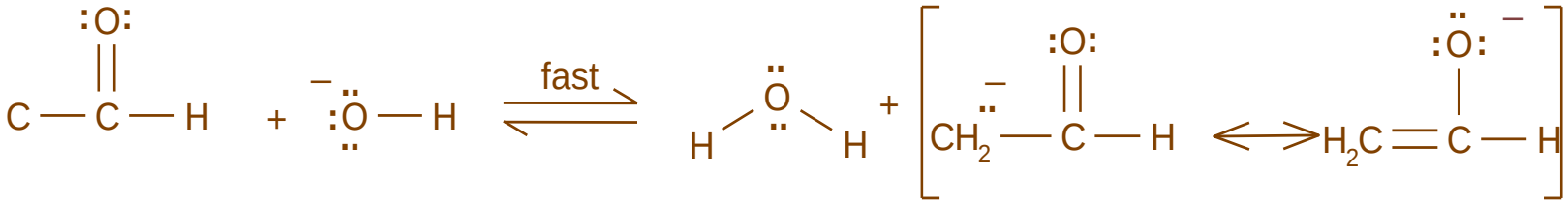
تراکم آلدولی :



a β–hydroxyaldehyde

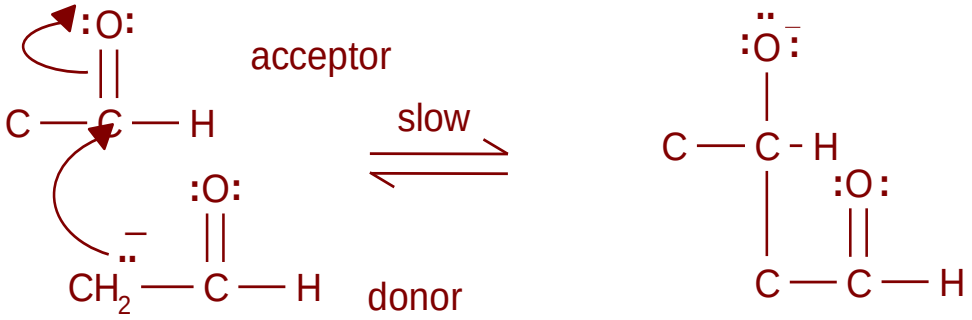
مكانيسم :

1)

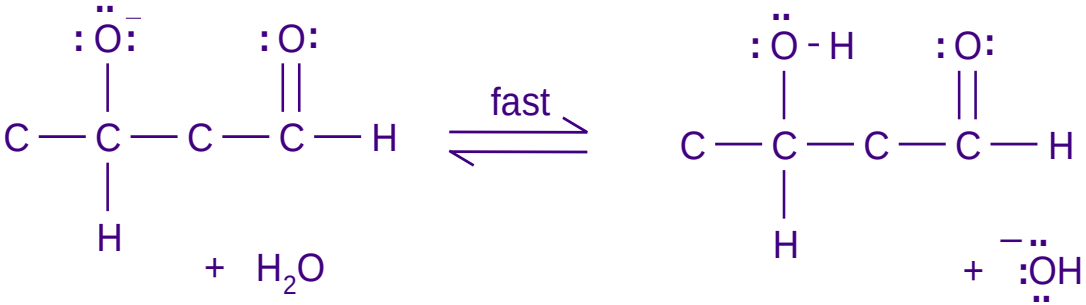


an enolate ion

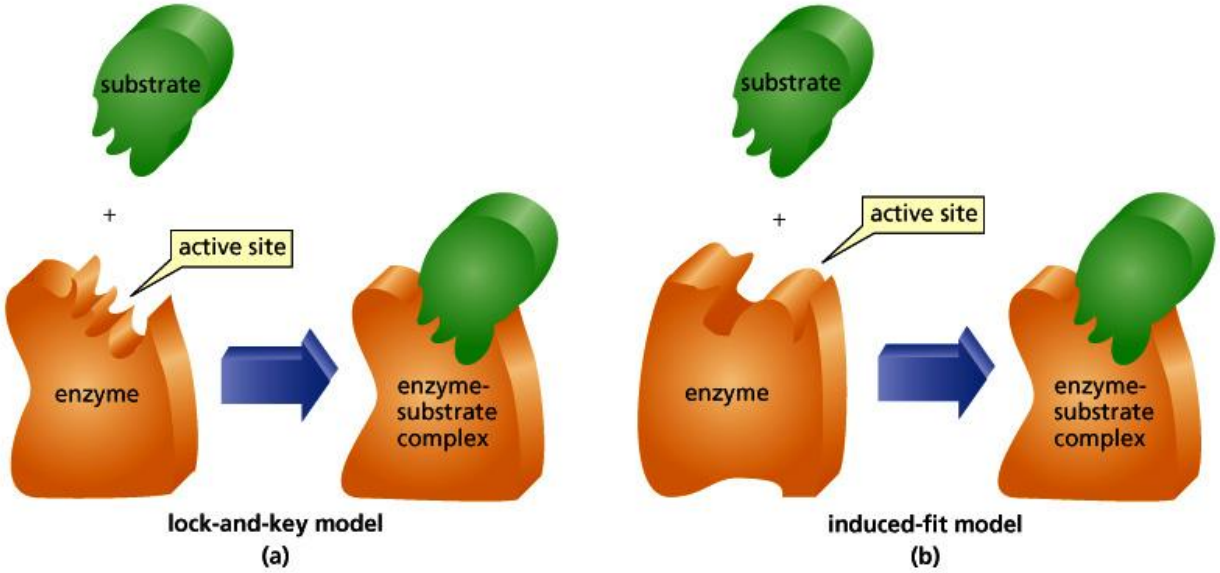
2)

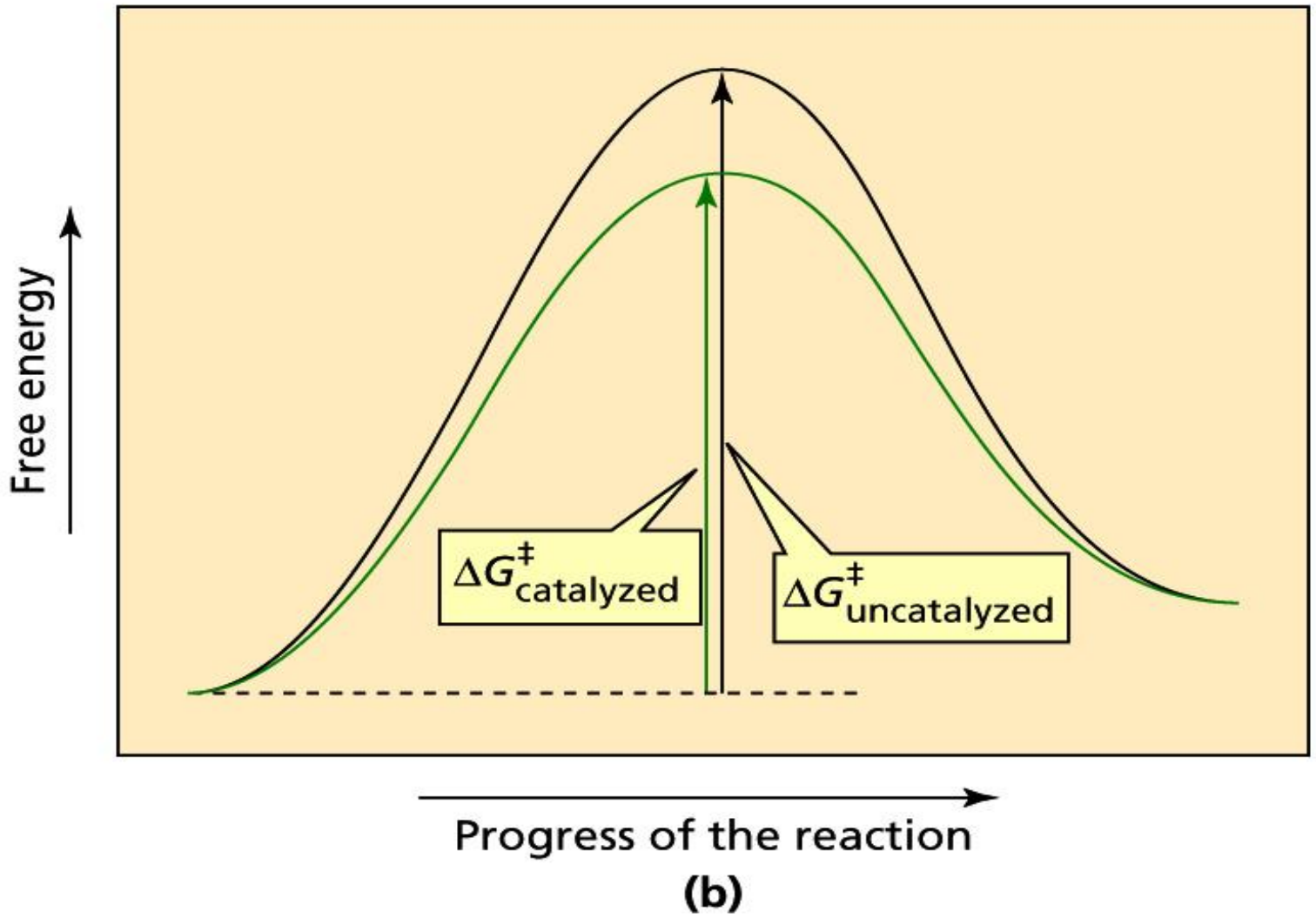


3)



نقش کاتالیزوری :



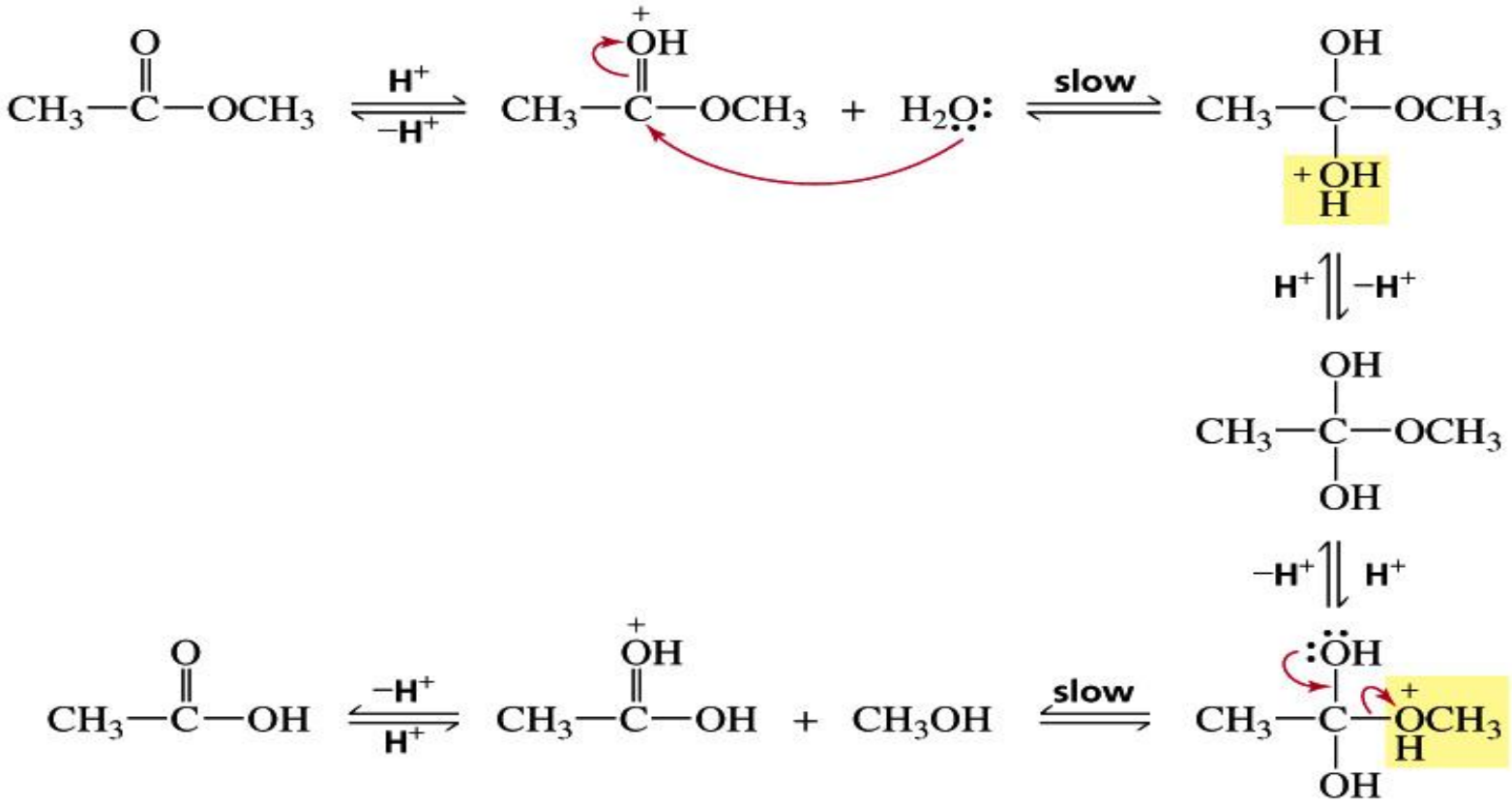

Free energy
$\Delta G^{\ddagger}_{\text{catalyzed}}$
$\Delta G^{\ddagger}_{\text{uncatalyzed}}$
Progress of the reaction

(b)

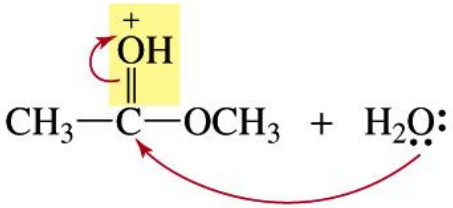
An Acid-Catalyzed Reaction

اسید کاتالیست :

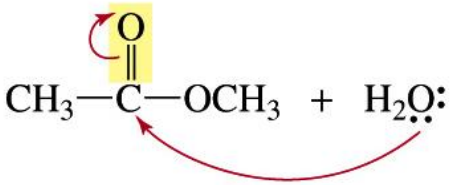
mechanism for the acid-catalyzed hydrolysis of an ester



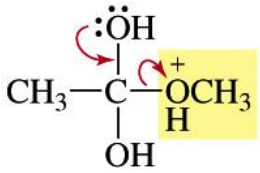
acid-catalyzed first slow step



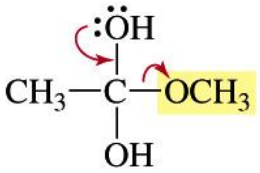
uncatalyzed first slow step



acid-catalyzed second slow step



uncatalyzed second slow step



$$HX + S \underset{k\text{-}1}{\overset{k_1}{\longleftrightarrow}} S - H^+ + X^-$$

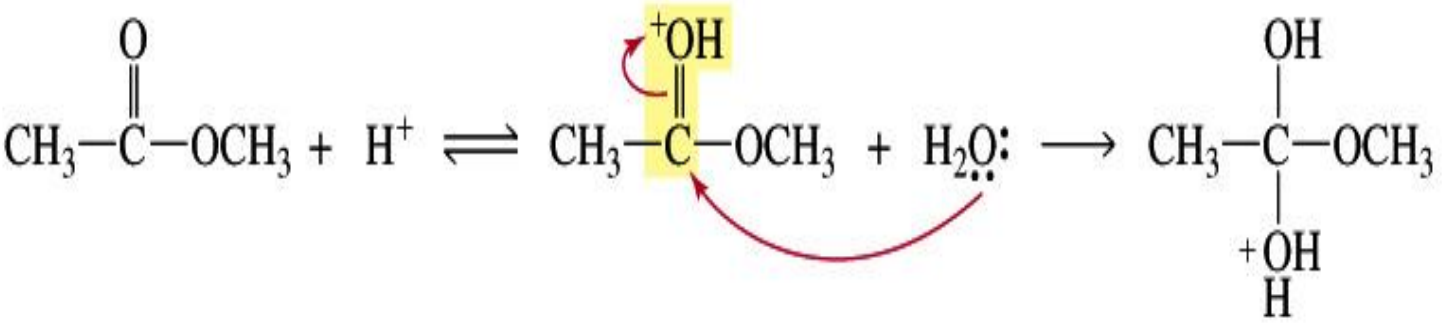
$$S - H \xrightarrow{k_2} product$$

$k_{-1} \langle\langle k_2$ کاتالیز عمومی اسید

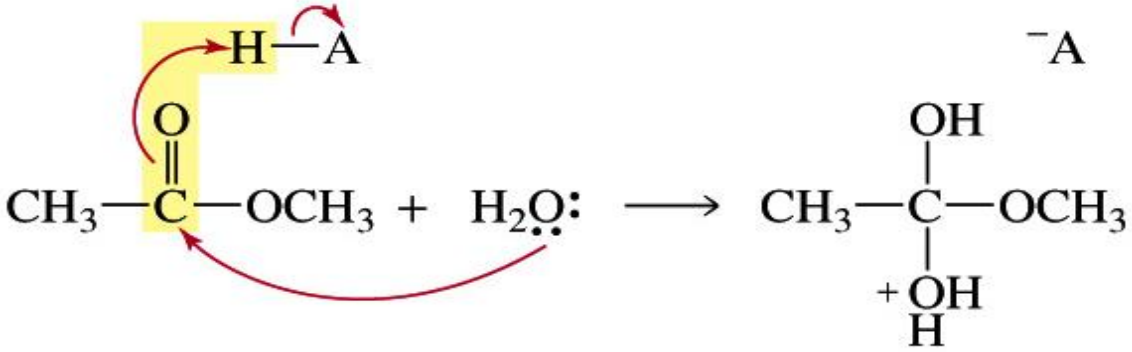
$k_{-1} \rangle\rangle k_2$ کاتالیز خاص اسید

مقایسه اسید خاص و عام :

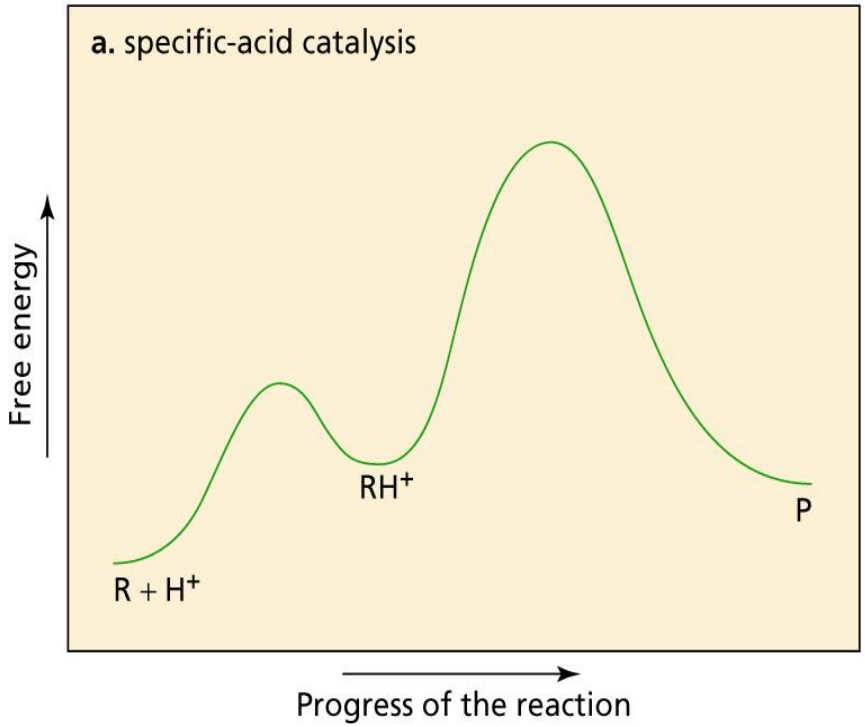
specific-acid-catalyzed attack by water

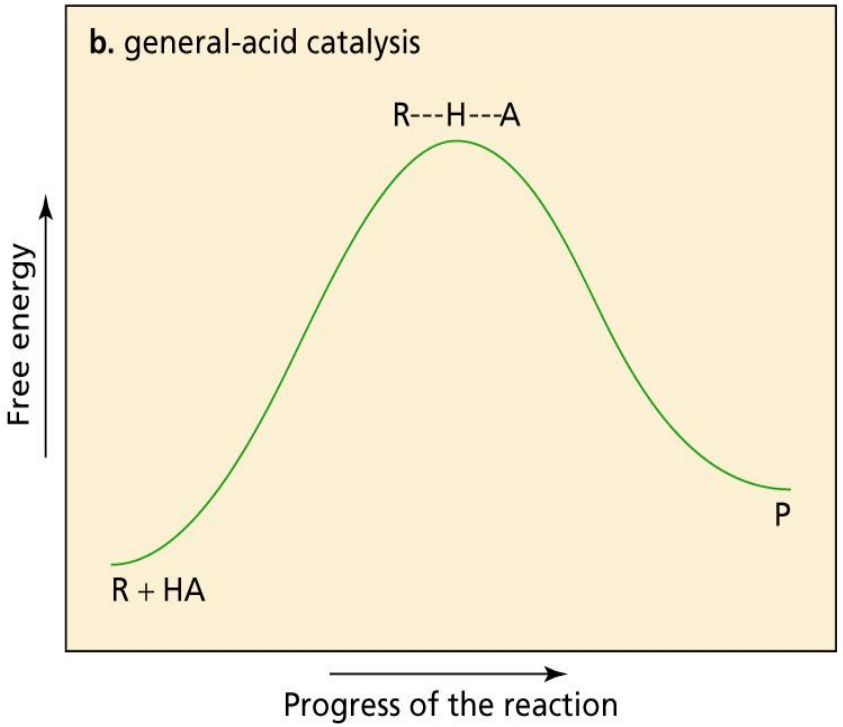


general-acid-catalyzed attack by water



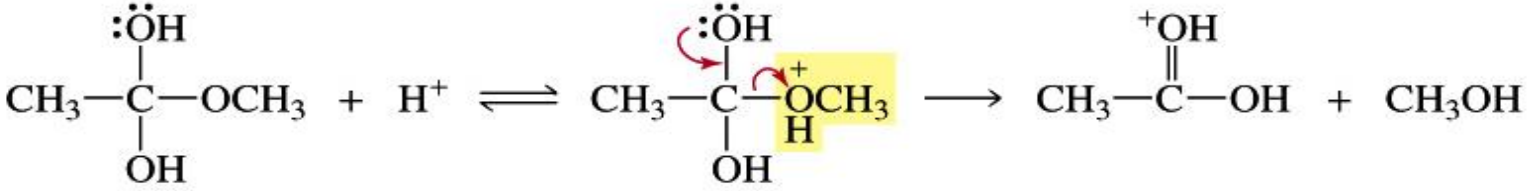
نمودار اسید کاتالیست خاص وعام :





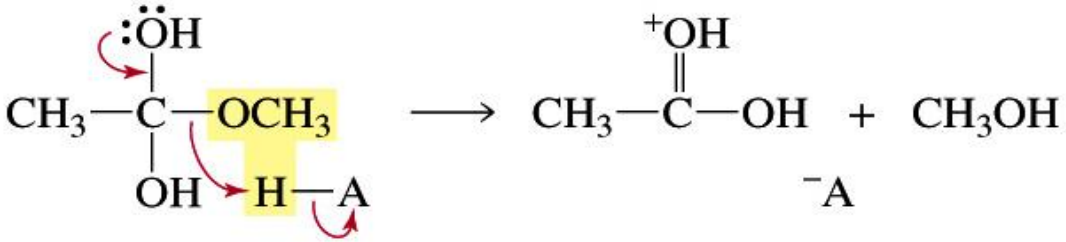
A specific-acid must be a strong acid

specific-acid-catalyzed elimination of the leaving group



A general-acid can be a weaker acid

general-acid-catalyzed elimination of the leaving group



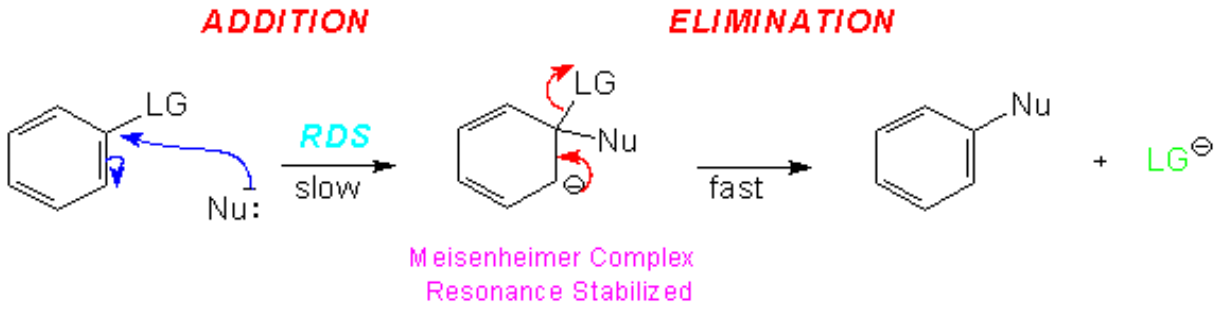
جایگزینی نوکلئوفیلی آروماتیک :

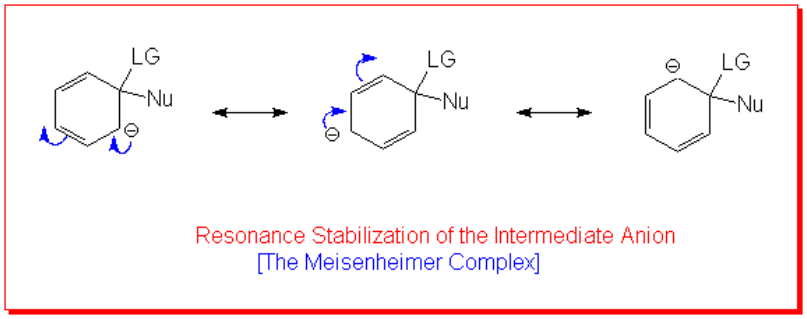
این عمل از دو طریق صورت میگیرد :

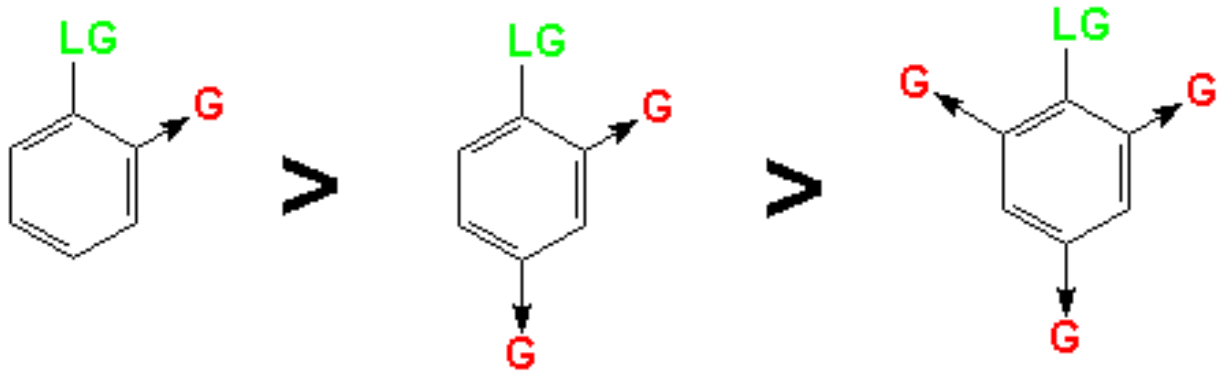
۱- مکانیسم افزایش – حذف

۲- مکانیسم حذف – افزایش (بنزاین)

