

1. Problem

(xếp các tác nhân sau vào loại tác nhân ái điện tử (electrophile) và loại tác nhân ái nhân (nucleophile)

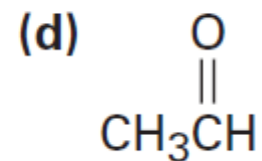
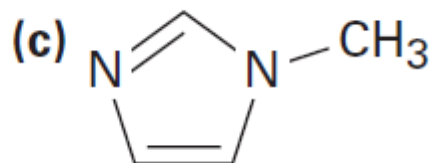
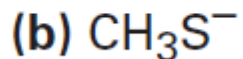
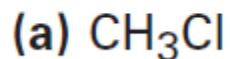
Which of the following species is likely a nucleophile or an electrophile?

(a) NO_2^+ (b) CN^- (c) CH_3NH_2 (d) $(\text{CH}_3)_3\text{S}^+$

2. Problem 6.4

(xếp các tác nhân sau vào loại tác nhân ái điện tử (electrophile) và loại tác nhân ái nhân (nucleophile))

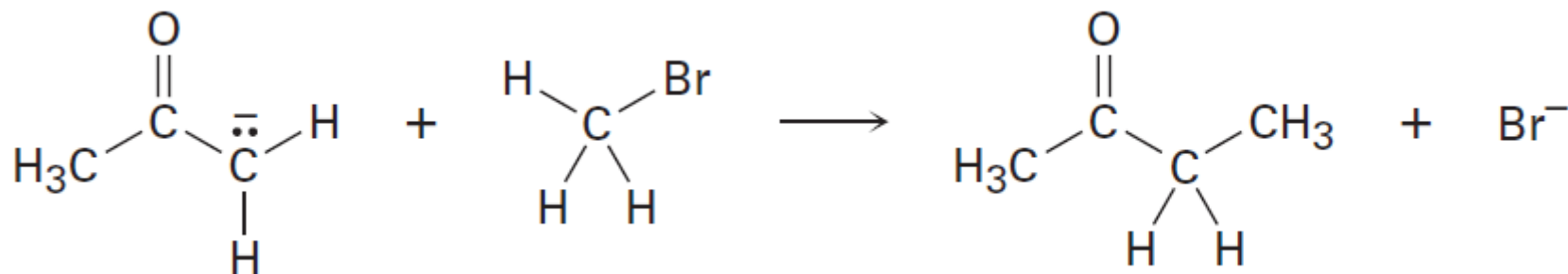
Which of the following species is likely a nucleophile or an electrophile? Which may be both?



3. Problem

(dùng mũi tên cong chỉ sự di chuyển của electrons trong phản ứng sau)

Show the movement of electrons in this reaction:

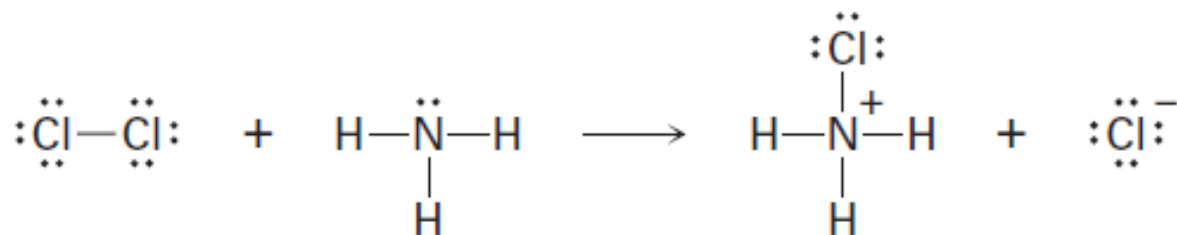


4. Problem 6.8

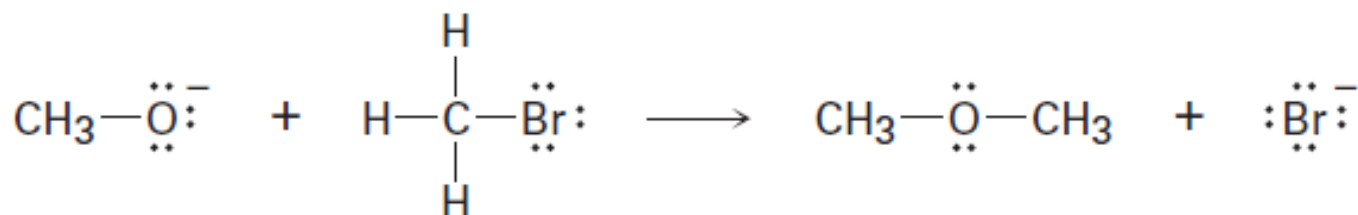
(dùng mũi tên cong chỉ sự di chuyển của electrons trong các phản ứng sau)

Show the flow of electrons in these reactions:

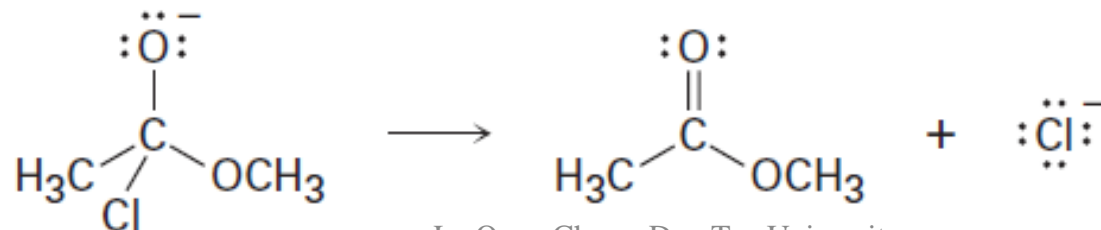
(a)



(b)



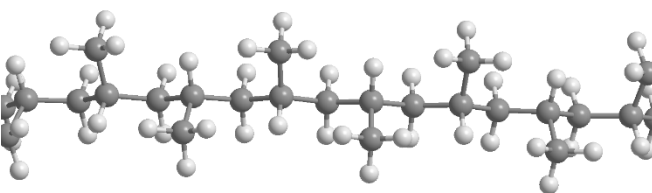
(c)



Nhà máy Nhựa Polypropylene Dung Quất



Chủ đầu tư	Tập đoàn Dầu khí Quốc gia Việt Nam (PVN)
Địa điểm	Bình Sơn – Dung Quất – Quảng Ngãi
Diện tích	15 ha
Quy mô	là dự án hóa dầu đầu tiên nằm trong cụm công nghiệp lọc hóa dầu Dung Quất, nằm cạnh Nhà máy lọc dầu Dung Quất, có công suất chế biến: 150.000 tấn/năm
Tổng mức đầu tư	232 triệu USD (tương đương 4.000 tỷ đồng)
Thời gian hoàn thành	02/2010



Plastic packaging (nhựa làm bao bì)

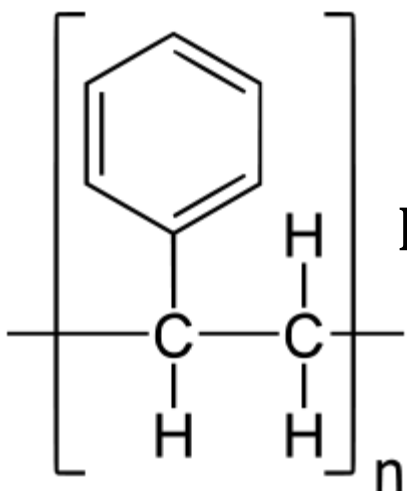
SCOPE

Plastic packaging systems for pharmaceutical use include bags, bottles, cartridges, dry powder and metered-dose inhalers, nebulizers, prefillable syringes, vials, and bottles as packaging systems for capsules and tablets. Commonly used plastic materials include polyethylene, polypropylene, polyolefins, polyethylene terephthalate, polyethylene terephthalate G, and poly(vinyl chloride). Some, but not all plastic packaging systems are formed from a single plastic material. For example, bags can be formed from layers of different plastic materials, and solid plastic containers can be manufactured from more than one plastic material by co-molding. These differences notwithstanding, plastic materials used in the construction of plastic packaging systems should be fully



Bao bì trong ngành dược

(pharmaceutical plastic packaging)

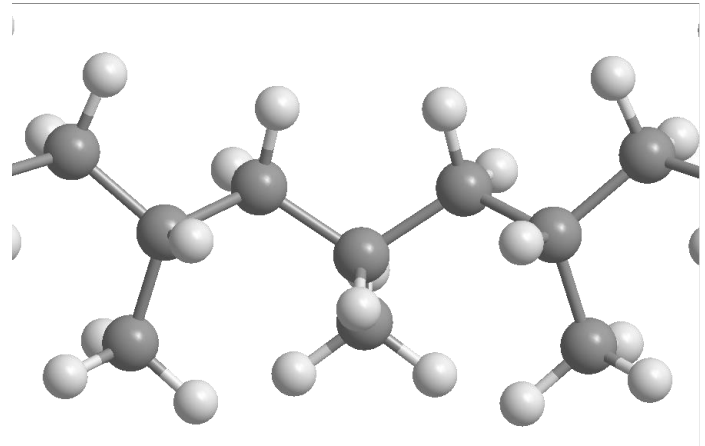
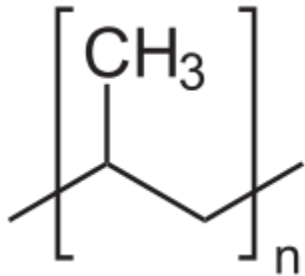


polystyrene

Expanded polystyrene (EPS)

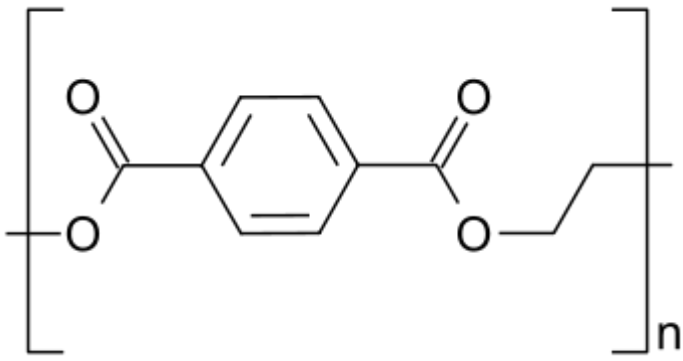
Bao bì trong ngành thực phẩm

Bao bì trong ngành thực phẩm



Polypropylene

Bao bì trong ngành thực phẩm



Polyethylene terephthalate



Food Grade Plastic



Organic Chemistry

CHE 203

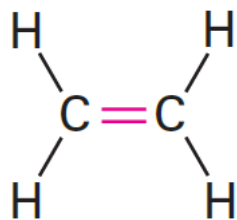
Lecture 7: Alkenes

Le Quoc Chon – Duy Tan University

Key concepts

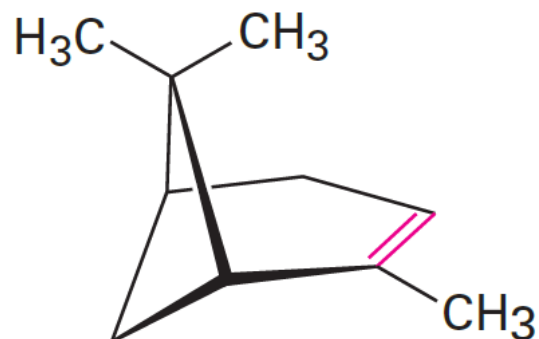
- Naming Alkenes (tên alkene)
- Cis-trans isomers (đồng phân cis/trans của alkene)
- E, Z configuration (cấu hình E, Z của alkene)
- Electrophilic addition reactions (phản ứng cộng ái điện tử vào alkene)
- Markovnikov's rules (quy tắc Markovnikov)
- Stability of carbocation (độ bền của carbocation)

Alkenes



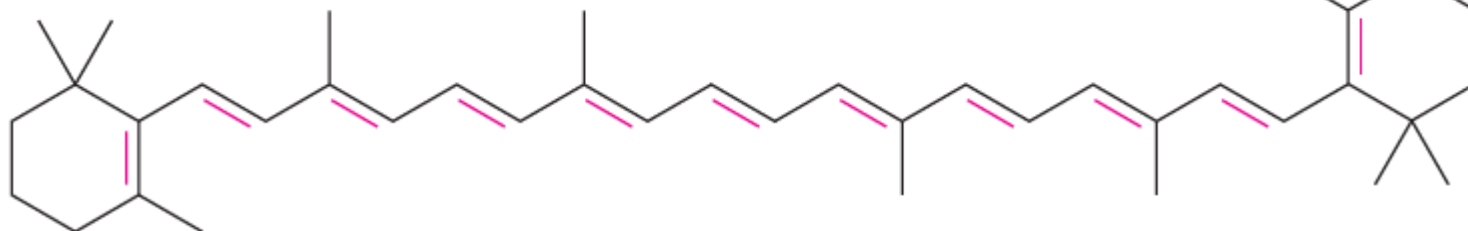
Ethylene

(a plant hormone –
hormone thực vật)



α -Pinene

(from resin of live tree
– từ nhựa cây)



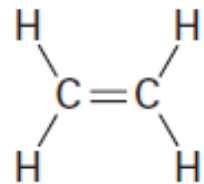
β -Carotene

(orange pigment and vitamin A precursor)

Chất tạo màu cam, và chất nguồn cho vitamin A

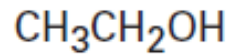
Industry of alkenes

(alkenes trong công nghiệp)

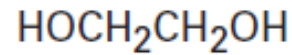


**Ethylene
(ethene)**

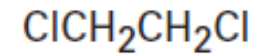
127 MT/year



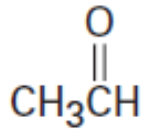
Ethanol



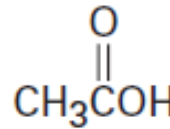
Ethylene glycol



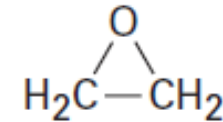
Ethylene dichloride



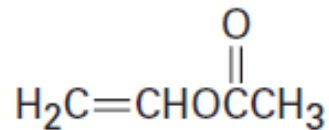
Acetaldehyde



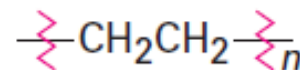
Acetic acid



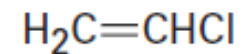
Ethylene oxide



Vinyl acetate

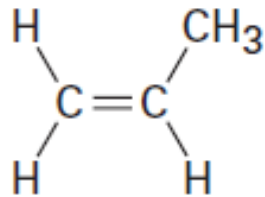


Polyethylene



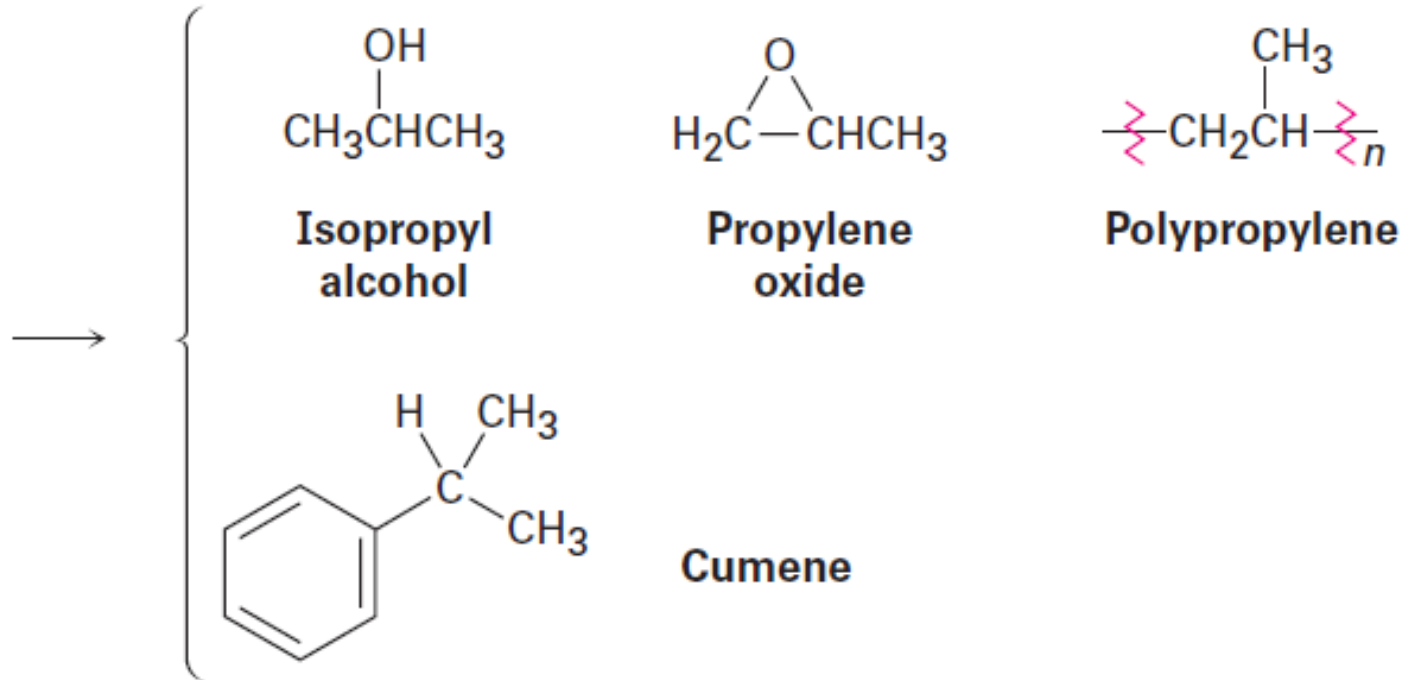
Vinyl chloride

Industry of alkenes (alkenes trong công nghiệp)

