

Poglavlje 12: Reakcije alkena

TABELA 12-3

Uobičajeni polimeri i njihovi monomeri

Monomer	Struktura	Polimer (uobičajeno ime)	Struktura	Primena
eten	$\text{H}_2\text{C}=\text{CH}_2$	polietilen	$-(\text{CH}_2\text{CH}_2)_n-$	čuvanje hrane, posude



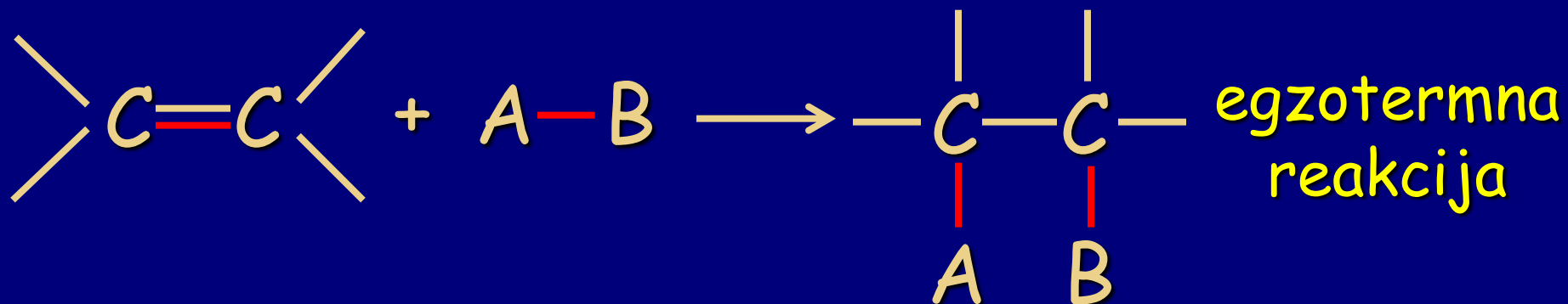
Polietilen

otporna na habanje



Adicione reakcije alkena

π veza je nezasićena, karakteristične reakcije adicije.



$$\Delta H^\circ = (DH^\circ_{\pi\text{-veza}} + DH^\circ_{\text{A-B}}) - (DH^\circ_{\text{C-A}} + DH^\circ_{\text{C-B}})$$

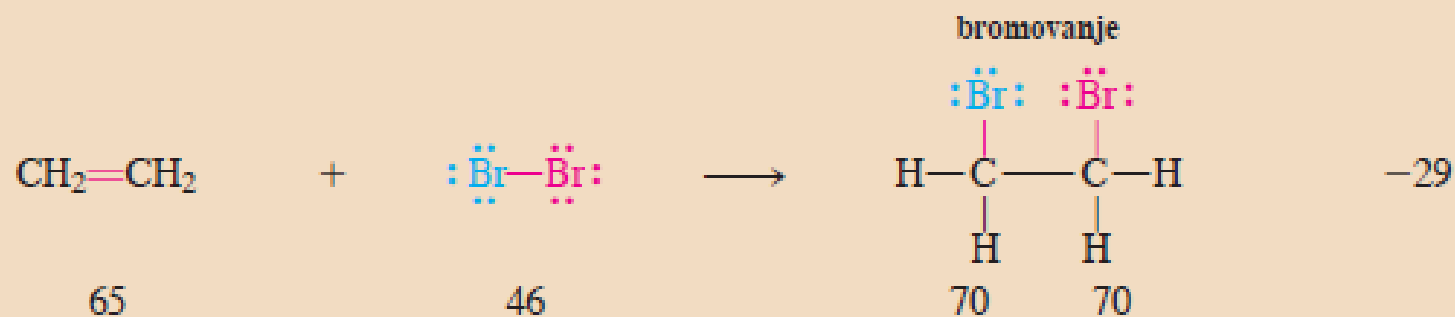
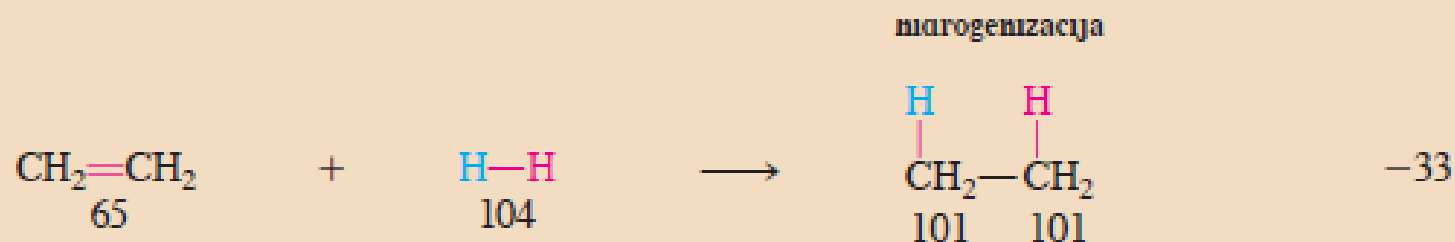
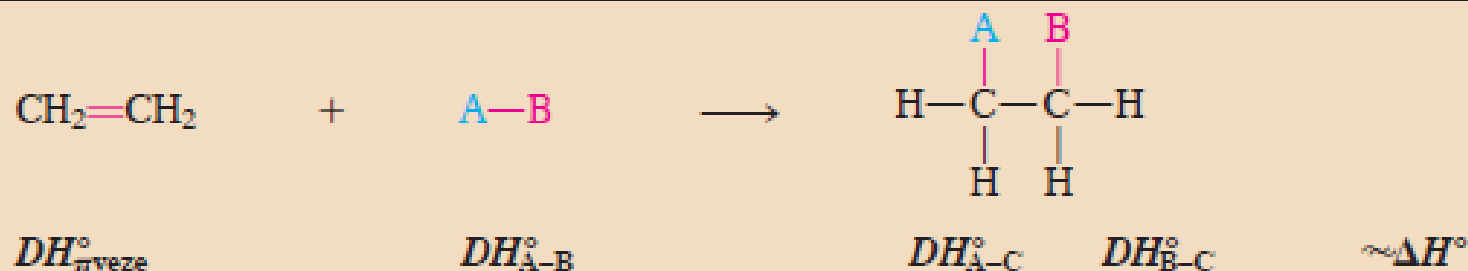
Vežba 12-1

Izračunajte ΔH° adicije H_2O_2 na eten, pri čemu se dobija 1,2-etandiol (etilen-glikol) ($DH^\circ_{\text{HO-OH}} = 51 \text{ kcal mol}^{-1}$).

$$\Delta H^\circ = (65 + 51) - (94 + 94)$$

TABELA 12-1

Izračunajte ΔH° (sve vrednosti u kcal mol^{-1}) za reakcije adicije na alkene^a



hidrohlorovanje

^a Ovo su samo izračunate vrednosti: one ne uzimaju u obzir promene u jačini C-C i C-H σ -veza koje uključuju i promenu u hibridizaciji. (Uporedite vrednosti hidrogenizacije u tabeli sa onima izračunatim u zadatku 48 u poglavlju 11.)

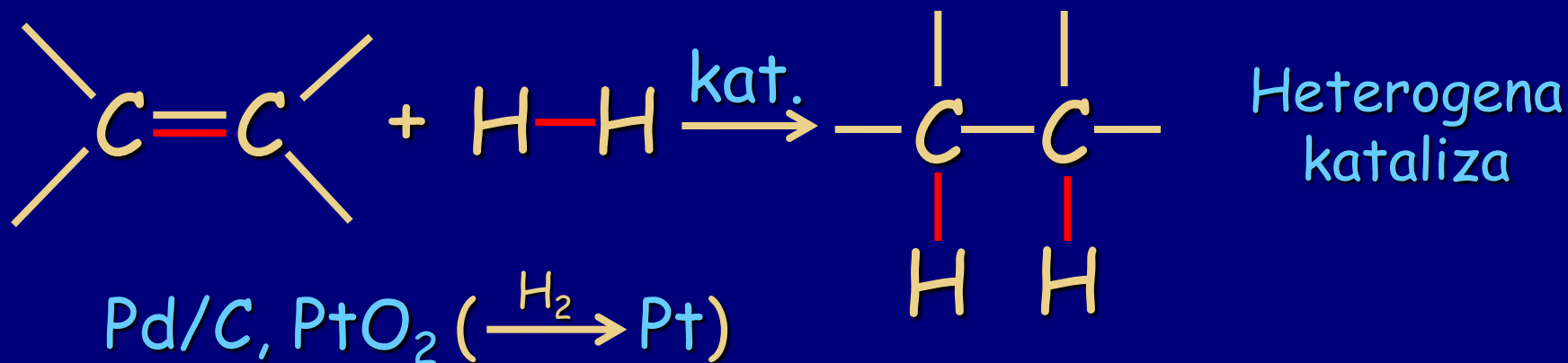
TABELA 12-1

Izračunajte ΔH° (sve vrednosti u kcal mol^{-1}) za reakcije adicije na alkene^a

$\text{CH}_2=\text{CH}_2$	+	$\text{A}-\text{B}$	\longrightarrow	$\begin{array}{c} \text{A} \quad \text{B} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	
DH_{veze}°		$DH_{\text{A-B}}^\circ$		$DH_{\text{A-C}}^\circ$ $DH_{\text{B-C}}^\circ$	$-\Delta H^\circ$
				hidrochlorovanje	
$\text{CH}_2=\text{CH}_2$	+	$\text{H}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}$	\longrightarrow	$\begin{array}{c} \text{H} \quad \overset{\cdot\cdot}{\text{Cl}} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	-17
65		103		101 84	
				hidratacija	
$\text{CH}_2=\text{CH}_2$	+	$\text{H}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{H}$	\longrightarrow	$\begin{array}{c} \text{H} \quad \overset{\cdot\cdot}{\text{O}}\text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	-11
65		119		101 94	

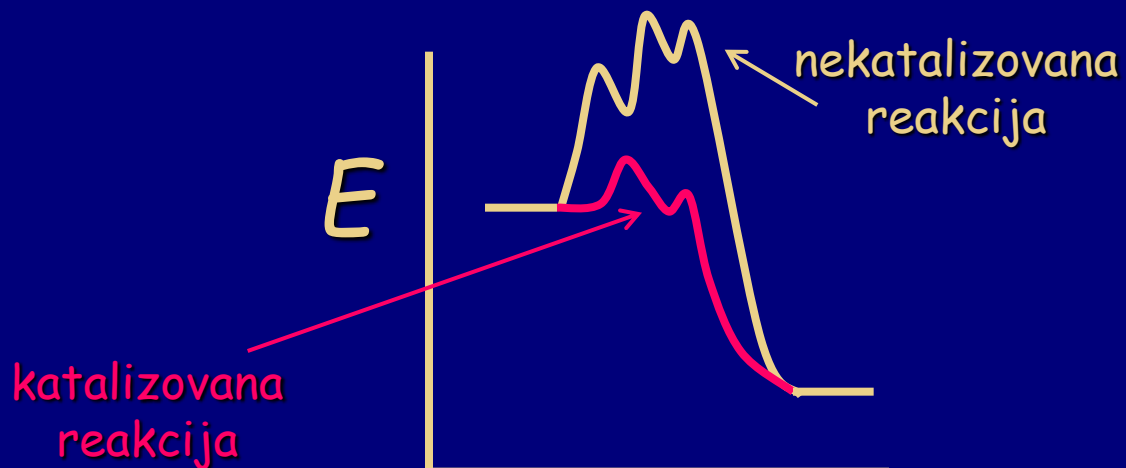
^a Ovo su samo izračunate vrednosti: one ne uzimaju u obzir promene u jačini C-C i C-H σ-veza koje uključuju i promenu u hibridizaciji. (Uporedite vrednosti hidrogenizacije u tabeli sa onima izračunatim u zadatku 48 u poglavlju 11.)