مکانیسم افزایش – حذف :

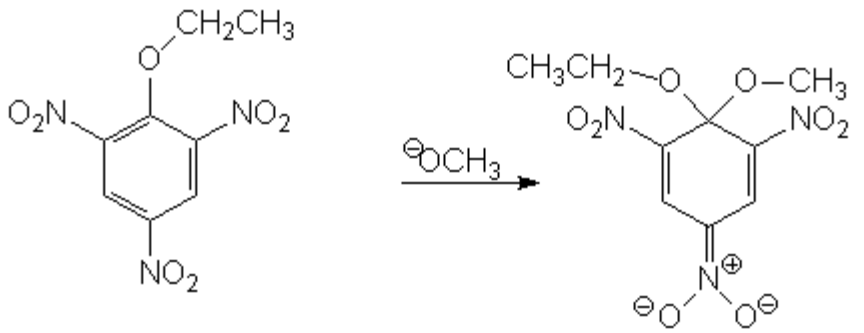




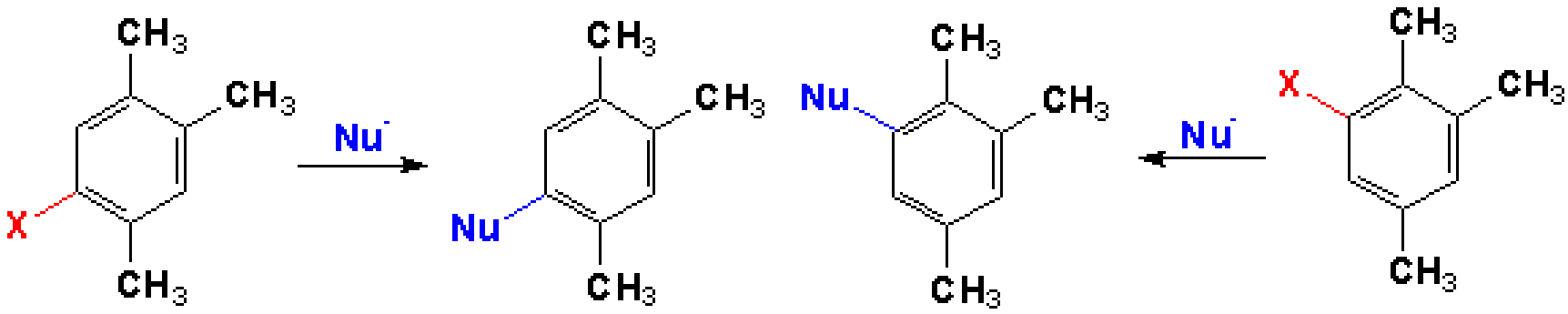


CF_3, CN, CHO, COR, COOH, Br, Cl, I

Common Activating Groups for NAS

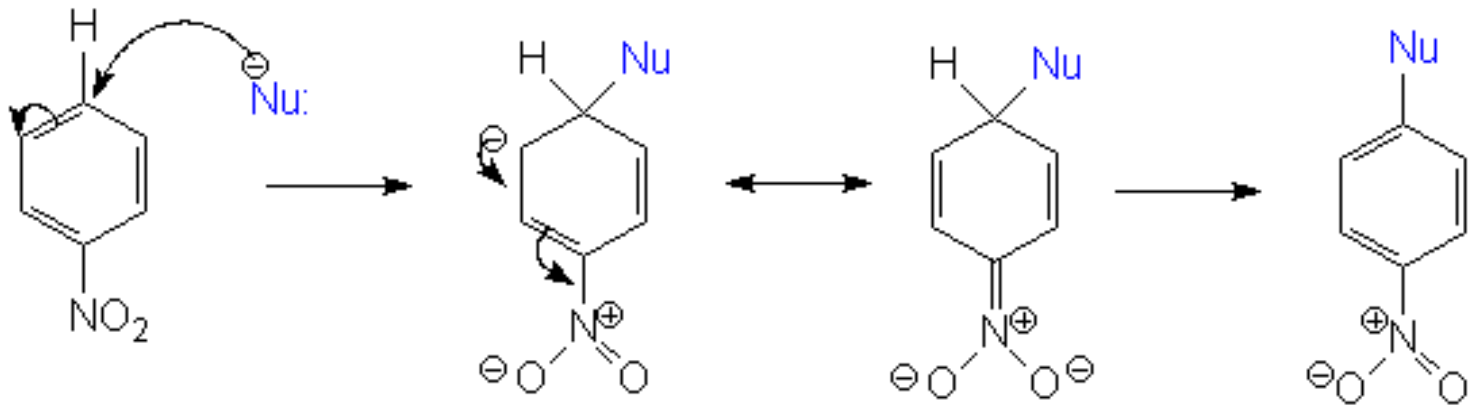


Meisenheimer Complex

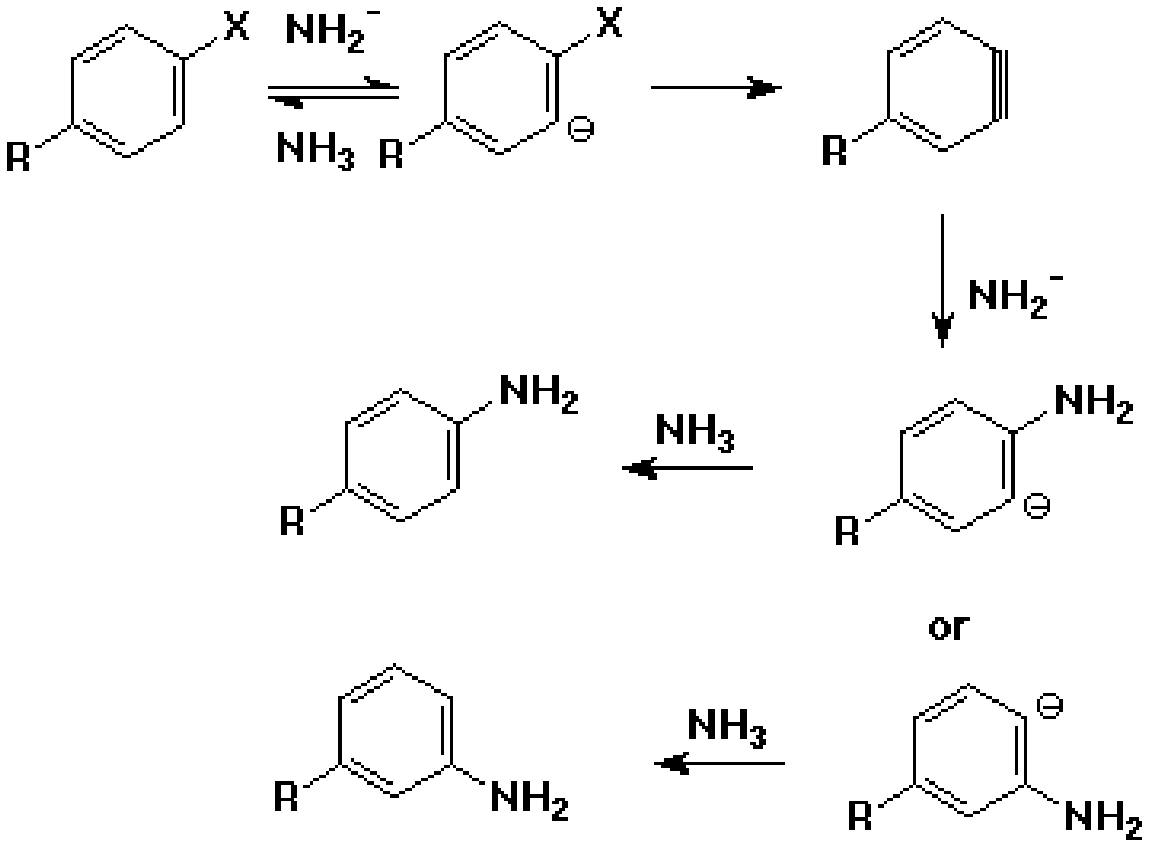


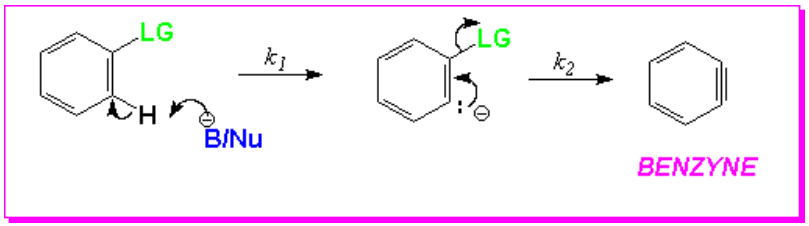
X = Cl,Br	1	:	1.5
X = I	1	:	5.9

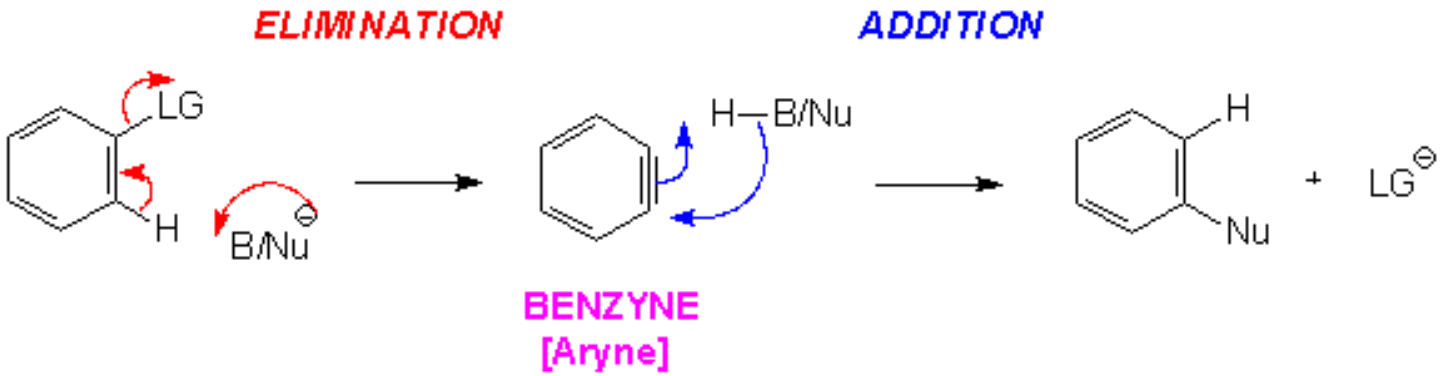
Nucleophilic Aromatic Substitution for Hydrogen NASH

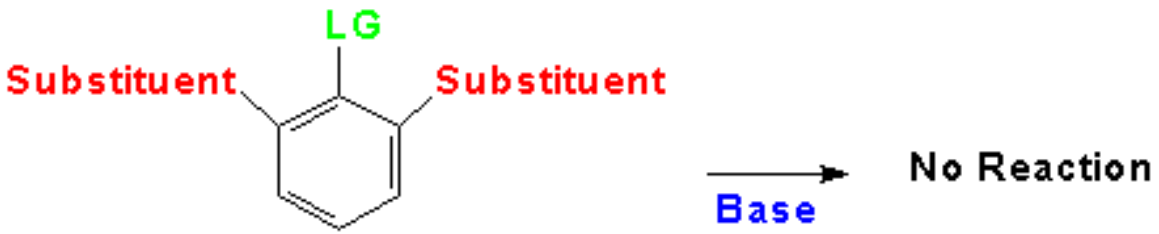


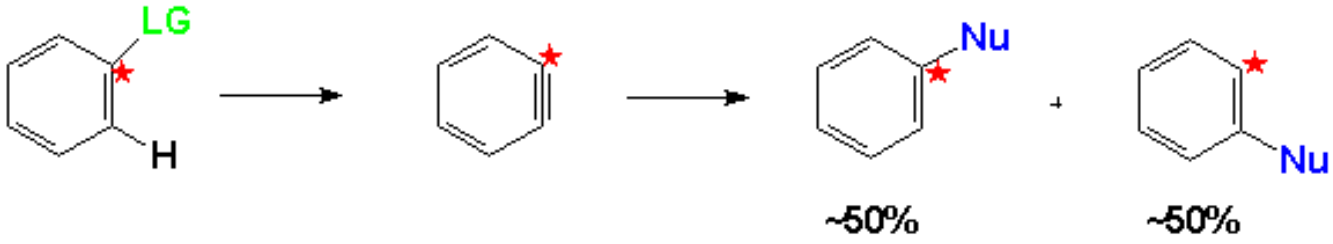
مکانیسم حذف – افزایش :

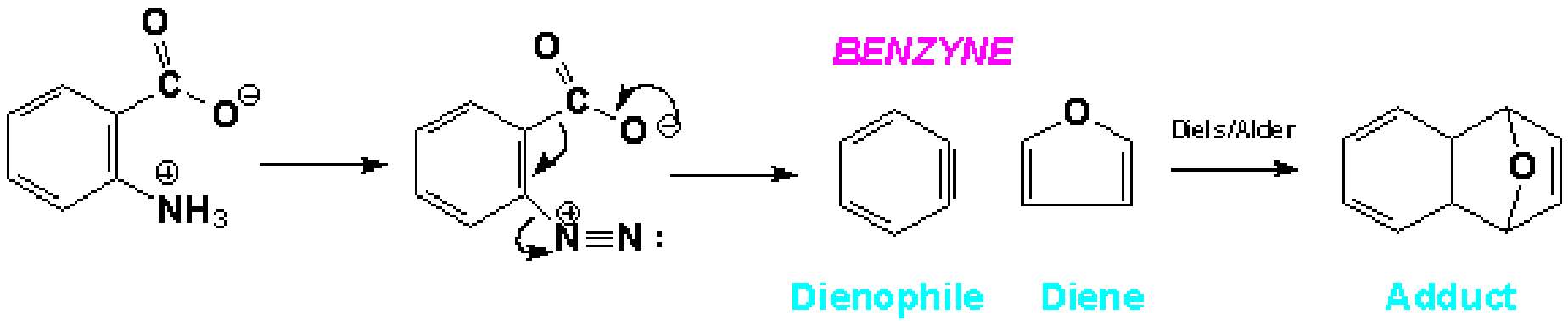



LG
H
B/Nu
k_1
LG
k_2
BENZYNE


ELIMINATION
ADDITION
LG
H
B/Nu
H—B/Nu
H
Nu
+
LG
BENZYNE
[Aryne]


LG
Substituent
Substituent
Base
No Reaction


LG
H
Nu
Nu
~50%
~50%


BENZYNE
Diels/Alder
Dienophile
Diene
Adduct

فصل ۶ : رادیکالهای آزاد

هدفهای کلی :

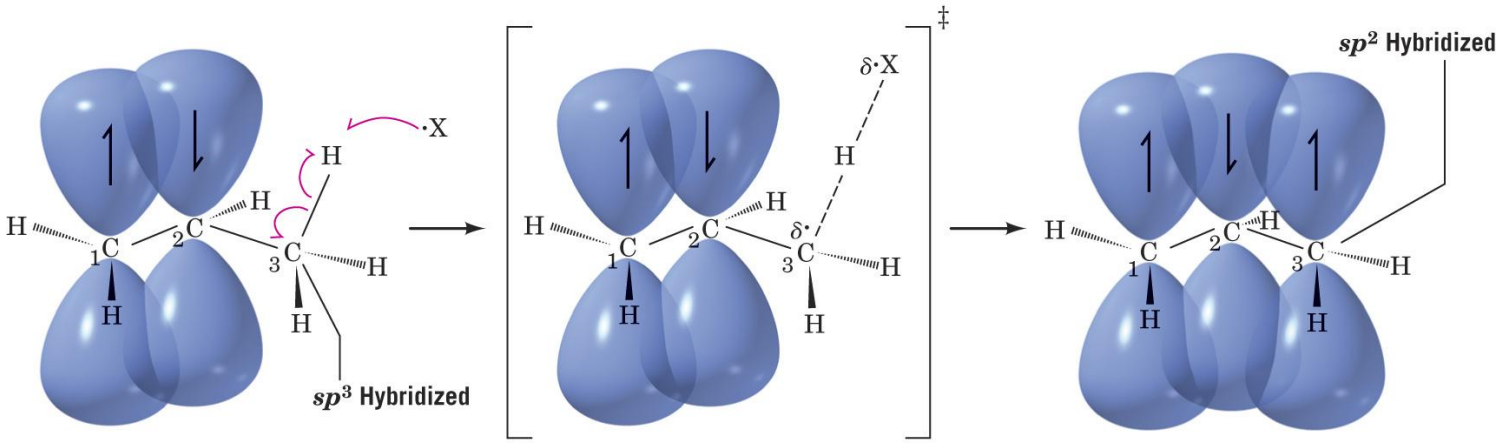
در این فصل سعی میشود دانشجویان با مفاهیم رادیکال آزاد ، روشهای تهیه ، واکنشهای مربوطه (هومولیز، زنجیری، پلیمری شدن و....) آشنا شوند.

رادیکا لهای آزاد:

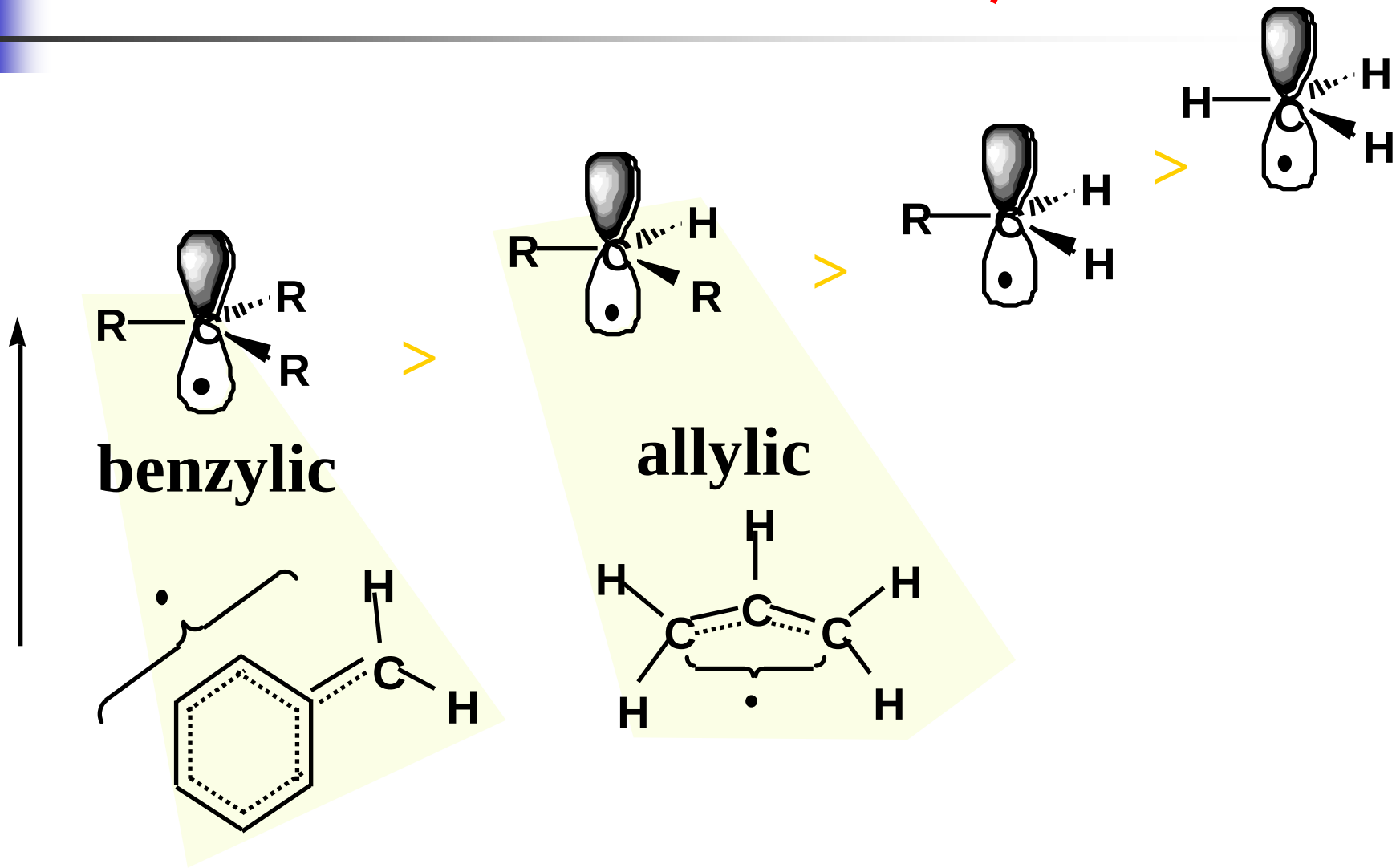
تاریخچه:

اصطلاح رادیکال اولین بار توسط لاوازیه در سال ۱۷۸۹ معرفی گردید

رادیکال آزاد: یک رادیکال آزاد معمولا" به صورت یک مولکول یا اتم با یک جفت الکترون جفت نشده تعریف می شود.



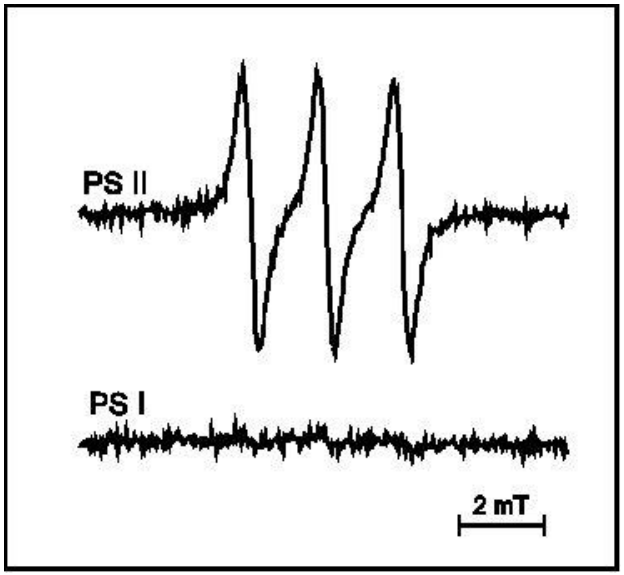
پایداری رادیکالهای آزاد :



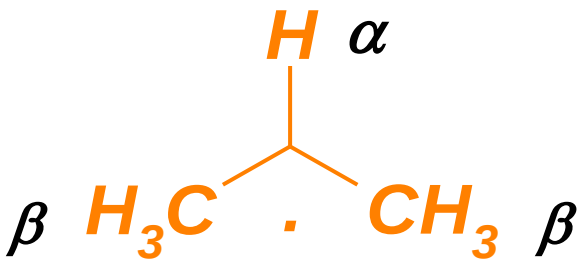
تشخیص رادیکالهای آزاد:

۱- ترازوی گوی : وجود الکترون منفرد باعث پارا مغناطیس شدن ذره می گردد.

۲- رزونانس اسپین الکترون (esr) :رزونانس پارامغناطیس الکترون (epr) موسوم است مفید ترین و قابل استفاده ترین تکنیک برای تشخیص رادیکالهای آزاد است.

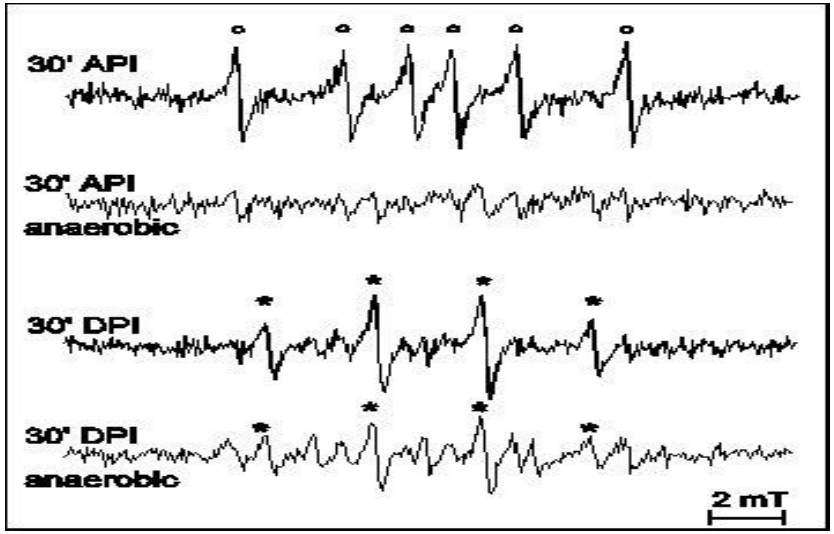


علاوه بر هسته های هیدروژن ، سایر عناصری که دارای اسپین هسته ای غیر از صفر هستند باعث شکافت در جذب esr می گردد.



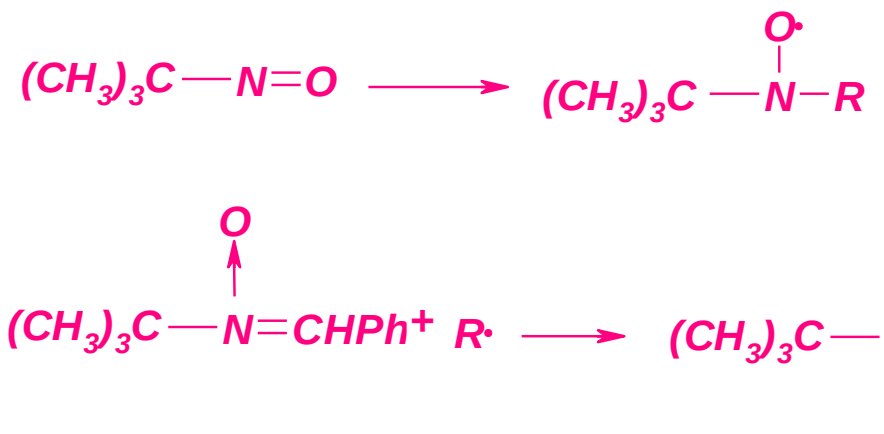
$$a_{H_\alpha} = 22 gauss$$

$$a_{H_\beta} = 25 gauss$$



روش پایدارکردن رادیکالهای آزاد:

به دام انداختن رادیکال بوسیله برخی واکنش های شیمیایی است.