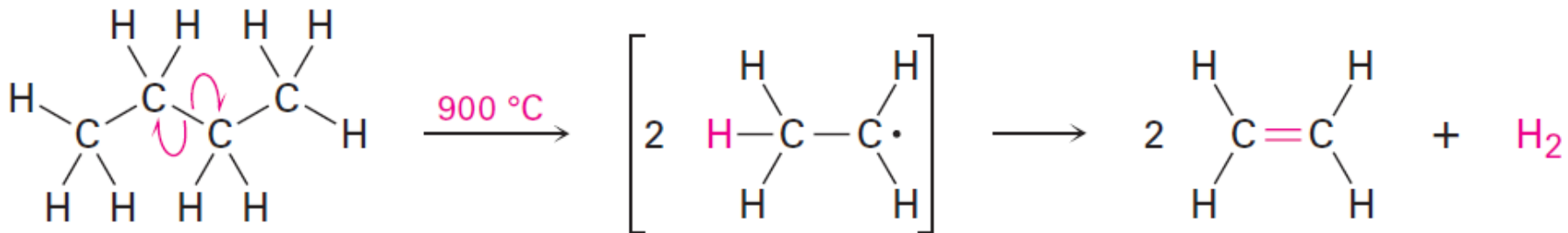
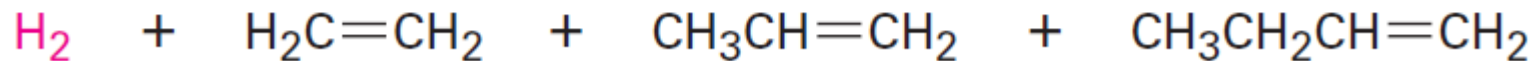
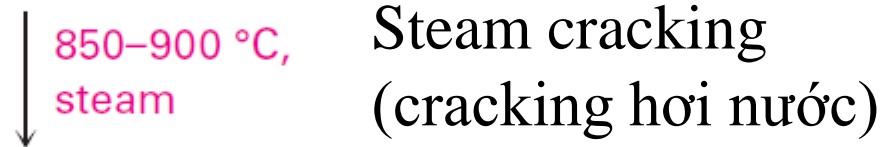
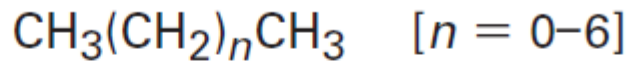


**Propylene
(propene)**

54 MT/year



Industry of alkenes (alkenes trong công nghiệp)



Naming alkenes

Đọc tên Alkenes

Step 1. Name the parent hydrocarbon

Step 2. Number the Carbon atoms in the chain

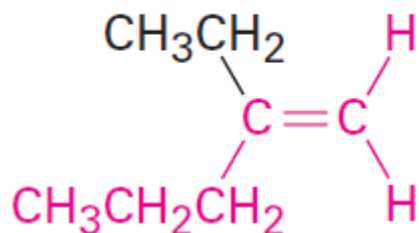
Step 3. Write full name with position of double bond

(Xác định mạch chính chứa liên kết đôi,
Đếm số carbon trên mạch chính,
Viết tên với vị trí nhánh và vị trí liên kết đôi)

Naming alkenes

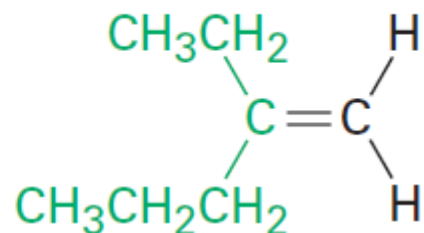
Xác định mạch chính chứa liên kết đôi

Step 1. Name the parent hydrocarbon



Named as a *pentene*

NOT

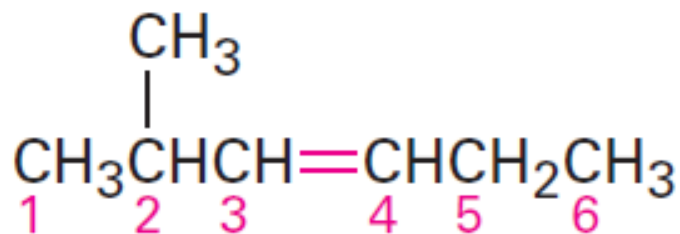
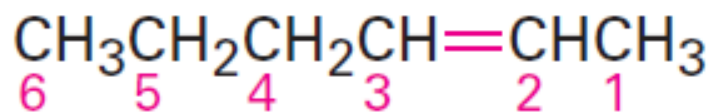


as a hexene, since the double bond is not contained in the six-carbon chain

Naming alkenes

Đếm số carbon trên mạch chính

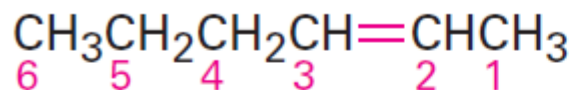
Step 2. Number the Carbon atoms in the chain



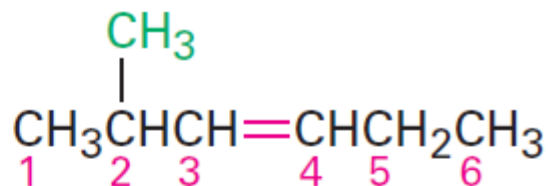
Naming alkenes

Viết tên với vị trí nhánh và vị trí liên kết đôi

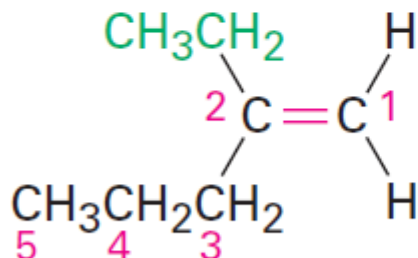
Step 3. Write full name



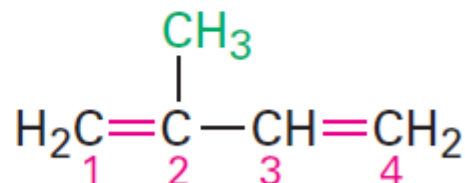
2-Hexene



2-Methyl-3-hexene



2-Ethyl-1-pentene



2-Methyl-1,3-butadiene

IUPAC

Tên theo quy ước quốc tế

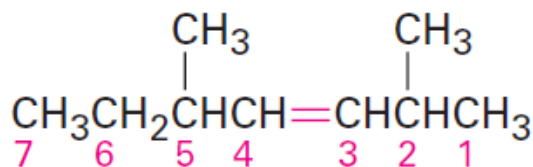


Tên kiểu mới

Newer naming system:

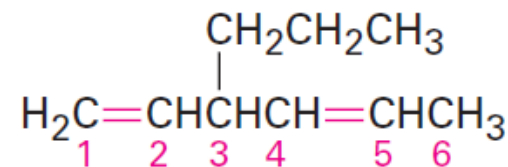
(Older naming system:

Tên kiểu cũ



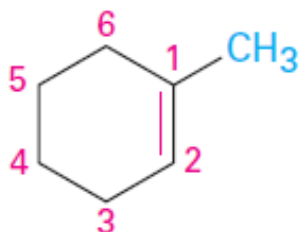
2,5-Dimethylhept-3-ene

2,5-Dimethyl-3-heptene

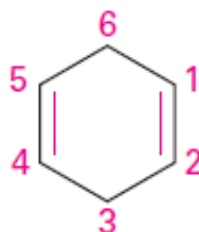


3-Propylhexa-1,4-diene

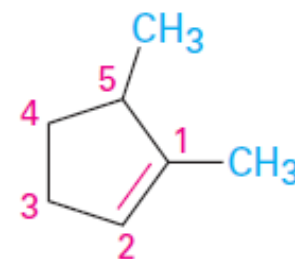
3-Propyl-1,4-hexadiene)



1-Methylcyclohexene

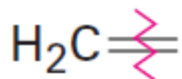


1,4-Cyclohexadiene
(New: Cyclohexa-1,4-diene)

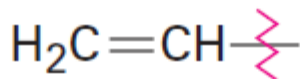


1,5-Dimethylcyclopentene

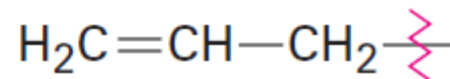
Tên thông thường IUPAC vs Common names



A methylene group



A vinyl group



An allyl group

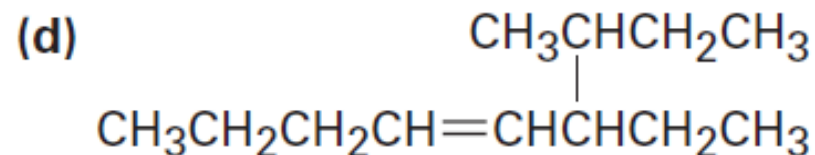
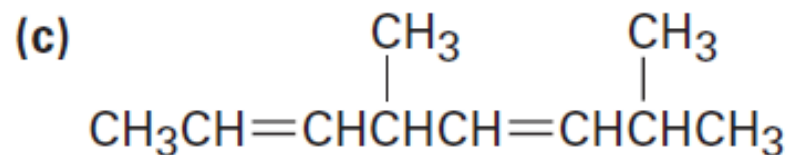
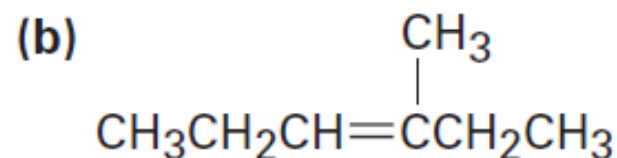
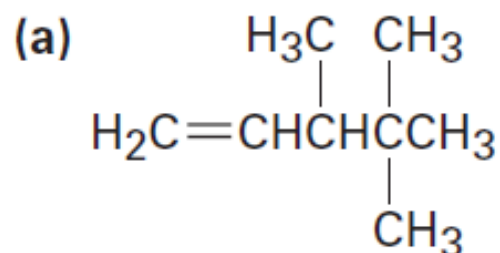
TABLE 7-1 Common Names of Some Alkenes

Compound	Systematic name	Common name
$\text{H}_2\text{C}=\text{CH}_2$	Ethene	Ethylene
$\text{CH}_3\text{CH}=\text{CH}_2$	Propene	Propylene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$	2-Methylpropene	Isobutylene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	2-Methyl-1,3-butadiene	Isoprene

Problem

PROBLEM 7-4 (đọc tên IUPAC các chất sau)

Give IUPAC names for the following compounds:



Problem

(vẽ công thức cấu tạo các chất sau với tên IUPAC cho dưới đây)

PROBLEM 7-5

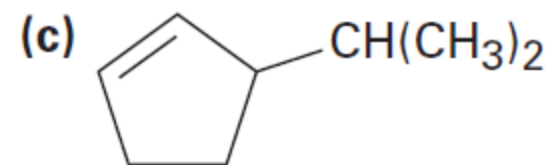
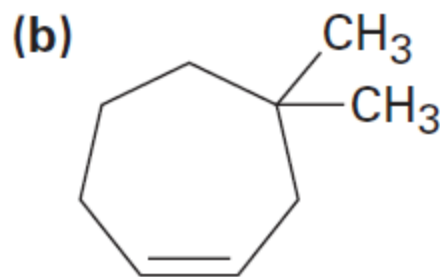
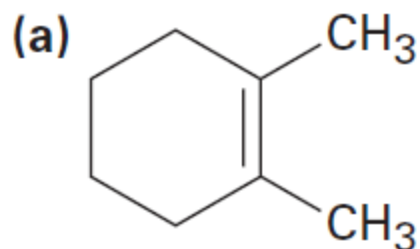
Draw structures corresponding to the following IUPAC names:

- (a) 2-Methyl-1,5-hexadiene
- (b) 3-Ethyl-2,2-dimethyl-3-heptene
- (c) 2,3,3-Trimethyl-1,4,6-octatriene
- (d) 3,4-Diisopropyl-2,5-dimethyl-3-hexene

Problem

PROBLEM 7-6

Name the following cycloalkenes:



(Ghi chú: chọn số thứ tự sao cho liên kết đôi ở vị trí C1 và C2, và vị trí nhánh thấp nhất có thể)

Problem

PROBLEM 7-7

Change the following old names to new, post-1993 names, and draw the structure of each compound:

- (a) 2,5,5-Trimethyl-2-hexene
- (b) 2,3-Dimethyl-1,3-cyclohexadiene

(Chuyển từ tên IUPAC cũ sang mới rồi vẽ công thức cấu tạo)

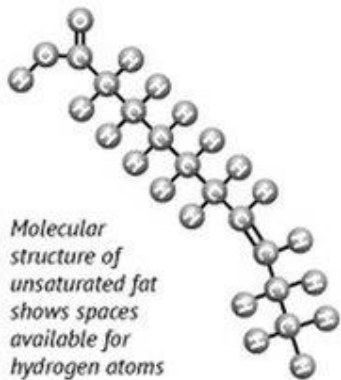
Different Kinds of Fat

Fatty acids, which are the building blocks of fat, are long chains of carbon and hydrogen atoms. Essential fatty acids are those needed by the human body that can only be obtained through food. Some fats are harmful, however.



UNSATURATED FATS

The so-called "good" fats can be found in nuts, avocados and other vegetables. The molecular structure of unsaturated fat causes it to be lower in calories than other fats.

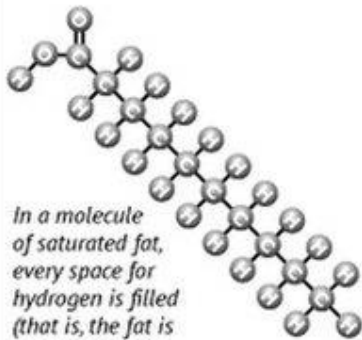


Molecular structure of unsaturated fat shows spaces available for hydrogen atoms to bond



SATURATED FATS

These fats are found mostly in animal products. It is recommended that people reduce their consumption of saturated fats in order to stay healthy.

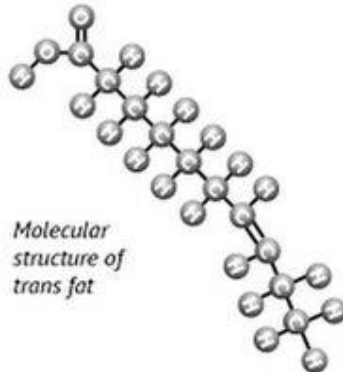


In a molecule of saturated fat, every space for hydrogen is filled (that is, the fat is "saturated" with hydrogen)



TRANS FATS

Trans fats are unsaturated (good) fats which have been partially saturated with hydrogen to extend their shelf life. Unfortunately, these trans fats are found to elevate "bad" cholesterol and should be avoided.



Molecular structure of trans fat

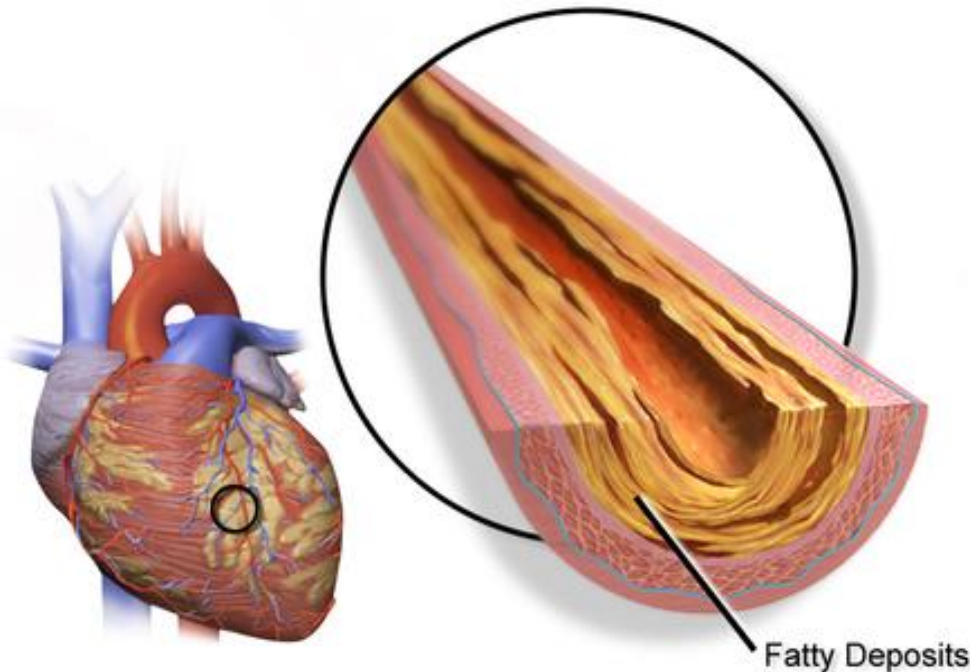
In 1994, it was estimated that trans fats caused 20,000 deaths annually in the United States from heart disease.