1. Katalitička hidrogenizacija: H_2 + katalizator

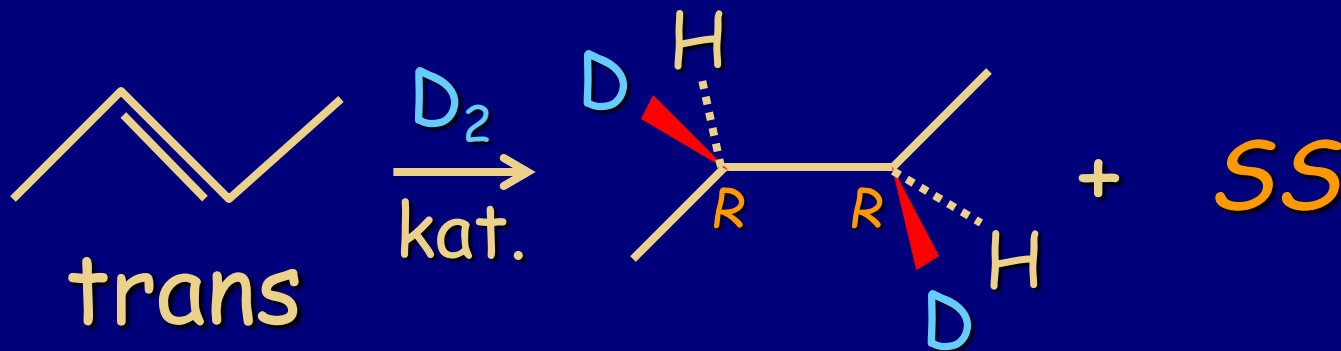
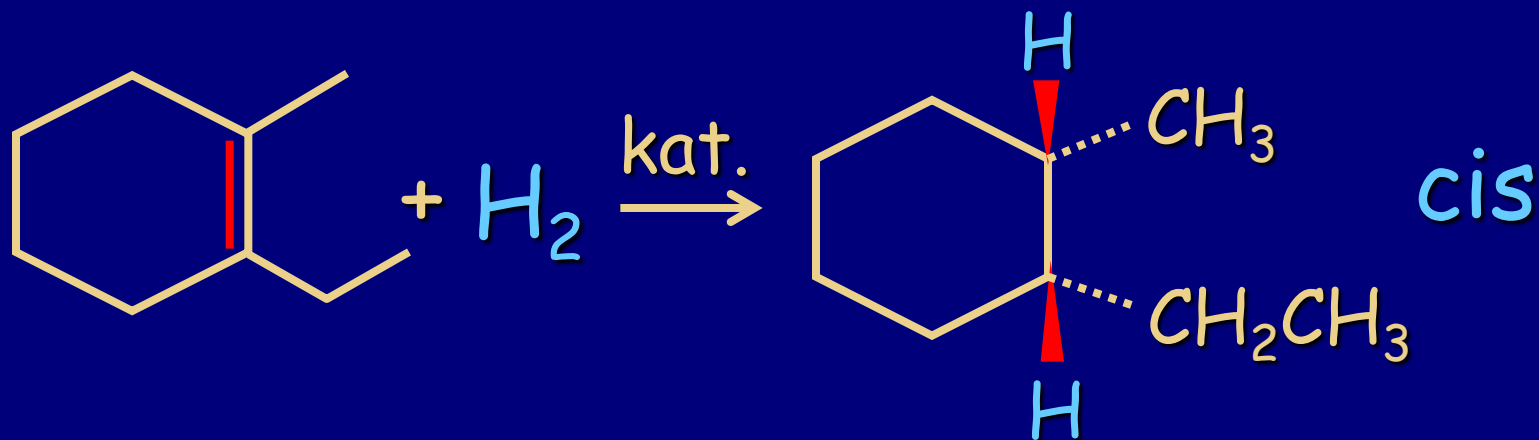


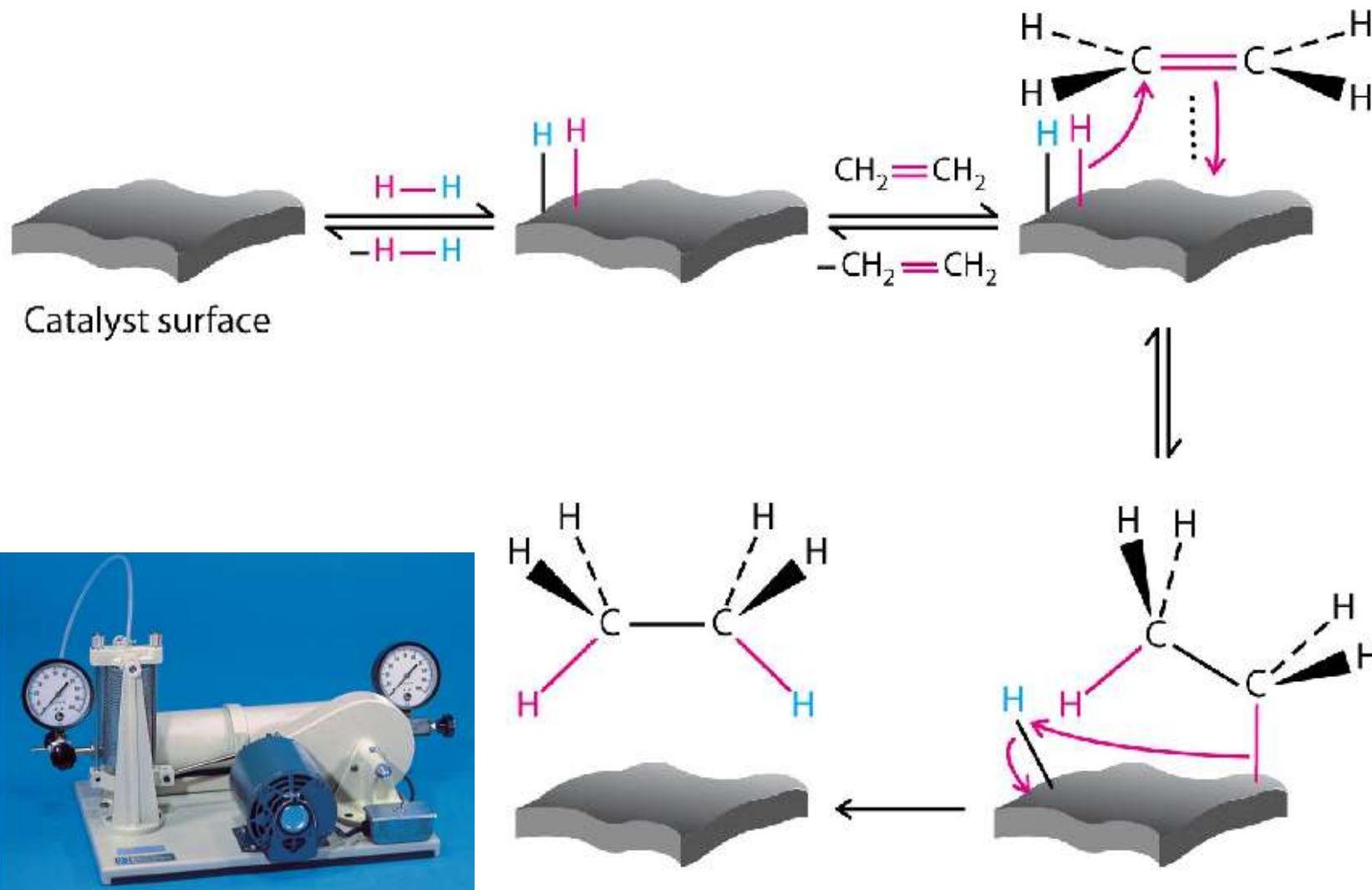
Zašto kataliza? Mehanizam snižavanj E_a

Alkeni + H_2 $\not\rightarrow$
nema reakcije
bez katalizatora



Mehanizam hidrogenizacije: do reakcije dolazi na površini katalizatora. Dolazi do stereospecifične adicije sa iste strane dvostruke veze (sin adicija).





Vežba 12-2

Katalitička hidrogenizacija (S)-2,3-dimetil-1-pentena daje samo jedan optički aktivni proizvod. Nacrtajte proizvod i objasnite rezultat. [Pomoć: da li adicija H_2 (1) stvara novi stereocentar ili (2) utiče na neku od veza u okolini već postojećeg stereocentra?]