واکنش های هومولیز :

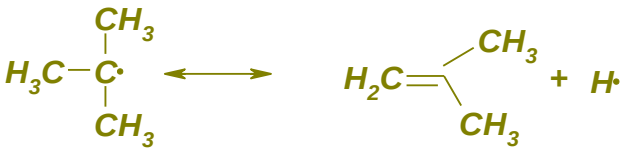
انرژی تفکیک پیوند :

$$A - B \longrightarrow A^{\cdot} + B^{\cdot}$$

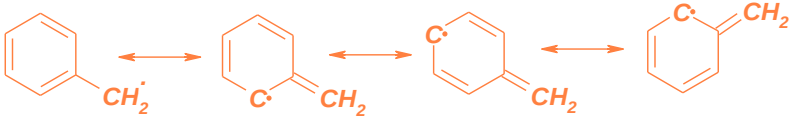
انرژی پیوند تفکیک نمونه ها Kcal/mol	
H-H	104
F-F	38
Cl-Cl	58
Br-Br	46
CH3-H	104
1˚C-H	98
2˚C-H	95
3˚C-H	91
Ar-H	112

پایداری رادیکالها:

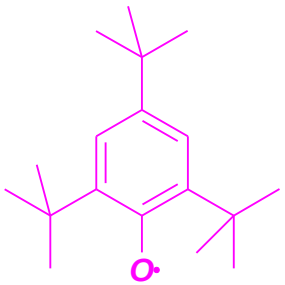
۱-هایپر کانجوگه شدن



۲-رزونانس

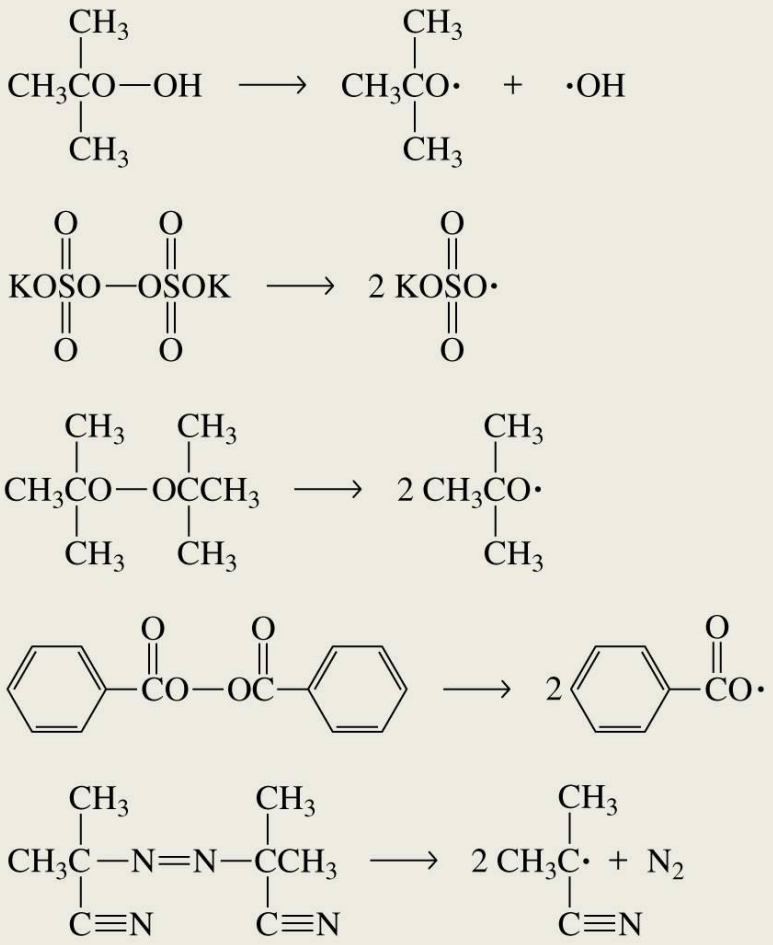


۳-پایداری بوسیله ممانعت فضایی



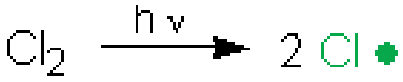
آغازگرها :

Table 28.3 Some Radical Initiators

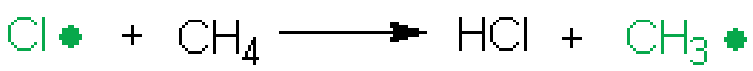


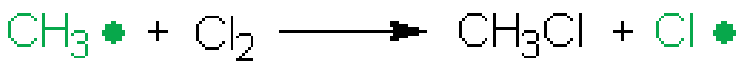
واکنش های زنجیری :

1. Initiation reaction

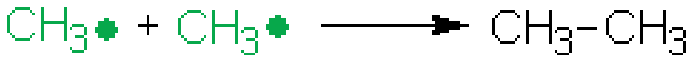


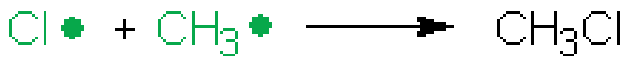
2. Chain propagation





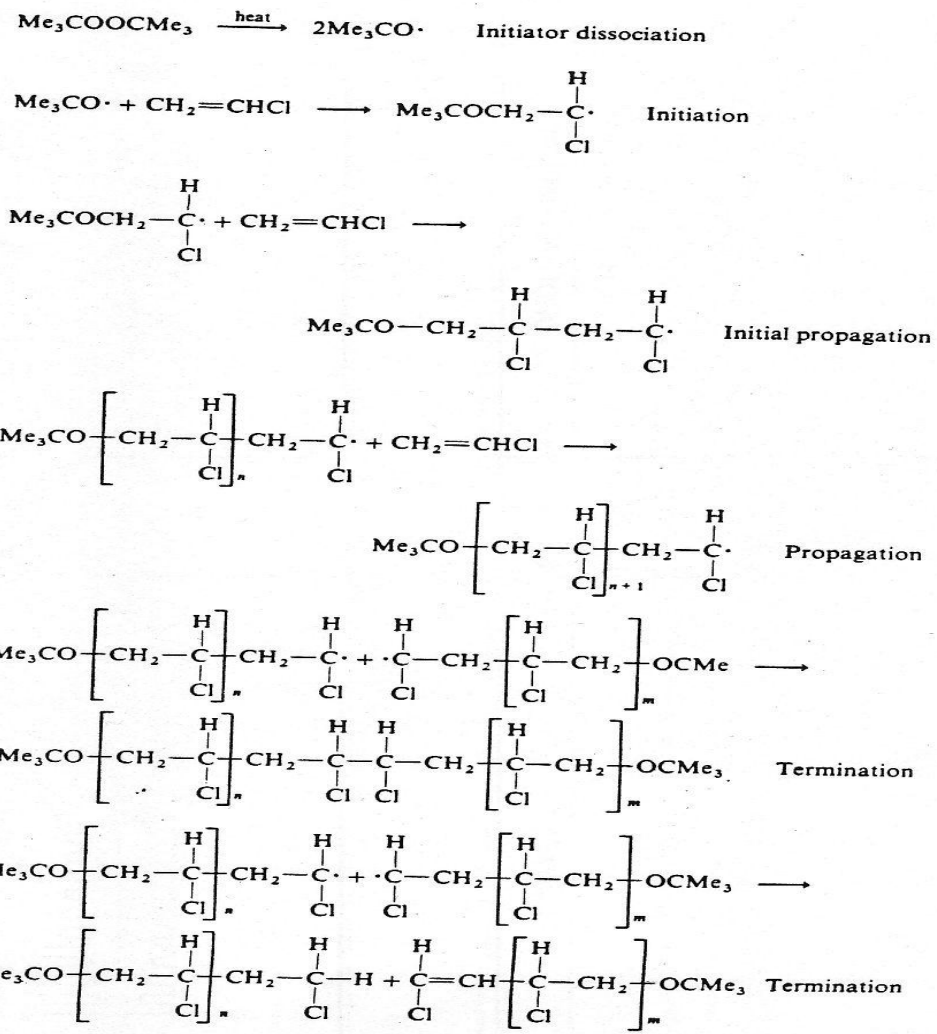
3. Chain termination reactions



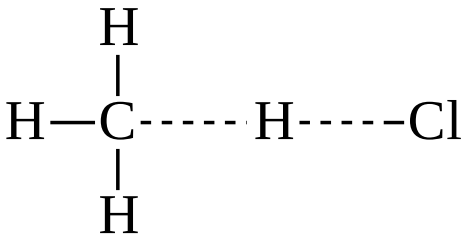


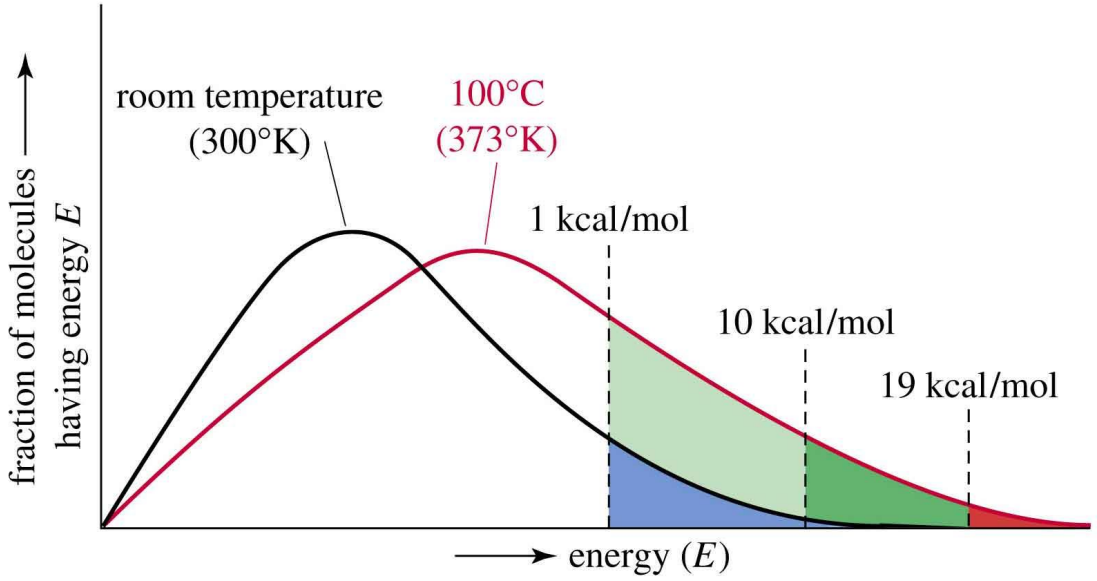
مثال :

CHAIN REACTIONS



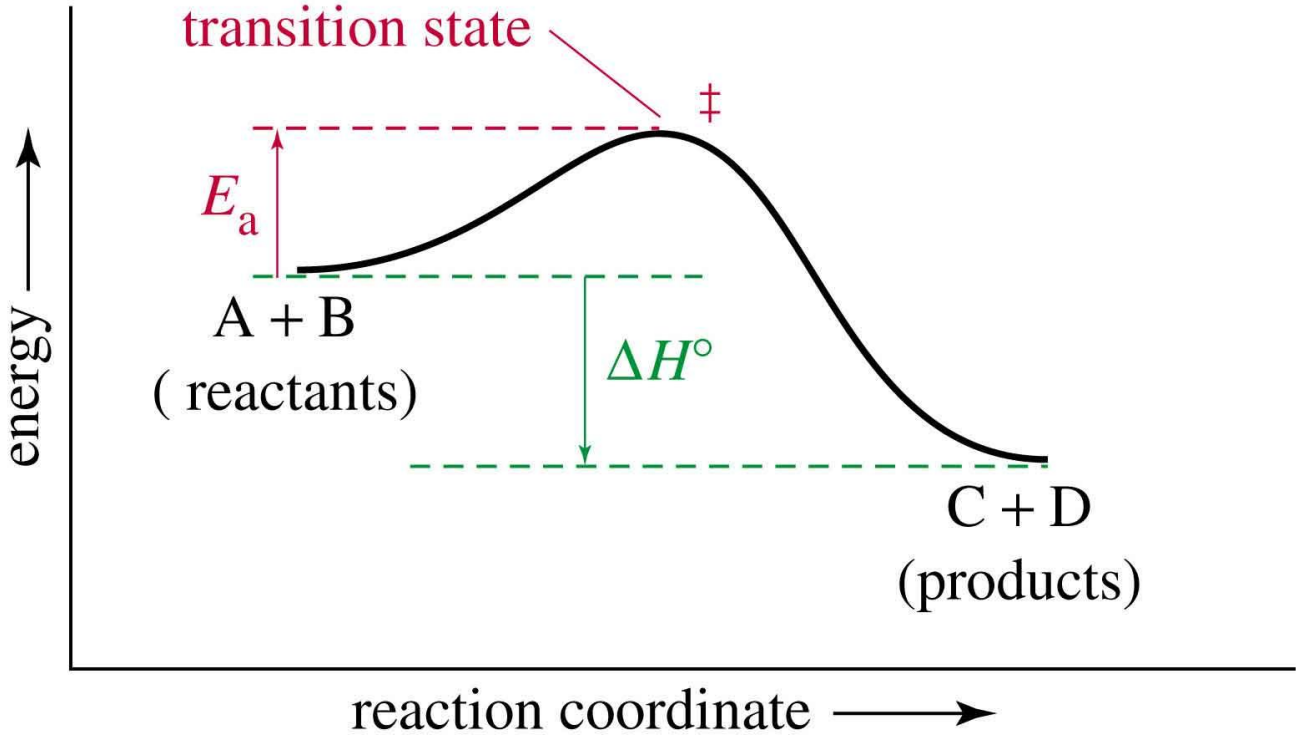
سینیتیک :


H
H—C-----H-----Cl
H


fraction of molecules having energy E
room temperature (300°K)
100°C (373°K)
1 kcal/mol
10 kcal/mol
19 kcal/mol
energy (E)

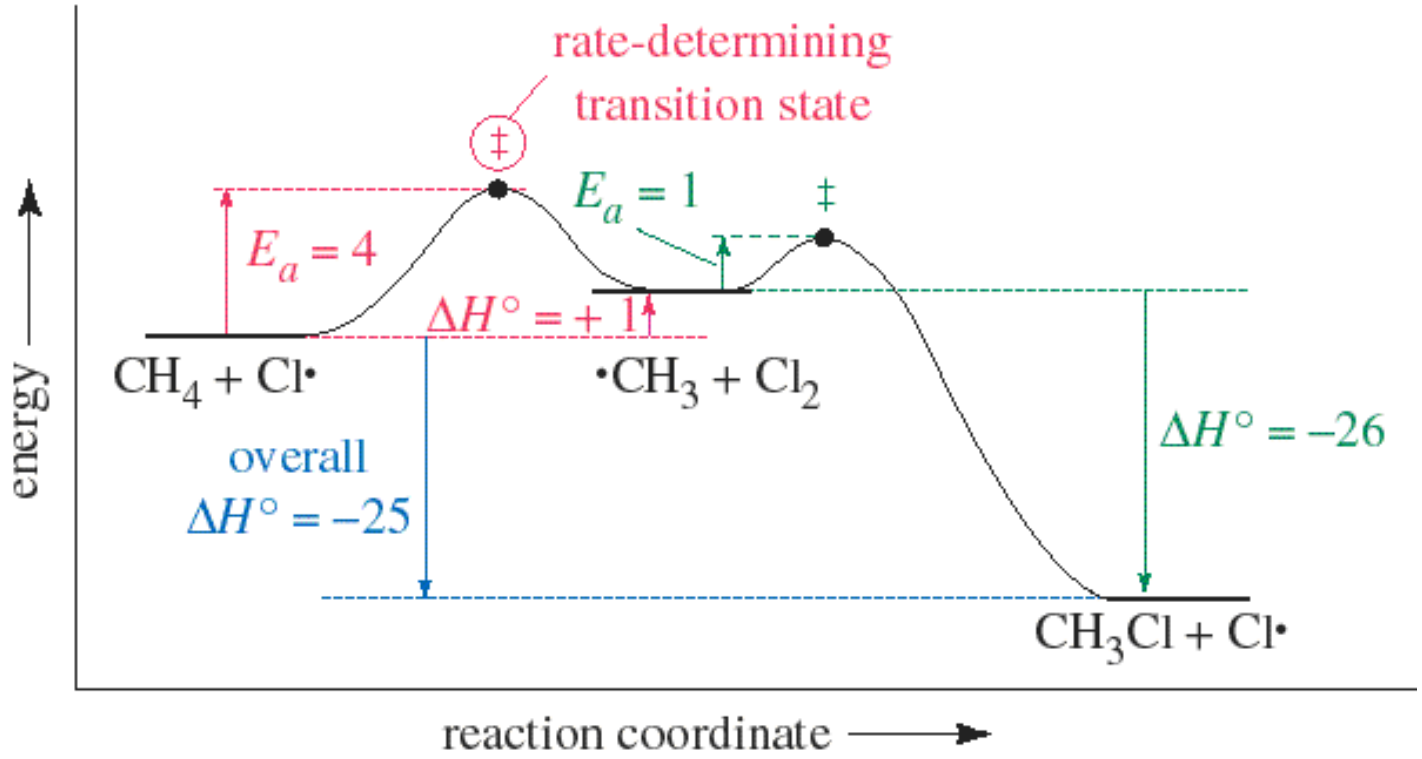
Reaction-Energy Diagrams

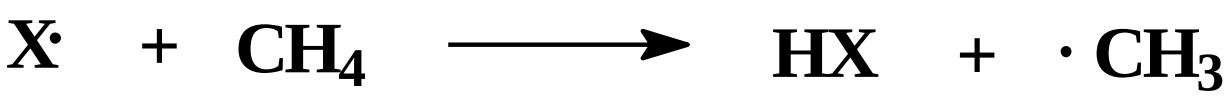
- For a one-step reaction:
  reactants → transition state → products
- A catalyst lowers the energy of the transition state.



Energy Diagram for aTwo-Step Reaction

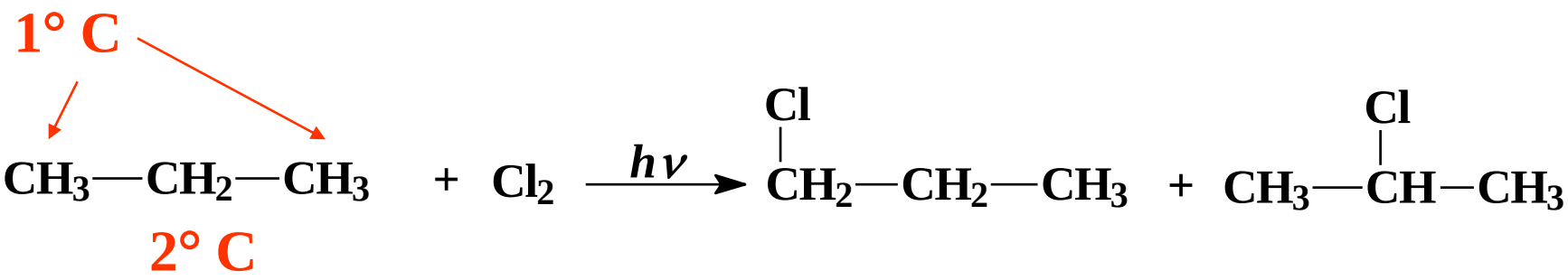
- Reactants → transition state → intermediate
- Intermediate → transition state → product

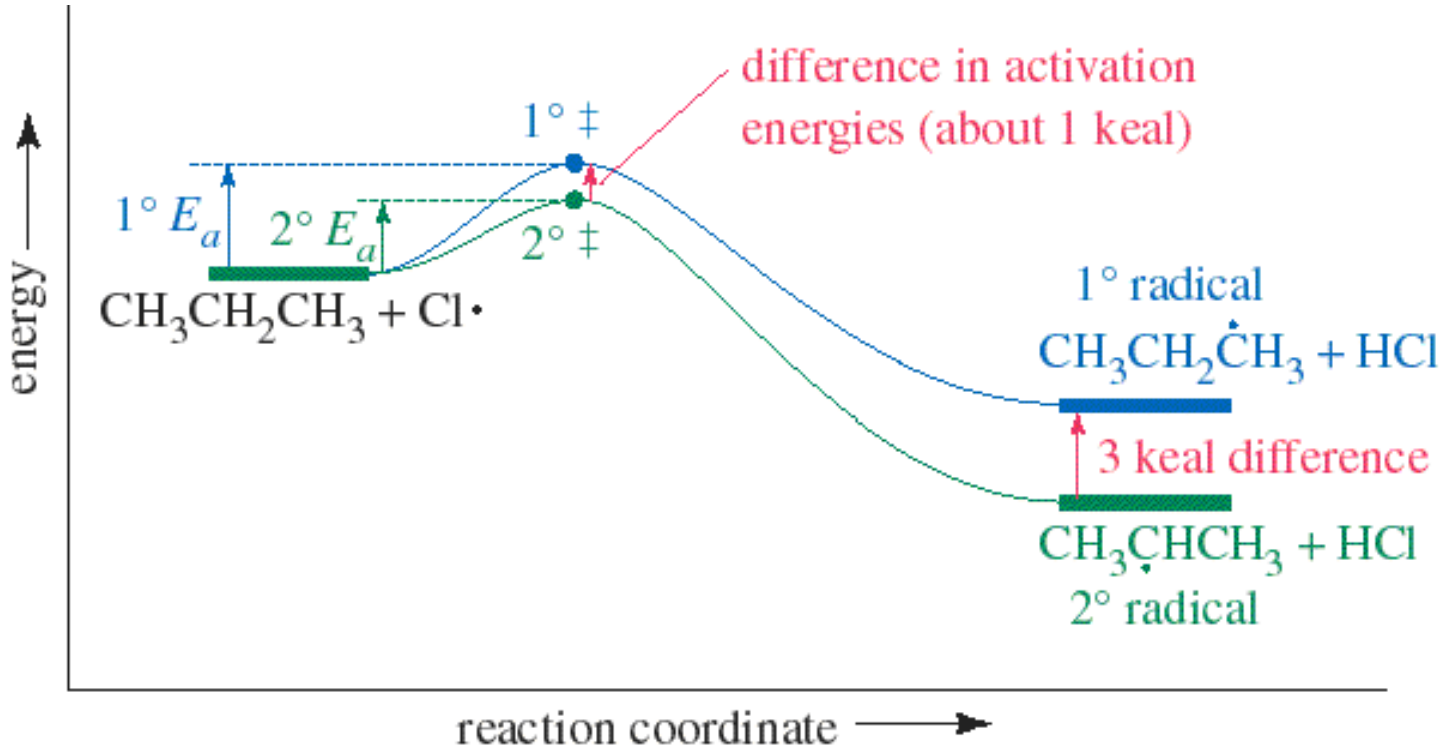




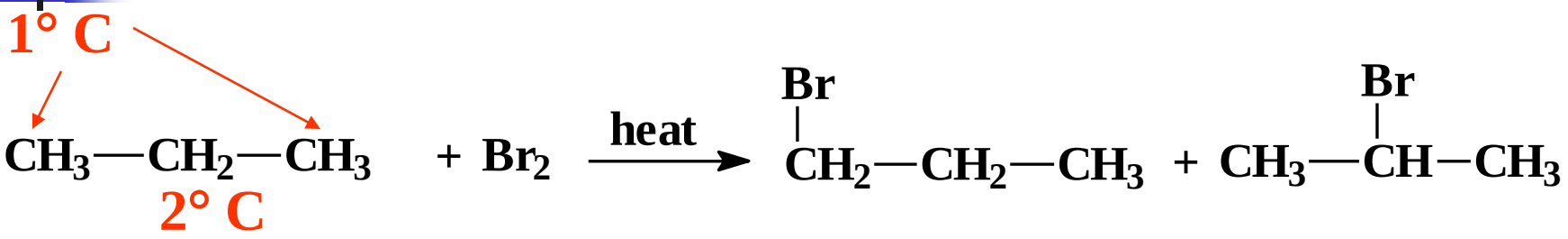
X	E_a	Rate @ 300K	Rate @ 500K
F	1.2 kcal	140,000	300,000
Cl	4 kcal	1300	18,000
Br	18 kcal	9×10^{-8}	0.015
I	34 kcal	2×10^{-19}	2×10^{-9}