(1994: trans fat gây ra khoảng 20000 người chết/năm ở Mỹ)

Coronary artery disease (CAD)

(Bệnh động mạch vành)

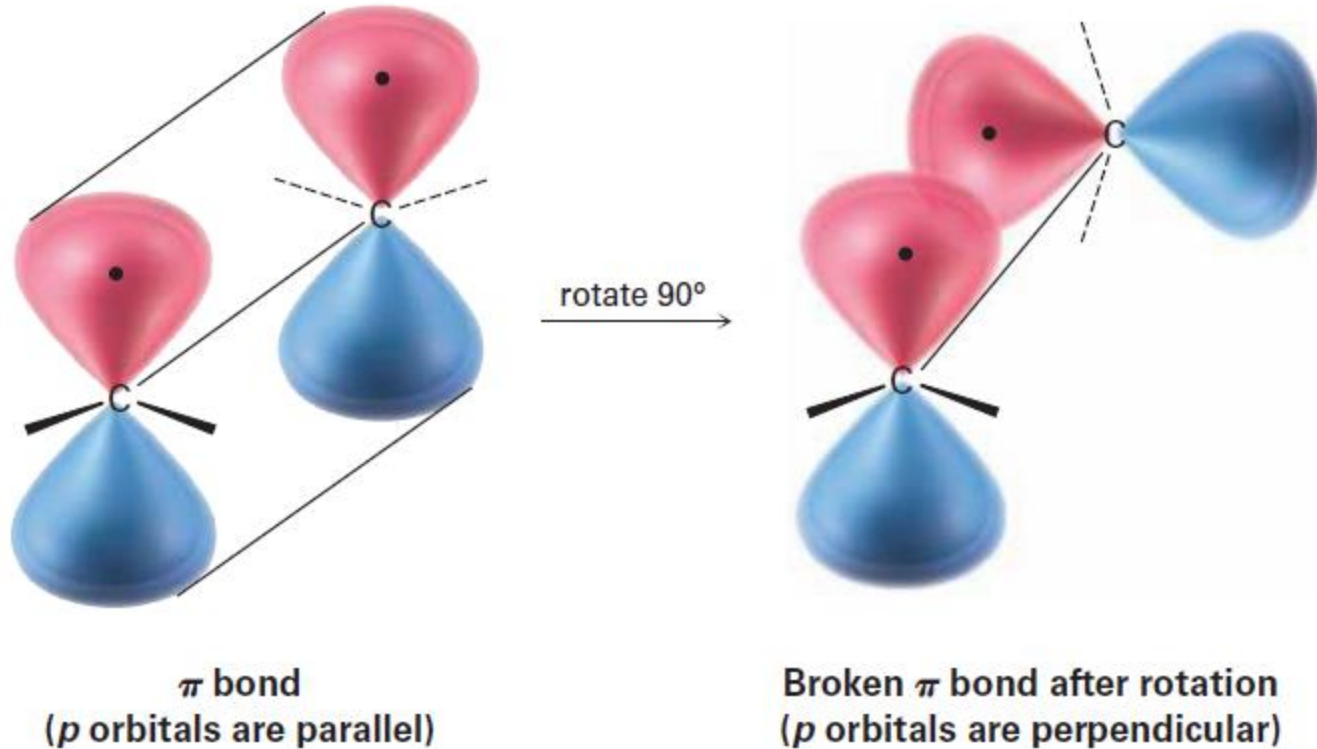
In 2015 CAD affected 110 million people and resulted in 8.9 million deaths. It is the most common cause of death globally.



Ways to reduce CAD risk include eating a healthy diet, regularly exercising, maintaining a healthy weight, and not smoking

Cis-trans isomerism in alkenes

Đồng phân cis/trans với Alkenes

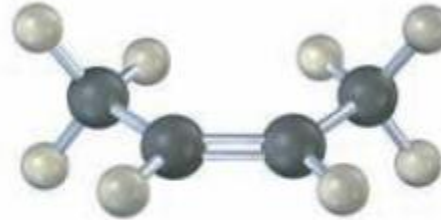
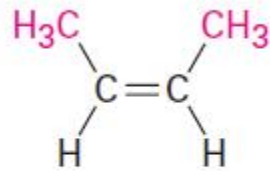


Can not rotate without breaking bond

Cis-trans isomerism in alkenes

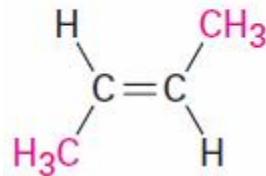
Đồng phân cis/trans với Alkenes

Hai nhóm
thế cùng
phía



cis-2-Butene

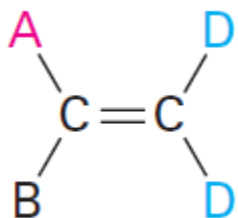
Hai nhóm thế
khác phía



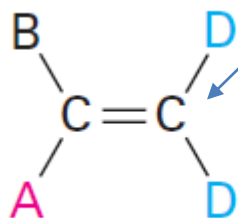
trans-2-Butene

Đồng phân cis/trans với Alkenes

Cis-trans isomerism in alkenes



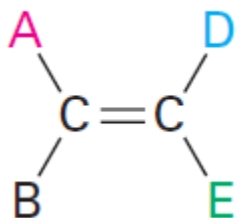
=



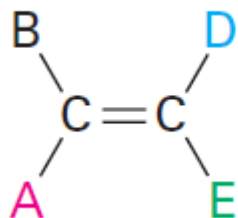
One of the double-bond carbons is attached to two identical groups

These two compounds are identical; they are not cis-trans isomers.

(hai chất này giống nhau, không phải đồng phân cis-trans của nhau)



≠



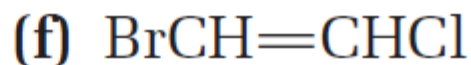
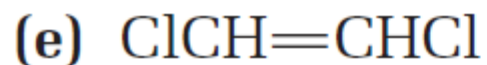
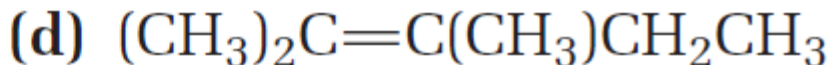
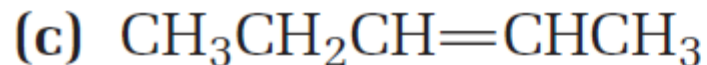
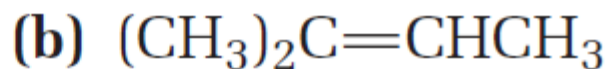
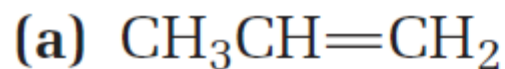
These two compounds are not identical; they are cis-trans isomers.

(hai chất khác nhau và là đồng phân cis-trans của nhau)

Problem 7.8

Which of the following compounds can exist as pairs of cis-trans isomers? Draw each cis-trans pair.

(chất nào sau đây có đồng phân cis-trans, hãy vẽ chúng).

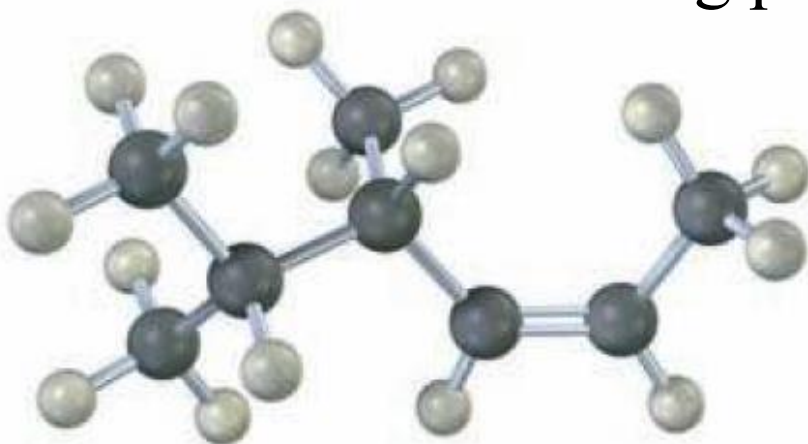


Problem 7.8

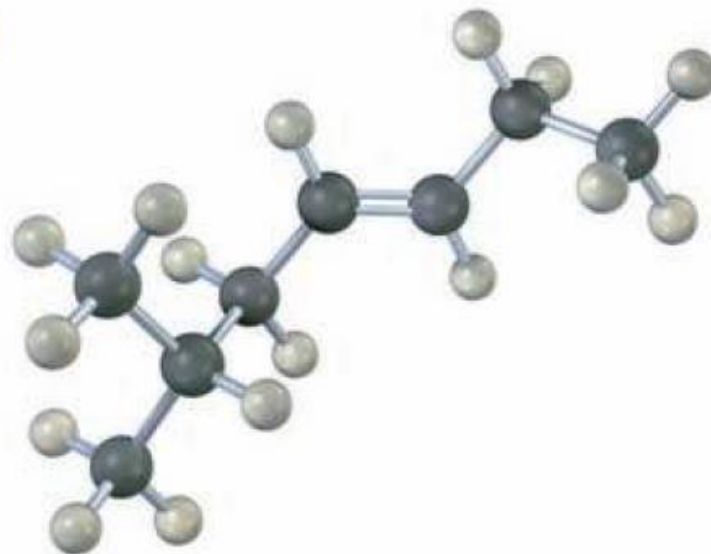
Name the following alkenes, including a cis/trans designation.

Đọc tên alkenes sau với
đồng phân cis/trans

(a)



(b)



Alkene Stereochemistry: E, Z system

Cahn-Ingold-Prelog rules

(xem xét hai nhóm thế trên mỗi C có liên kết đôi, rồi sắp xếp chúng

RULE 1 theo mức độ ưu tiên)

Considering each of the double-bond carbons separately, look at the two substituents attached and rank them according to the atomic number of the first atom in each. An atom with higher atomic number ranks higher than an atom with lower atomic number.

(nếu mức độ ưu tiên không được xác lập bởi nguyên tử thứ 1 thì xem nguyên tử thứ 2, 3...)

RULE 2

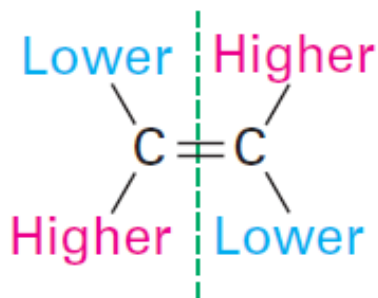
If a decision can't be reached by ranking the first atoms in the two substituents, look at the second, third, or fourth atoms away from the double-bond until the first difference is found.

(nguyên tử có liên kết bội thì tương đương đúng với số nguyên tử có liên kết đơn)

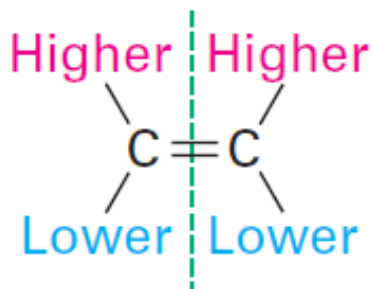
RULE 3

Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.

Alkene Stereochemistry: E, Z system

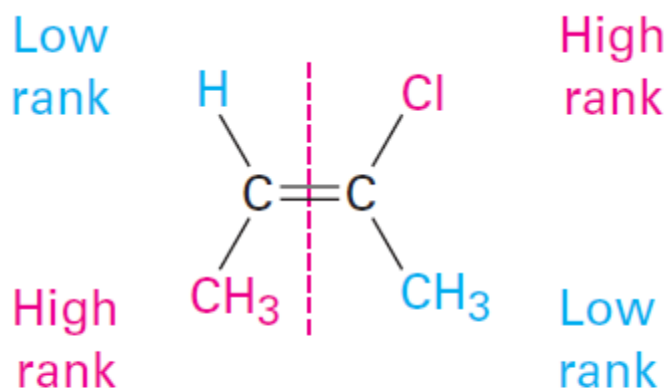


E double bond
(Higher-ranked groups are on **opposite** sides.)
(hai nhóm ưu tiên khác phía)

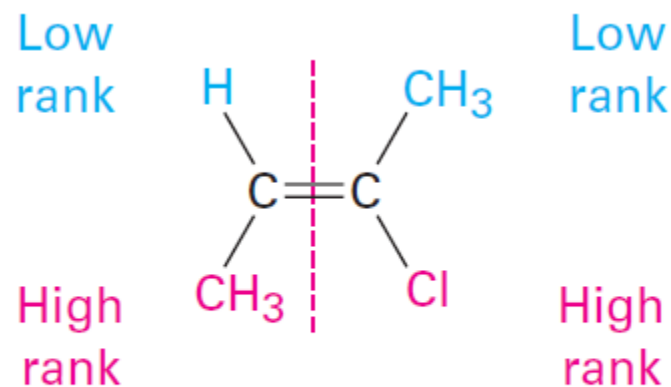


Z double bond
(Higher-ranked groups are on the **same** side.)
(hai nhóm ưu tiên cùng phía)

Alkene Stereochemistry: E, Z system



(a) (*E*)-2-Chloro-2-butene

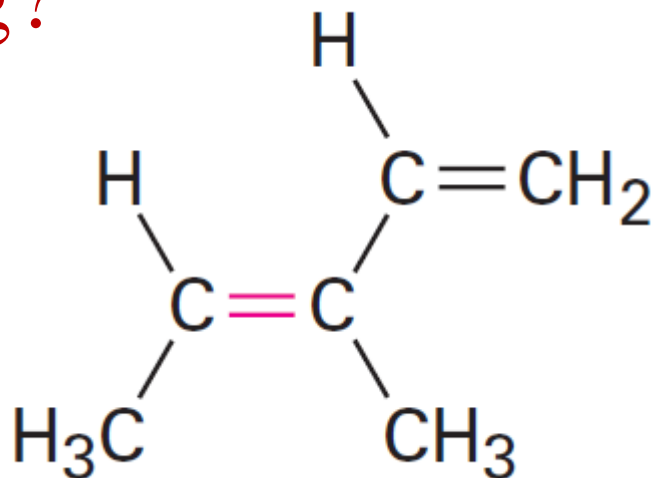


(b) (*Z*)-2-Chloro-2-butene

Problem

Right or wrong?

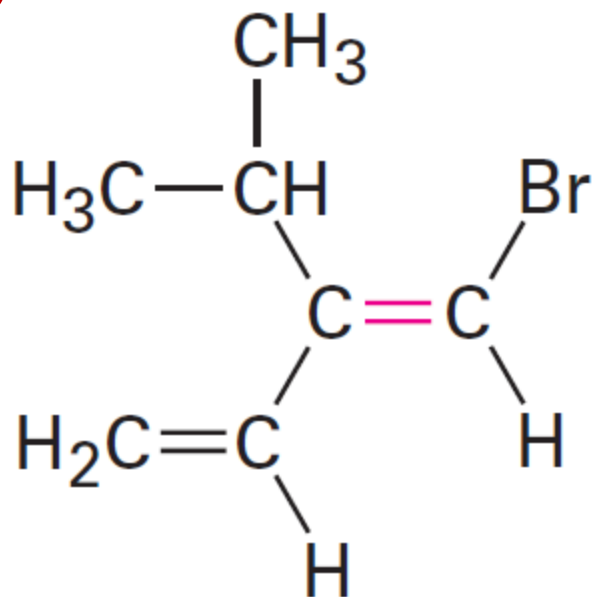
Ví dụ: cấu hình E chất
sau là đúng hay sai?



(E)-3-Methyl-1,3-pentadiene

Problem

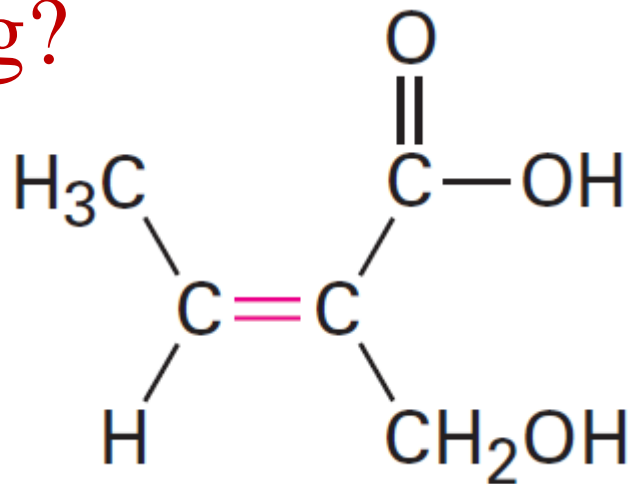
Right or wrong?



**(E)-1-Bromo-2-isopropyl-
1,3-butadiene**

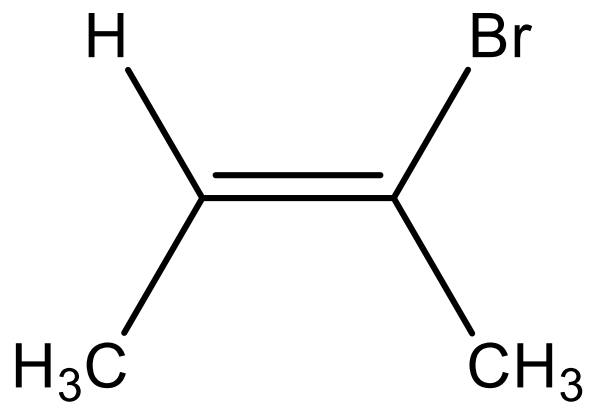
Problem

Right or wrong?