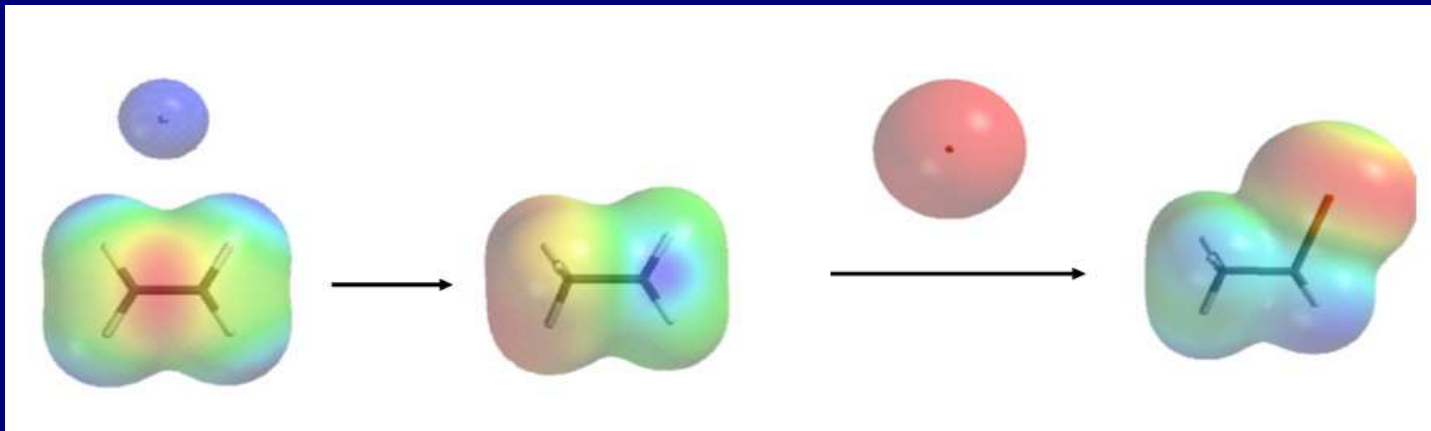
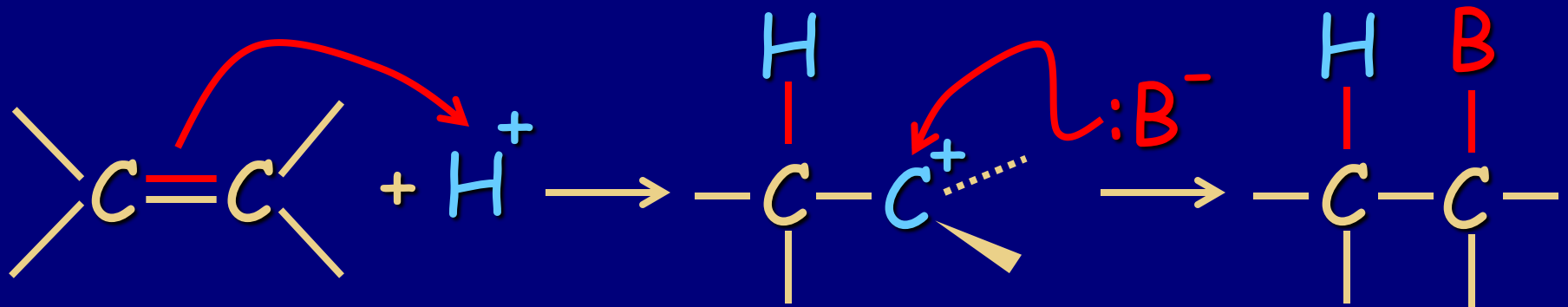
Biljna ulja, margarine, i buter: "očvršćavanje" nakon hidrogenizacije



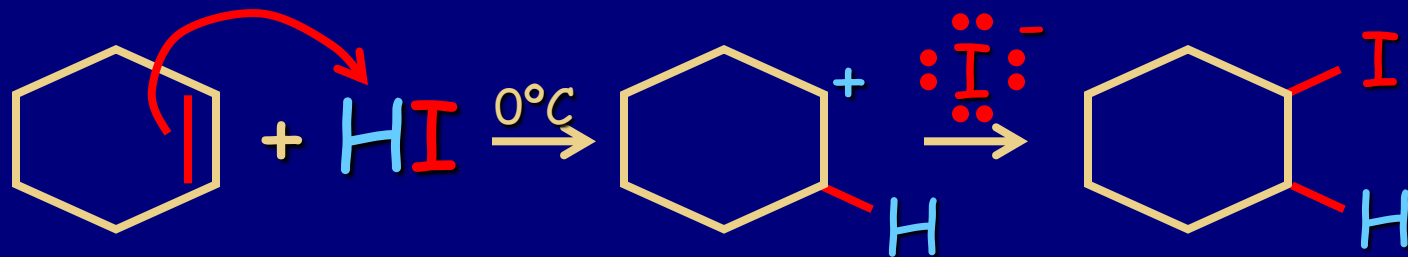
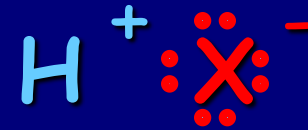
Elektrofilne adicije

π veza je elektron-bogata. Adicija polarnih reagenasa $A^{\delta+}-B^{\delta-}$.

Mehanizam za $A^{\delta+} = H^+$ Obrnuto od E1!

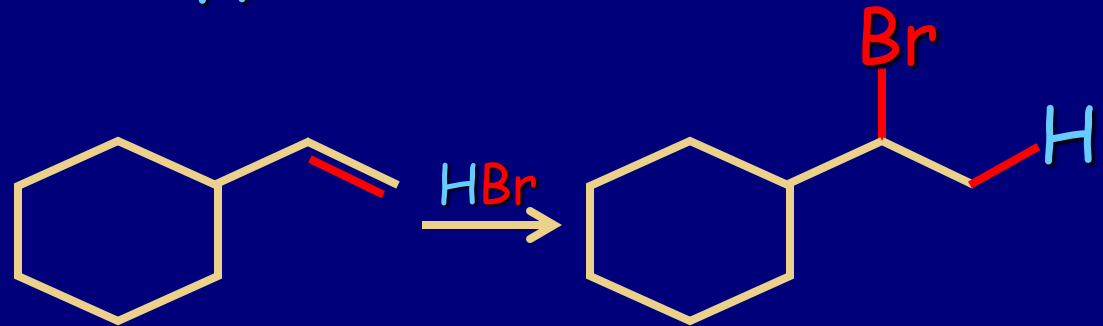


Hidrohalogenovanje



Obrnuto u odnosu na eliminaciju

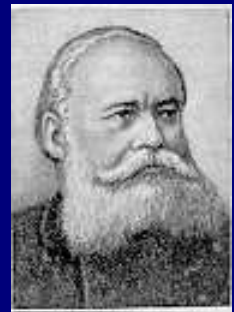
Regioselektivna reakcija:



Markovnikov-ljevo pravilo

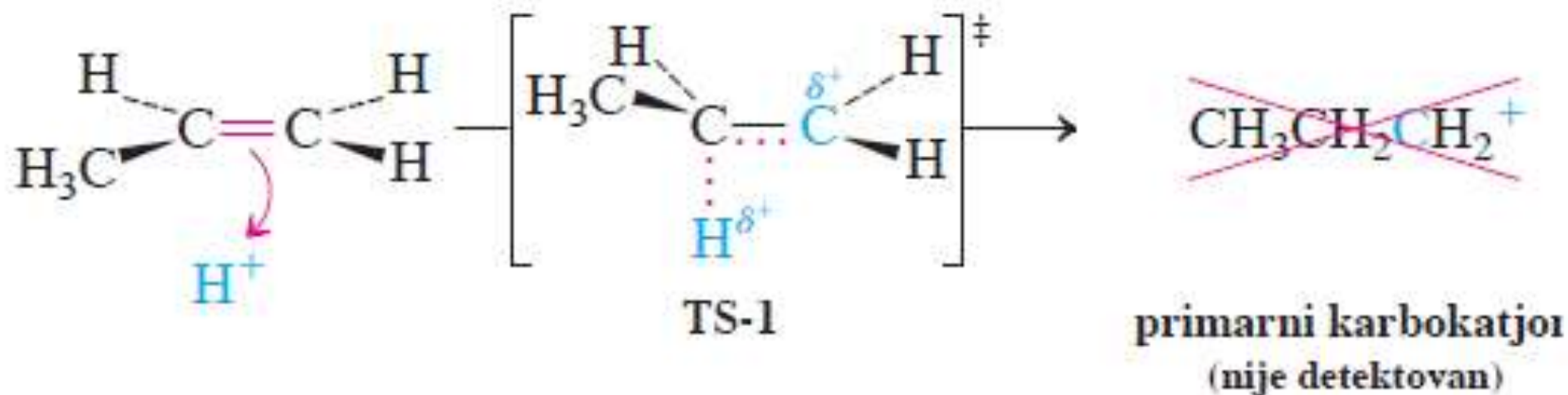
H⁺ (A^{δ+}) se adira na manje supstituisan ugljenik