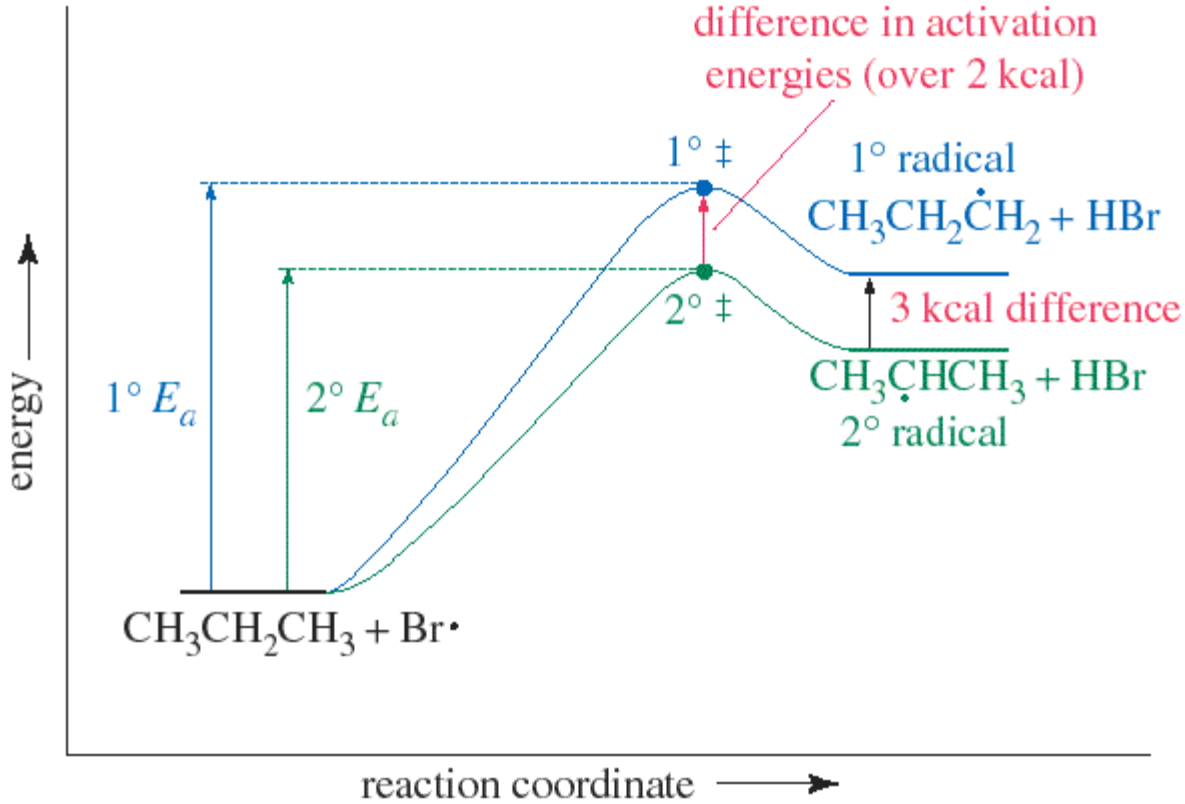
Chlorination of Propane



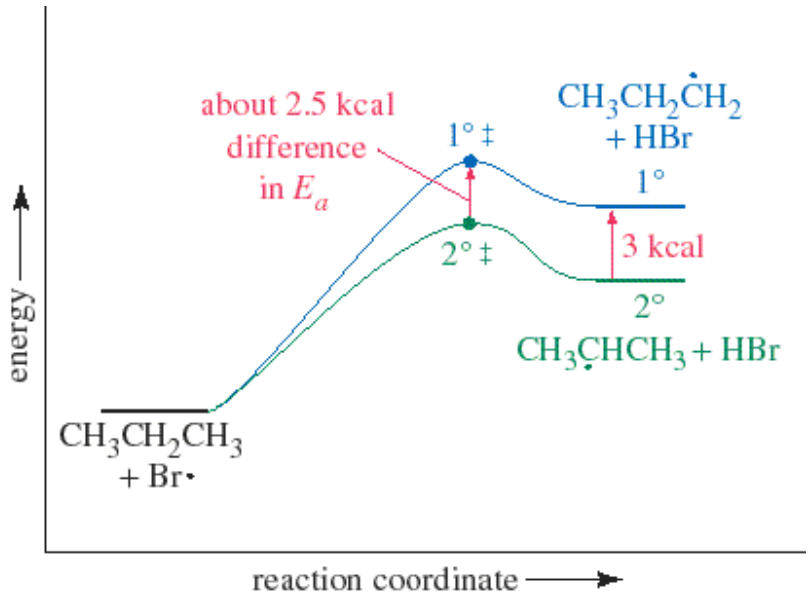


Bromination of Propane

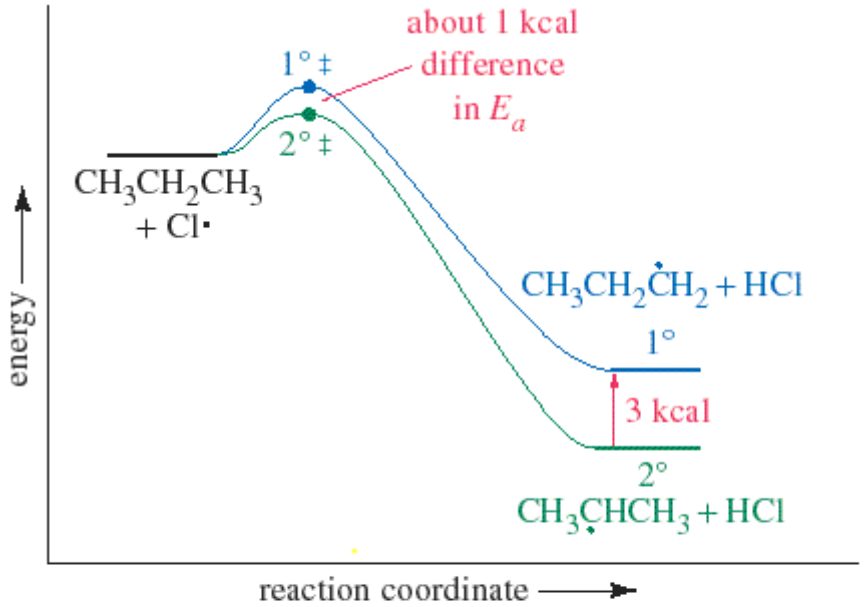




Bromination vs. Chlorination

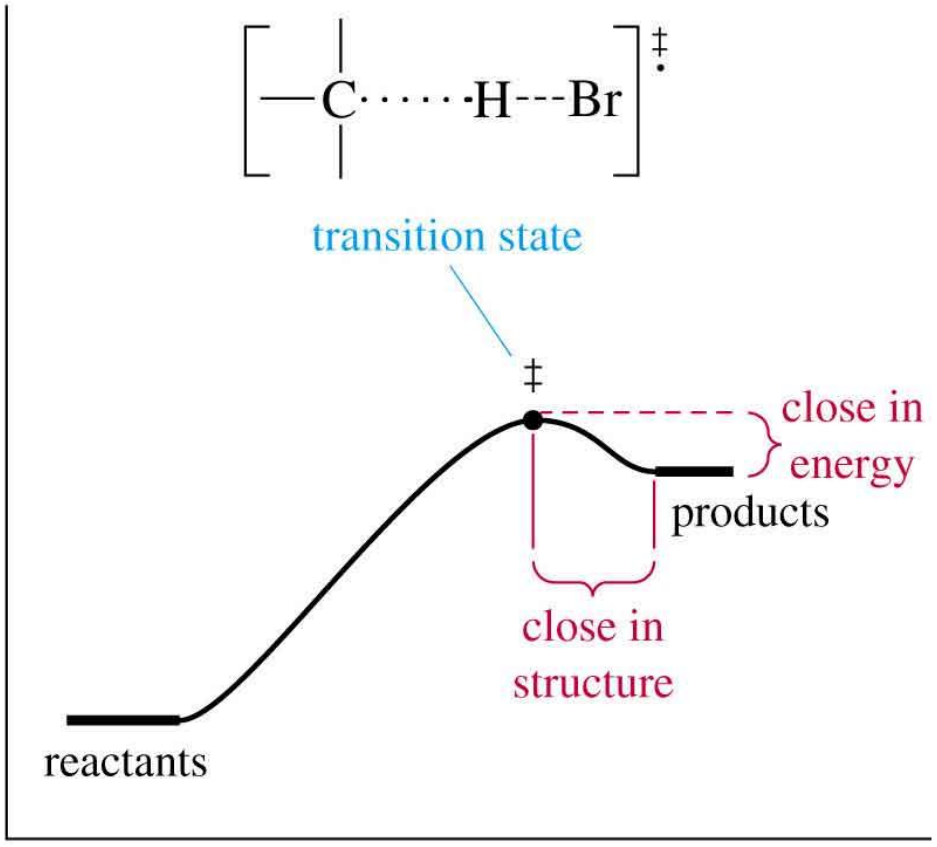


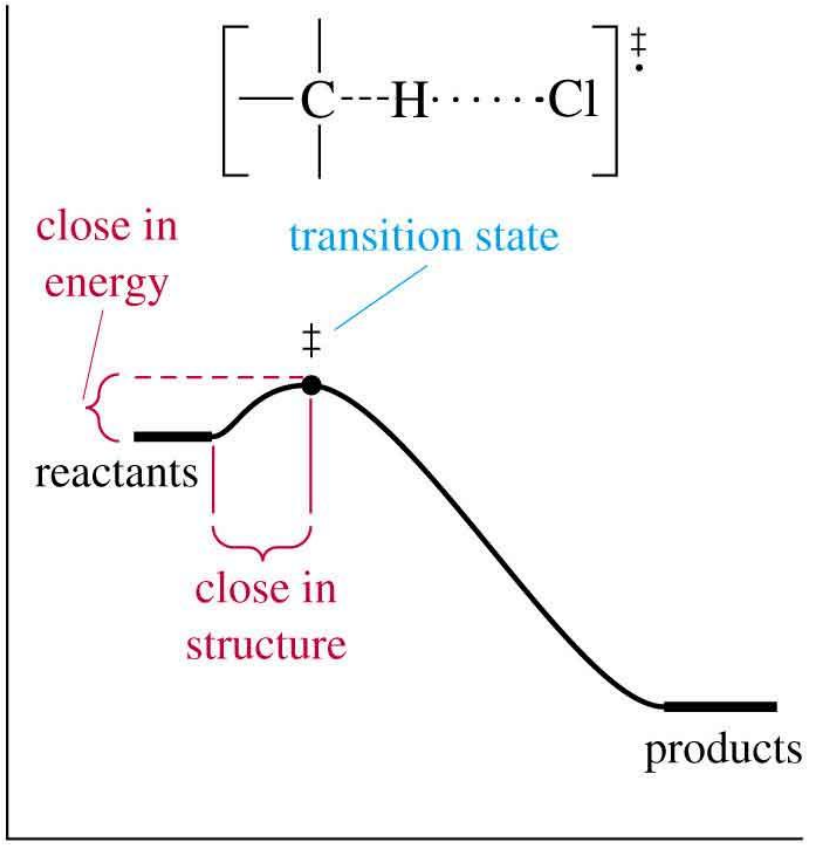
(a) BROMINATION
endothermic
TS close to products
large difference in E_a



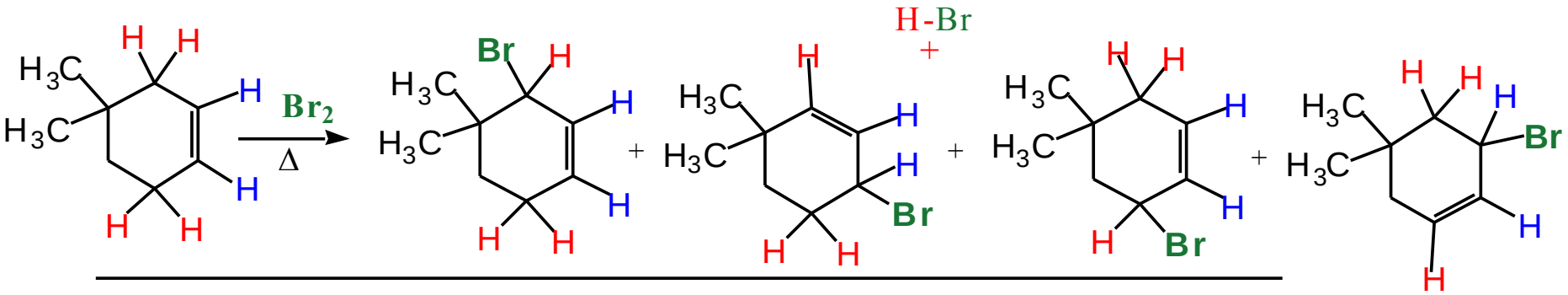
(b) CHLORINATION
exothermic
TS close to reactants
small difference in E_a

Endothermic and Exothermic Diagrams

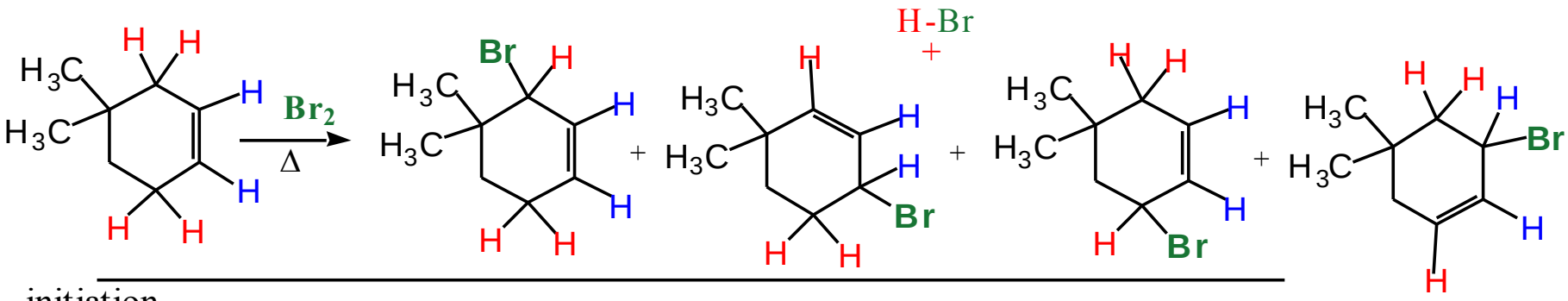




Reaction

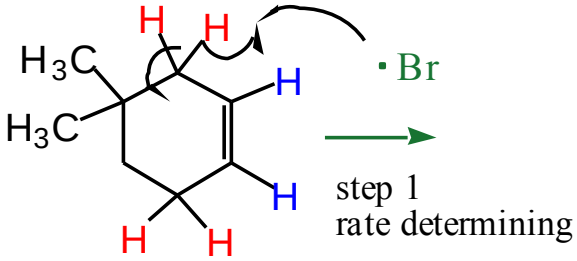

H
H
H3C
H3C
H
H
H
Br2
Δ
Br
H
H3C
H3C
H
H
H
+
H
H3C
H3C
H
H
Br
H
H
H-Br
+
+
H
H
H3C
H3C
H
H
Br
H
+
H
H
H
H3C
H3C
Br
H
H

Reaction



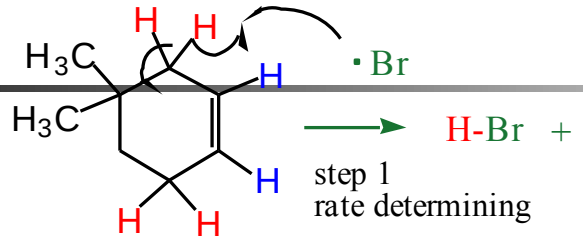
initiation

propagation



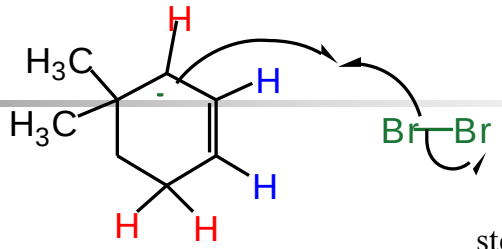
step 1
rate determining

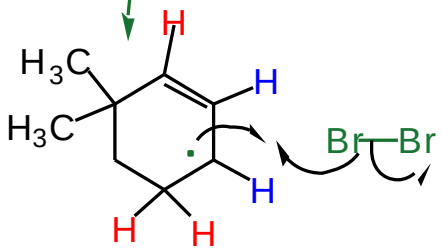
propagation



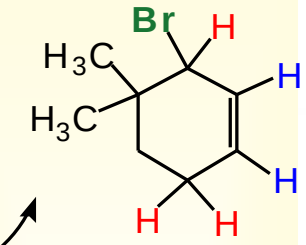
step 1
rate determining

H-Br +

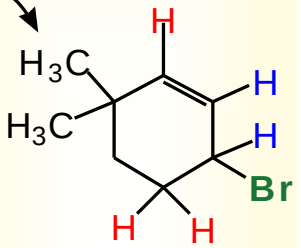




step 2

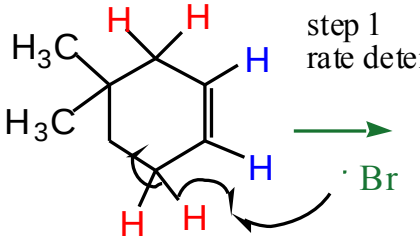


and



+ · Br

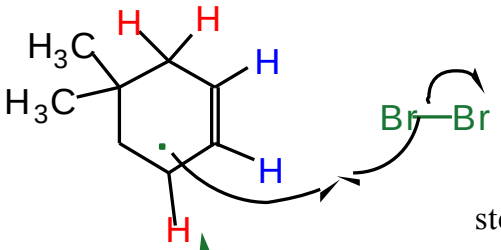
two different allylic sites

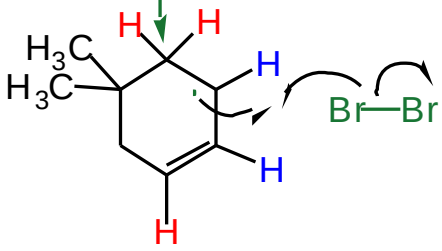


step 1
rate determining

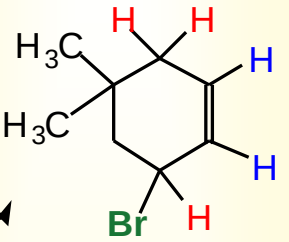
H-Br +

· Br

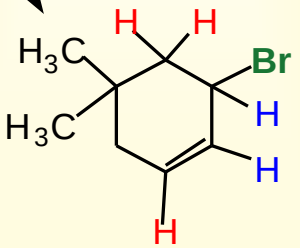




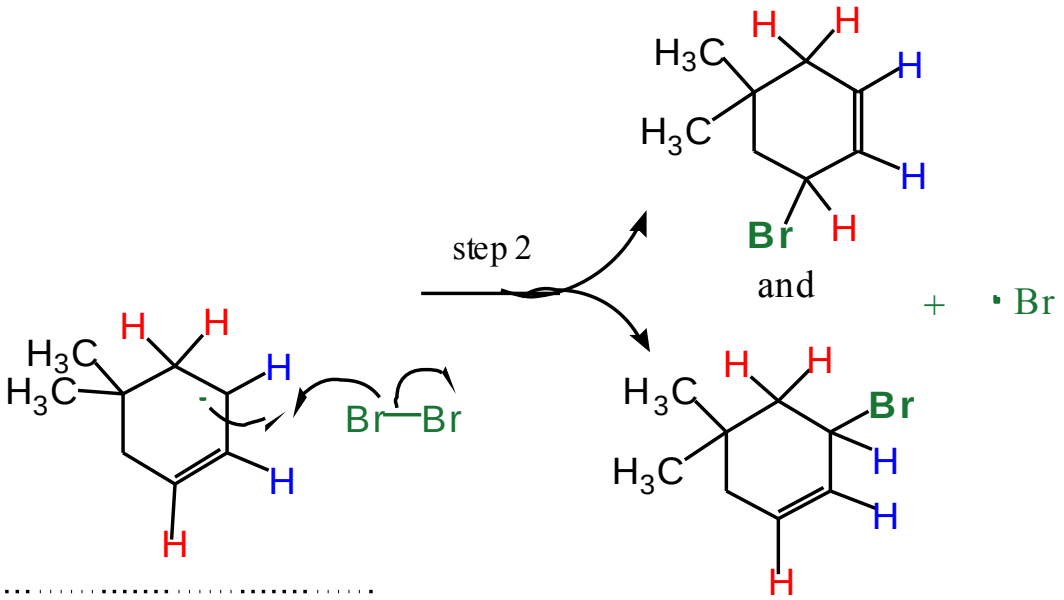
step 2



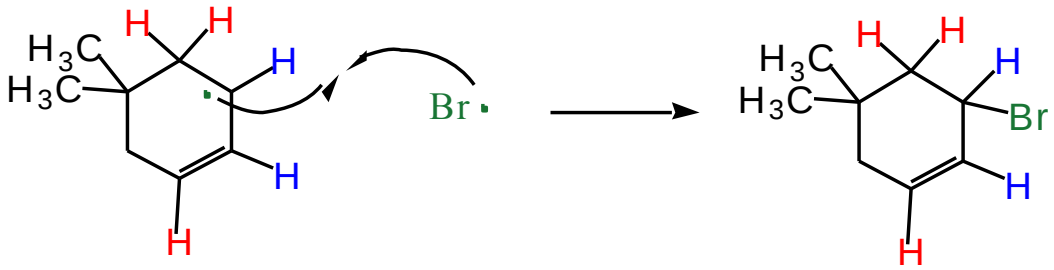
and



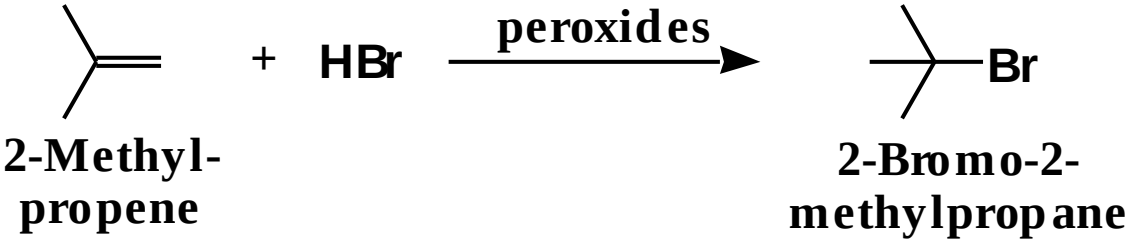
+ · Br



termination - one of many

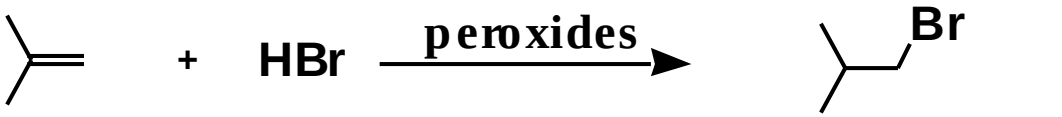


Markovnikov addition



2-Methyl-propene → 2-Bromo-2-methylpropane

Non-Markovnikov addition

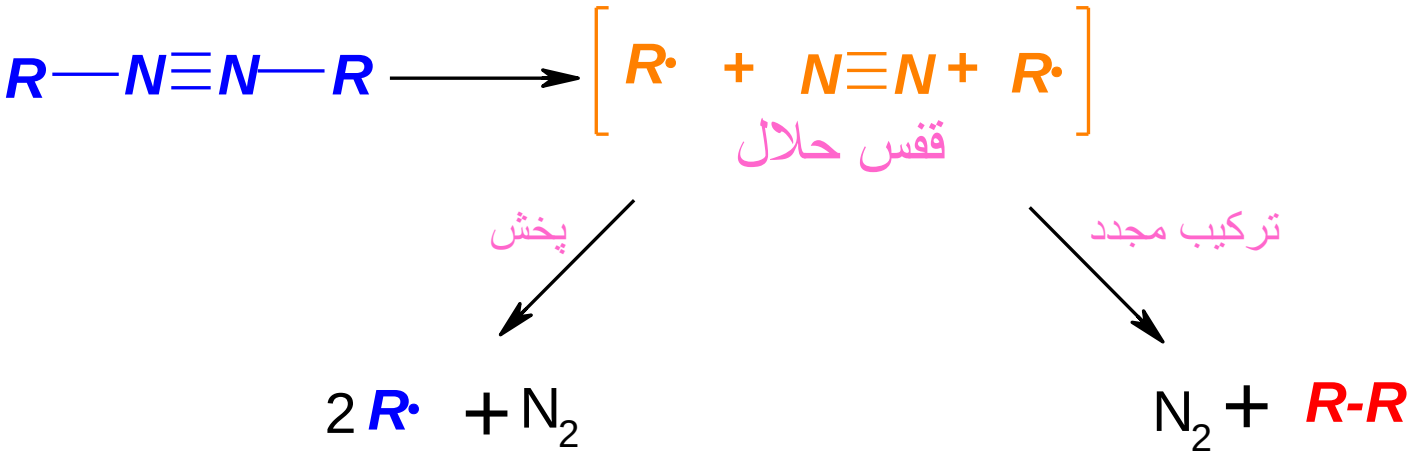


2-Methyl-propene → 1-Bromo-2-methylpropane

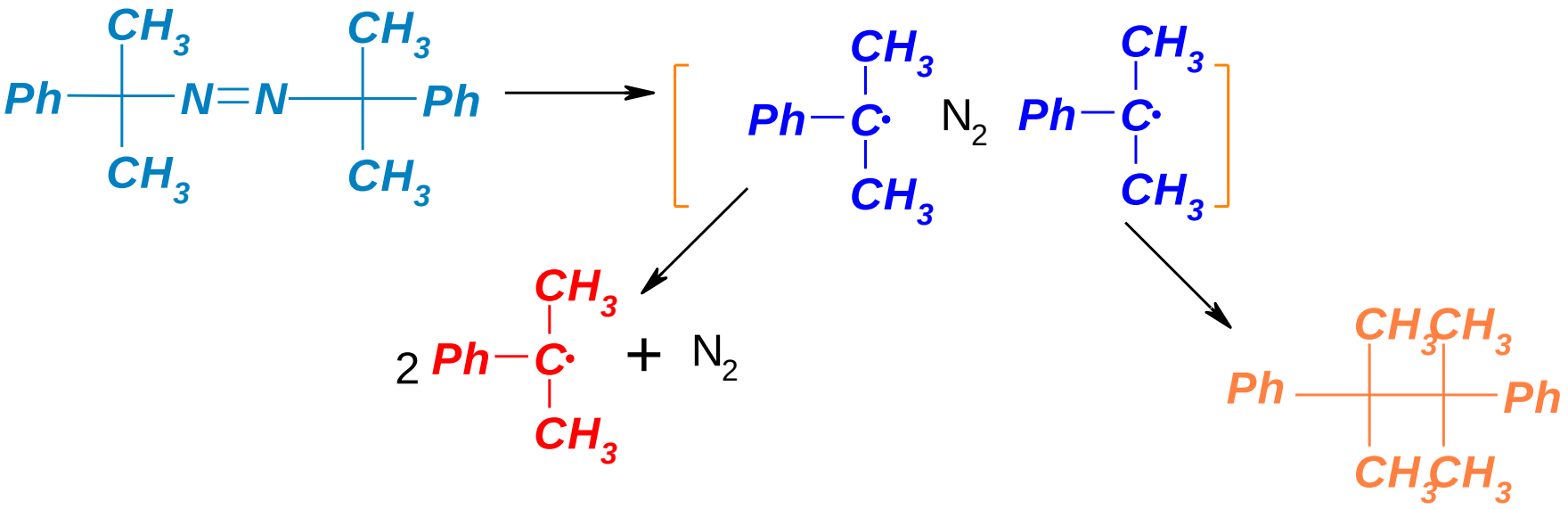
اثرهای قفس:

Cage effects

اثرهای قفس: مولکولهای حلال محیط برای رادیکالها یک قفس به وجود می آورند که باعث جدایی دو رادیکال از یکدیگر می شود .



مثال :


CH3
Ph
N=N
Ph
CH3
CH3
CH3
Ph
C·
N2
Ph
C·
CH3
CH3
CH3
CH3
2 Ph
C·
+ N2
CH3
CH3
CH3CH3
Ph
Ph
CH3CH3

دی رادیکالها :

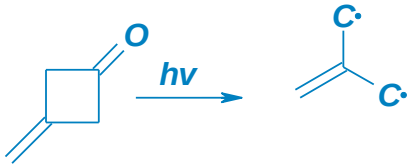
یک مولکول با دو مرکز رادیکالی یک دی رادیکال خوانده می شود .