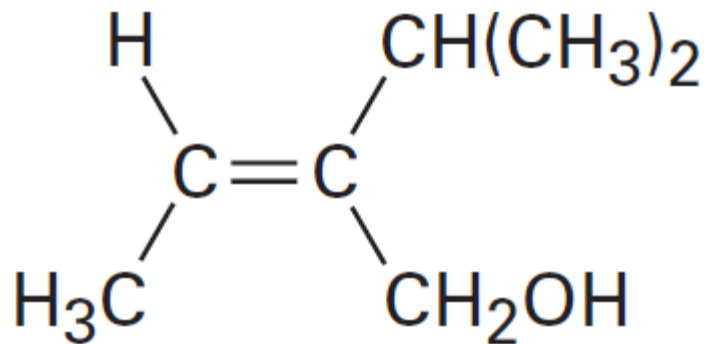
**(Z)-2-Hydroxymethyl-
2-butenoic acid**

Cis/trans vs E/Z

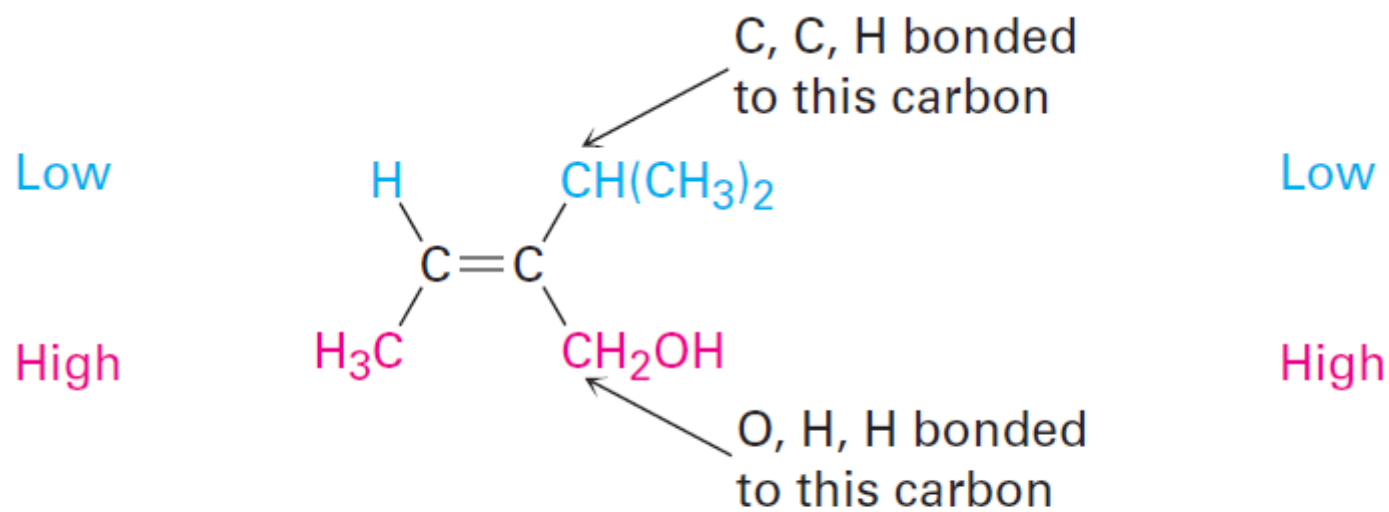


Problem

Assign E, Z configuration:
(xác định cấu hình E/Z chất sau)



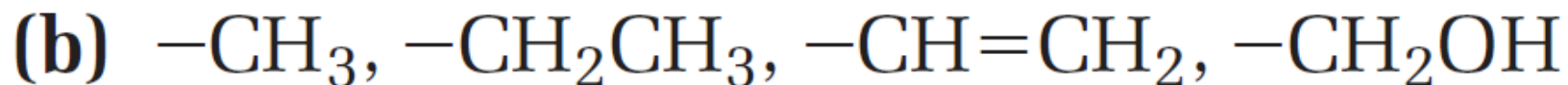
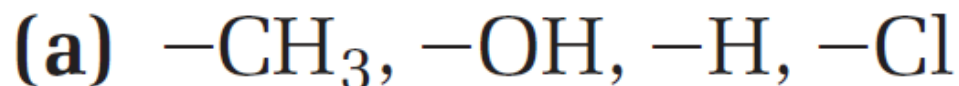
Problem: answer



Z configuration

Problem 7.12

Rank the substituents in each of the following sets according to the sequence rules: (sắp xếp theo thứ tự ưu tiên các nhóm thế sau).

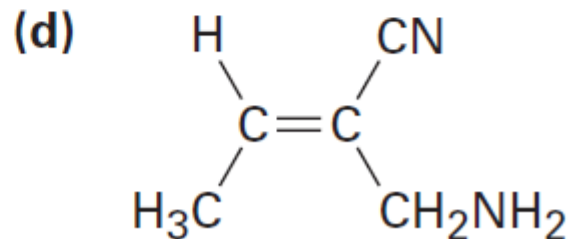
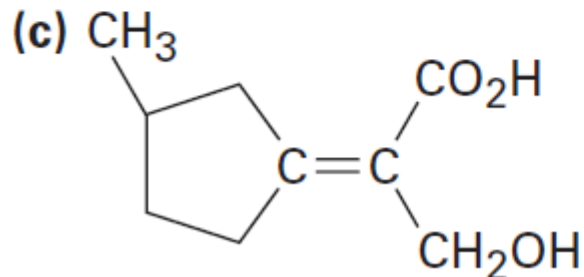
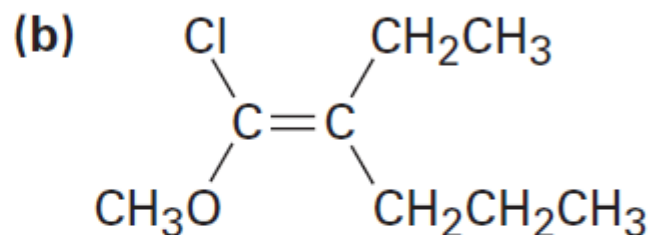
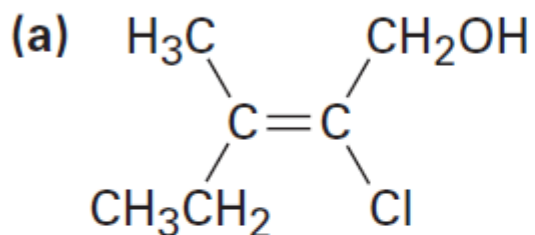


Problem

PROBLEM 7-13

(các chất sau có cấu hình E hay Z?)

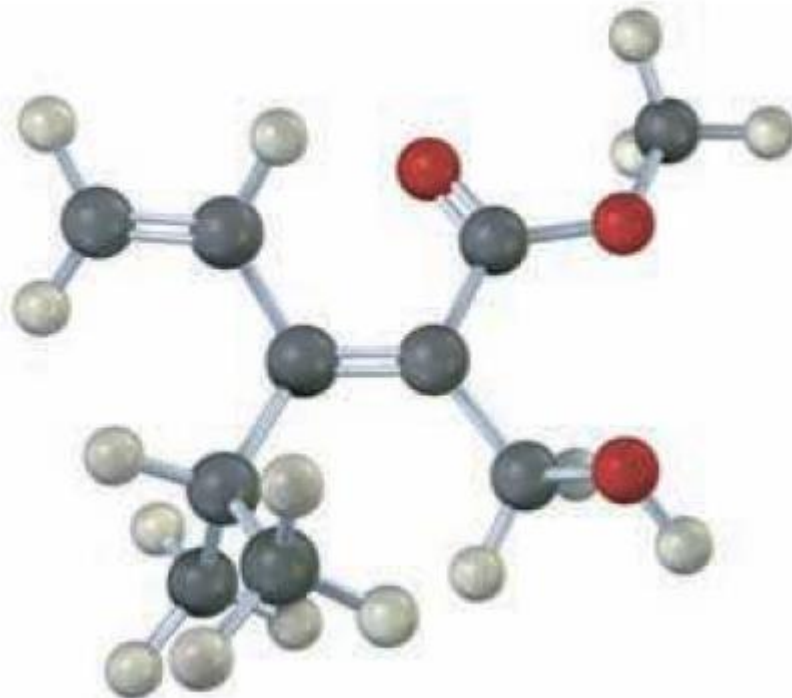
Assign *E* or *Z* configuration to the following alkenes:



Problem 7.14

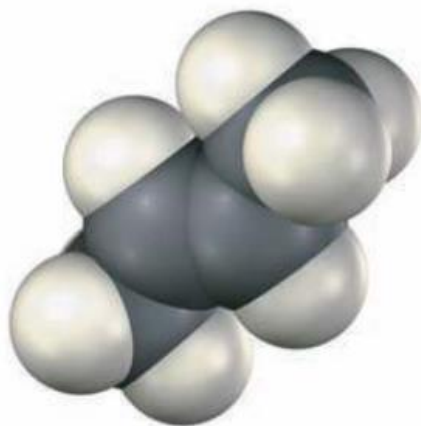
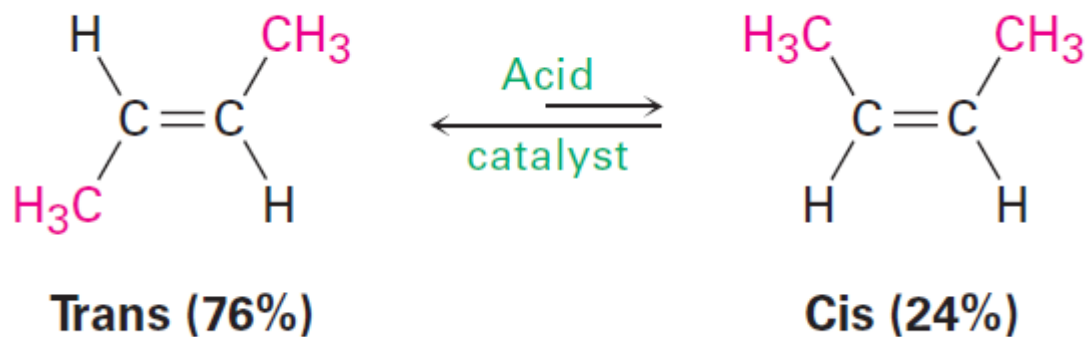
Red is O. Assign E or Z configuration for this molecule and convert into skeletal structure.

(xác định cấu hình E, Z cho alkene sau)

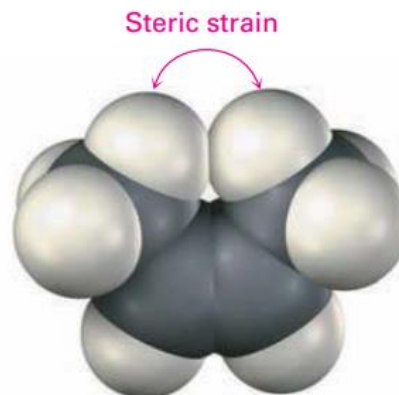


Stability of Alkenes

(độ bền của alkenes)

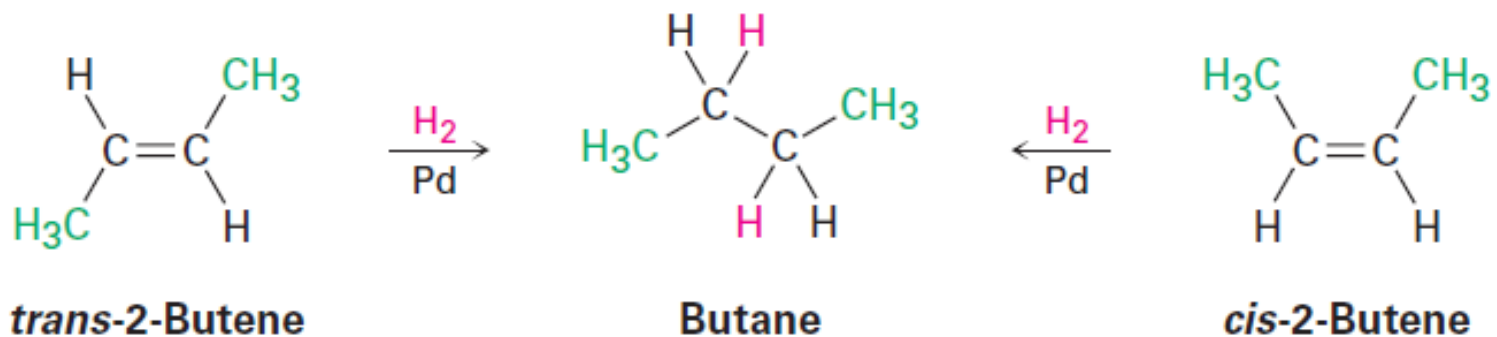


trans-2-Butene



cis-2-Butene

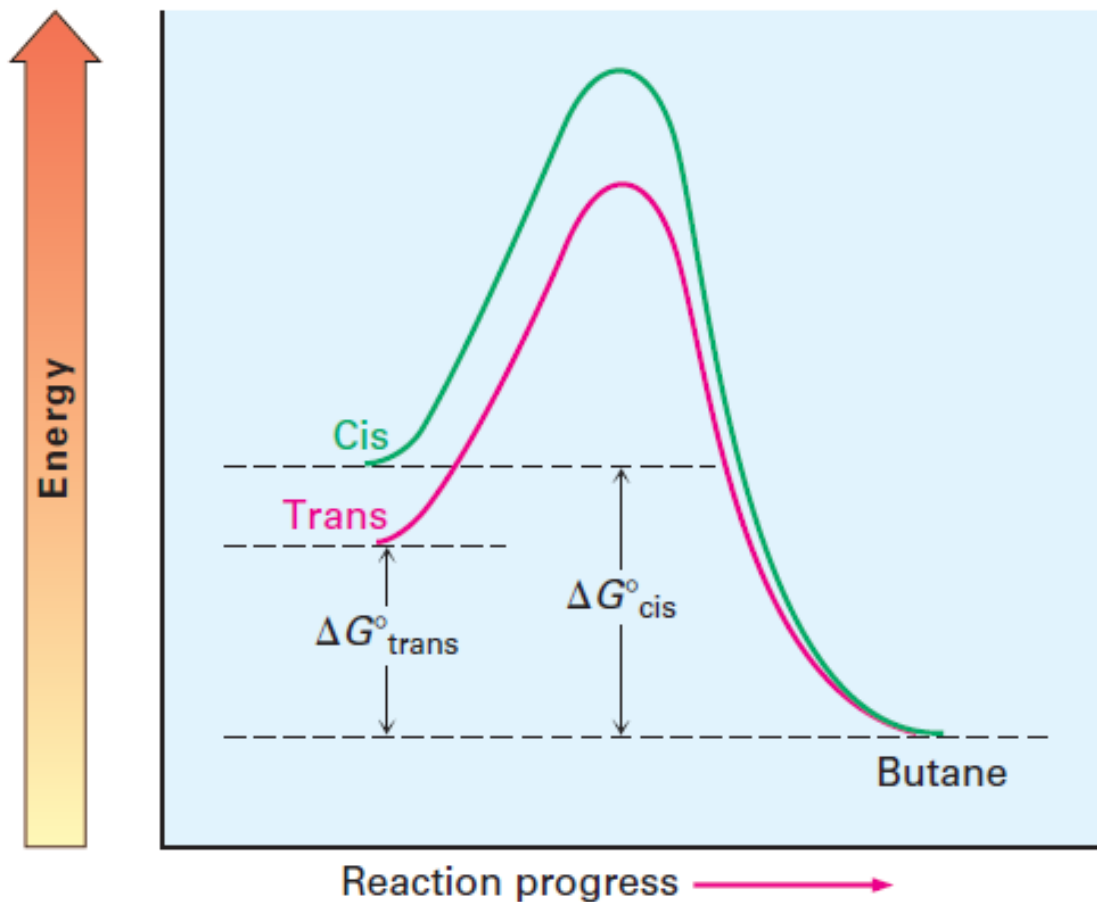
Stability of butene



$$\Delta H^\circ_{\text{hydrog}} = -116 \text{ kJ/mol}$$

$$\Delta H^\circ_{\text{hydrog}} = -120 \text{ kJ/mol}$$

Stability of butene



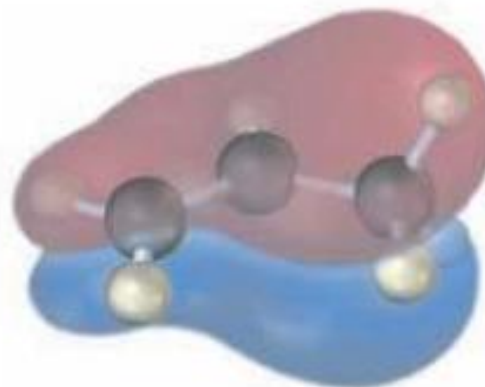
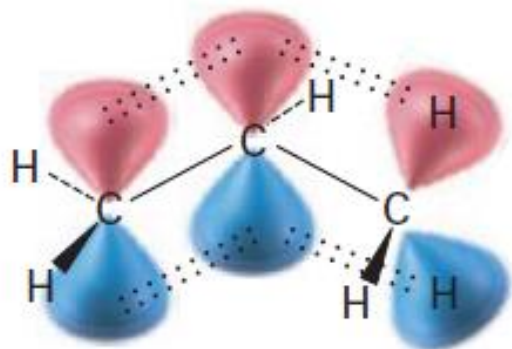
Stability of Alkenes

TABLE 7-2 Heats of Hydrogenation of Some Alkenes

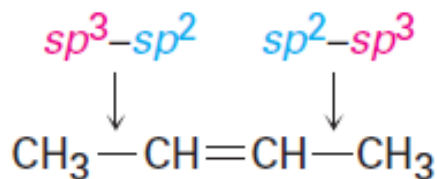
Substitution	Alkene	$\Delta H^\circ_{\text{hydrog}}$	
		(kJ/mol)	(kcal/mol)
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	-136	-32.6
Monosubstituted	$\text{CH}_3\text{CH}=\text{CH}_2$	-125	-29.9
Disubstituted	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (cis)	-119	-28.3
	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (trans)	-115	-27.4
	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	-118	-28.2
Trisubstituted	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	-112	-26.7
Tetrasubstituted	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	-110	-26.4

Influential factors: hyperconjugation and bond strength

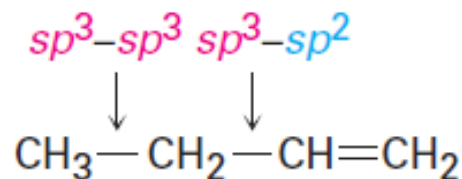
Stability of Alkenes



Hyperconjugation: C=C and adjacent C-H interaction



2-Butene
(more stable)



1-Butene
(less stable)

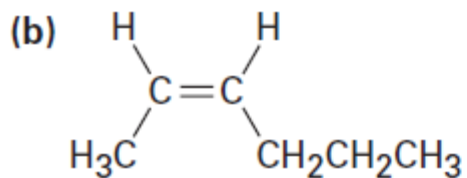
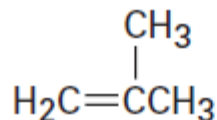
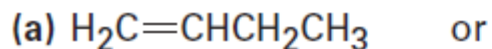
2 factors

$\text{sp}^3\text{-sp}^2$ is stronger than $\text{sp}^3\text{-sp}^3$

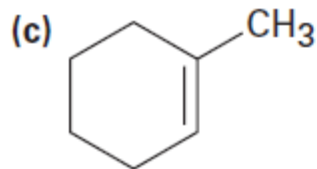
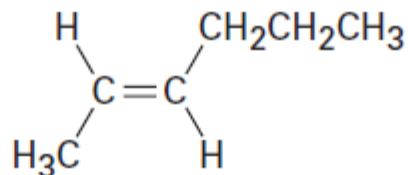
Problem