1838-1904

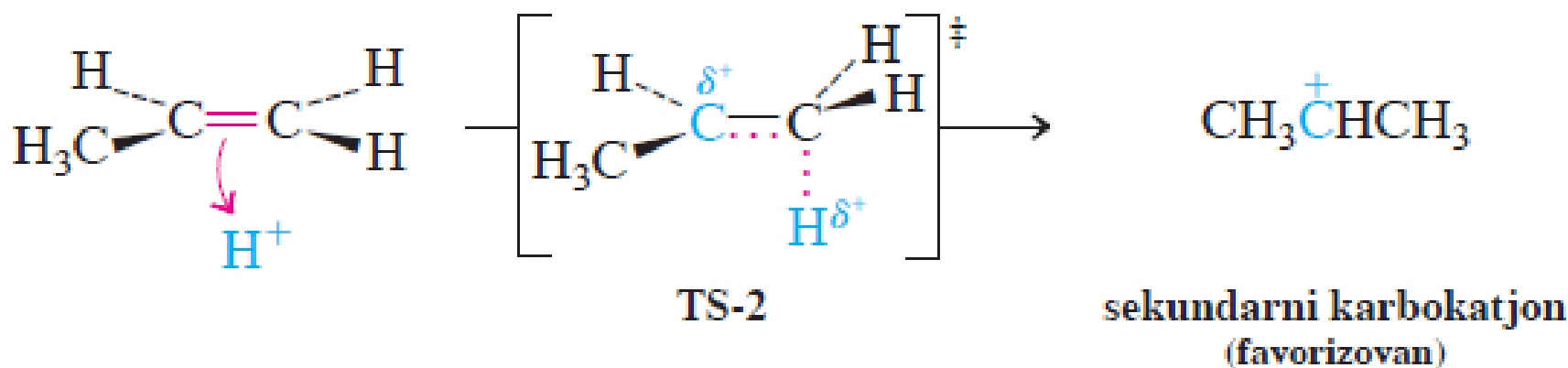


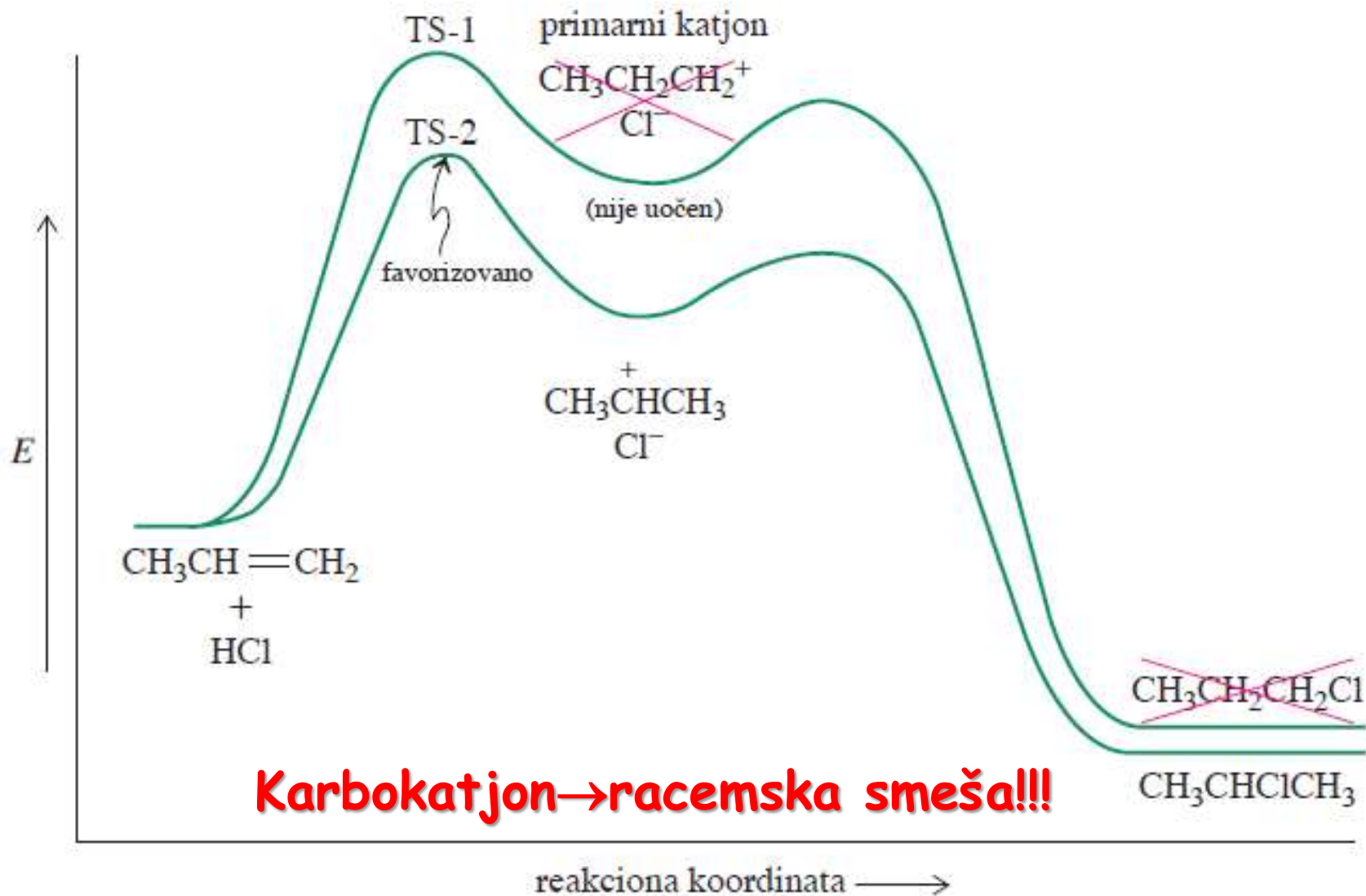
Zašto? Protonovanjem nastaje više supstituisani katjon

Protonovanje propena na C2



Protonovanje propena na C1



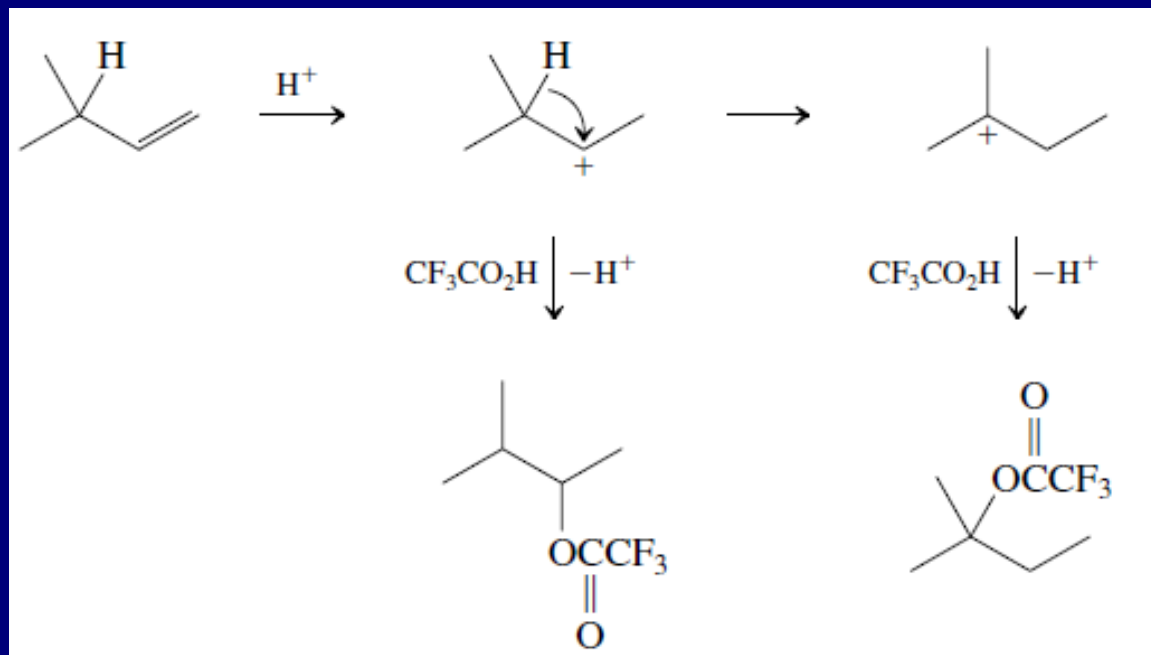
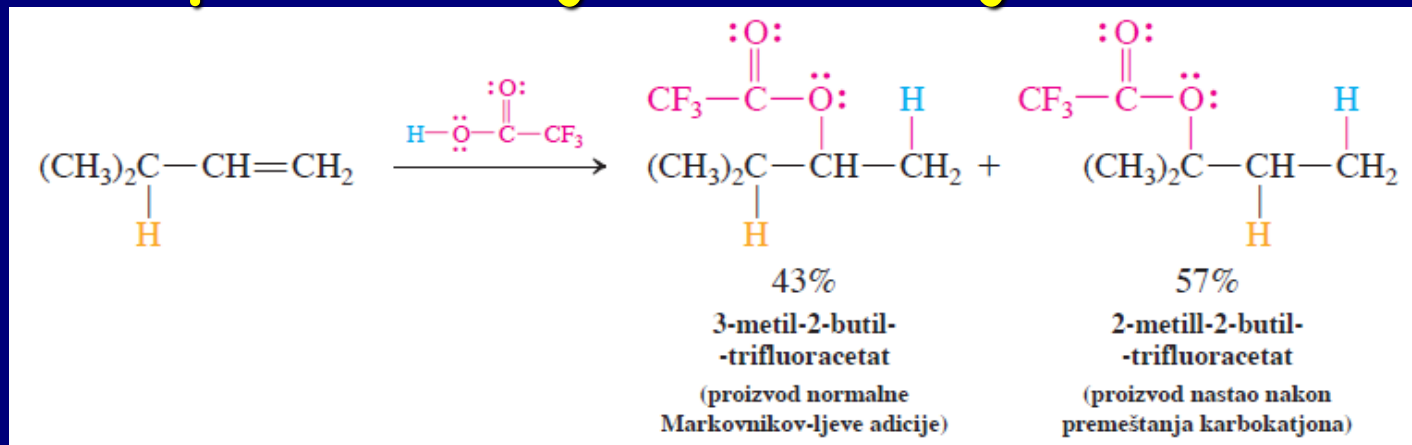


Karbokatjon \rightarrow racemska smeša!!!

Vežba 12-3

Predvidite ishod adicije HBr na: (a) 1-heksen; (b) *trans*-2-penten; (c) 2-metil-2-buten; (d) 4-metilcikloheksen. Koliko se izomera gradi u svakom pojedinačnom slučaju?

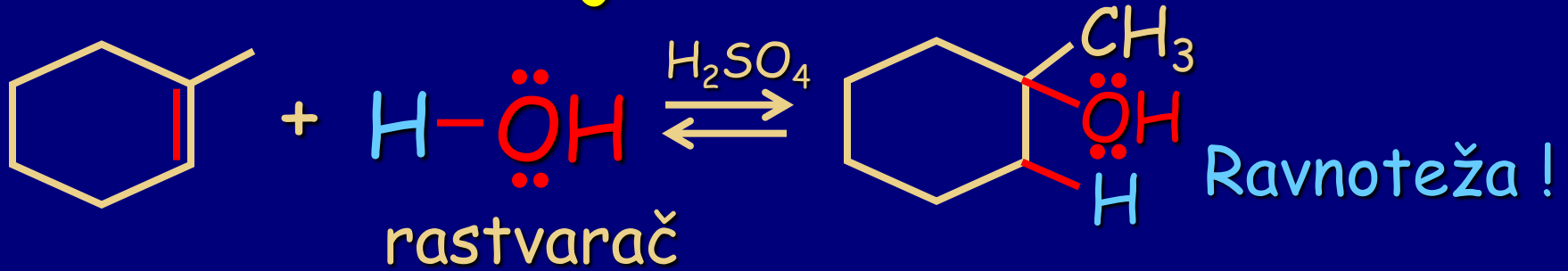
U toku elektrofilne adicije može doći do premeštanja karbokatjona



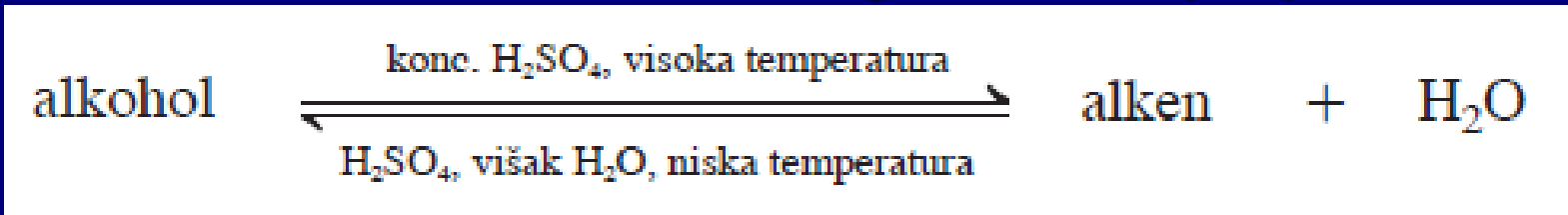
Uslovi za premeštanje: jaka kiselina + slab nukleofil