انواع دی رادیکالها:

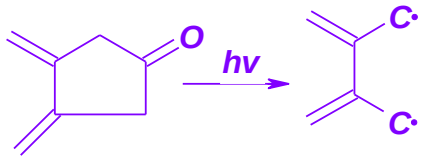
۱ و ۱- دی رادیکال :(کارین) فصل ۷

۱ و۲- دی رادیکالها (فصل ۸)

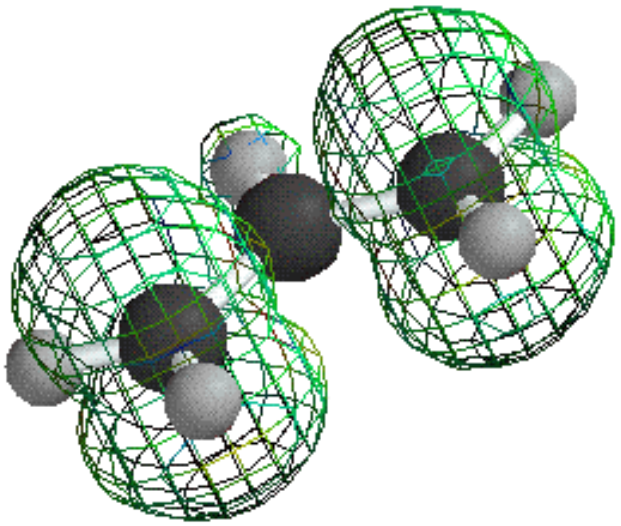
۱و۳- دی رادیکالها



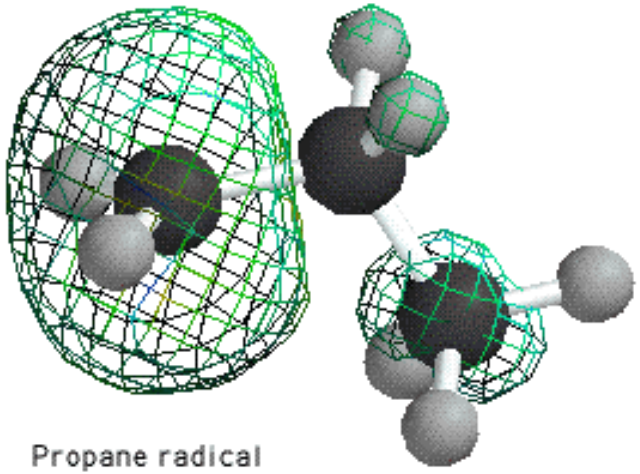
۱و٤- دی رادیکالها



۱و ٥- دی رادیکالها



Propene radical



Propane radical

واکنشهای رادیکالی شاخص:

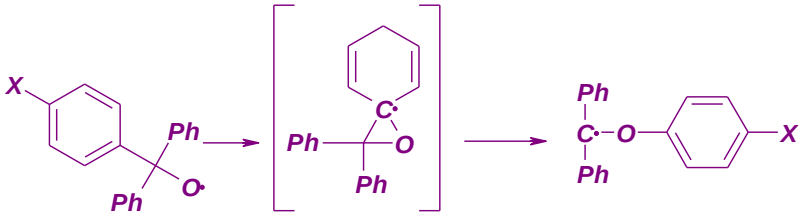
۱- نو آرایی های تک مولکولی و قطعه قطعه شدنها

۲- واکنشهای دو مولکولی رادیکال – رادیکال (پایان)

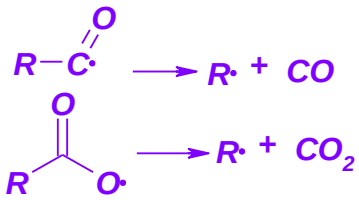
۳- واکنشهای دو مولکولی انتقال الکترون (کاهش)

۴- واکنشهای دو مولکولی رادیکال مولکول (جدا کردن ، افزایش ، جایگزینی)

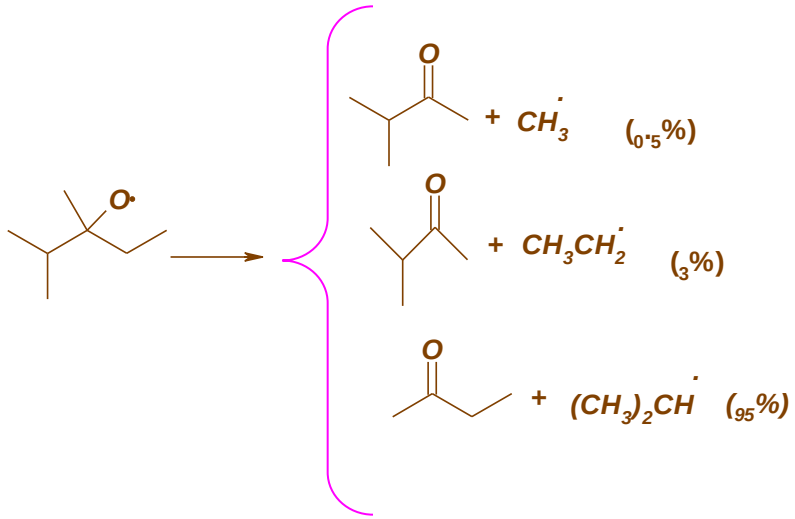
نوآرایی های تک مولکولی و قطعه قطعه شدن :



نو آرایی رادیکالی نسبتا"نادر هستند.



از هم پاشی رادیکالی:



شکستن β

واکنشهای رادیکال – رادیکال :

این واکنشها لزوما" به تخریب رادیکالها منجر می شوند .مراحل پایانی واکنشهای زنجیری :

$$2CH_3CH_2CH_2^{\cdot} \xrightarrow{Combination} CH_3CH_2CH_2CH_2CH_2CH_3$$

$$2CH_3CH_2CH_2^{\cdot} \xrightarrow{Disproportionation} CH_3CH_2CH_3 + CH_3CH=CH_2$$

واکنشهای اکسایش – کاهش رادیکالی :

در حضور اکساینده ها یا کاهنده های مناسب رادیکالها ممکن است به کاتیونها اکسایش و یا به آنیونها کاهش یابند .

$$Fe^{+2} + ROOH \longrightarrow RO^{\cdot} + OH^{-} + Fe^{+3}$$

$$RO^{\cdot} + Fe^{+2} \longrightarrow RO^{-} + Fe^{+3}$$

واکنشهای رادیکال – مولکول :

1-واکنشهای کند شدن رادیکال :

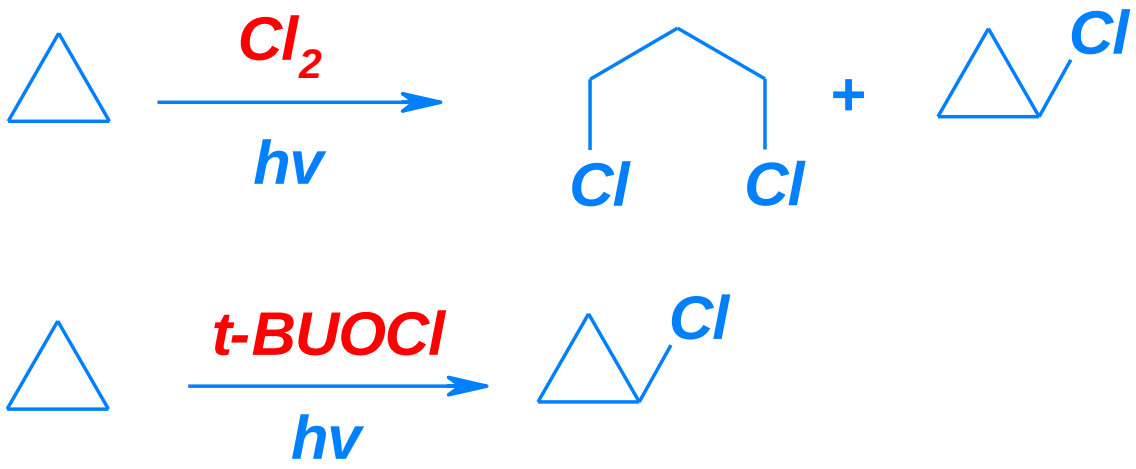
$$B-A+R^{\cdot} \longrightarrow B^{\cdot}+R-A$$

$$tBUOCl \xrightarrow{\Delta} tBUO^{\cdot}+Cl^{\cdot}$$

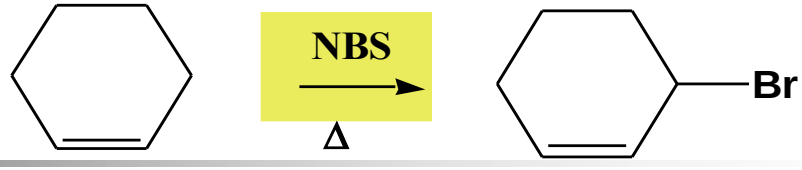
$$tBUO^{\cdot}+RH \longrightarrow tBUOH+R^{\cdot}$$

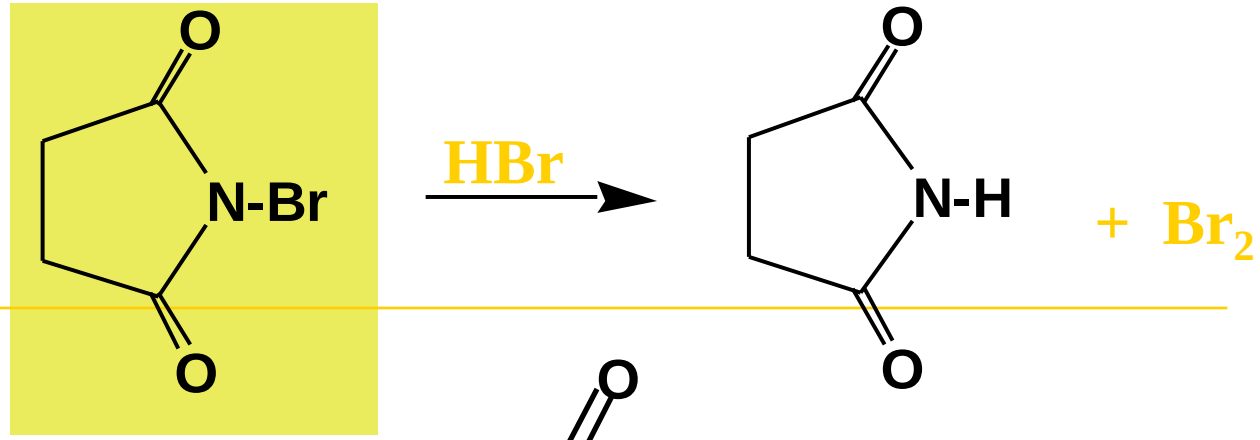
$$R^{\cdot}+tBUOCl \longrightarrow RCl+tBUO^{\cdot}$$

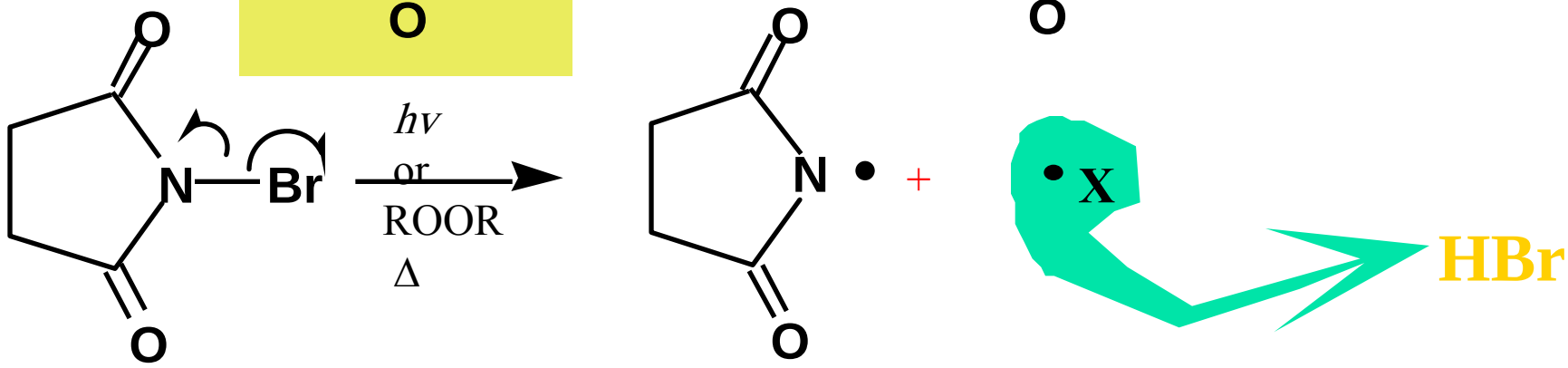
مثال :

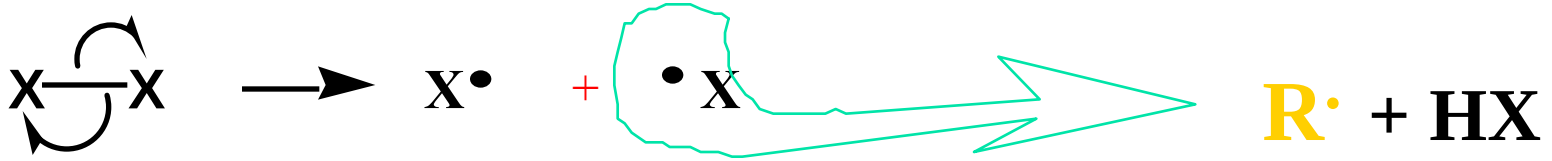


NBS for Br_2

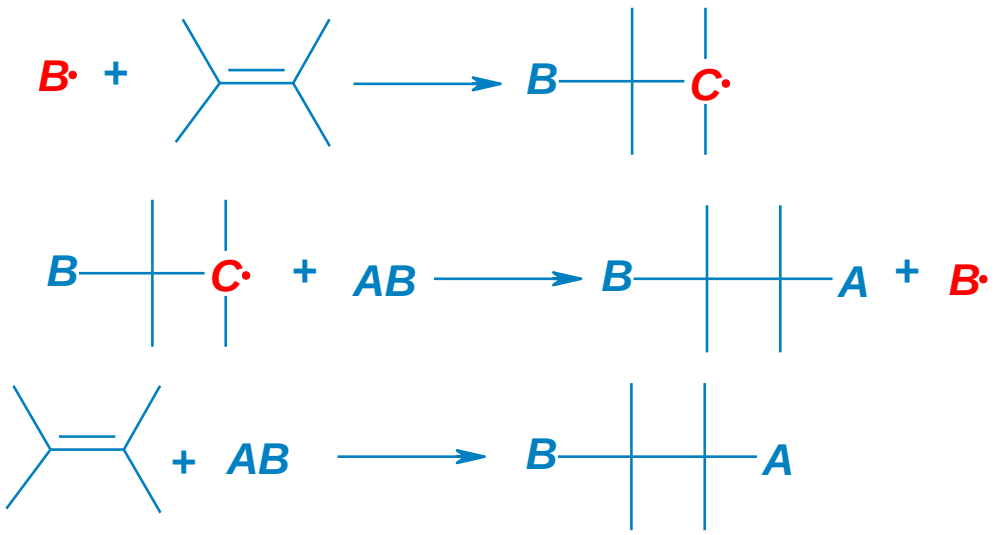








۲- واکنشهای افزایشی رادیکالی:



خود اکسایش :

خود اکسایش را میتوان به عنوان موردی خاص از افزایش رادیکالی در نظر گرفت ،به ویژه افزایش رادیکال به یک مولکول اکسیژن .

$$\phi CH(CH_3)_2 + \phi C^{\cdot}(CH_3)_2 + RH$$

$$\phi C^{\cdot}(CH_3)_2 + O_2 \longrightarrow \phi C(CH_3)_2 OO^{\cdot}$$

$$\phi C(CH_3)_2 OO^{\cdot} + \phi CH(CH_3)_2 \longrightarrow \phi C(CH_3)_2 OOH + \phi C^{\cdot}(CH_3)_2$$

$$Overall : \phi CH(CH_3)_2 + O_2 \longrightarrow \phi C(CH_3)_2 OOH$$

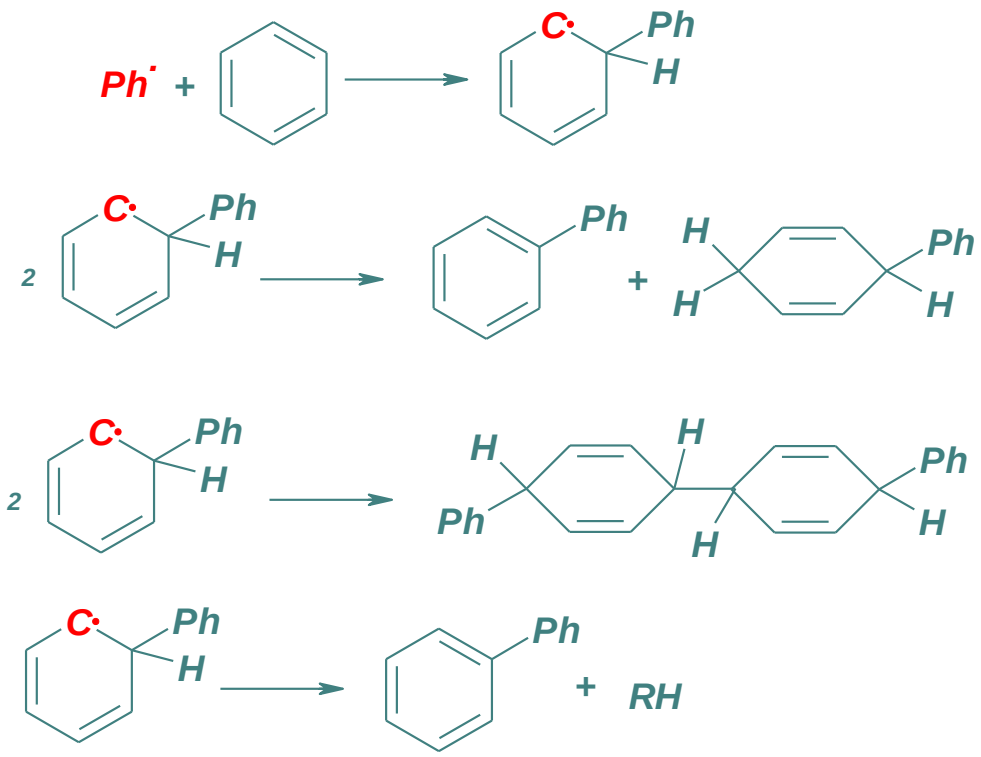
اکسایش کیومن با هوا :

$$\phi C(CH_3)_2OOH \xrightarrow{H^+} \phi C(CH_3)_2OOH_2^+ \xrightarrow{-H_2O} +C(CH_3)_2O\phi$$

$$+C(CH_3)_2O\phi \xrightarrow{H_2O} OHC(CH_3)_2O\phi \longrightarrow O=C(CH_3)_2 + HO\phi$$

آریل دار شدن :

افزایش به حلقه آروماتیک نوعی دیگر از واکنشهای ممکن رادیکال آزاد است فنیل دار شدن توسط رادیکالهای فنیل بهترین روش سنتزی برای ایجاد بی آریل می باشد .



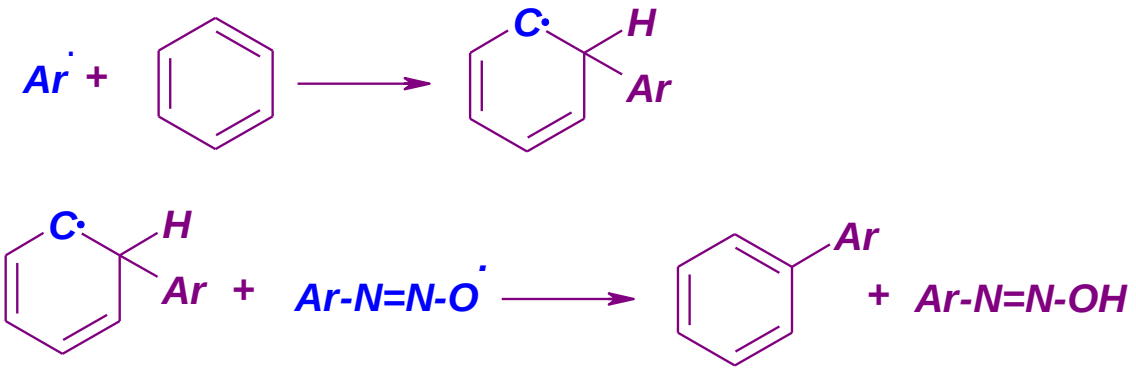
واکنش گومبرک :

$$ArN_2^+ + OH^- \longrightarrow ArN = N - OH$$

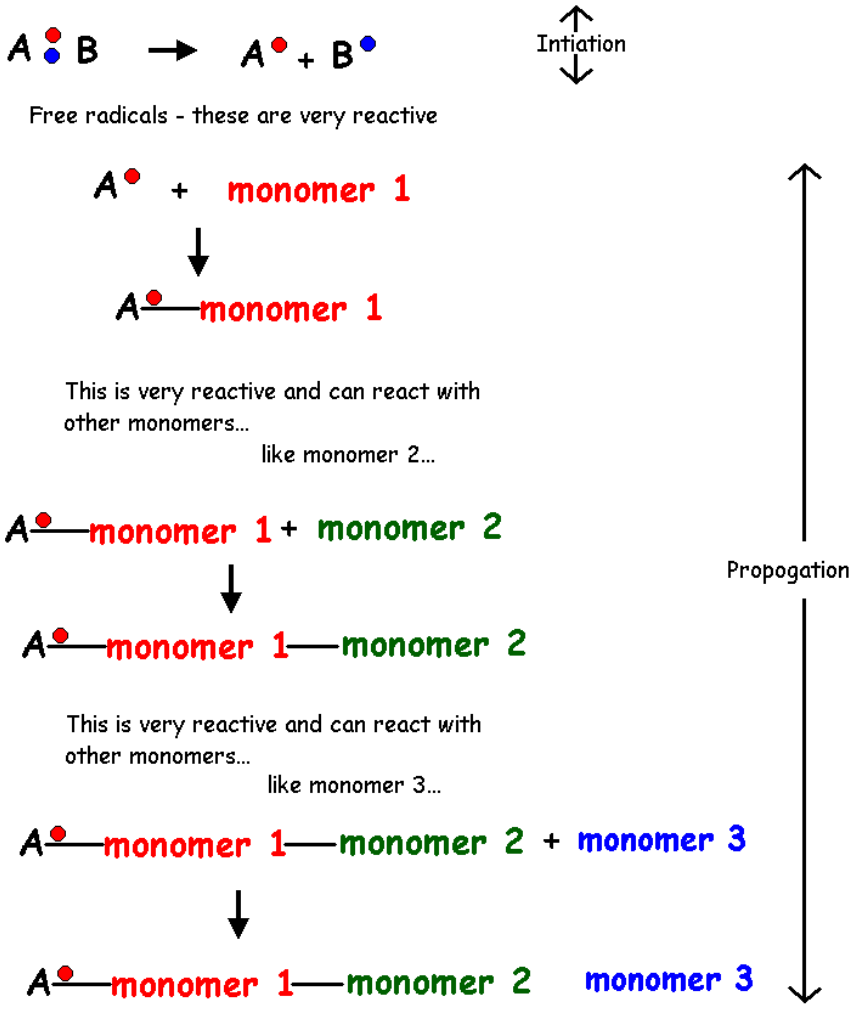
$$ArN = N - OH + OH^- \Leftrightarrow ArN = N - O^- + H_2O$$

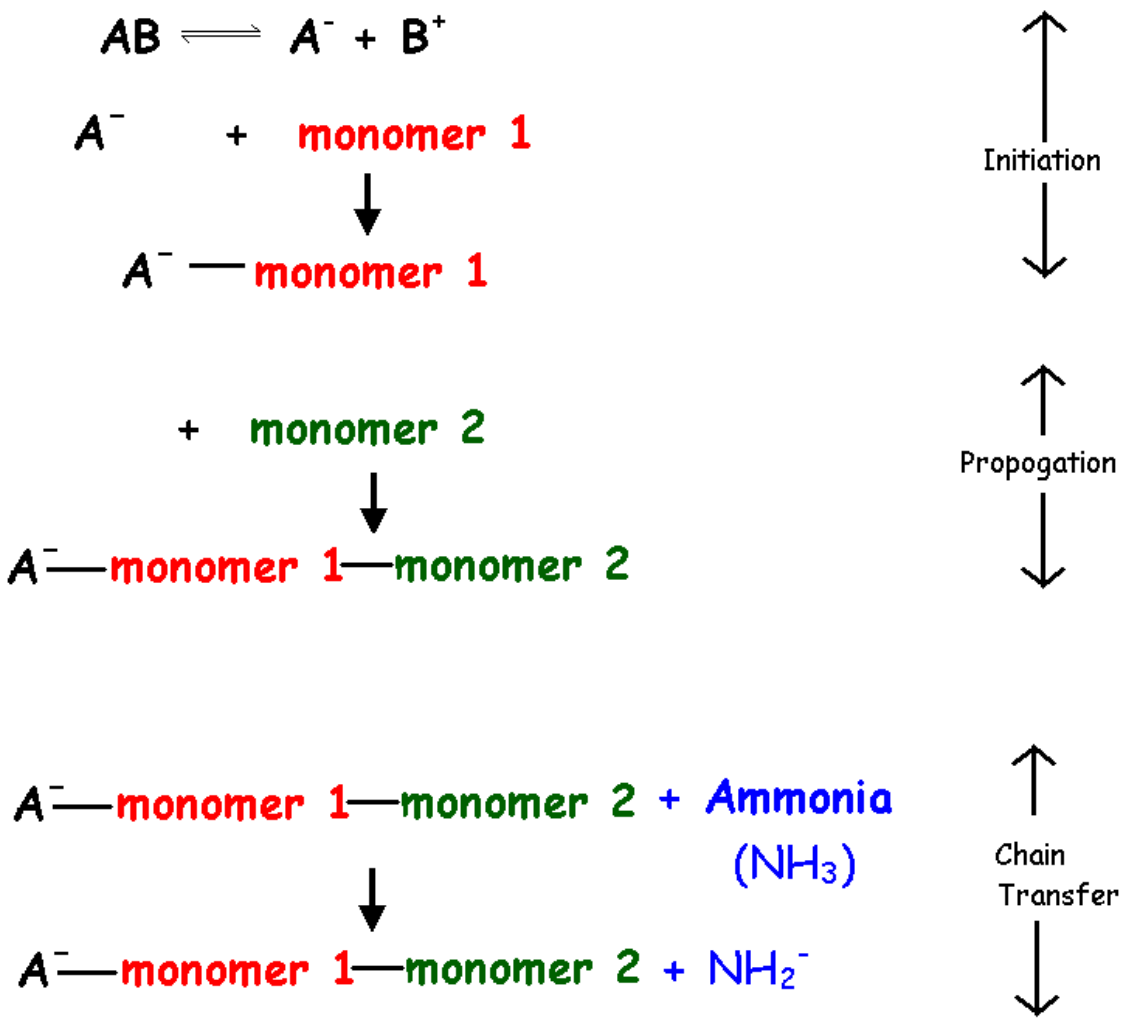
$$ArN = N - O^- + ArN_2^+ \longrightarrow ArN = N - O - N = NAr$$

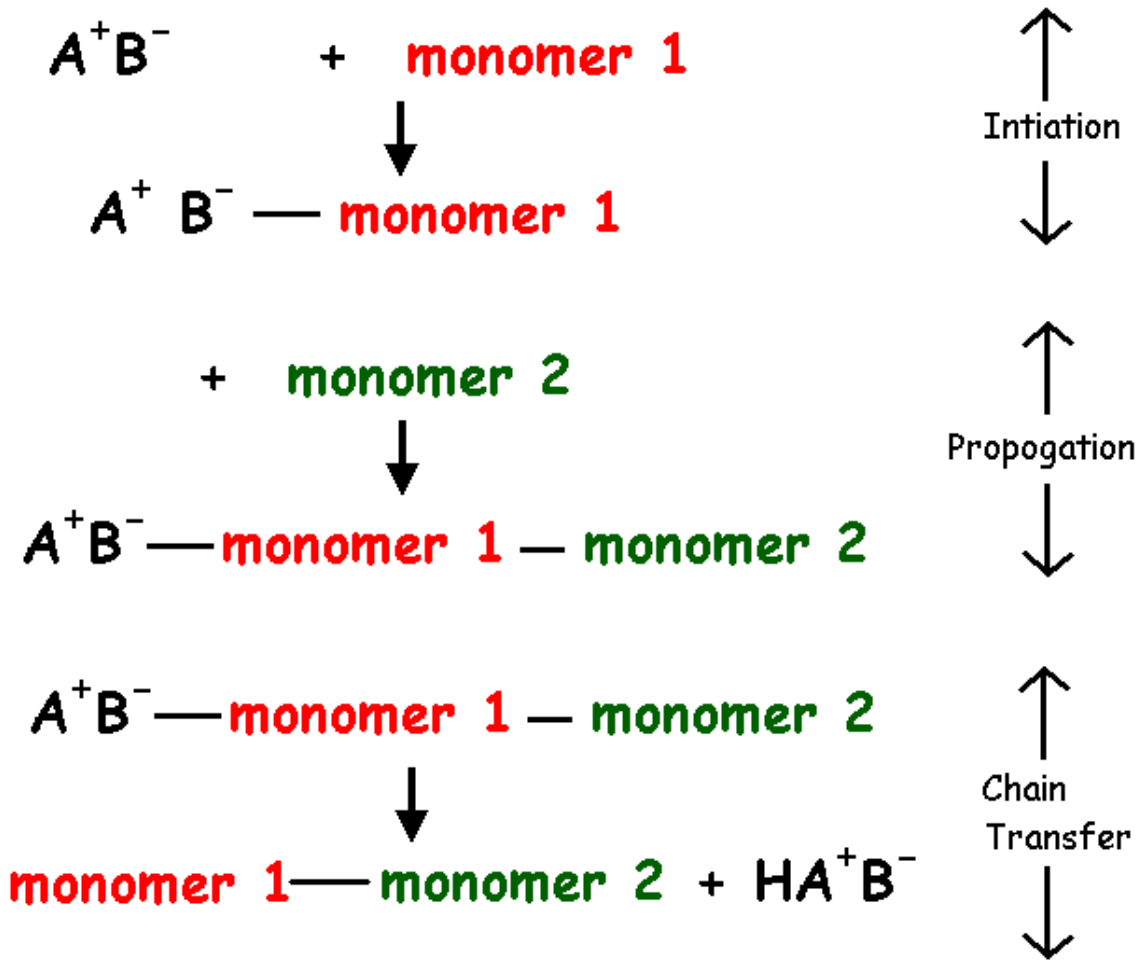
$$ArN = N - O - N = NAr \longrightarrow Ar^{\cdot} + N_2 + ArN = N - O^{\cdot}$$