PROBLEM 7-15

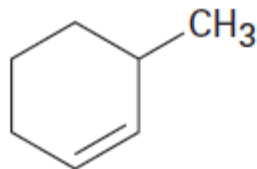
Name the following alkenes, and tell which compound in each pair is more stable:



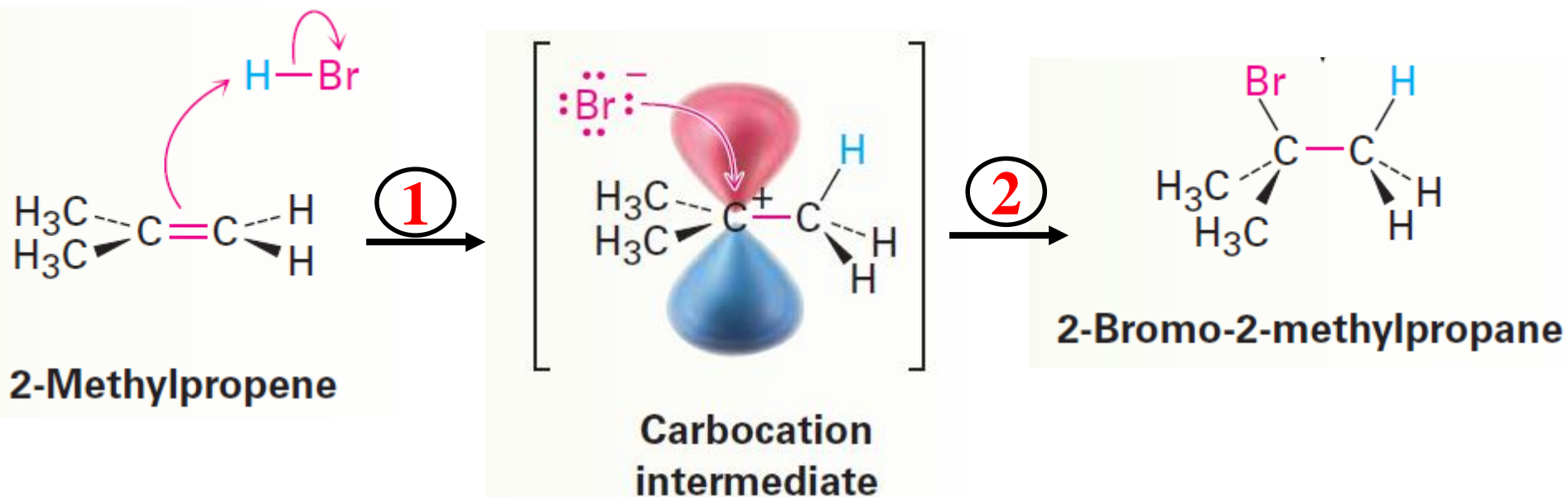
or



or

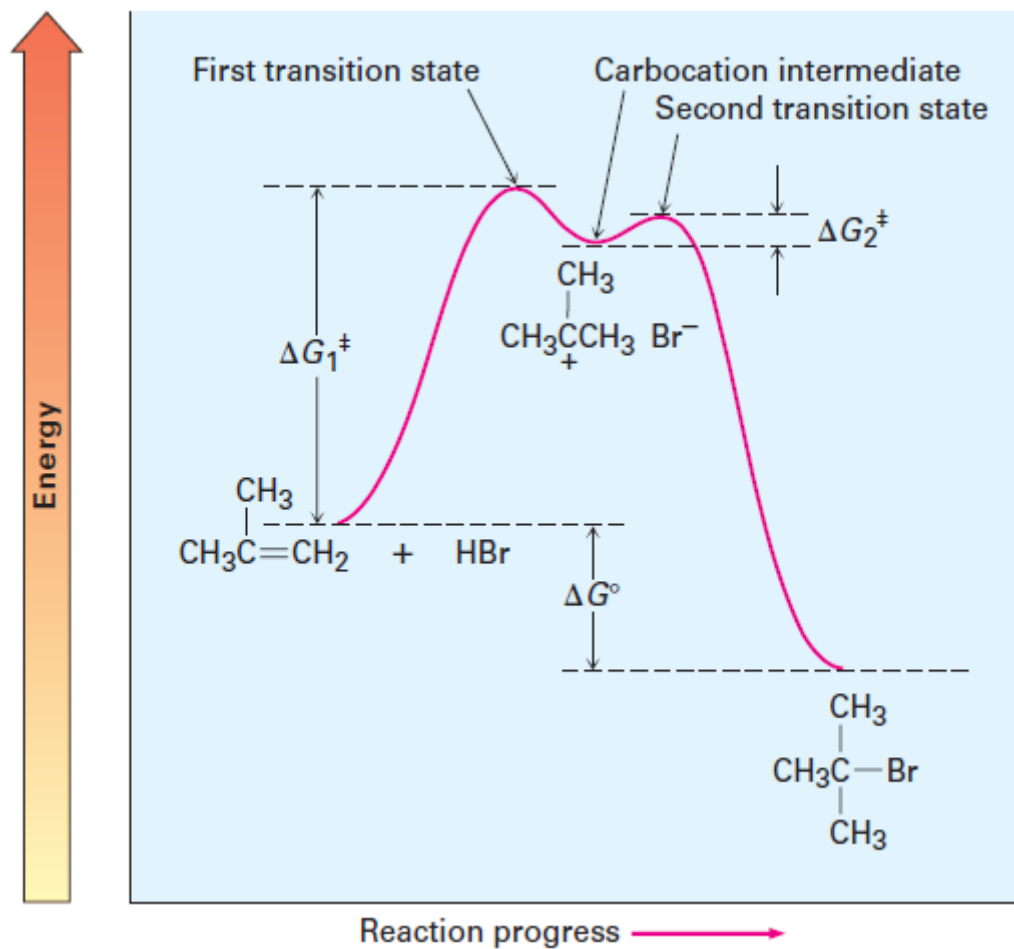


Electrophilic additions reaction of alkenes (phản ứng cộng ái điện tử của alkene)

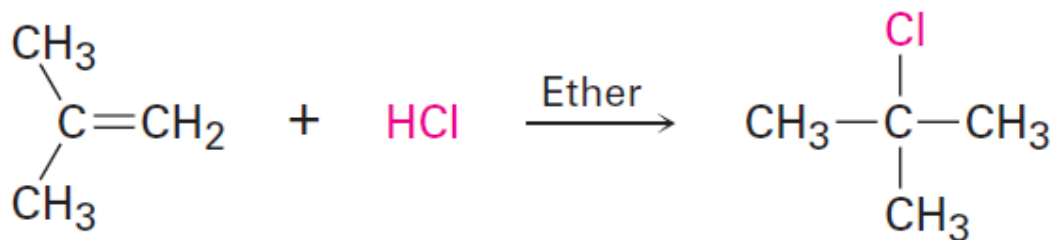


1 A hydrogen atom on the electrophile HBr is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant p orbital. Simultaneously, two electrons from the H–Br bond move onto bromine, giving bromide anion.

2 The bromide ion donates an electron pair to the positively charged carbon atom, forming a C–Br bond and yielding the neutral addition product.

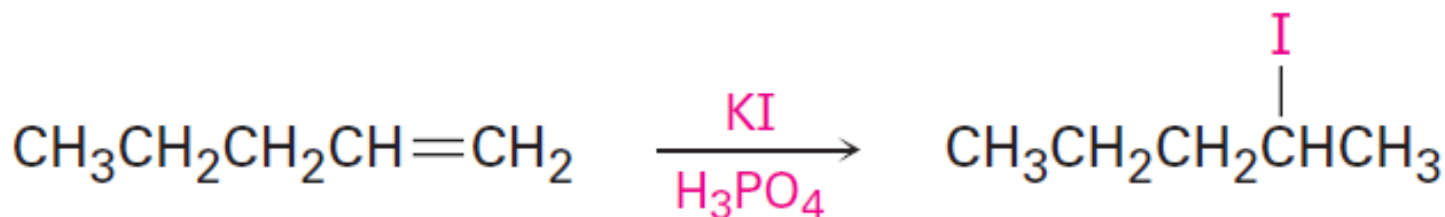


Electrophilic additions reaction of alkenes



2-Methylpropene

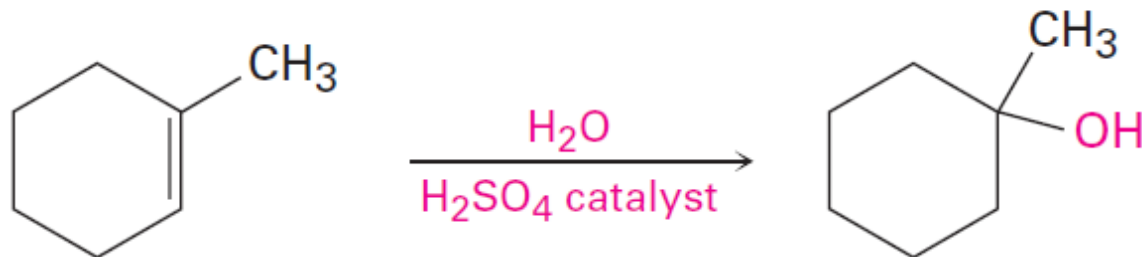
**2-Chloro-2-methylpropane
(94%)**



1-Pentene

(HI)

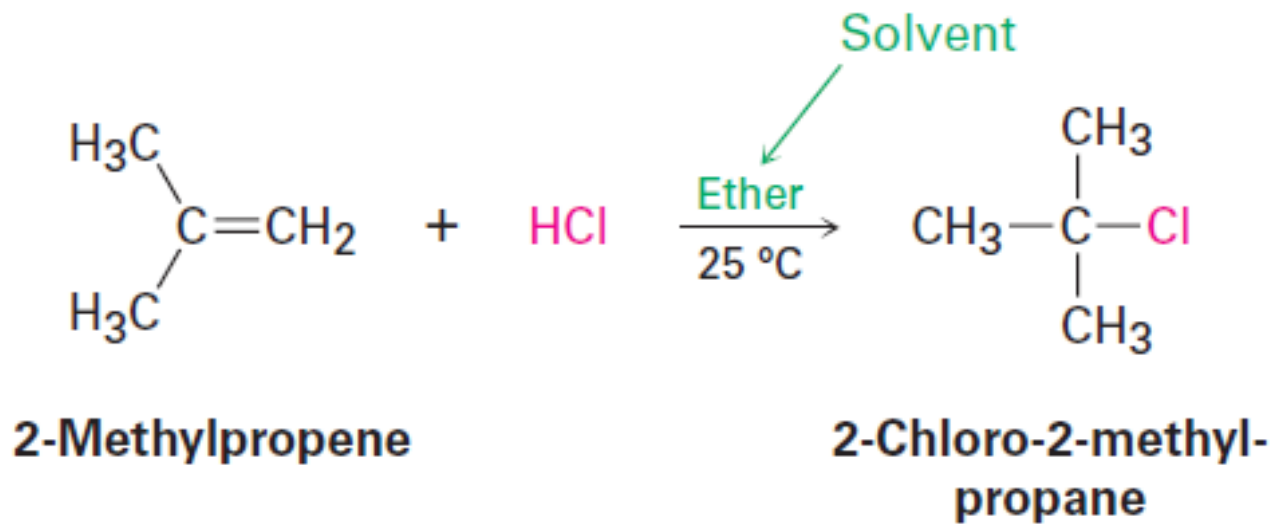
2-Iodopentane



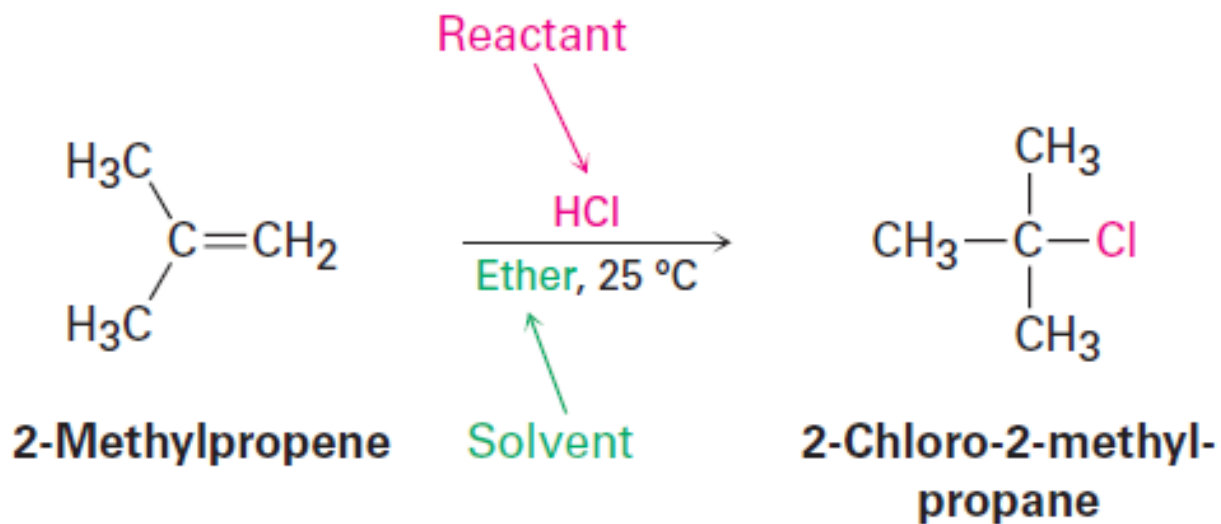
1-Methylcyclohexene

1-Methylcyclohexanol

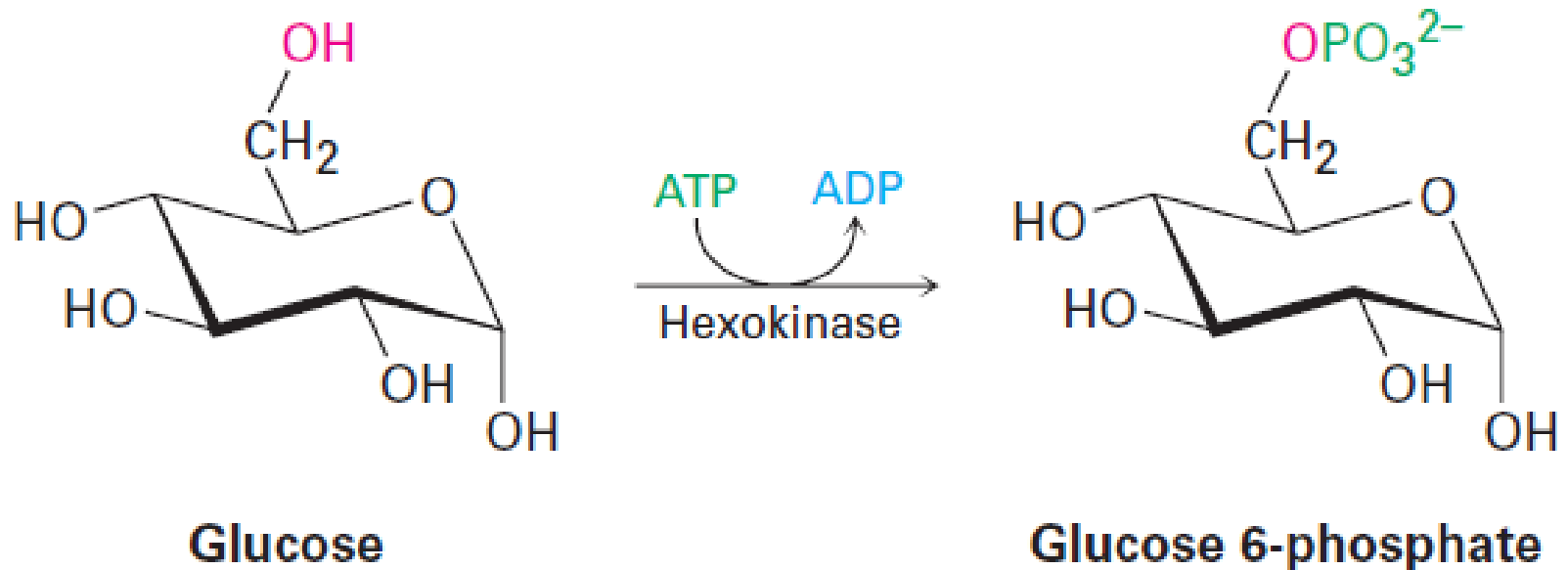
Write reaction?