Markovnikov-Ijeva hidratacija

H_2O, H^+ katalizator

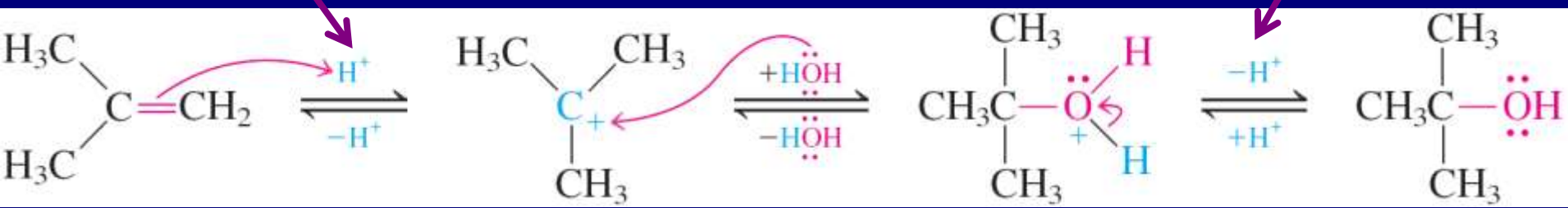


Reverzibilna hidratacija 2-metilpropena:



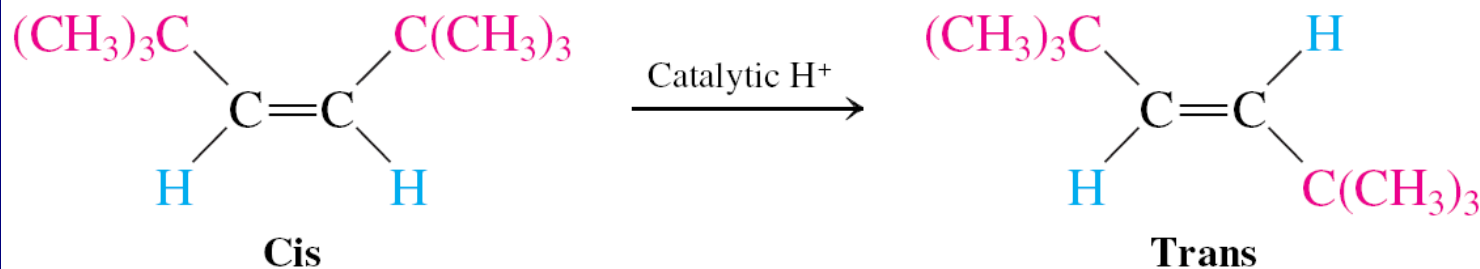
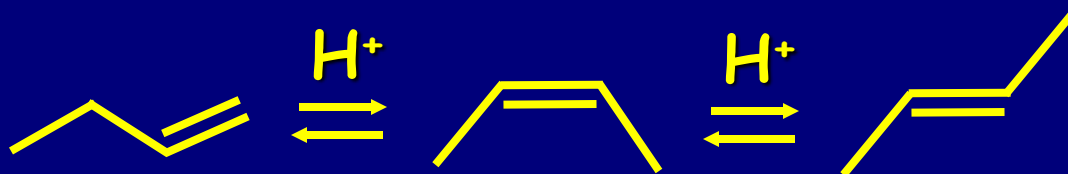
H^+ se koristi

H^+ regeneracija

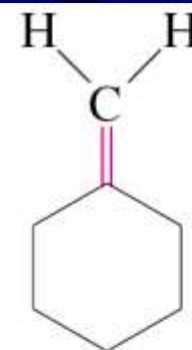


Posledice reverzibilnosti E1

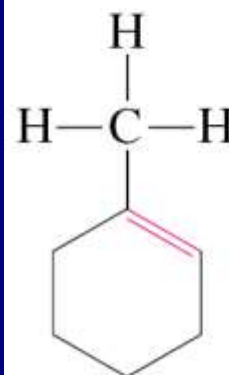
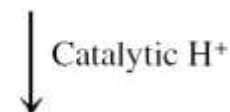
Izomerizacija alkena



ravnoteža = termodinamička kontrola



Terminal



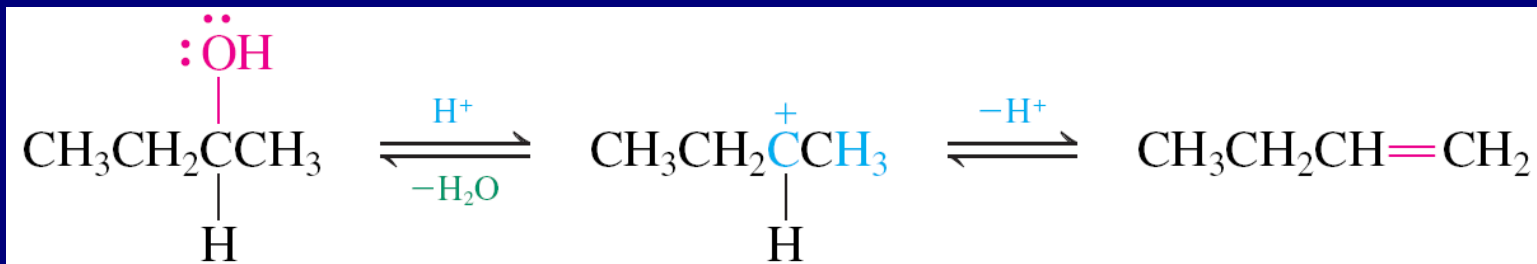
Internal

Vežba 12-6

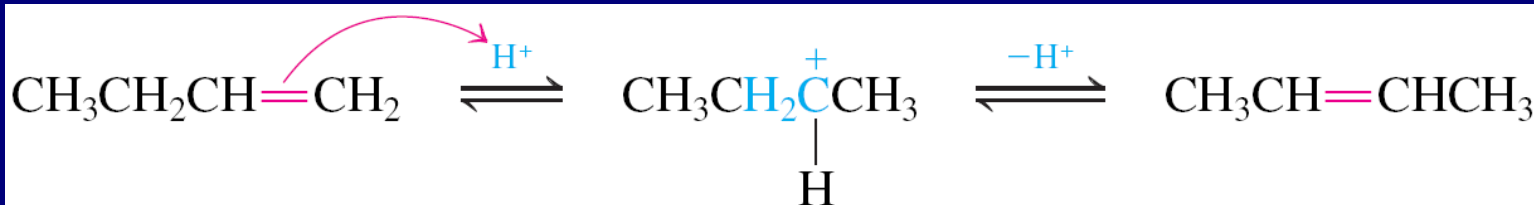
Dejstvo katalitičke količine deuterisane sumporne kiseline na 2-metilpropen u D_2O daje $(CD_3)_3COD$. Objasnite mehanizam.

Mehanizam termodinamičke kontrole

Faza 1

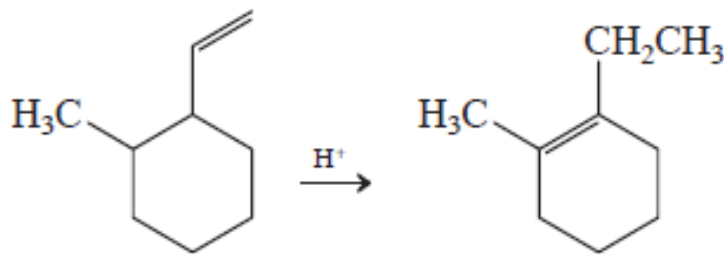


Faza 2

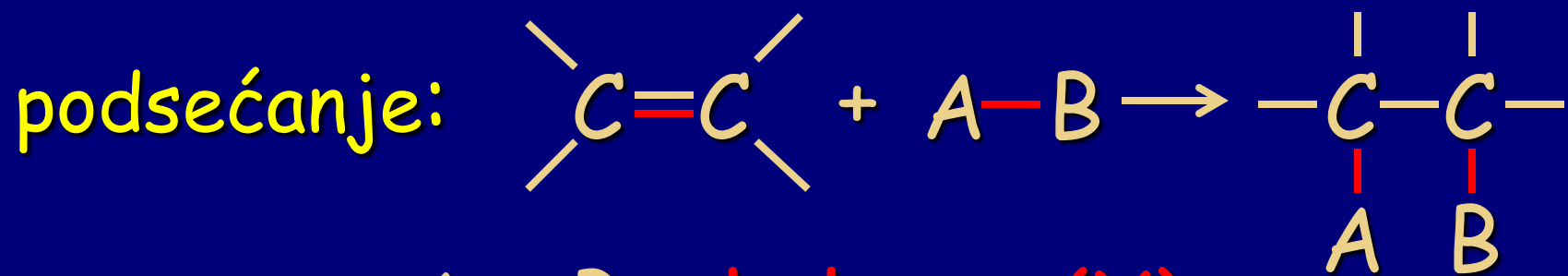


Vežba 12-7

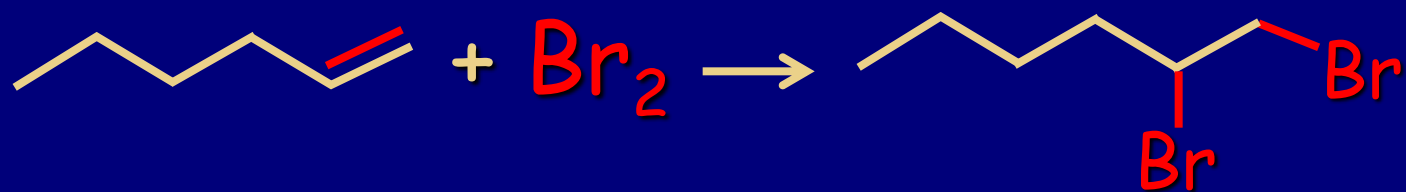
Napišite mehanizam predstavljenog premeštanja. Zbog čega se ova reakcija vrši?