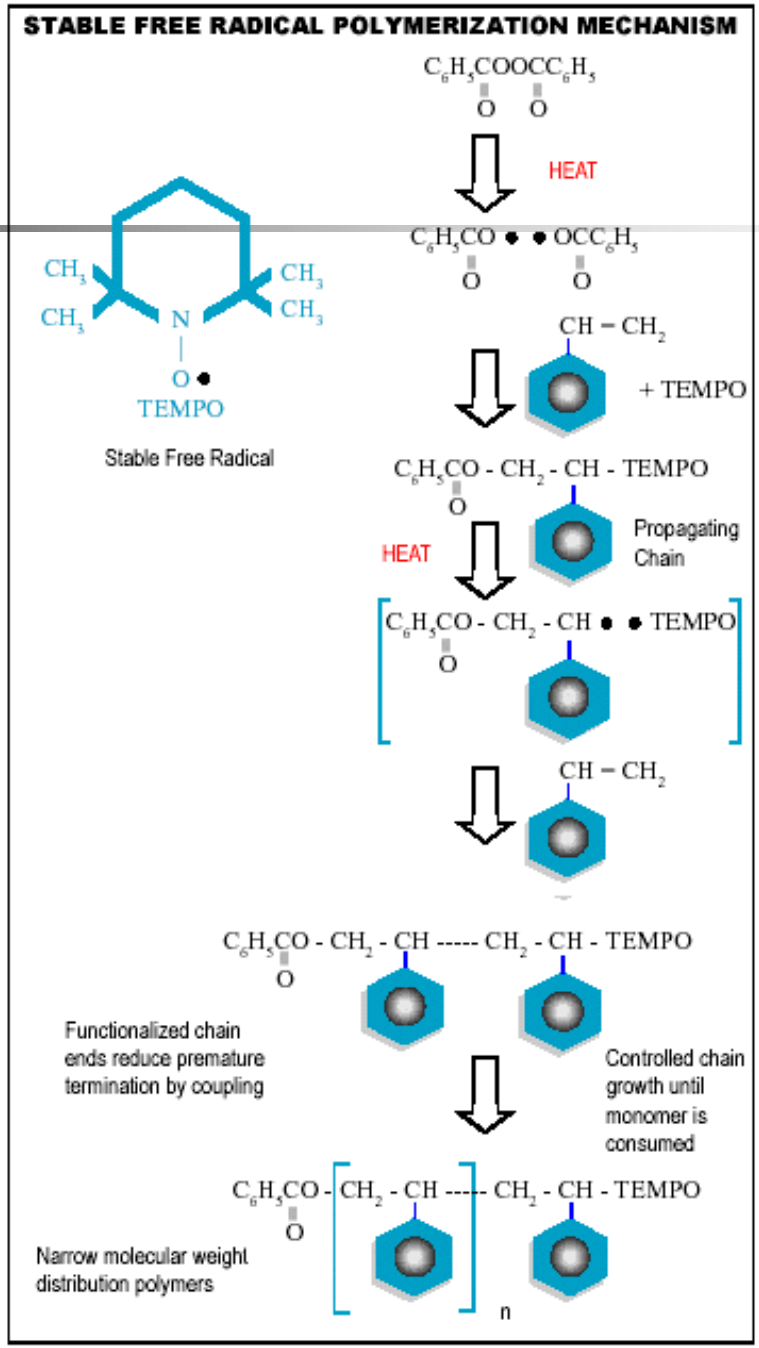
پلیمری شدن رادیکالی :




AB ⇌ A⁻ + B⁺
A⁻ + monomer 1
A⁻ — monomer 1
Initiation
+ monomer 2
A⁻—monomer 1—monomer 2
Propogation
A⁻—monomer 1—monomer 2 + Ammonia
(NH3)
A⁻—monomer 1—monomer 2 + NH2⁻
Chain
Transfer

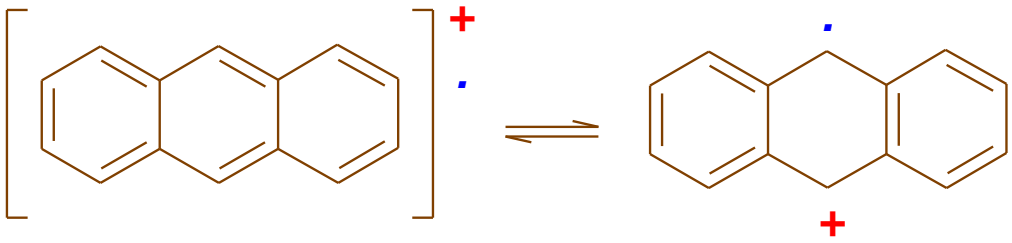

A+B−
+ monomer 1
A+ B− — monomer 1
Intiation
+ monomer 2
A+B− — monomer 1 — monomer 2
Propogation
A+B− — monomer 1 — monomer 2
monomer 1 — monomer 2 + HA+B−
Chain
Transfer

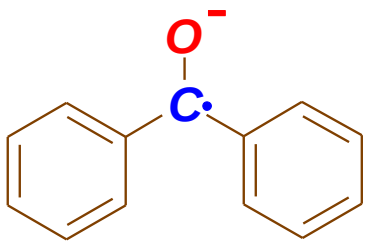
مثال :

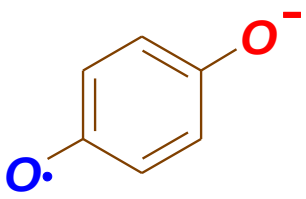

STABLE FREE RADICAL POLYMERIZATION MECHANISM
HEAT
TEMPO
Stable Free Radical
+ TEMPO
Propagating Chain
HEAT
Functionalized chain ends reduce premature termination by coupling
Controlled chain growth until monomer is consumed
Narrow molecular weight distribution polymers
n

یون رادیکالها:

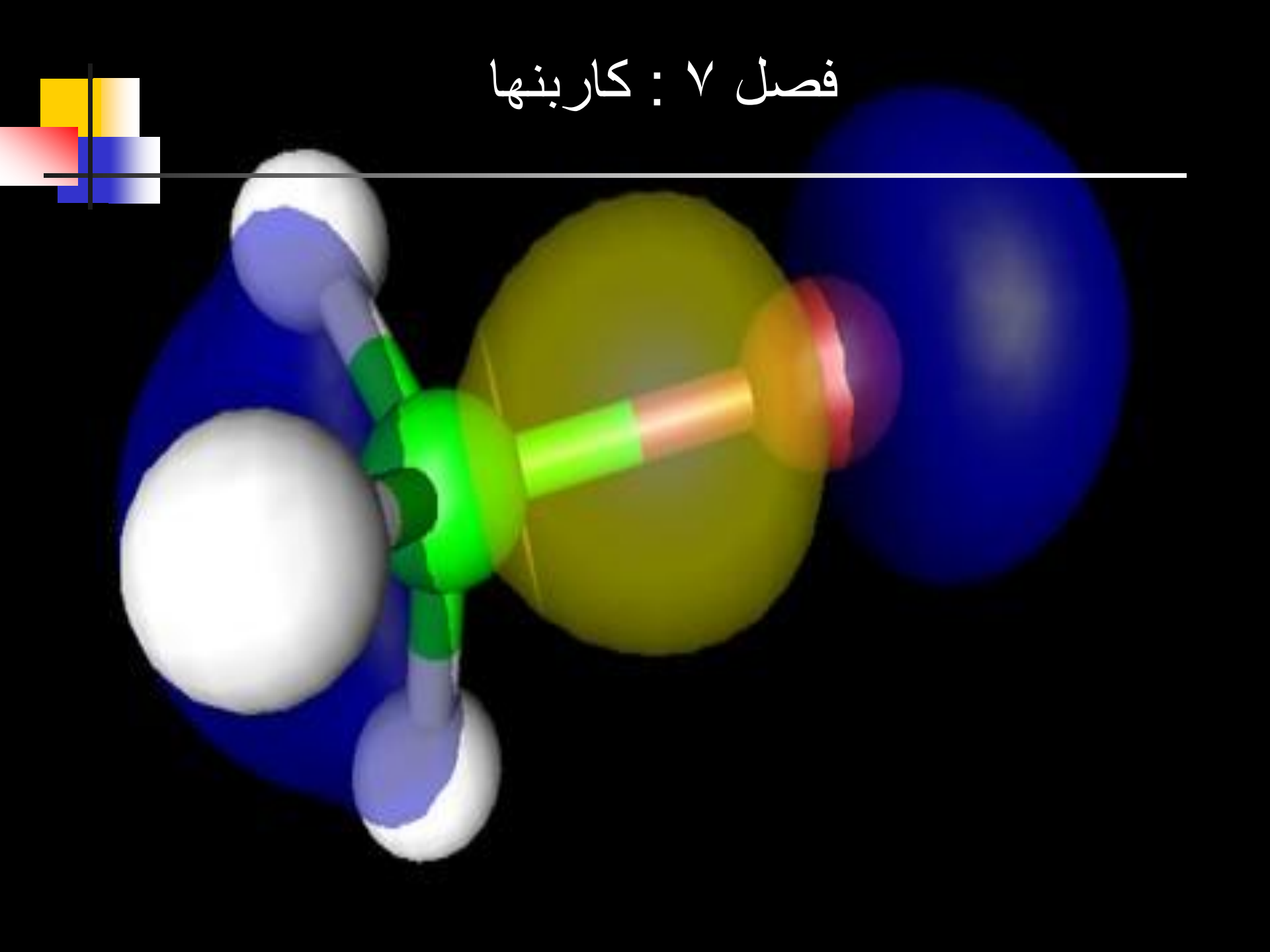
یون رادیکالها جزو واسطه های مهم در شیمی آلی هستندکه حاوی یک الکترون جفت نشده وهمچنین حامل یک بار مثبت یا منفی می باشند .







فصل ۷ : کاربنها



هدفهای کلی :

کاربن ها به عنوان ترکیباتی که دارای اتم کربن دوظرفیتی می باشند شناخته شده اند ودر این فصل دانشجویان عزیز با مطالعه کاربن ها به تمایز فرم یکتایی وسه تایی پی برده و همچنین واکنشهای آنها اعم از تولید و نوآرایی و... را فرا خواهند گرفت .

Carbenes

کاربن :

کاربن ترکیبی است که دارای کربن دو ظرفیتی می باشد. چنین کربنی دارای شش الکترون ظرفیتی می باشد که چهار تای آن در دو پیوند کووالانسی شرکت دارند و دوتای دیگر به صورت الکترونهای غیر پیوندی می باشد .

States of Carbenes and ساختمان کاربن ها :

- **Singlet state: carbocation-like in nature, trigonal planar geometry, electrophilic character**

متیلن یکتایی :

متیلین سه تایی :

- **Triplet state: diradical-like in nature, linear geometry**

واکنشهای تهیه کاربن :

a) $R_2C{=}\overset{+}{N}{=}\overset{-}{\underset{\cdot\cdot}{N}}\cdot \xrightarrow[\text{or}\ \Delta]{h\nu} R-\overset{\cdot\cdot}{C}-R + N_2\uparrow$ (singlet)

b) $R_2C{=}C{=}O \xrightarrow[\text{or}\ \Delta]{h\nu} R-\overset{\cdot\cdot}{C}-R + CO\uparrow$ (singlet)

c) $RCHX_2 + \text{base} \longrightarrow R-\overset{\cdot\cdot}{C}X_2^{-} \xrightarrow{-X^-} R-\overset{\cdot\cdot}{C}-X$

d) $RCHX_2 + R'Li \xrightarrow{-R'X} R-\underset{X}{\overset{H}{C}}-Li \longrightarrow R-\overset{\cdot\cdot}{C}-H + LiX$
(where X = I & Br) (carbenoid)

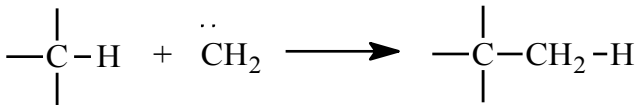
e) $RCHX_2 + R'Li \xrightarrow{-R'H} R-\underset{X}{\overset{X}{C}}-Li \longrightarrow R-\overset{\cdot\cdot}{C}-X + LiX$
(where X = F & Cl) (carbenoid)

f) $CH_2I_2 \xrightarrow[\text{ether}]{Zn\text{-}Cu} I-CH_2\cdot Zn-I$ (Simmons-Smith reagent)

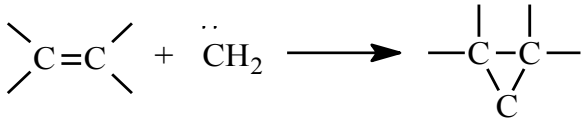
a carbenoid species that reacts stereospecifically with alkenes to give cyclopropanes but does not insert into alkane C-H bonds

انواع واکنشهای کاربن ها :

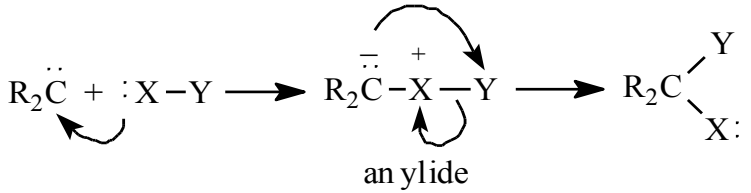
a) Insertion into a σ-bond:



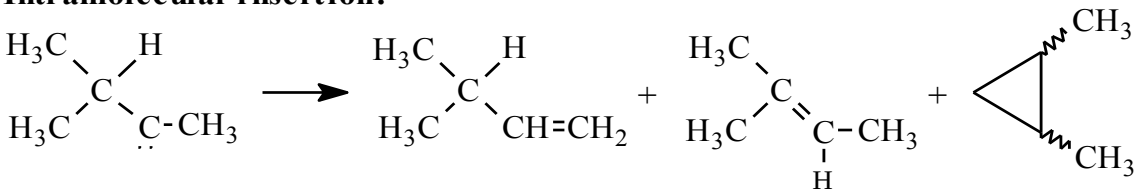
b) Addition to a π-bond:



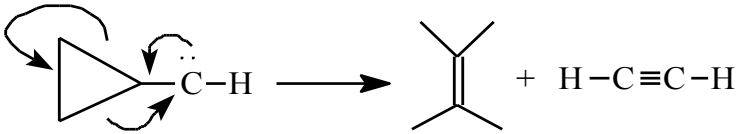
c) Ylide type rxn:



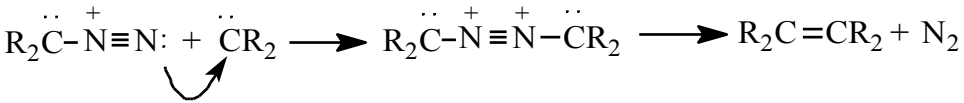
d) Intramolecular insertion:



e) Cracking:



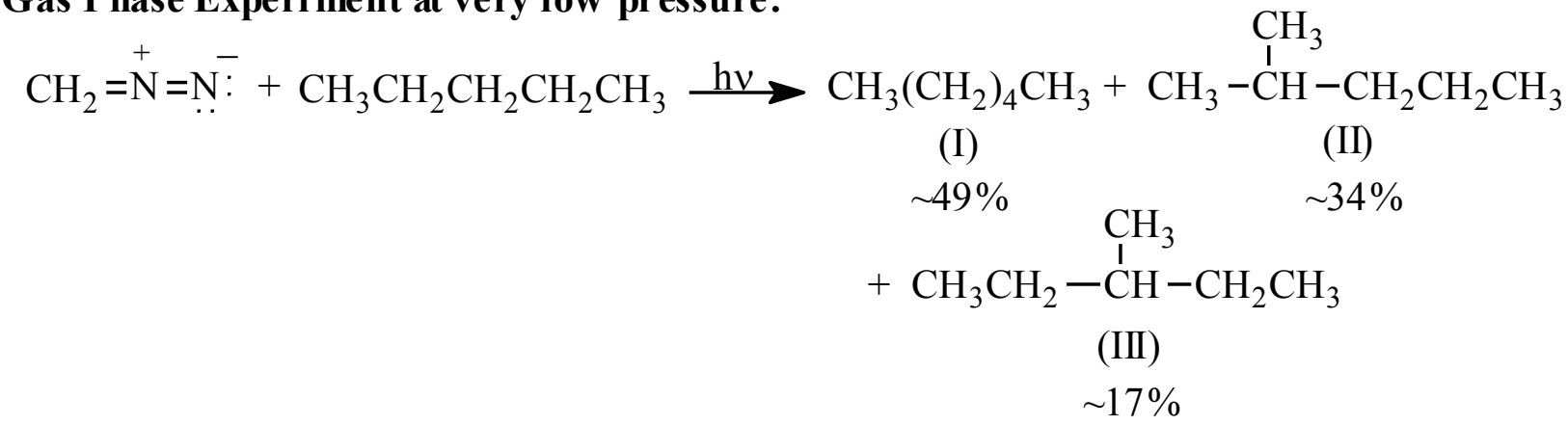
f) Dimerization:



Mechanistic Aspects of Carbene Chemistry

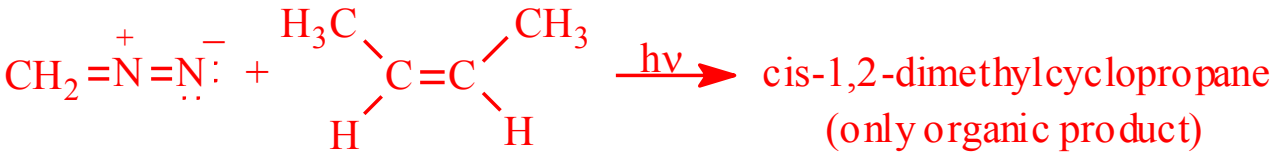
مشاهدات :

A. Gas Phase Experiment at very low pressure:



Point of Information: As the pressure of the system is increased (nitrogen or argon added), the yields of (II) and (III) increase at the expense of (I).

B. Liquid phase experiment :



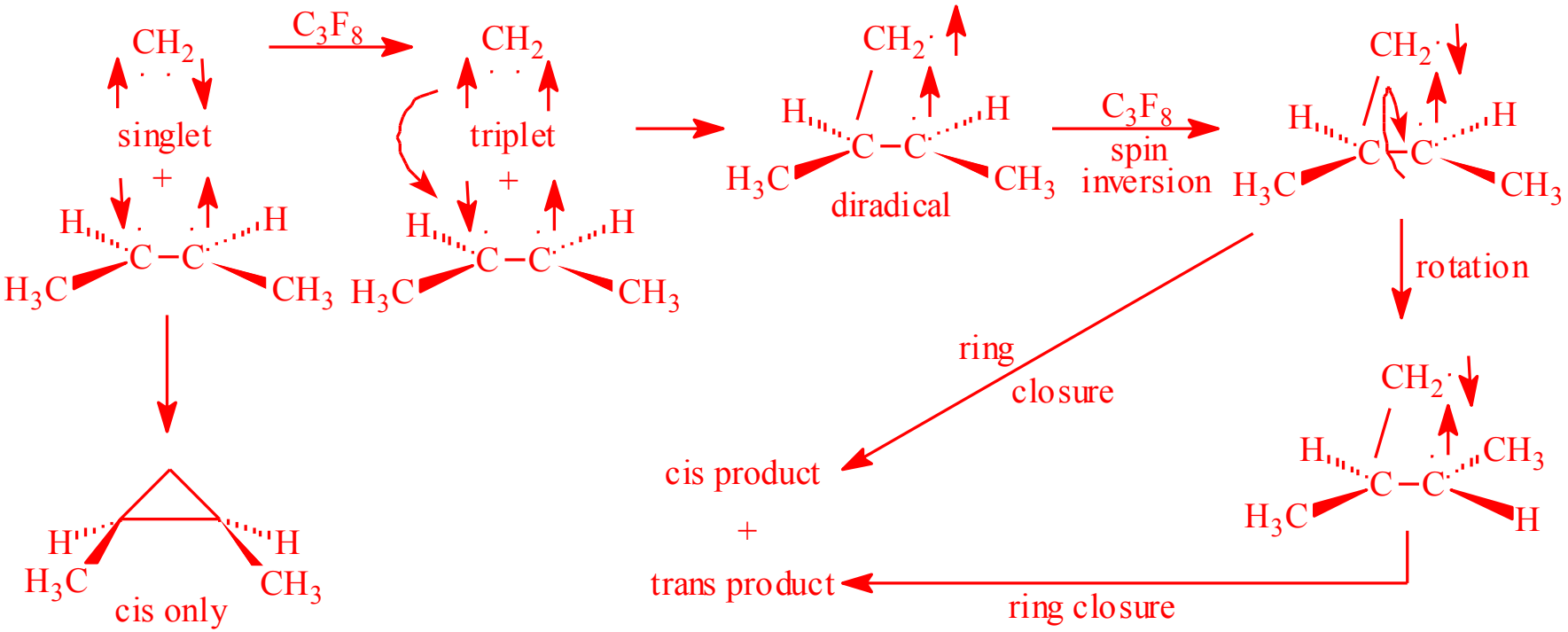
Point of Information: When an inert diluent such as perfluoropropane is added to the starting materials, a mixture of cis- and trans-1,2-dimethylcyclopropanes is obtained.

شیمی فضایی واکنش های کاربن :

Explanation for Gas Phase Experiment:

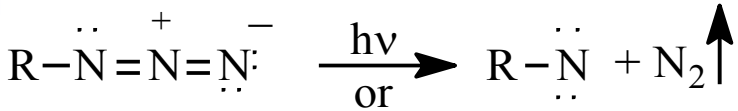
At very low pressure, reactive, singlet carbene inserts in the alkane C-H bonds in a completely random, statistical manner. However, upon addition of nitrogen or argon gas to the reaction, singlet carbene reverts to less reactive (more selective) triplet carbene via non-productive collisions with the inert diluent. Triplet carbene shows a preference for attacking tertiary and secondary hydrogen atoms rather than primary hydrogen atoms. Hence, formation of more tertiary and secondary abstraction products at the expense of primary abstraction product.