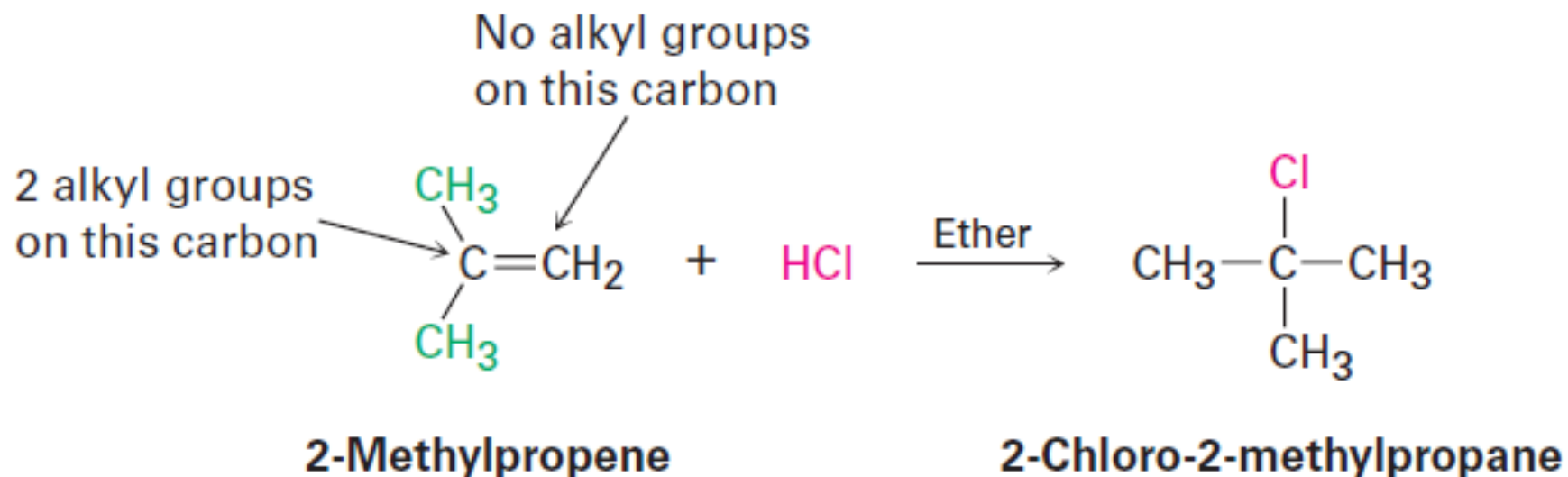
Write reaction?



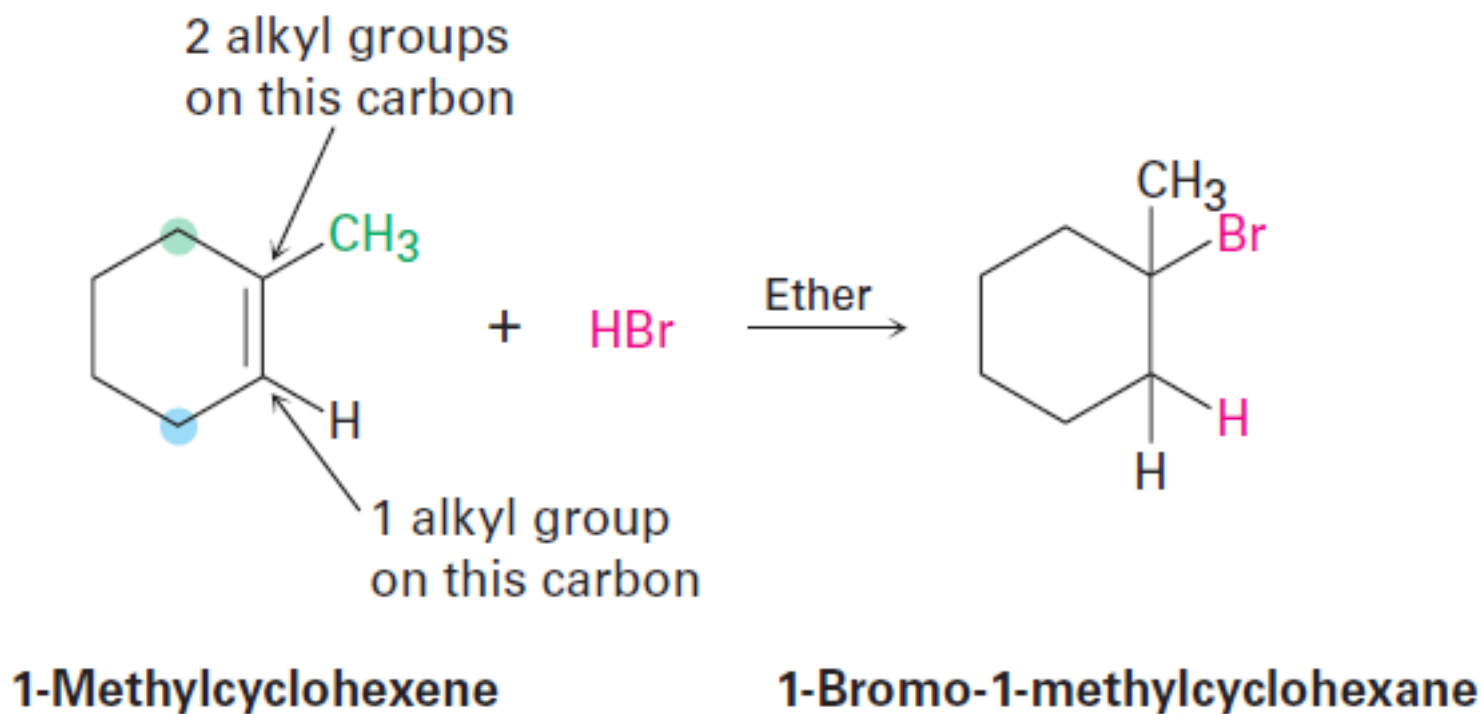
Write reaction?



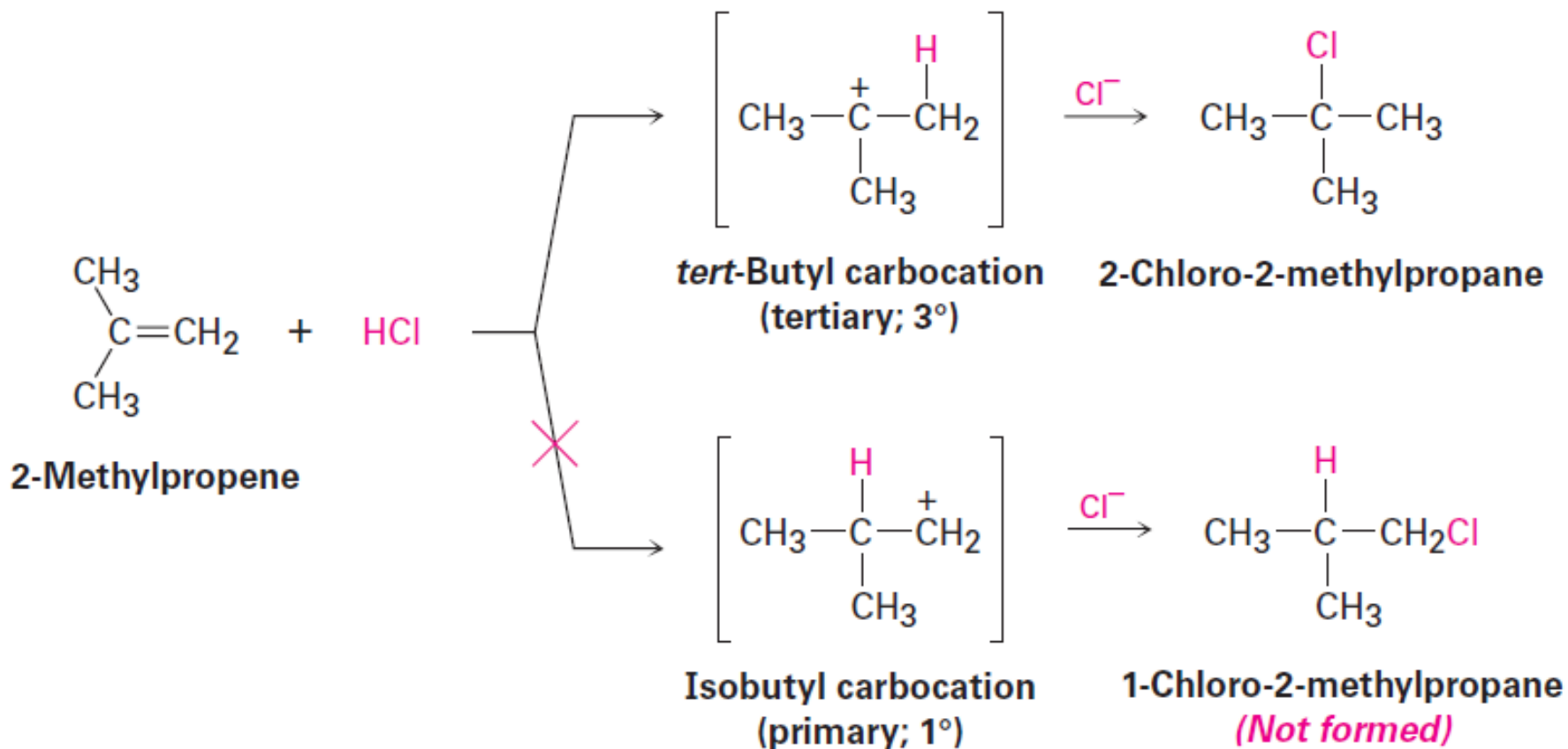
Markovnikov's rules



Markovnikov's rules



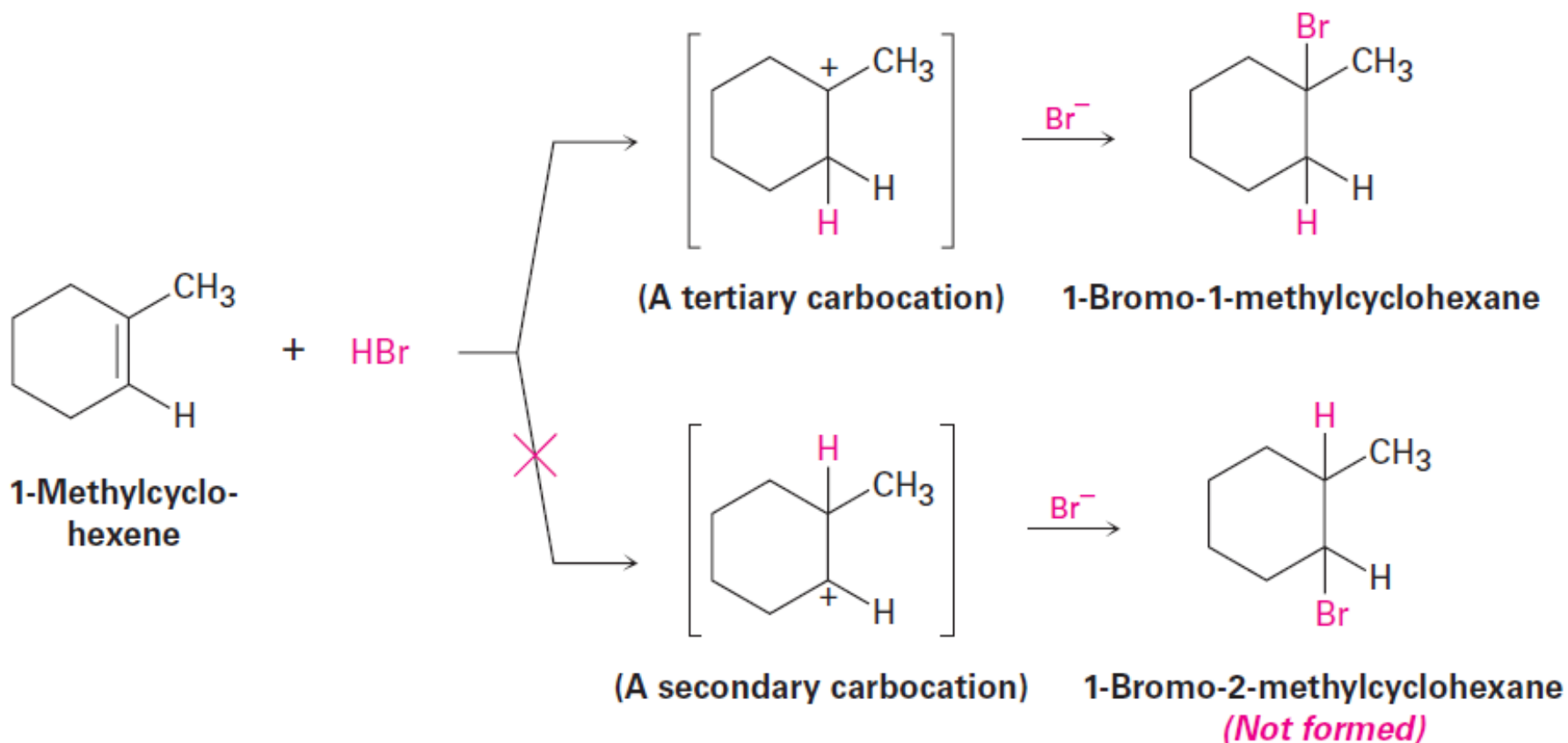
Markovnikov's rules



Markovnikov's rule (restated)

In the addition of HX to an alkene, the more highly substituted carbocation is formed as the intermediate rather than the less highly substituted one.

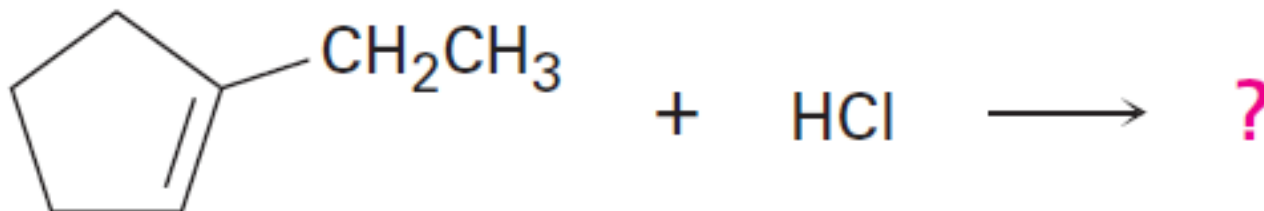
Markovnikov's rules



Problem

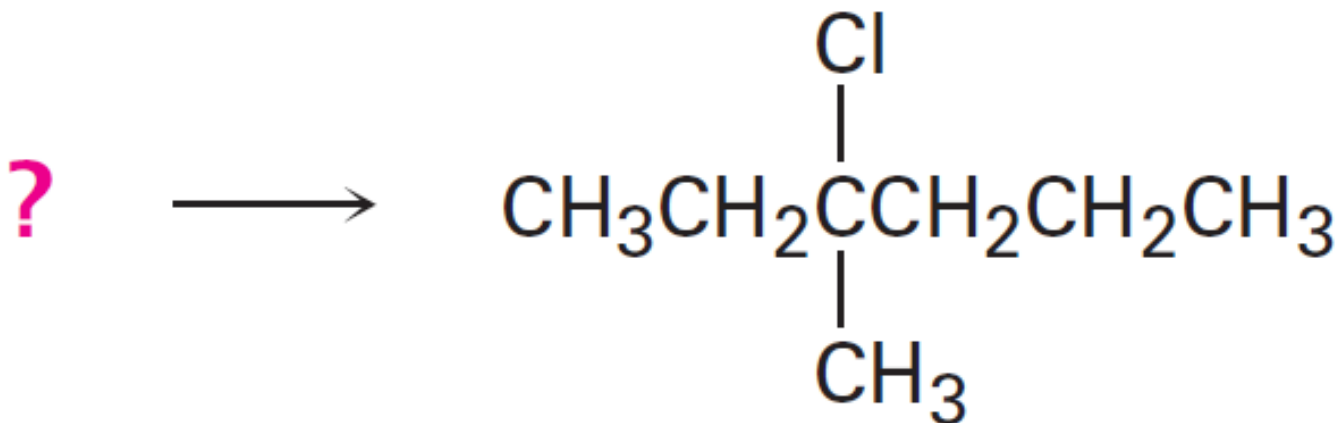
What product would you expect from the reaction of HCl with 1-ethylcyclopentene?

(phản ứng này tạo ra sản phẩm nào)



Problem

What alkene would you start with to prepare the following alkyl halide?
(có thể tổng hợp chất này từ alkene nào)

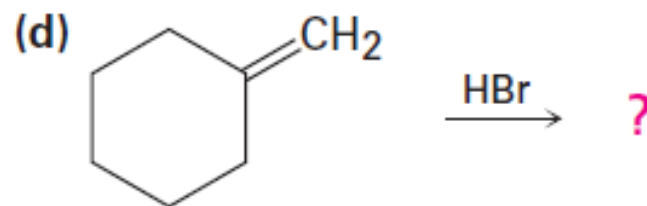
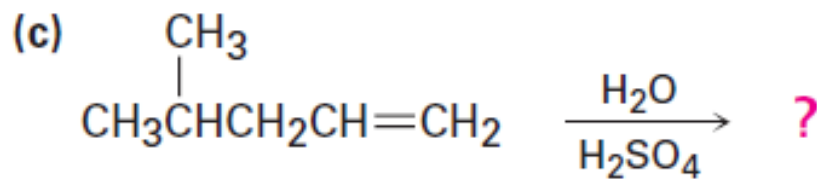
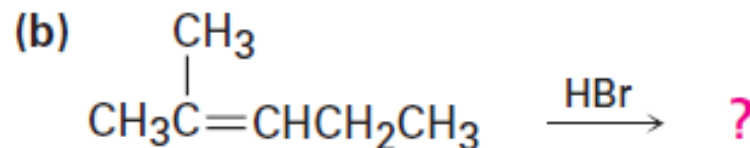
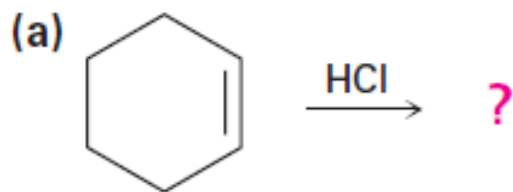


Work backward!

Problem 7.16

PROBLEM 7-16

Predict the products of the following reactions:

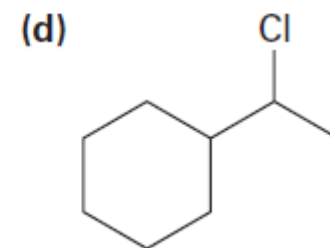
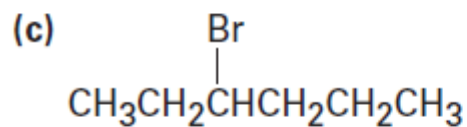
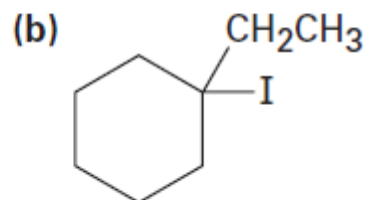
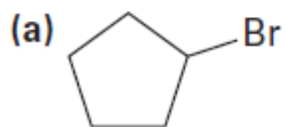


(Addition of H₂O occurs.)