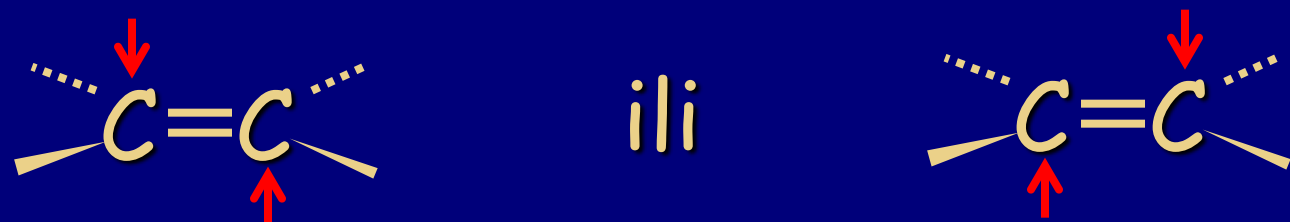
HALOGENIVANJE



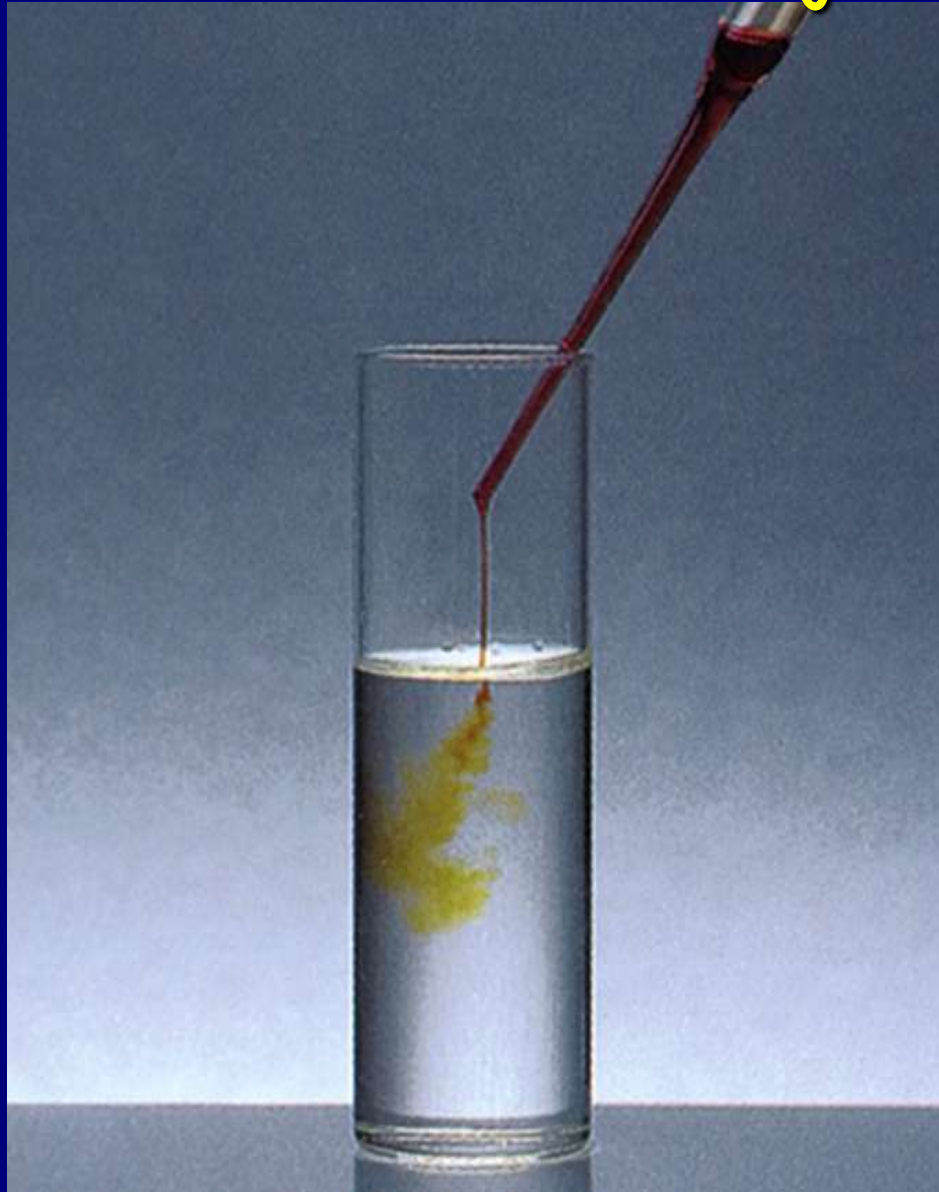
A = B = halogen (X)



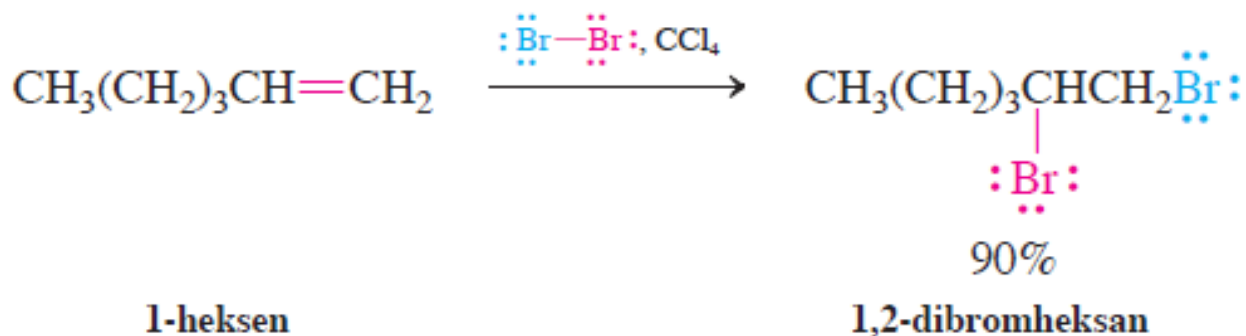
Stereospecifična adicija: anti (nije sin)