Explanation for Liquid Phase Experiment:



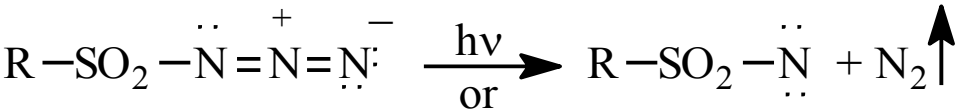
واسطه های شبه کاربنی :

a)



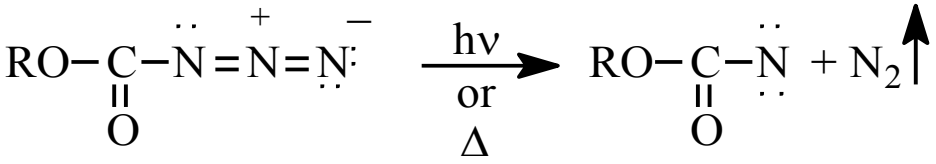
R = alkyl,aryl, H

b)



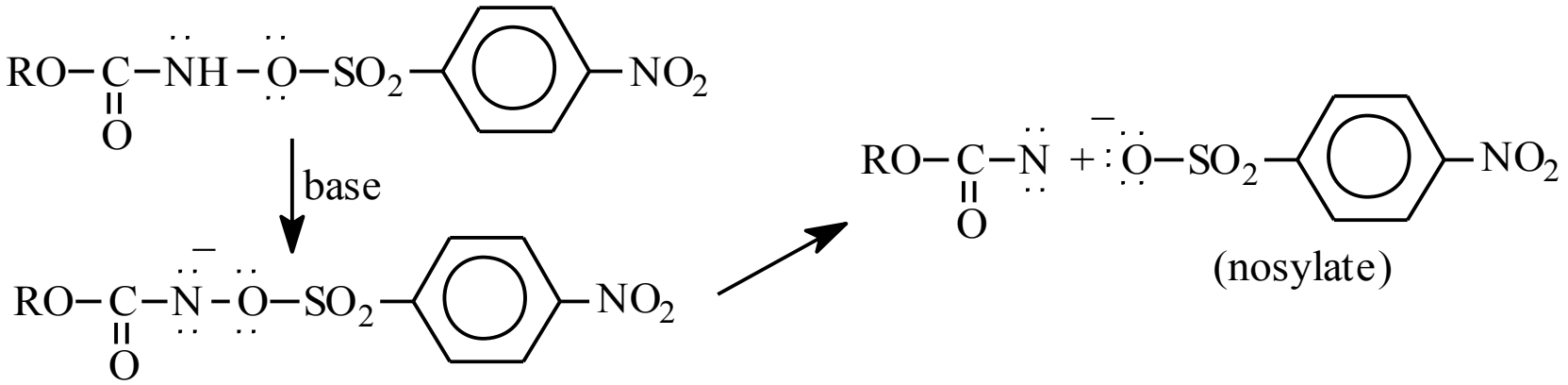
R = alkyl, aryl

c)

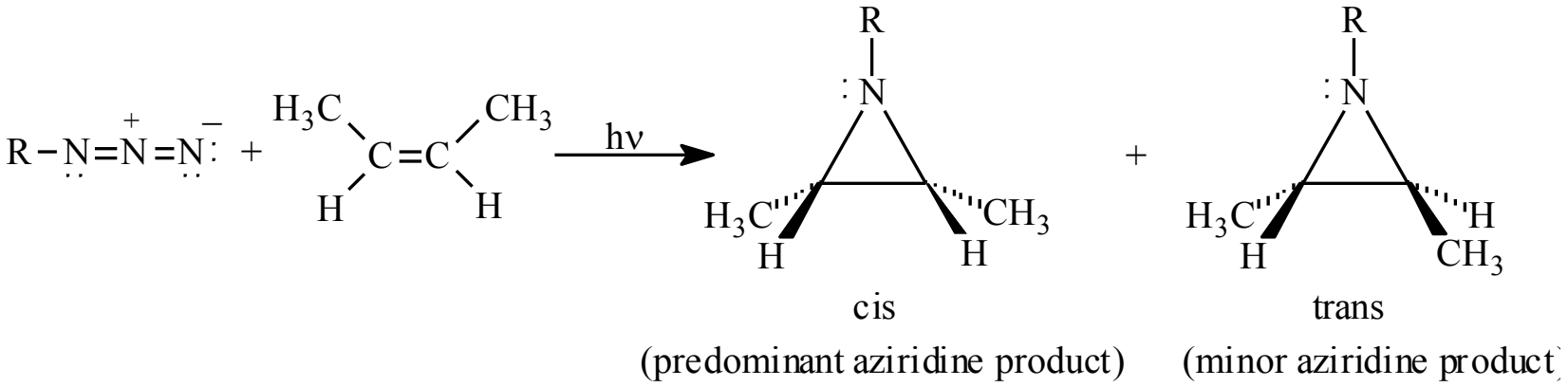


R = alkyl, aryl

d)



Liquid phase experiment

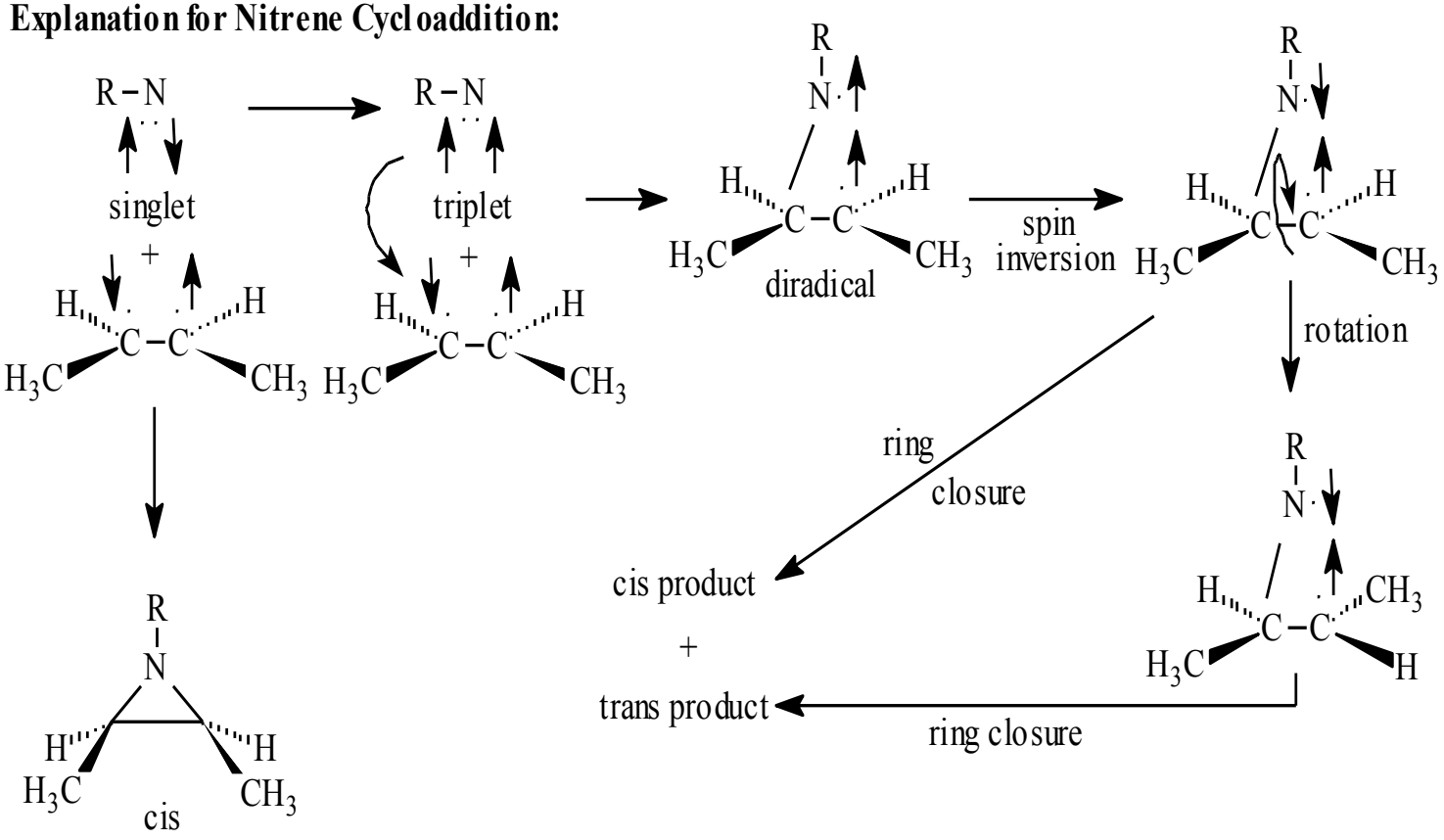


cis (predominant aziridine product)

trans (minor aziridine product)

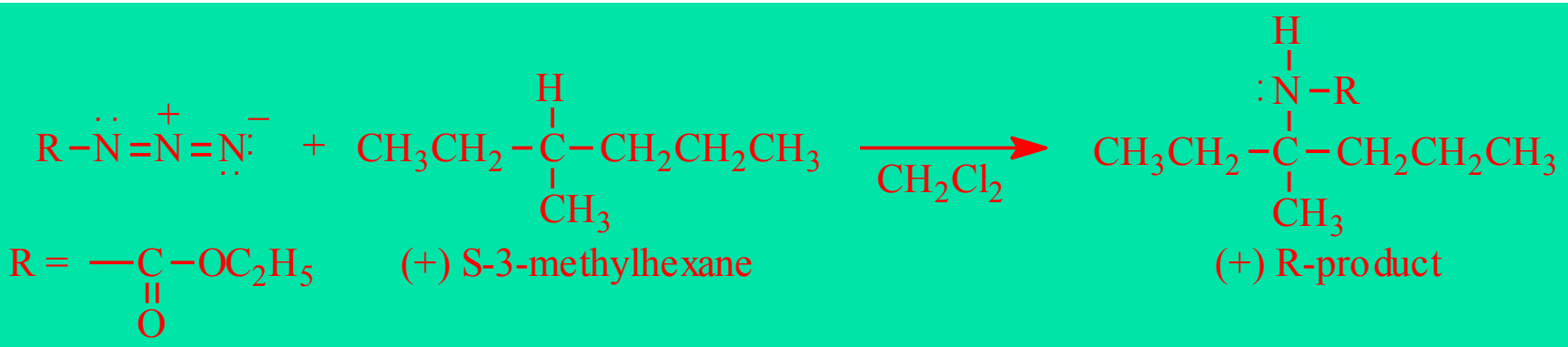
Point of Information: When an inert solvent is added to the reaction mixture, more trans-product is obtained at the expense of the cis-product.

Explanation for Nitrene Cycloaddition:

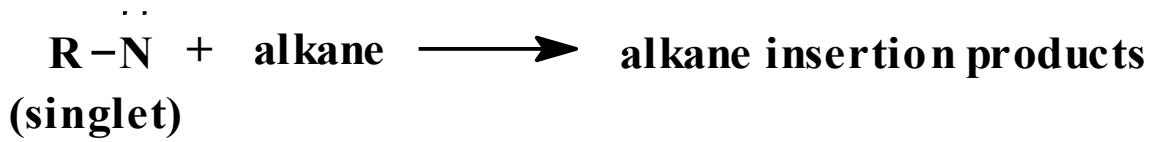


Insertion - Observations

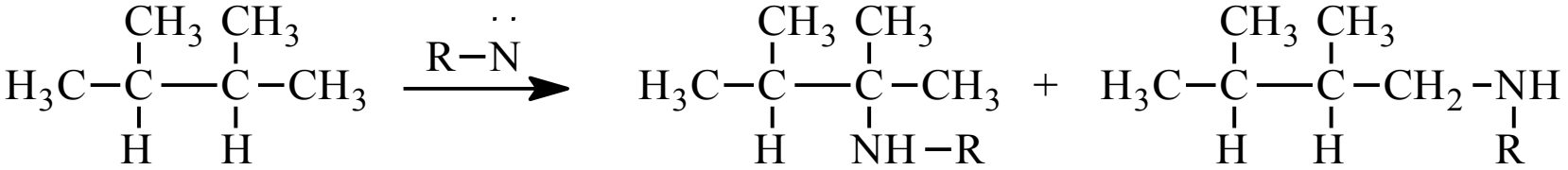
شواهد داخل شدن :



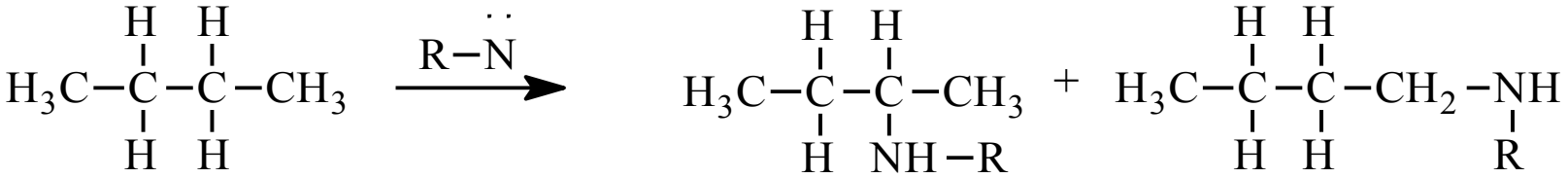
Method of Generation	Conc. of Alkane	Obs. rot. of prod.	Retention of Config
$R-N_3 \xrightarrow{\Delta}$	100%	$+1.69^{o}$	99%
$R-N_3 \xrightarrow{h\nu}$	1.2%	$+1.71^{o}$	100%
$R-N_3 \xrightarrow{h\nu}$	26.8%	$+1.69^{o}$	99%
$R-N_3 \xrightarrow{h\nu}$	100%	$+1.68^{o}$	98%



Alkane **Relative reactivities**



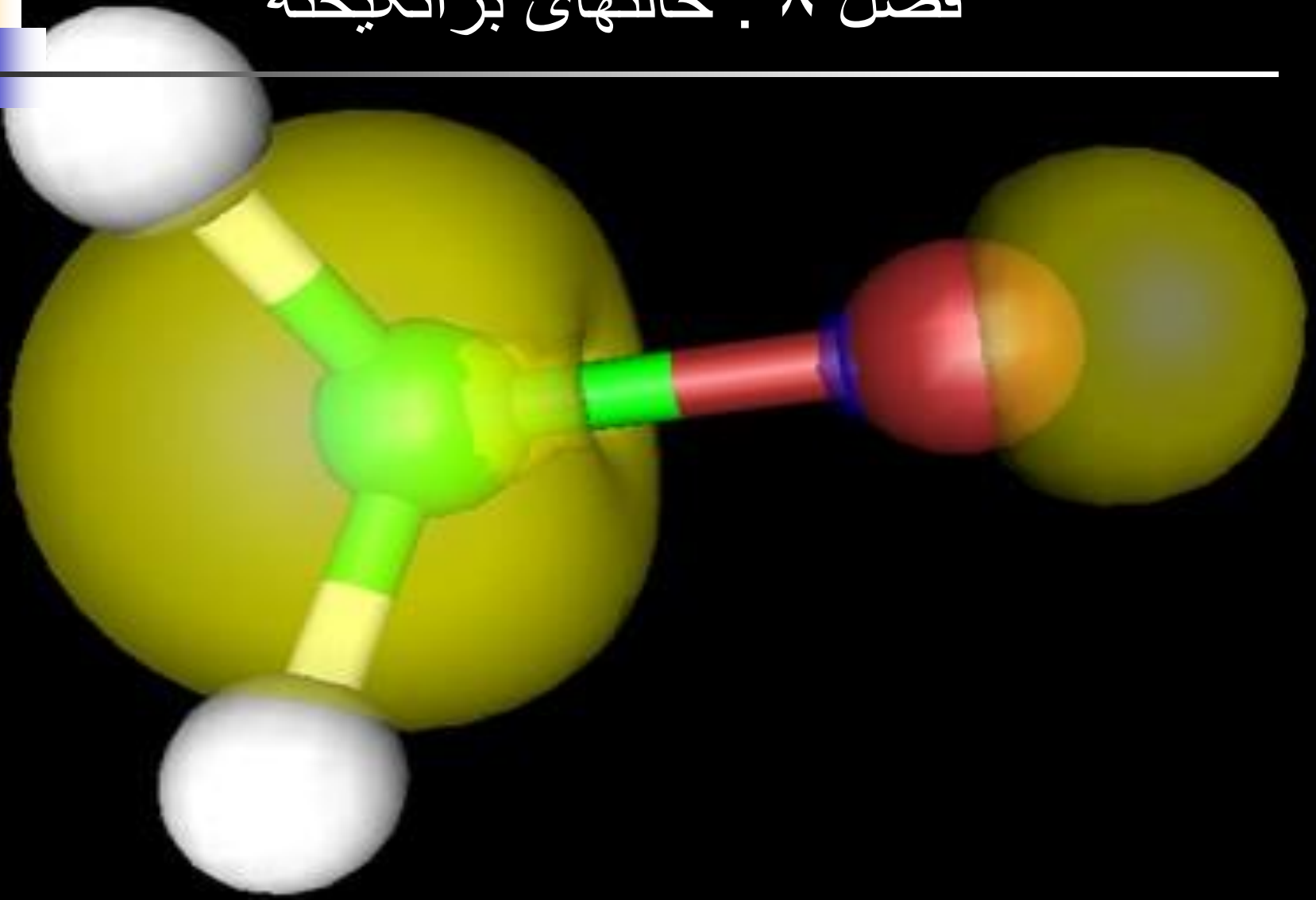
67.0 : 1.0



9.0 : 1.0

Singlet nitrene C-H insertion selectivity: tertiary C-H > secondary C-H > primary C-H

فصل ۸ : حالتهای برانگیخته



هدفهای کلی :

فوتوشیمی ،شیمی حالتهای برانگیخته الکترونی مولکولها می باشد.در این فصل دانشجویان با مفاهیم انتقالهای الکترونی (مجاز یا غیر مجاز) همچنین ایجاد حالتهای برانگیخته و واکنشهای نوری دی انها و عوامل کربونیل دار آشنا میشوند .

طیف های جذبی الکترونی :

$$C = \lambda \nu$$

$$E = h\lambda$$

وقتی فوتون توسط یک مولکول جذب می شود که انرژی فوتون دقیقا برای برانگیختن مولکول از حالت موجود به حالت بالاتر باشد .

$$\Delta E = E_f - E_i = h\nu$$

توانایی یک ماده ذر جذب نوری با طول موج معین توسط ضریب خاموشی سنجیده می شود (قانون بیر).

$$log(\frac{I_0}{I}) = A = \varepsilon Cl$$

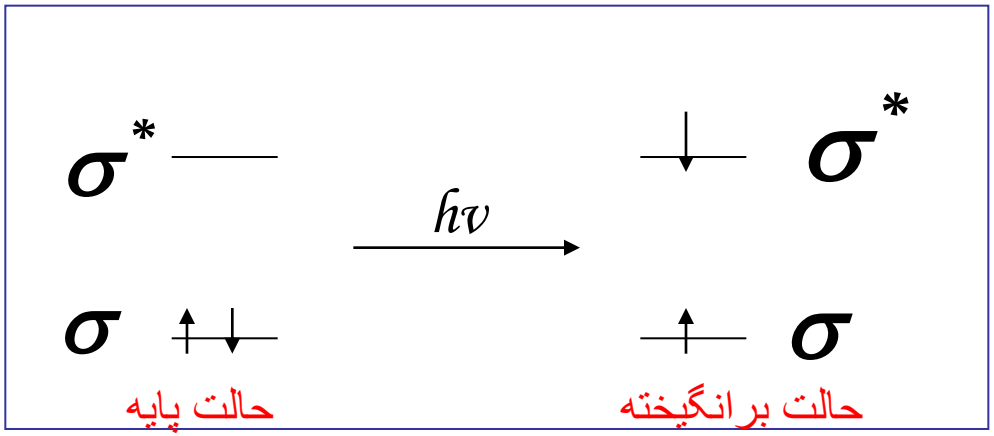
قانون هم ارزی فوتوشیمیایی انشتین :

۱- فقط نوری که جذب می شود در ایجاد تغییر فوتوشیمیایی موثر است .

۲- هر فوتون جذب شده فقط یک مولکول را در اولین مرحله برانگیختگی فعال می سازد .

انتقالهای اوربیتالی :

انتقالات $\sigma \longrightarrow \sigma^*$



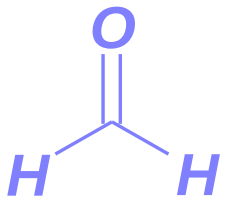
$$CH_3CH_3 \xrightarrow{147\,nm} H_2 + CH_3CH :$$

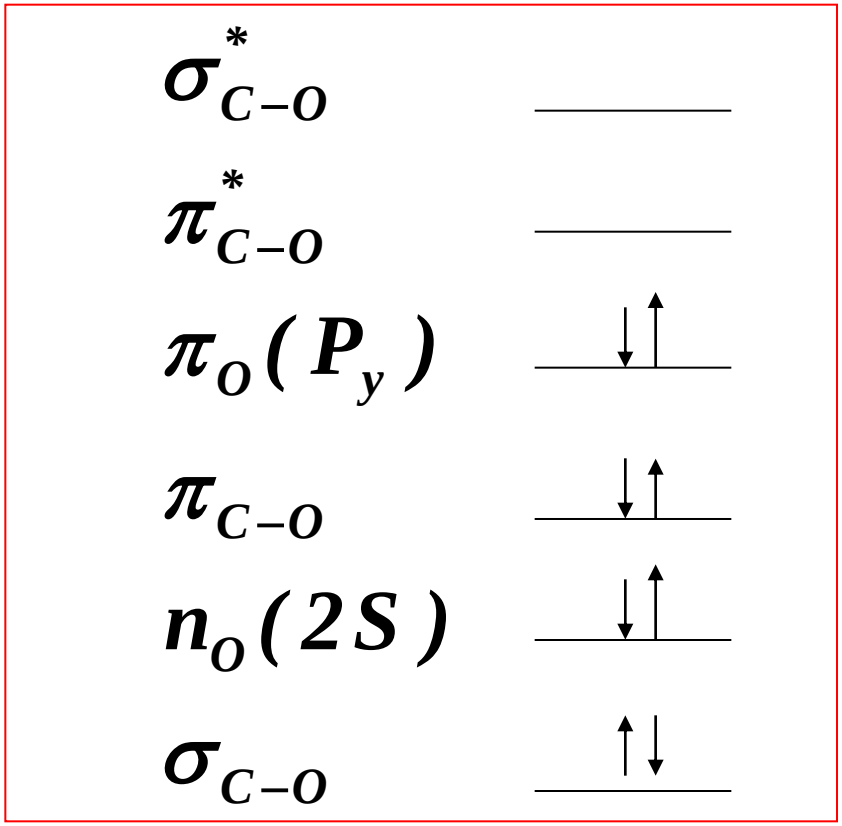
انتقالات $\pi \longrightarrow \pi^*$

با افزایش مزدوج سیستم پای ، فاصله انرژی بین بالاترین اوربیتال مولکولی اشغال نشده وپایین ترین اوربیتال مولکولی اشغال نشده به تدریج کاهش می یابد و هرچه مولکول بزرگتر باشد طول موج بزرگتری را جذب می کند .

انتقالات $n \longrightarrow \pi^*$

در برخی از مولکولهایی که هتروواتم دارند این انتقالات در آنها مشاهده میگردد.بنابراین انتقالات با پایین ترین انرژی مربوط به برانگیخته شدن یک الکترون غیر پیوندی به پایین ترین اوربیتال ضد پیوندی به صورت انتقال نامبرده انجام میشود .





ایجاد حالتهای برانگیخته به روش شیمیایی :

برانگیختگی شیمیایی دو مولکول اغلب در ترکیب مجدد یونهای با بار مخالف رخ میدهد .

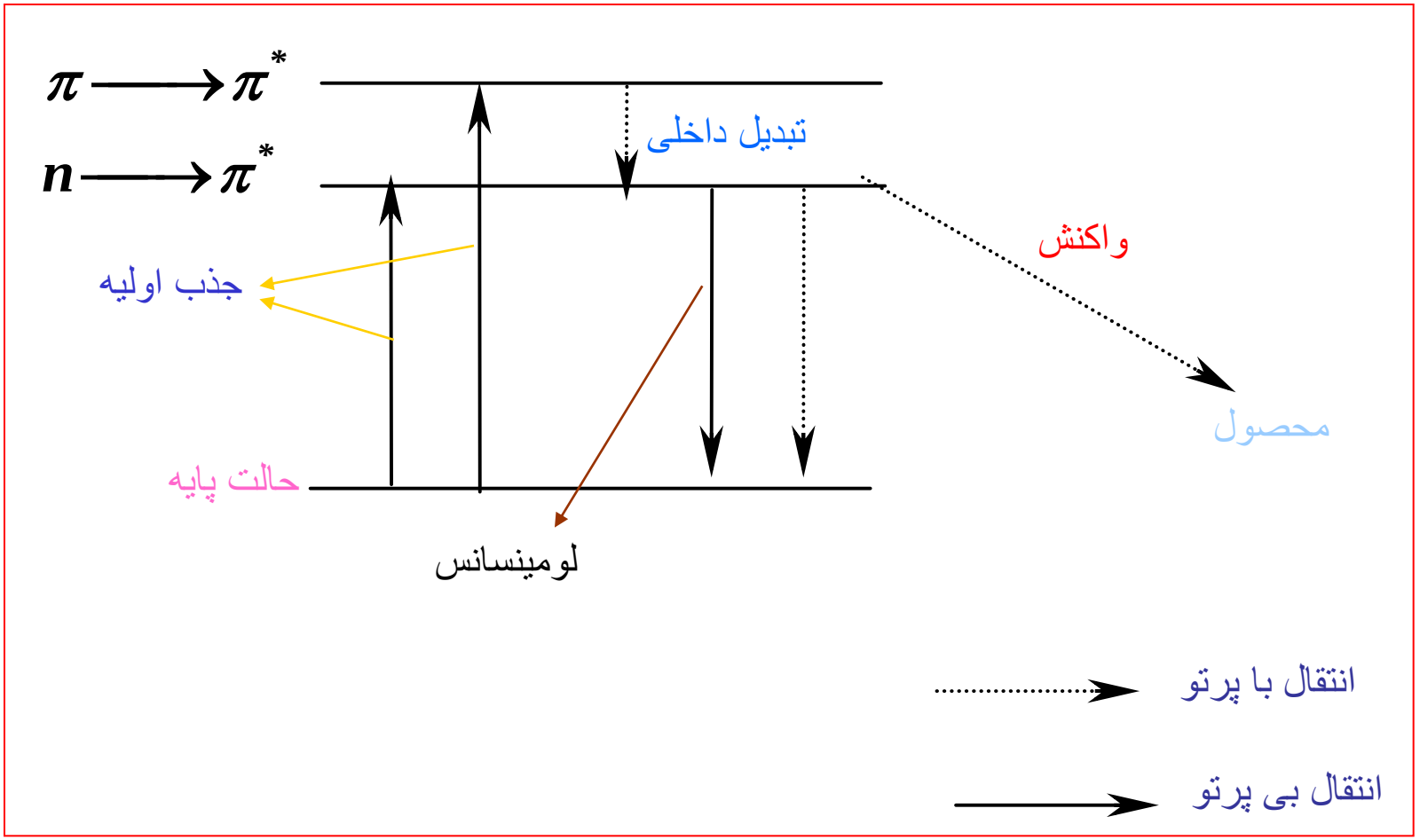
اکسایش: $A \xrightarrow{-e^-} A^+$

کاهش: $A \xrightarrow{+e^-} A^-$

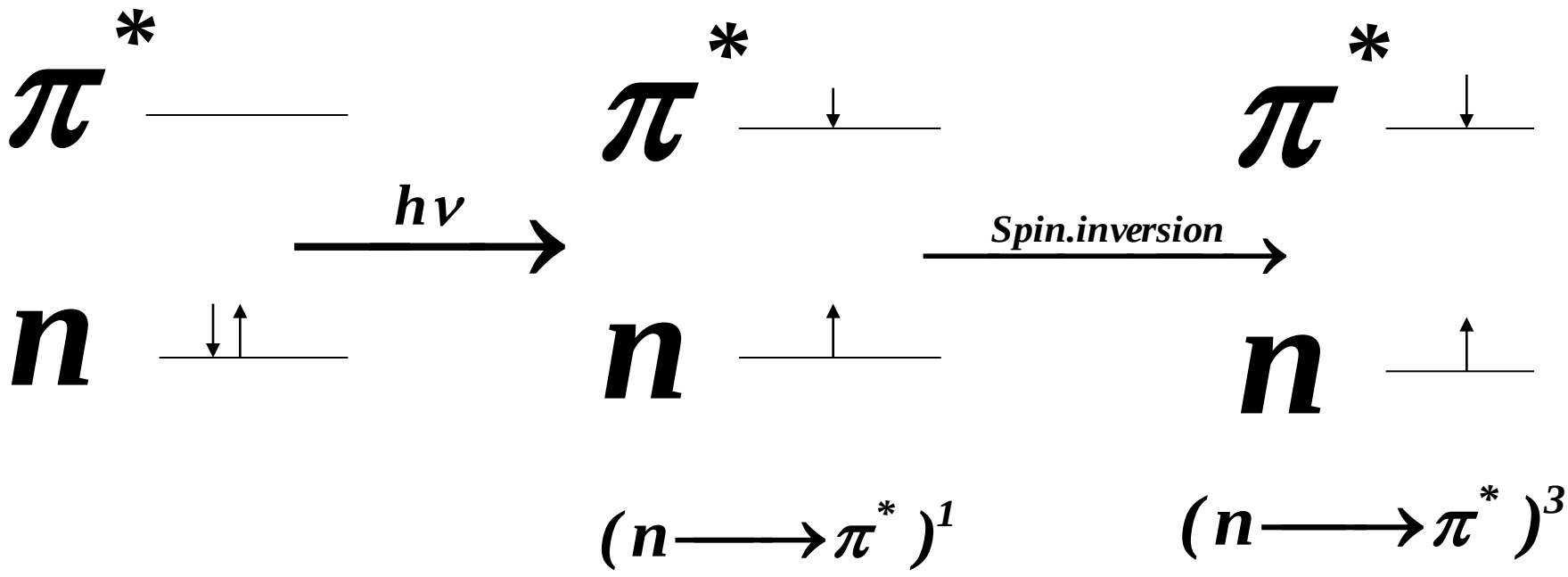
خنثی شدن: $A^+ + A^- \longrightarrow A + A^*$

انواع حالتهای برانگیخته وتبدیل آنها به یکدیگر :

فرایندهای مقدماتی فوتوفیزیکی :



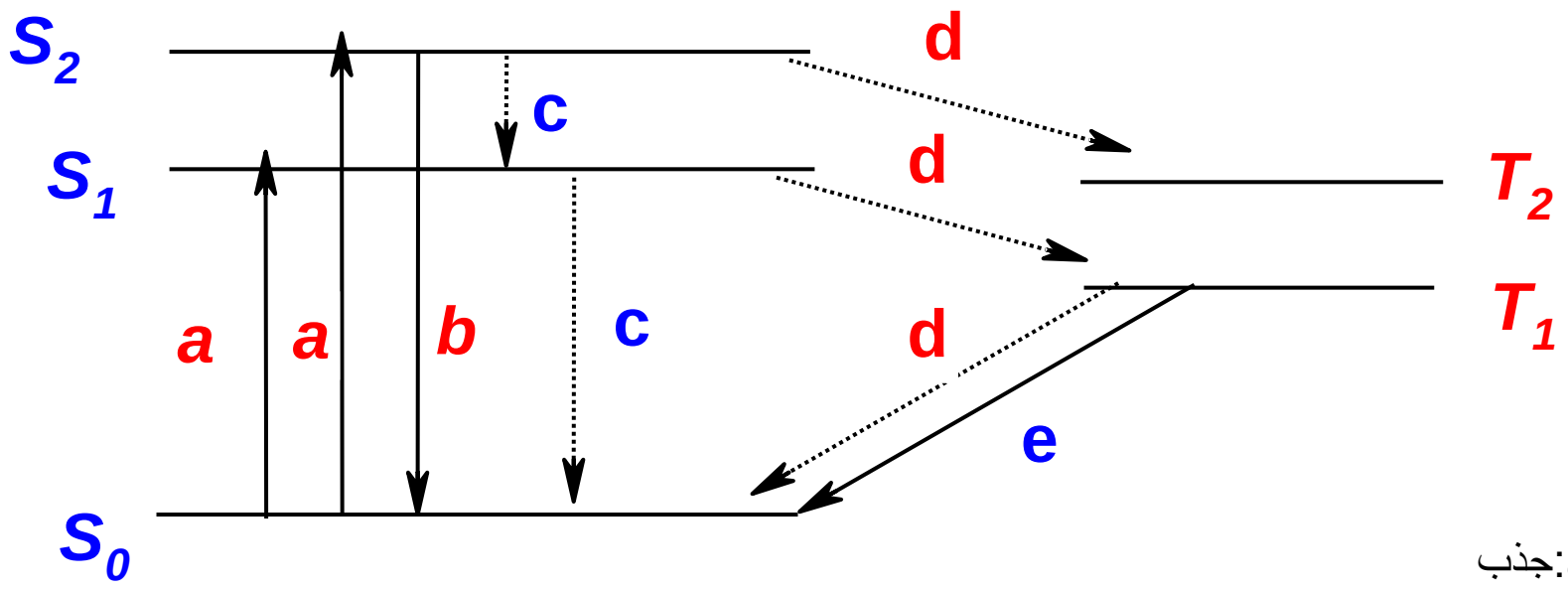
حالت های سه تایی :



یکی از مهمترین خواص حالت سه تایی ، انرژی کمتر آن از حالت یکتایی است

گذر بین سیستمی : *Intersystem crossing*

هر گذری از حالت یکتایی به سه تایی را گذر بین سیستمی گویند که اساسا یک فرآیند ممنوع است .