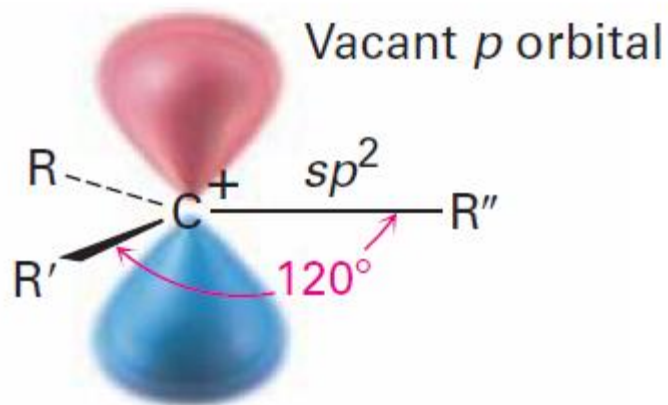
Problem 7.16

PROBLEM 7-17

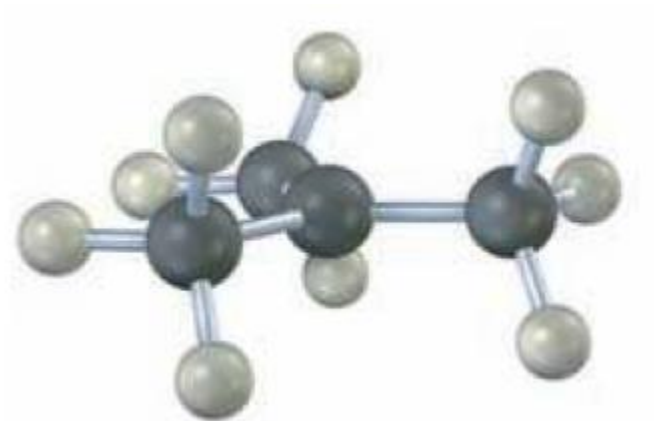
What alkenes would you start with to prepare the following products?



Carbocation structure and stability

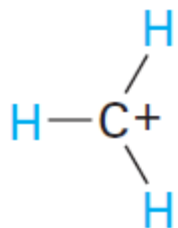


trivalent C is sp^2 -hybridized

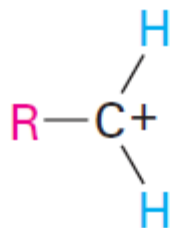


Carbocation is planar

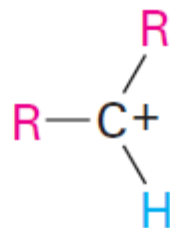
Carbocation structure and stability



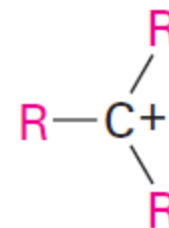
Methyl



Primary (1°)



Secondary (2°)

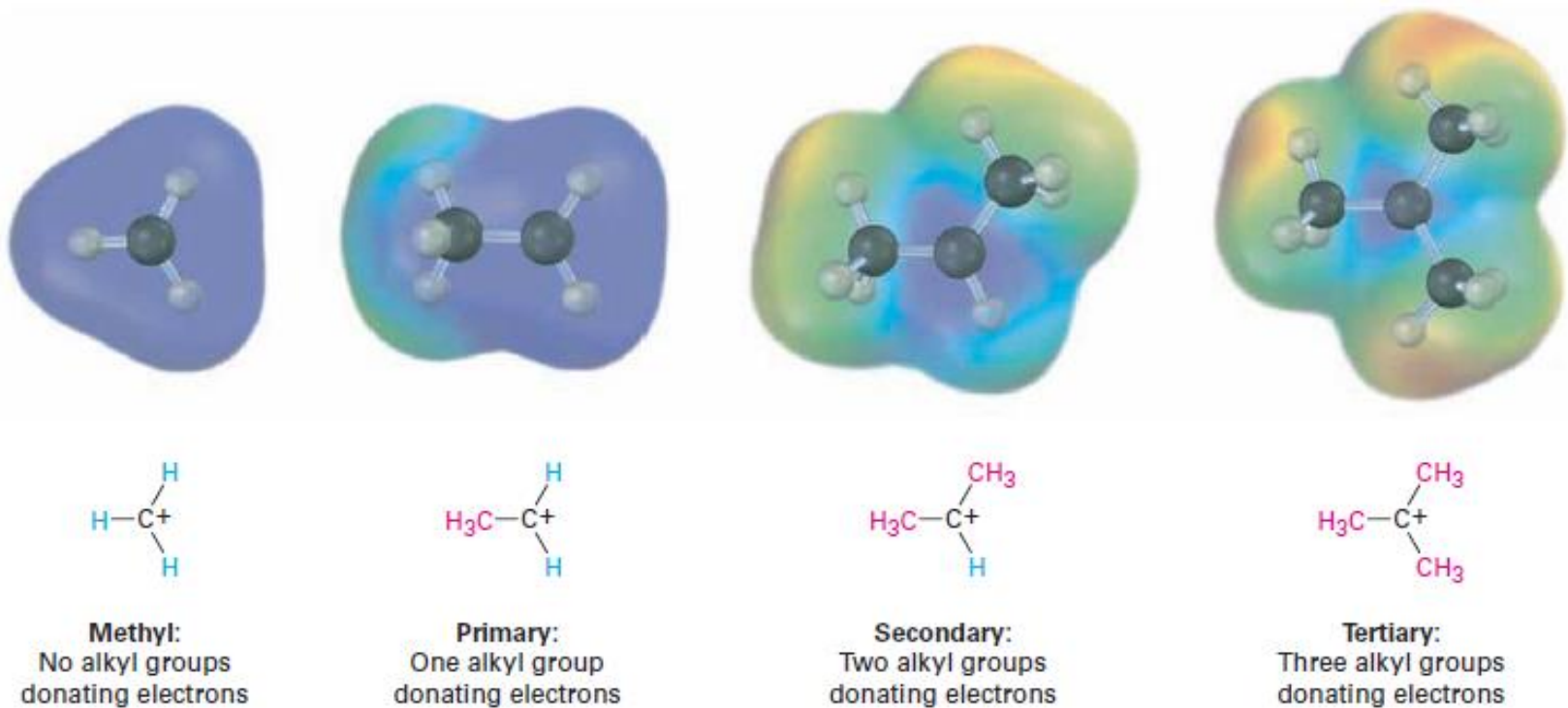


Tertiary (3°)



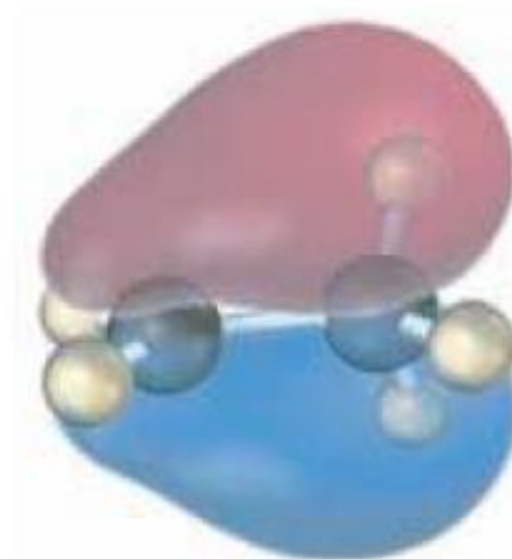
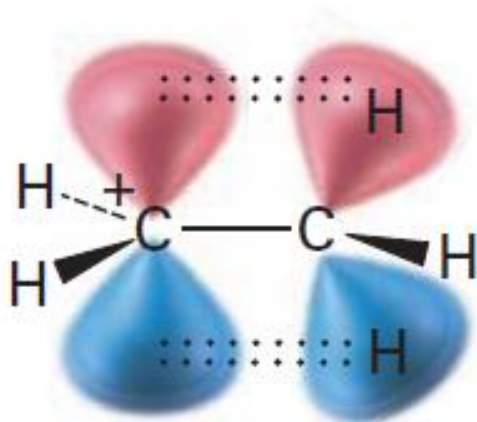
Carbocation structure and stability

Inductive effect stabilizes carbocation



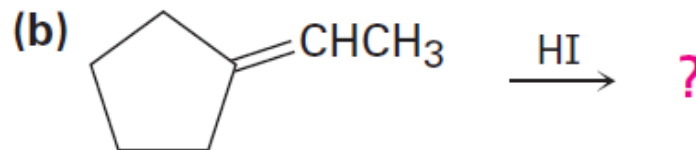
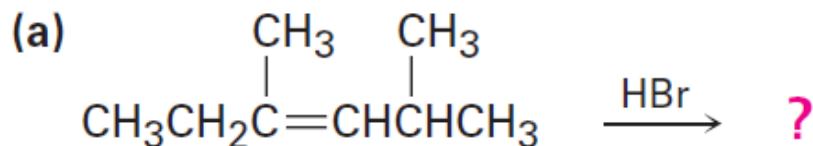
Carbocation structure and stability

Hyperconjugation stabilizes carbocation



Problem 7.18

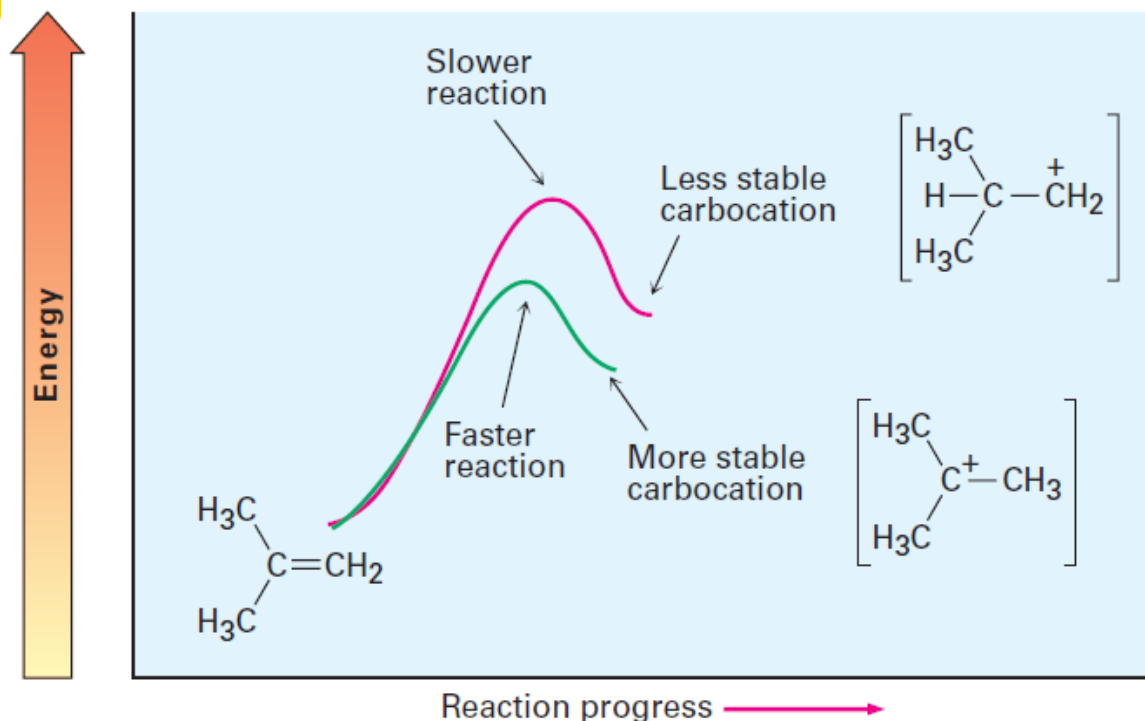
Show the structures of the carbocation intermediates you would expect in the following reactions: (hãy chỉ ra Carbocation trung gian của phản ứng sau)



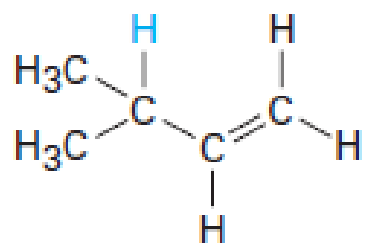
Hammond postulate

Hammond postulate

The structure of a transition state resembles the structure of the nearest stable species. Transition states for endergonic steps structurally resemble products, and transition states for exergonic steps structurally resemble reactants.



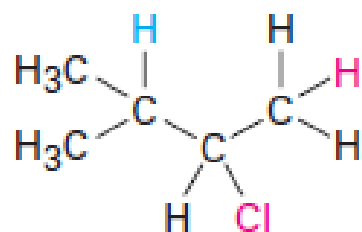
Carbocation rearrangement



3-Methyl-1-butene

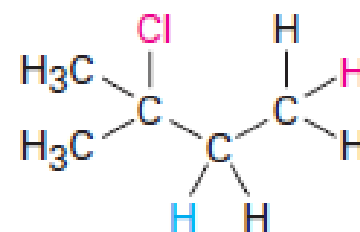
+

HCl



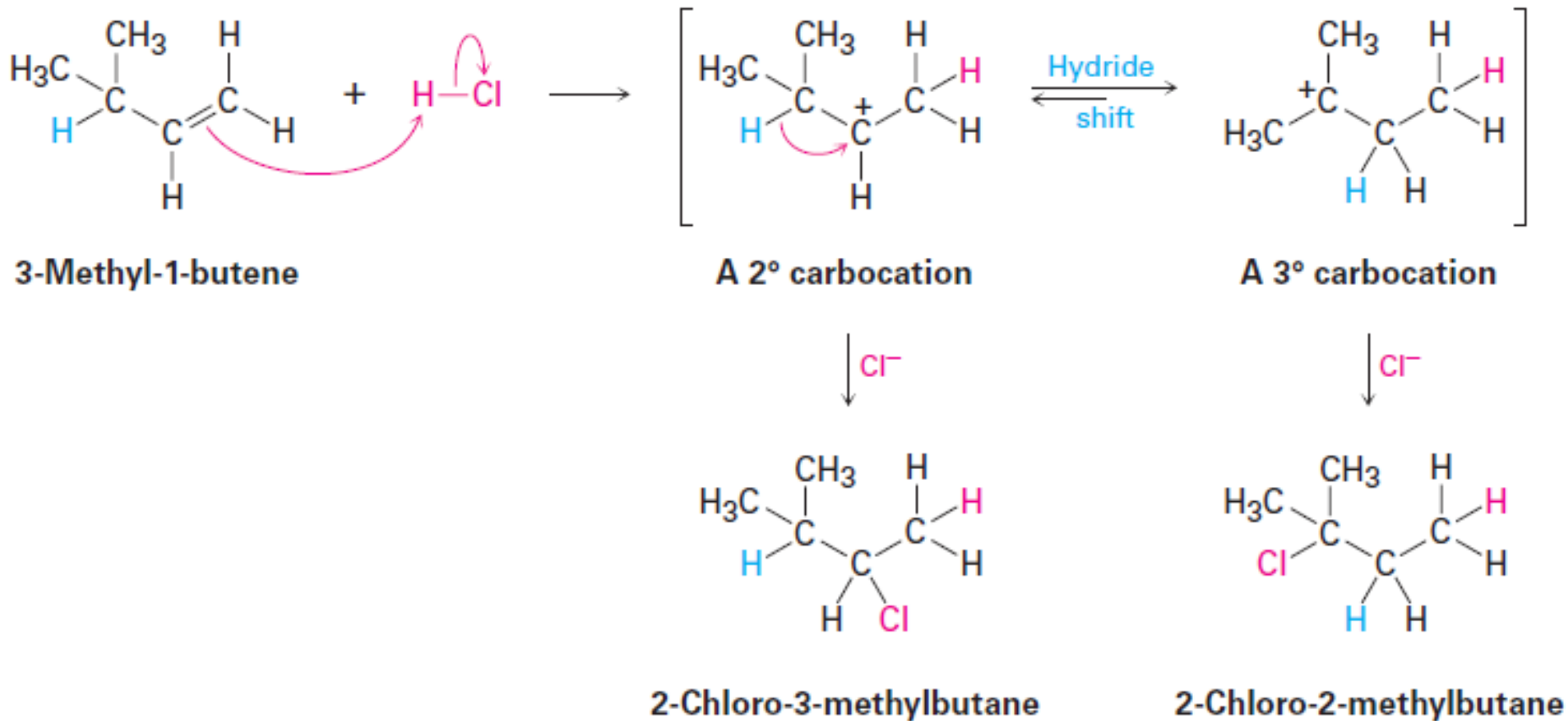
2-Chloro-3-methylbutane
(approx. 50%)