نمودار جابلونسکی

a:جذب
b:فلورسانس
c:تبدیل داخلی
d:گذربین سیستمی
e:فسفرسانس

بهره کوانتومی :

$$\phi = \frac{\text{تعداد مولکولهایی که متحمل یک فرآیند خاص شوند}}{\text{تعداد فوتونهای جذب شده}}$$

$$\phi_j^s = \frac{k_j}{\sum_s k}$$

بهره کوانتومی حالت یکتایی

$$\phi_j^T = \phi_{isc} \frac{k_j}{\sum_T k}$$

بهره کوانتومی حالت سه تایی

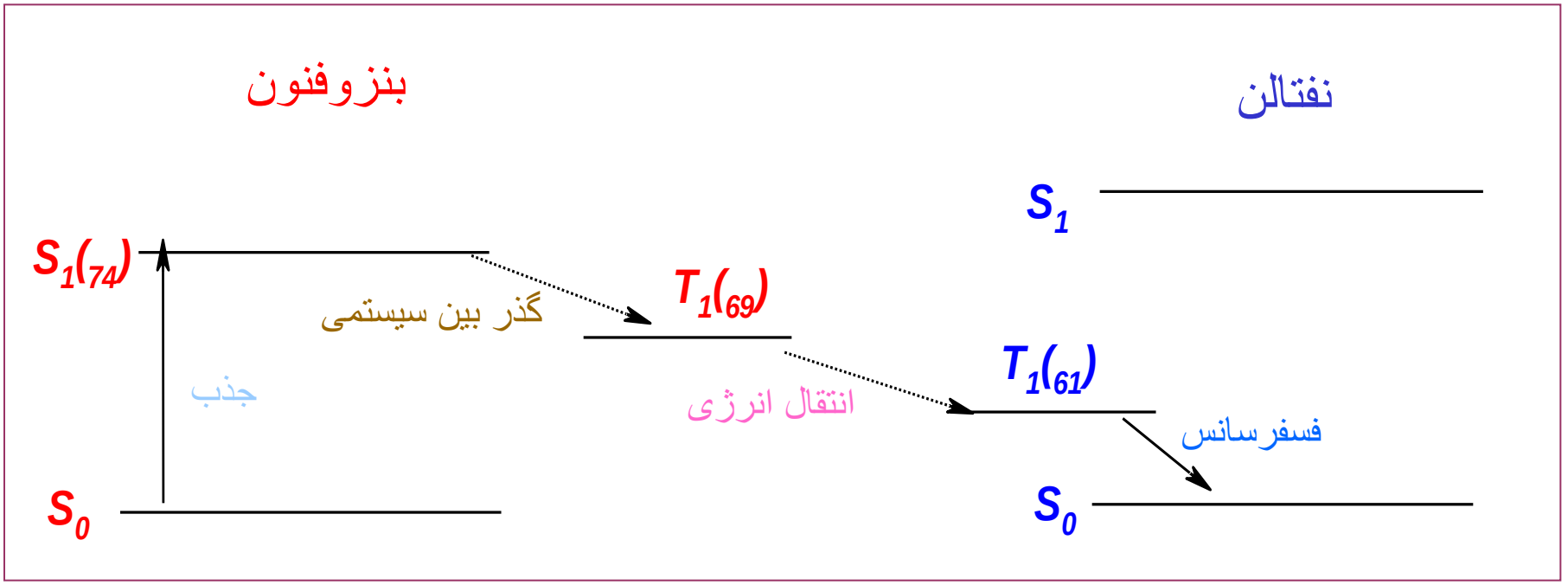
انتقال انرژی الکترونی :

انتقال انرژی الکترونی را می توان به صورت فرآیندی توصیف کرد که در آن برانگیختگی الکترونی از مولکول دهنده برانگیخته به یک مولکول گیرنده انتقال می یابد .

$$D^* + A \longrightarrow D + A^*$$

$$(\phi CO)^{*3} + C_{10}H_8 \longrightarrow \phi_2 CO + (C_{10}H_8)^{*3}$$

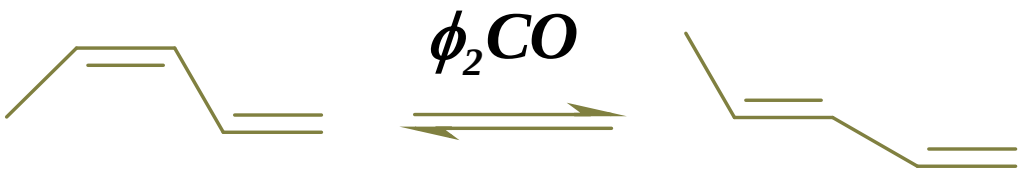
$$\Delta H = -8\,Kcal / mol$$



قاعده اسپین واینر: تا زمانی که اسپین کل سیستم (دهنده وگیرنده) پابت بماند , انتقال انرژی با یک مکانیسم مبادله الکترونی مجاز است

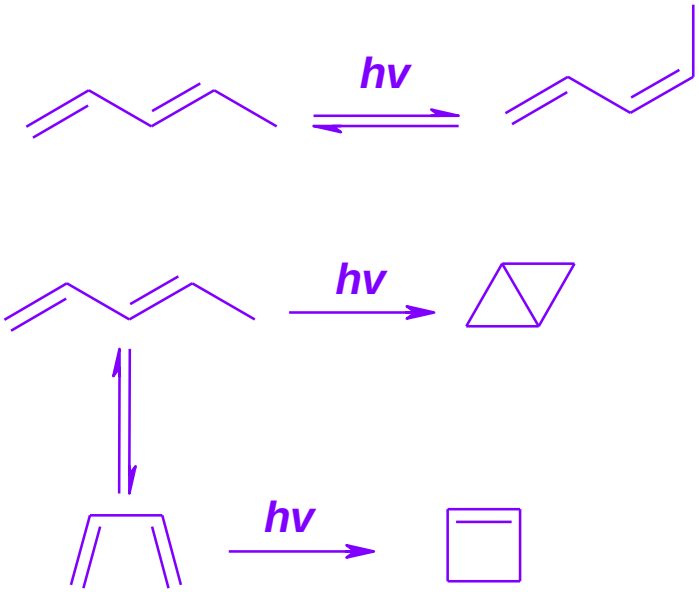
حساس شدن نوری:

ایزومری شدن سیس و ترانس در مقابل بنزوفنون :
بنزوفنون حساس کننده نوری

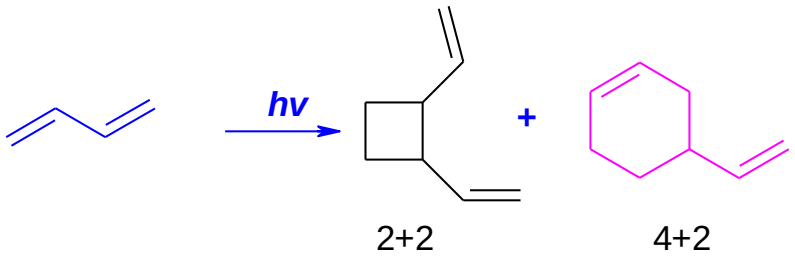


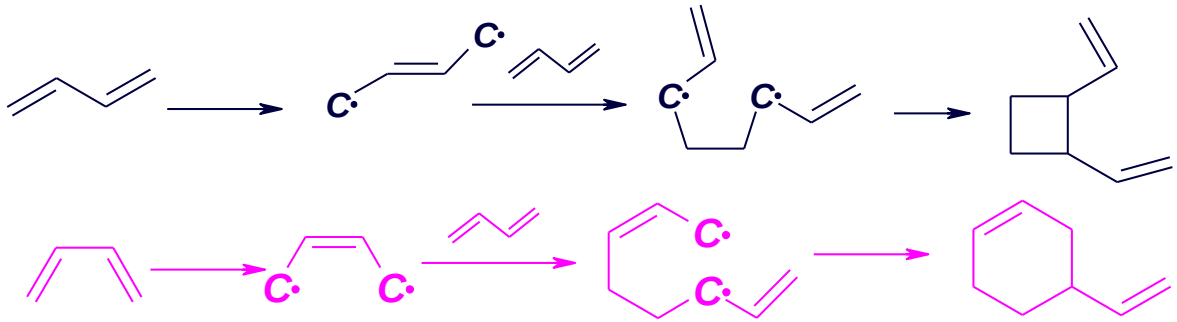
واکنشهای حالتهای برانگیخته :

۱- ایزومری شدن سیس –ترانس :



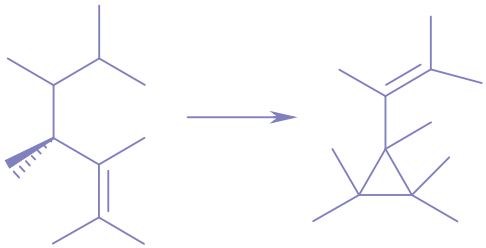
۲- دیمر شدن :

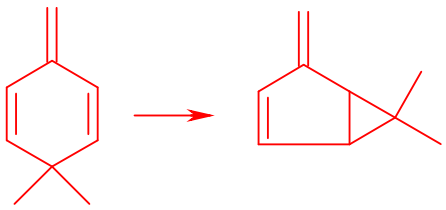


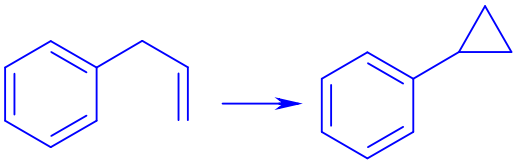


نوآرایی دی –Π– متان :

این واکنش معمولا در اثر فوتولیز مولکولهایی رخ می دهد که دارای دو پیوند پای متصل به یک کربن اشباع شده هستند.

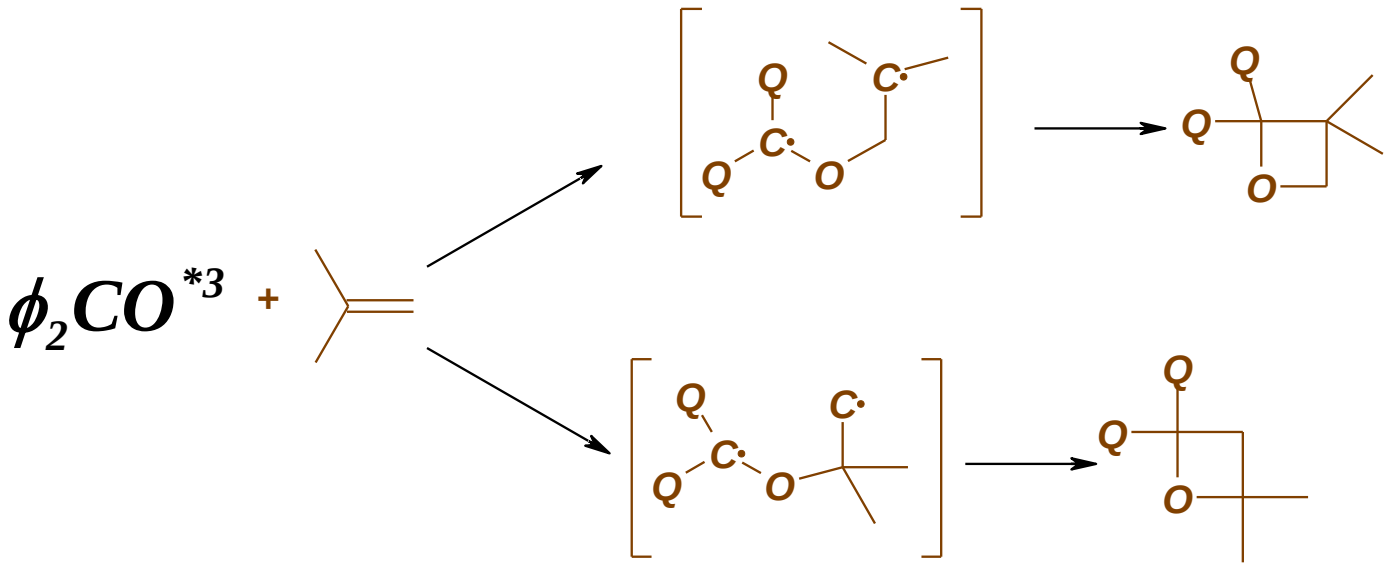






واکنشهای نوری عامل کربونیل :

تشکیل اکستان



کاهش نوری بنزوفنون :

$$2\phi_2CO \xrightarrow[(CH_3)_2CHO]{h\nu} \phi_2C(OH)-C(OH)\phi_2 + (CH_3)_2CO$$

مکانیسم:

$$2\phi_2CO \xrightarrow{h\nu} (\phi_2CO)^{*1} \longrightarrow (\phi_2CO)^{*3}$$

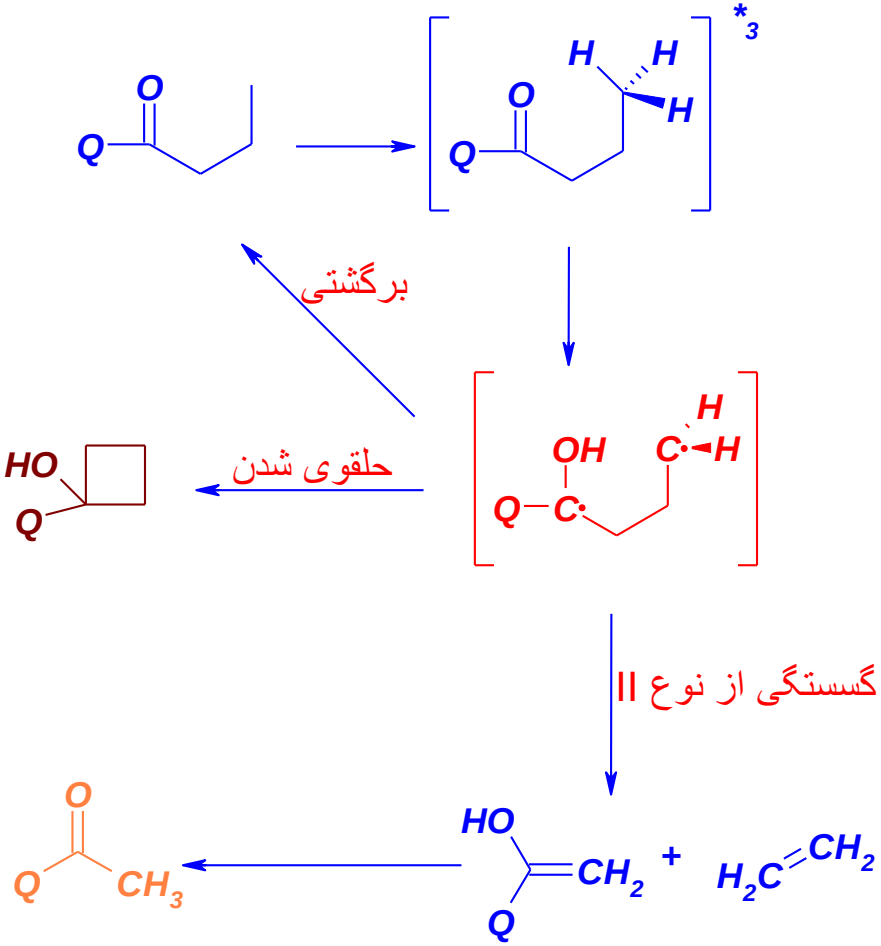
$$(\phi_2CO)^{*3} + Me_2CHOH \longrightarrow \phi_2C^{\cdot}OH + Me_2C^{\cdot}OH$$

$$Me_2C^{\cdot}OH + \phi_2CO \longrightarrow Me_2CO + \phi_2C^{\cdot}OH$$

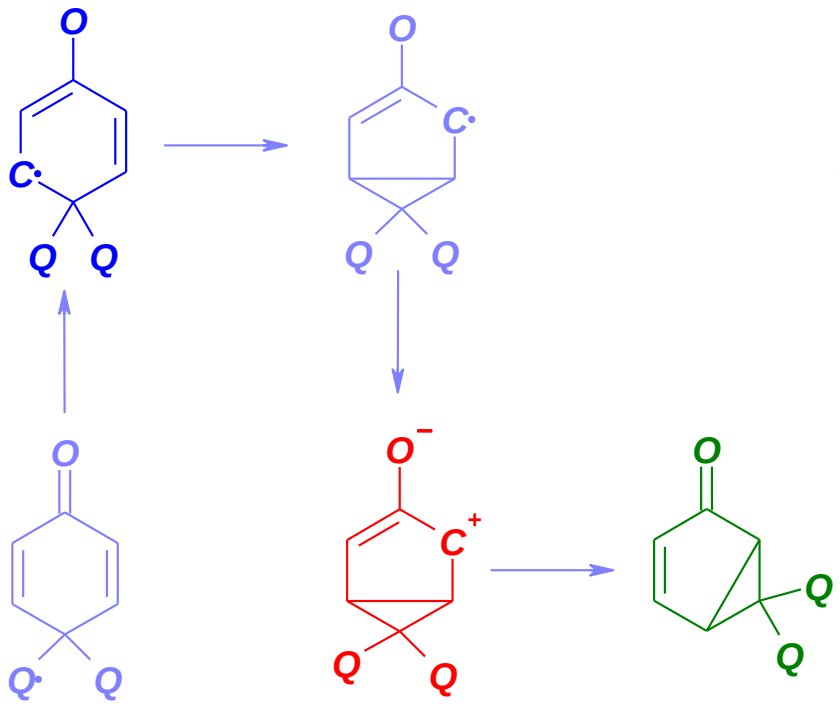
$$2\phi_2C^{\cdot}OH \longrightarrow \phi_2C(OH) - C(OH)\phi_2$$

گسستگی نوریش نوع II:

دی رادیکال ۱و۴ این نوع گسستگی را انجام میدهند .



نوآرایی نوری سیکلوهگزان دی انون :



حالت های برانگیخته سه تایی

حالت های پایه یکتایی

فوتوشیمیایی فاز بخار :

برای یک دسته از ترکیبات قطعه قطعه شدن نوری در فاز بخار به مقدار قابل ملاحظه ای تسریع میگردد.زیرا:

۱- عدم وجود قفس حلال

۲- عدم فعالسازی سریع ارتعاشی

گسستگی نوریش کتونها از نوع I:

$$CH_3COCH_3 \xrightarrow{h\nu} (CH_3COCH_3)^* \xrightarrow{Steam}$$

$$CH_3^{\cdot} + CH_3CO^{\cdot} \xrightarrow{\rangle 100} CH_3^{\cdot} + CO$$

$\phi(-CO) = 0.001$ در محلول

$\phi(-CO) = 0.1$ دربخار ۲۵درجه

$\phi(-CO) = 1$ دربخار ۱۲۰ درجه

اکسیژن مولکول یکتایی :

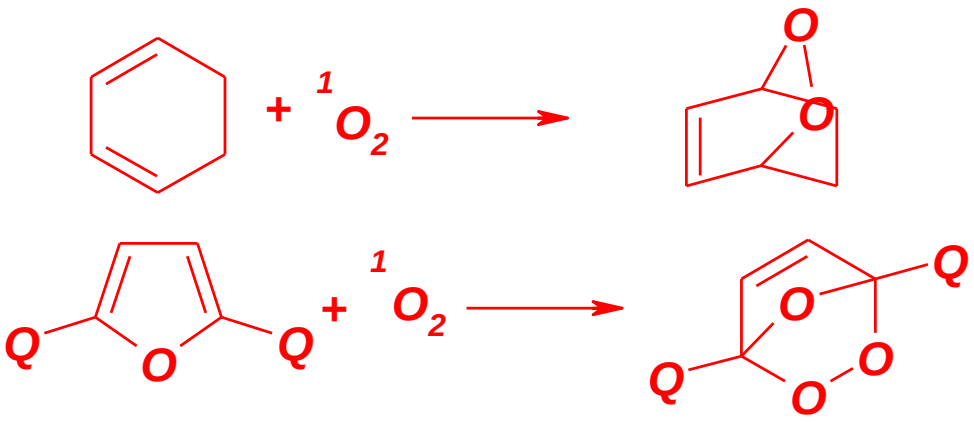
روشهای تهیه :

$$H_2O_2 + Cl_2 + 2OH^- \longrightarrow 2Cl^- + 2H_2O + {}^1O_2$$

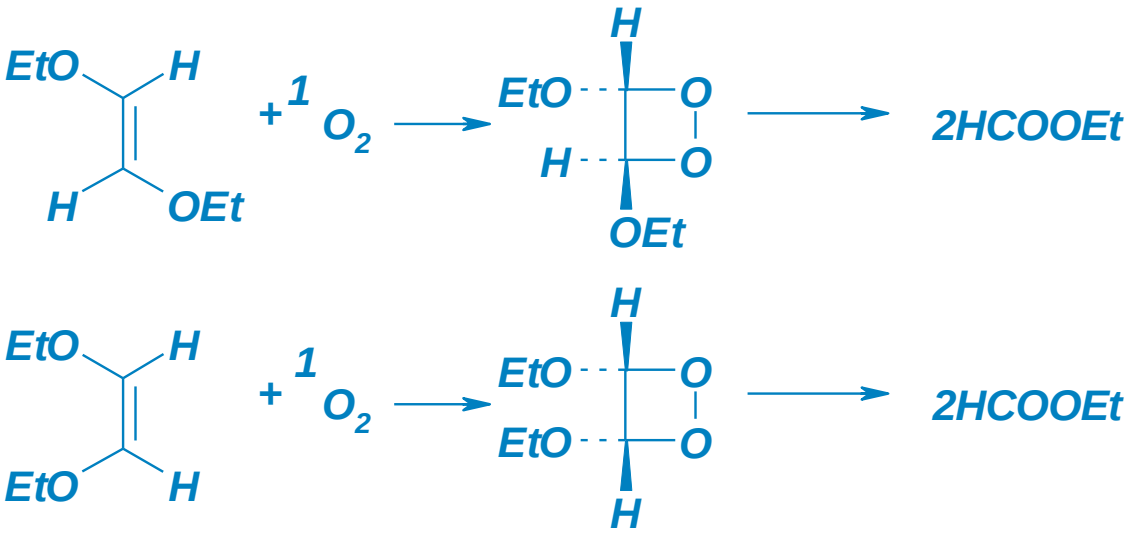
$$(\phi O)_3 P + O_3 \xrightarrow{-80^0\,C} (\phi O)_3 PO_3 \xrightarrow{-20^0\,C} (\phi O)_3 PO + {}^1O_2$$

واکنشهای اصلی اکسیژن یکتایی :

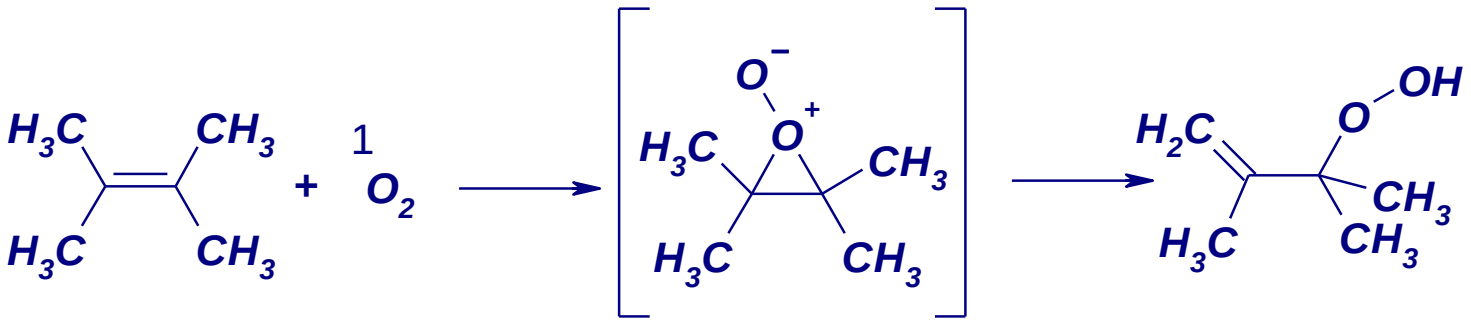
۱- حلقه زایی ۱و۴ :



۲- حلقه زایی ۱و۲ :



۳- تشکیل هیدروپراکسید :



پایان

با تشکر از توجه شما