+



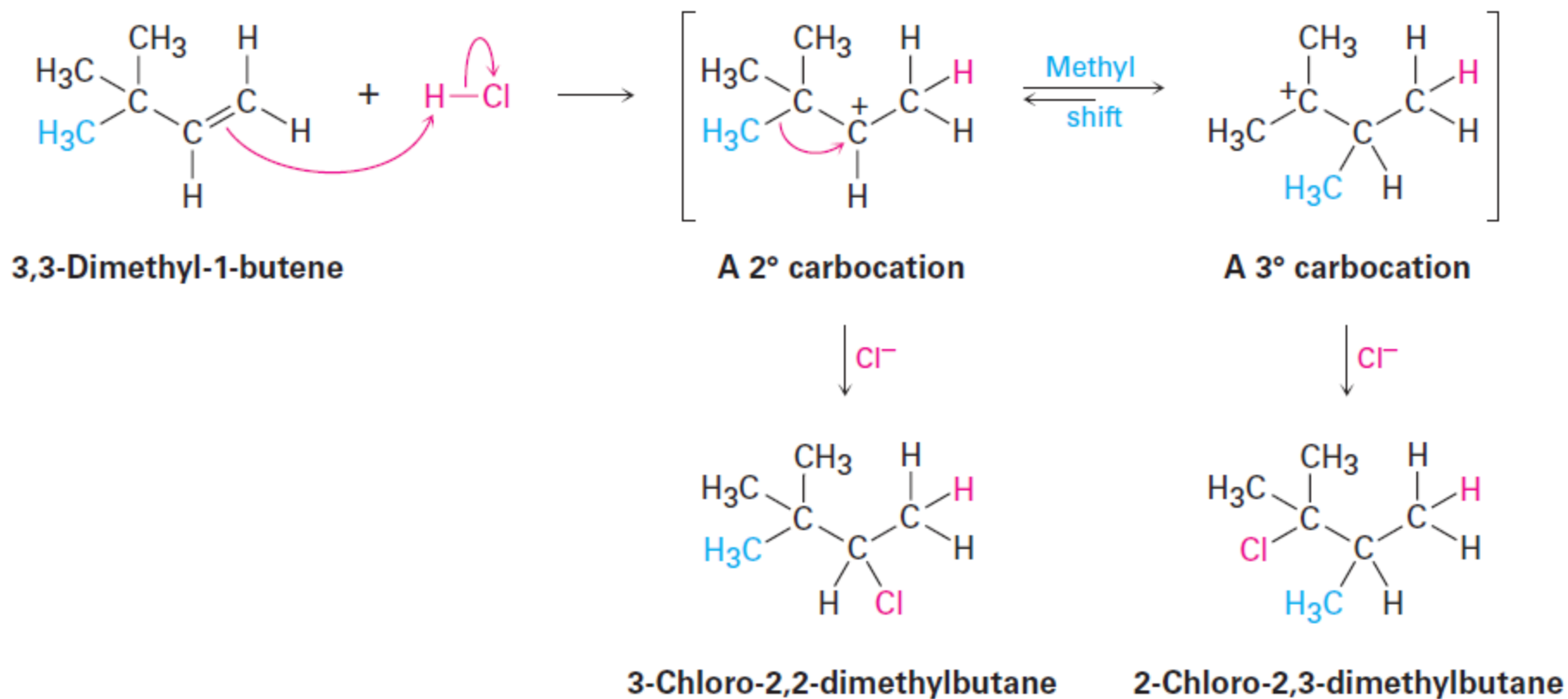
2-Chloro-2-methylbutane
(approx. 50%)

Carbocation rearrangement



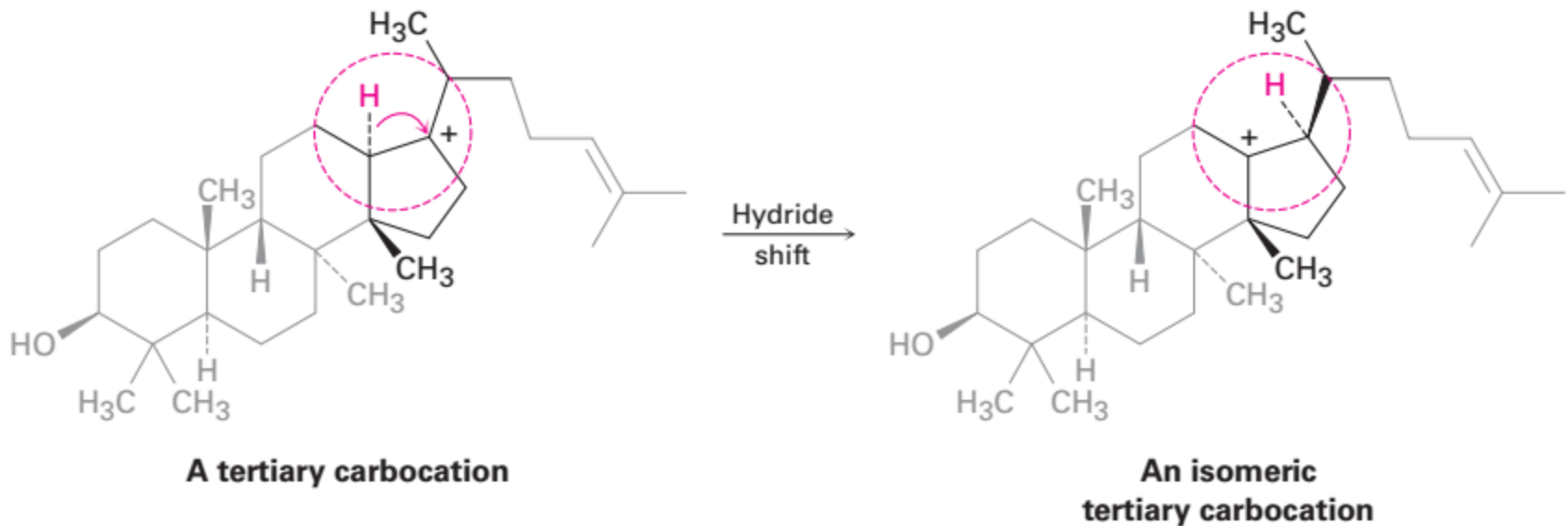
Arrangement of H.

Carbocation rearrangement



Arrangement of a methyl group.

Biosynthesis of cholesterol

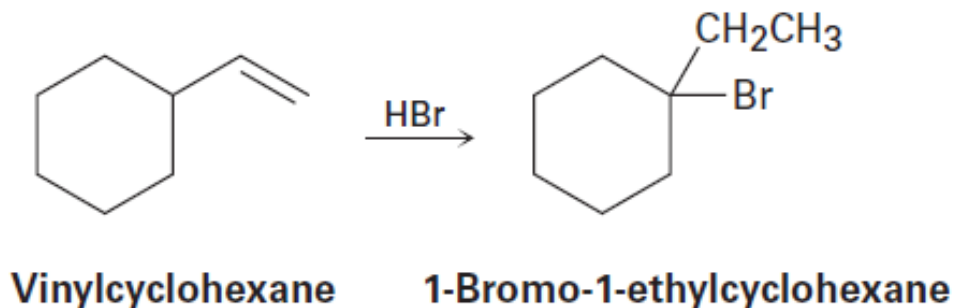


Hydride shift: :H^-

Problem

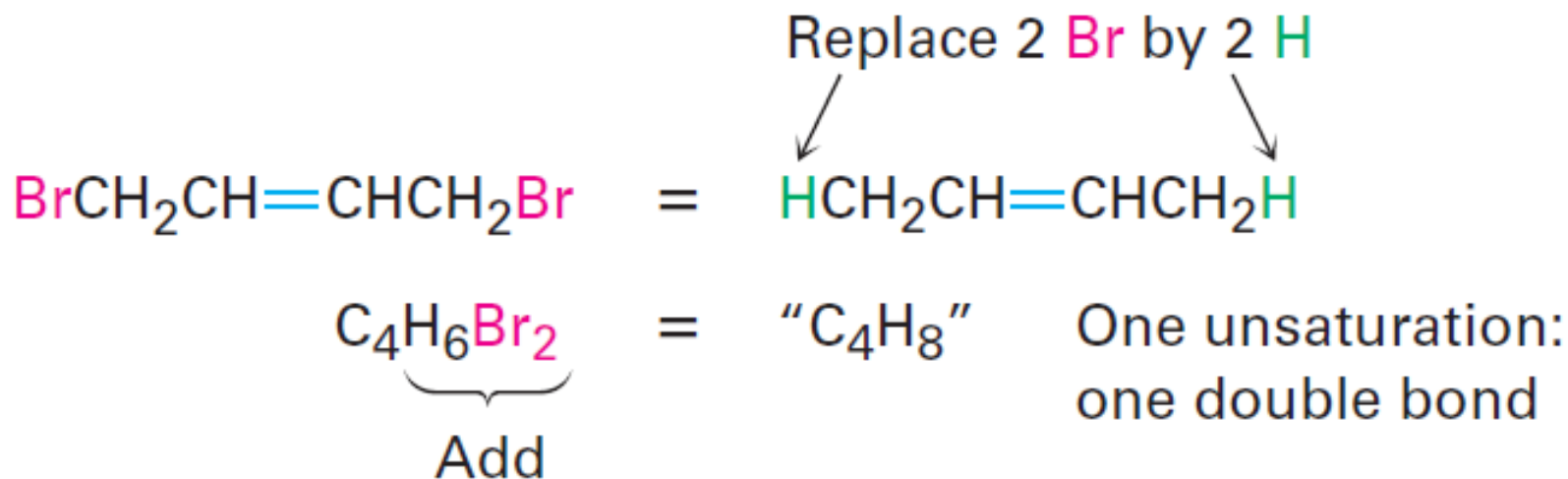
PROBLEM 7-21

On treatment with HBr, vinylcyclohexane undergoes addition and rearrangement to yield 1-bromo-1-ethylcyclohexane. Using curved arrows, propose a mechanism to account for this result.



Degree of unsaturation (độ chưa bão hòa)

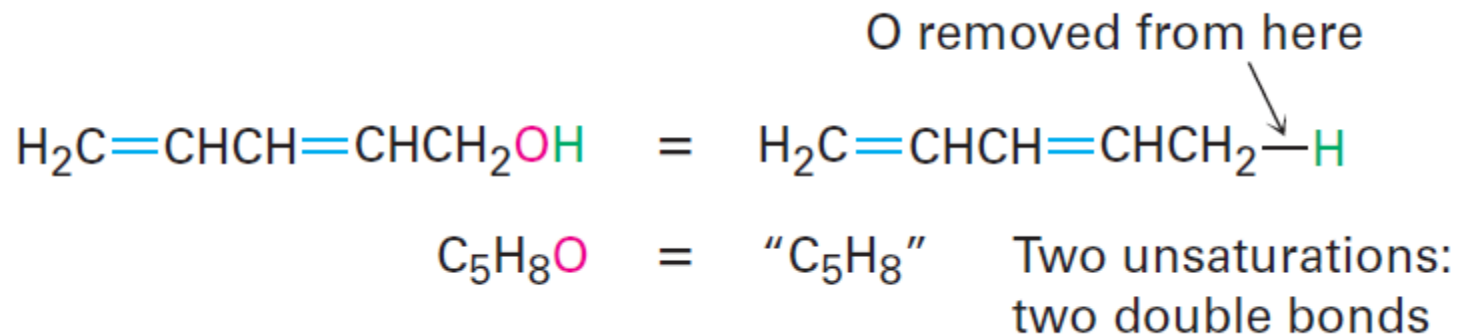
Organohalogen compounds (C, H, X, where X = F, Cl, Br, or I)



Consider X as H.

Degree of unsaturation (độ chưa bão hòa)

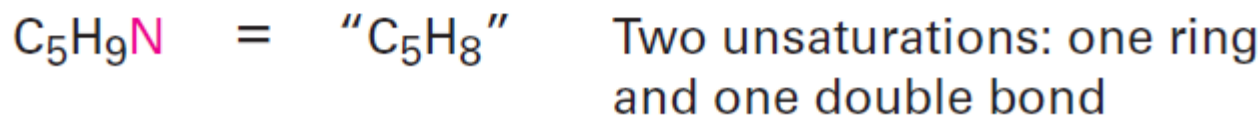
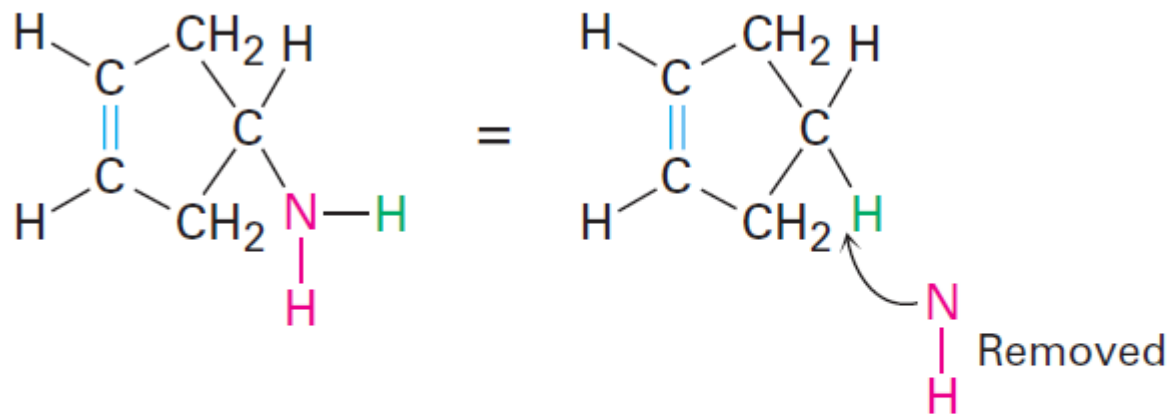
Organoxygen compounds (C, H, O)



The presence of O does not affect the number of H in the formula.

Degree of unsaturation (độ chưa bão hòa)

Organonitrogen compounds (C, H, N)



The presence of N add one more H to the formula.

Degree of unsaturation

To summarize:

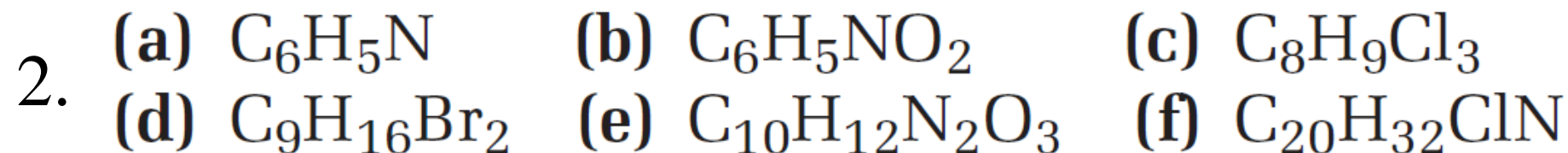
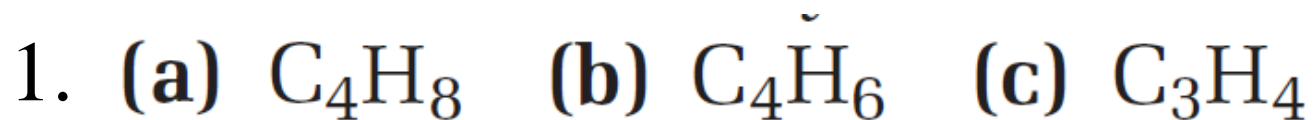
- **Add** the number of halogens to the number of hydrogens.
- **Ignore** the number of oxygens.
- **Subtract** the number of nitrogens from the number of hydrogens.

(Cộng số nguyên tử halogens vào số hydrogens,
Sự có mặt của oxygens không ảnh hưởng đến số hydrogens,
Có bao nhiêu nitrogens thì trừ bớt bấy nhiêu số hydrogens)

To calculate the degree of unsaturation

Problem 7.1

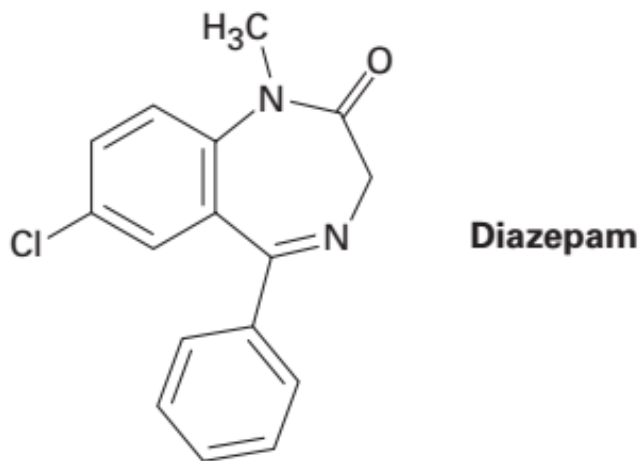
Calculate the degree of unsaturation in the following formulas:



(Diazepam dùng làm thuốc giảm triệu chứng lo lắng). Hãy tìm số H có mặt trong phân tử Diazepam mà không dùng cách đếm số H).

PROBLEM 7-3

Diazepam, marketed as an antianxiety medication under the name Valium, has three rings, eight double bonds, and the formula $C_{16}H_?ClN_2O$. How many hydrogens does diazepam have? (Calculate the answer; don't count hydrogens in the structure.)



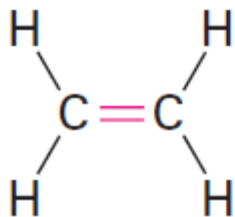
Problem 7.8

The sex attractant of the common housefly is an alkene named cis-9-tricosene. Draw its structure (Tricosane is the straight-chain alkane $C_{23}H_{48}$)

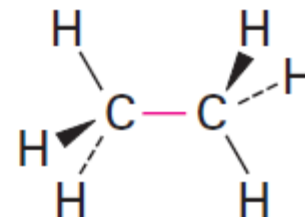
Degree of unsaturation (độ chưa bão hòa)

The number of rings and/or multiple bonds present in the molecule.

(số vòng, liên kết bội có trong phân tử)



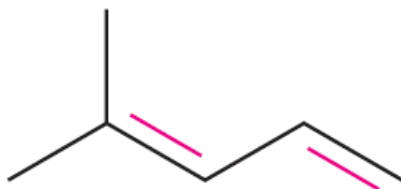
Ethylene: C₂H₄
(Fewer hydrogens – *Unsaturated*)



Ethane: C₂H₆
(More hydrogens – *Saturated*)



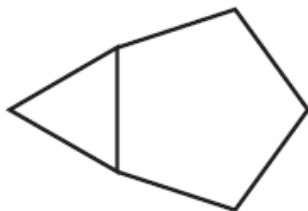
Degree of unsaturation (độ chưa bão hòa)



**4-Methyl-1,3-pentadiene
(two double bonds)**



**Cyclohexene
(one ring, one
double bond)**



**Bicyclo[3.1.0]hexane
(two rings)**



**4-Methyl-2-pentyne
(one triple bond)**