Bromovanje: moguća "titracija" test za nezasićenje

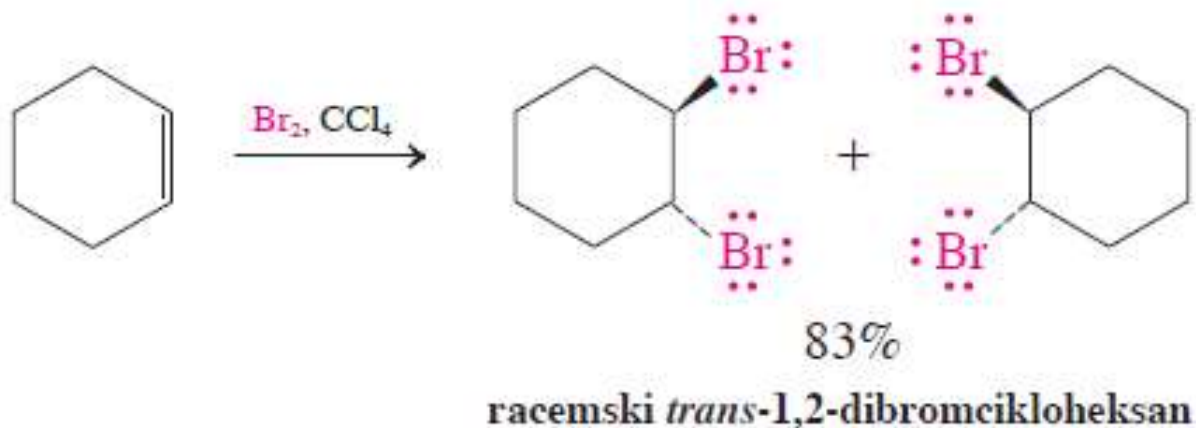


Elektrofilna adicija Br₂ na 1-heksen

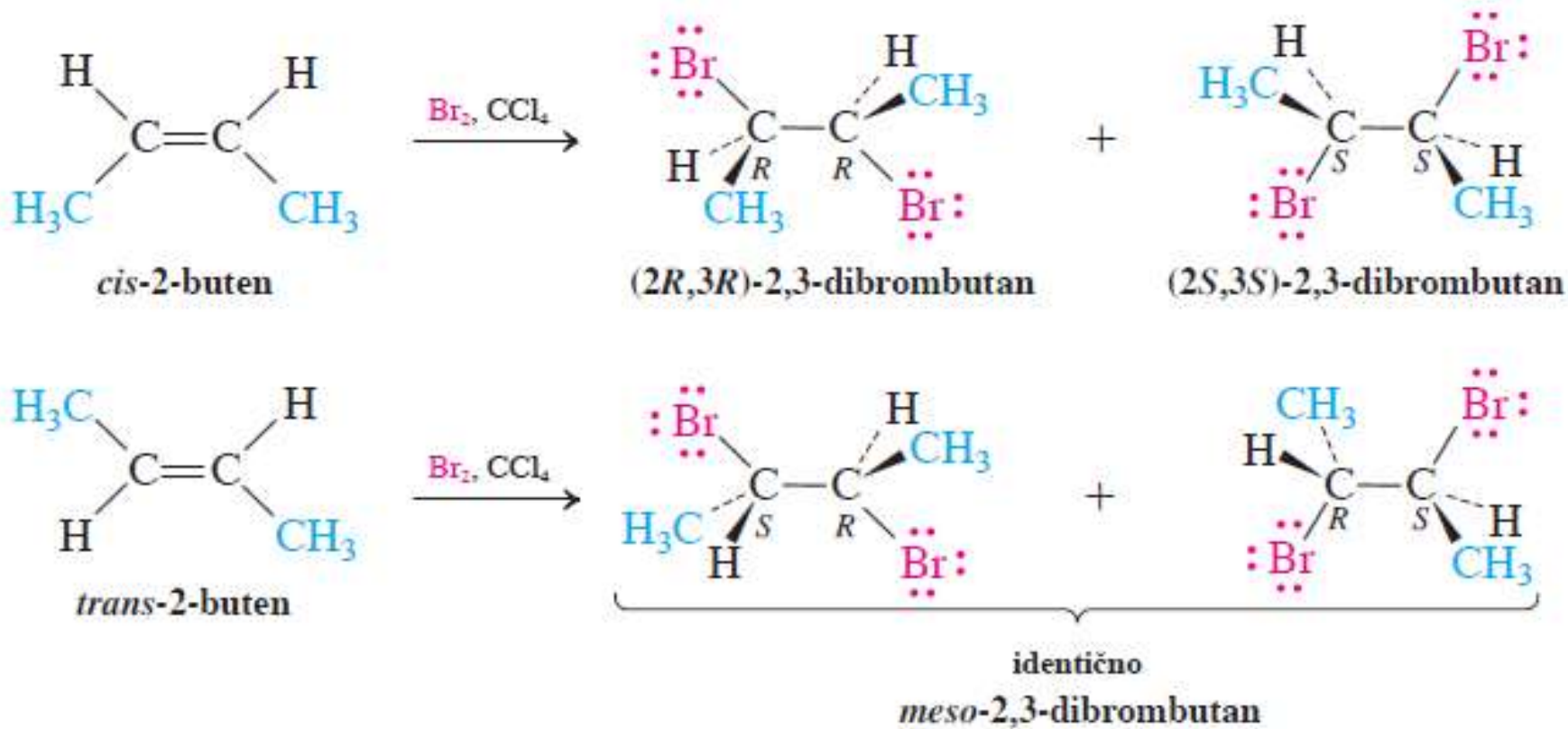


Bromovanje je anti adicija

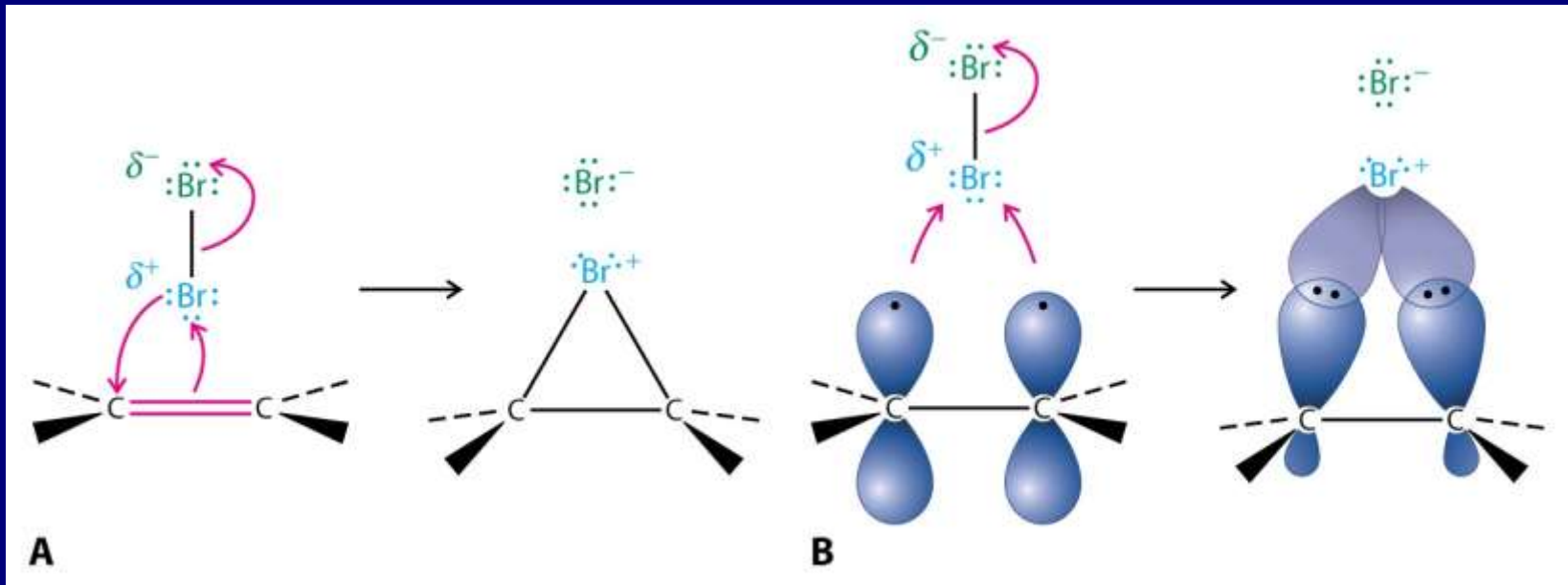
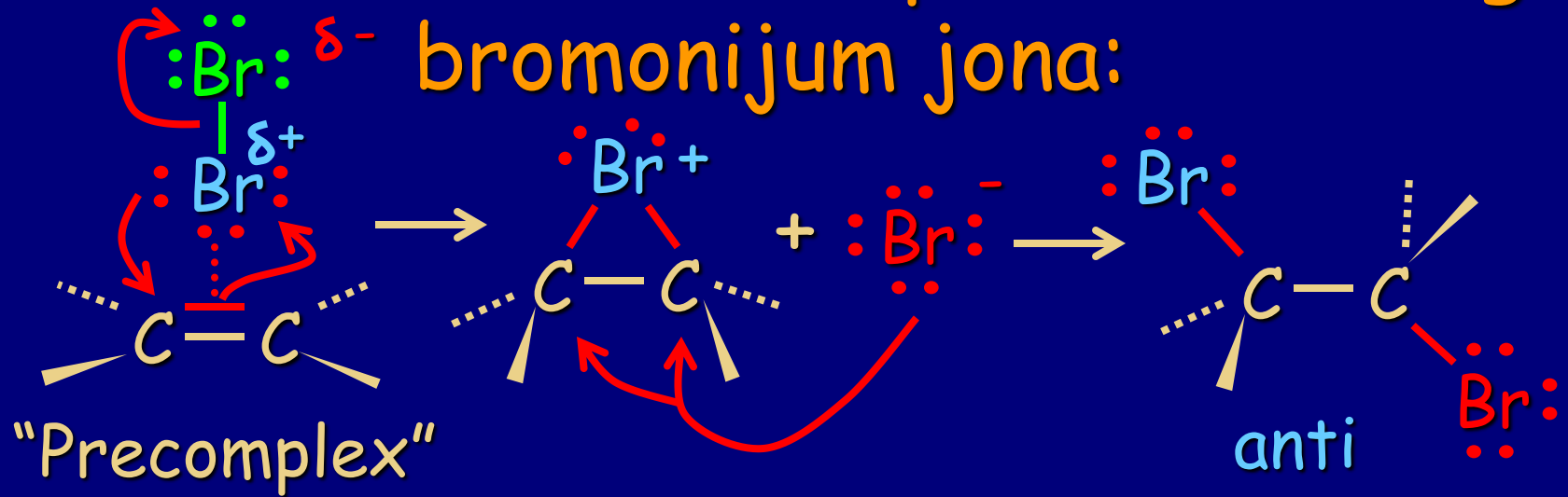
anti-bromovanje cikloheksena



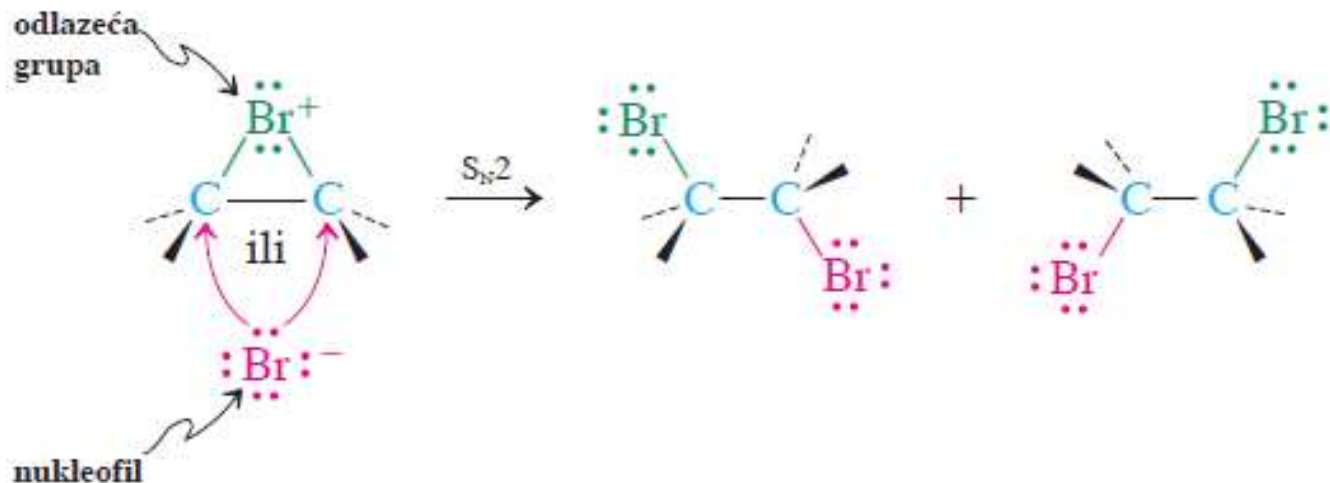
Stereospecifično bromovanje 2-butena



Mehanizam preko cikličnog bromonijum jona:

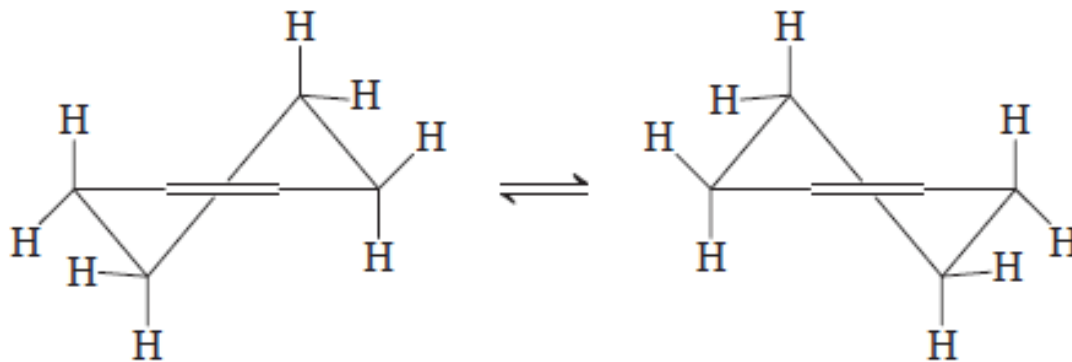


Nukleofilno otvaranje cikličnog bromonijum jona



Vežba 12-9

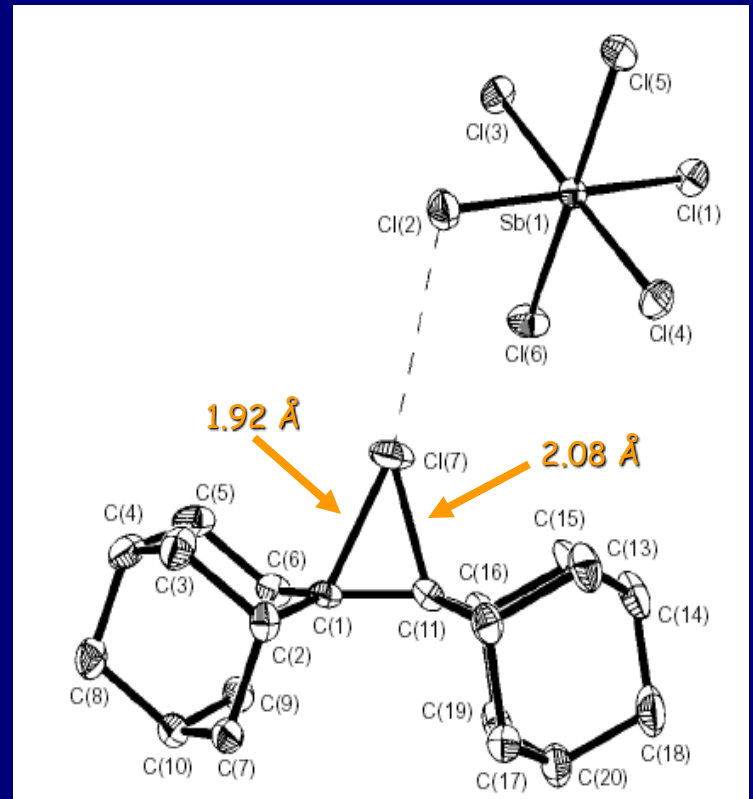
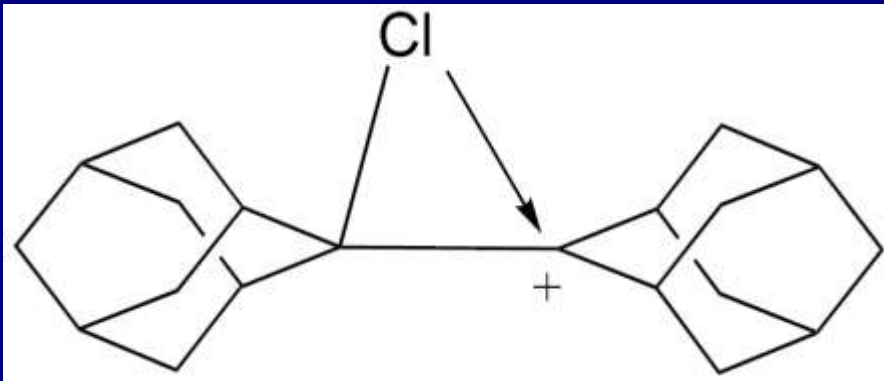
Nacrtajte intermedijer koji nastaje bromovanjem cikloheksena, koristeći dole date konformacije. Pokažite zašto se dobija racemski proizvod. Šta možete reći o početnoj konformaciji proizvoda?



konformaciona ravnoteža cikloheksena

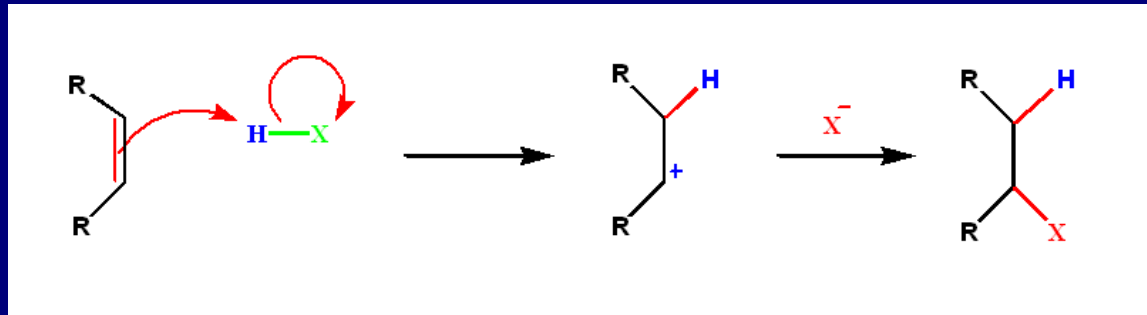
Struktura hloronijum jona

Kochi, *Chem. Commun.* 1998

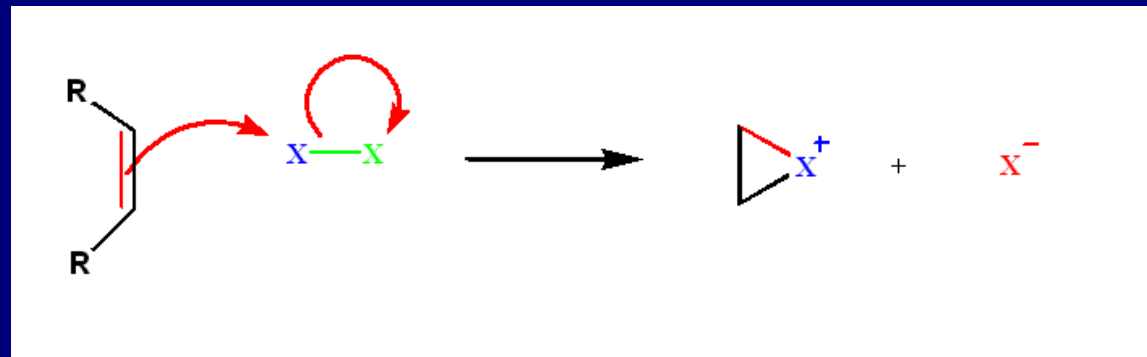


Alkeni kao nukleofili/baze

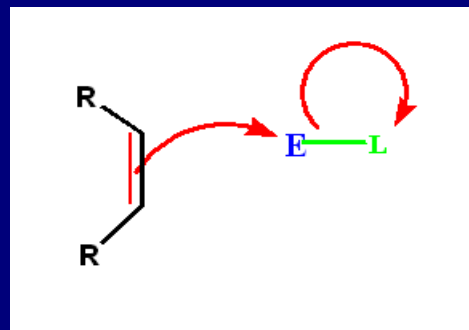
Baze:



Nukleofili:

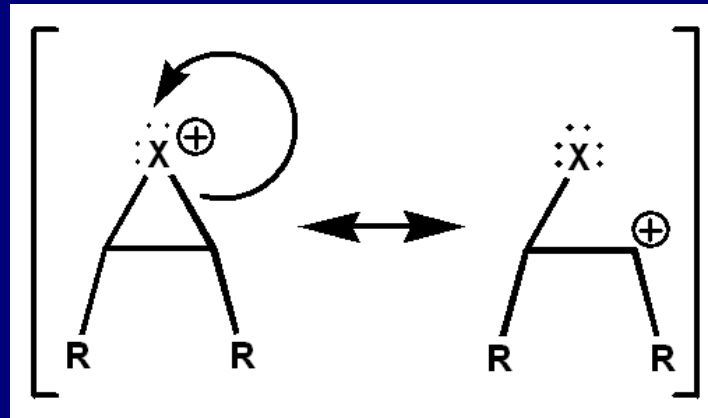


Generalno:

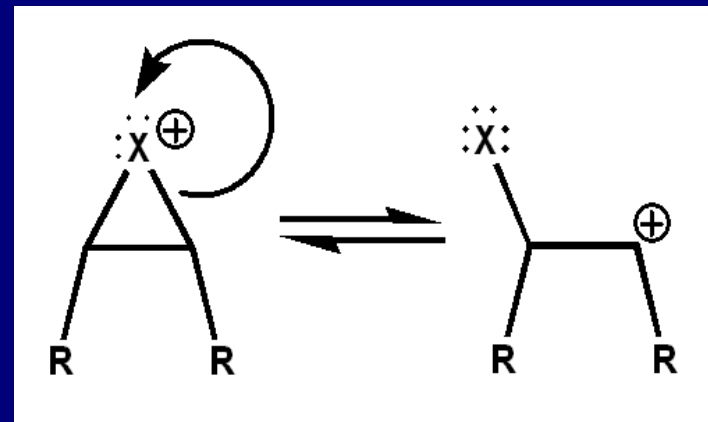


Ciklični halonijum joni: rezonancija naspram ravnoteže

Rezonancija:

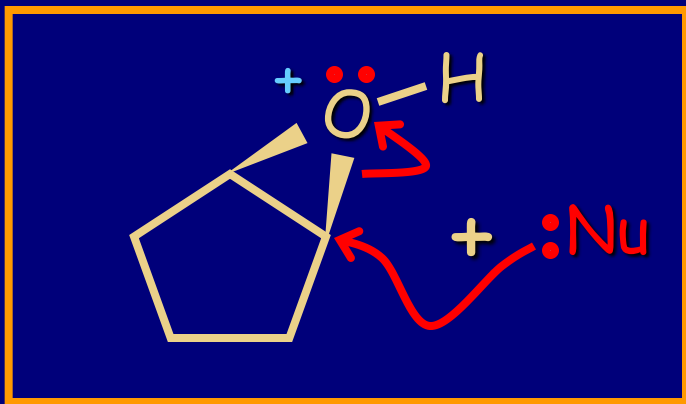
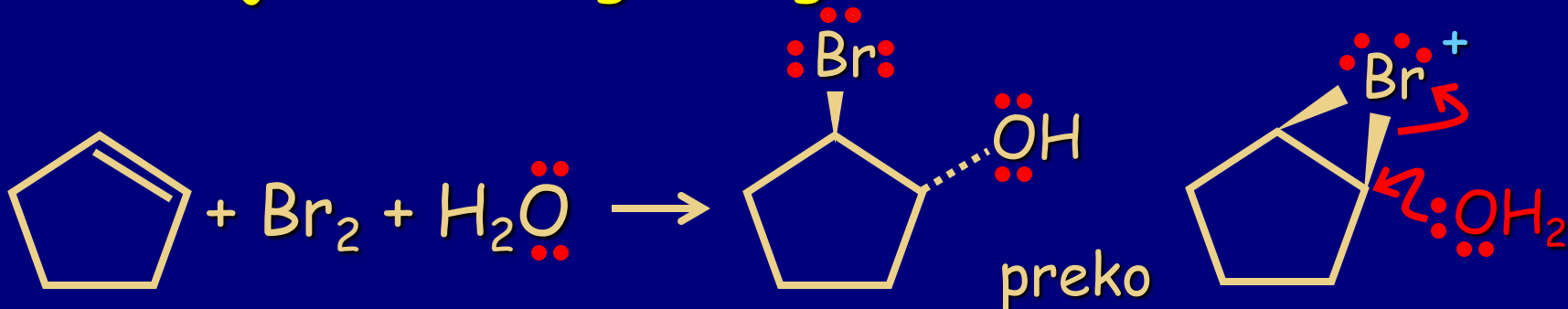


Ravnoteža:

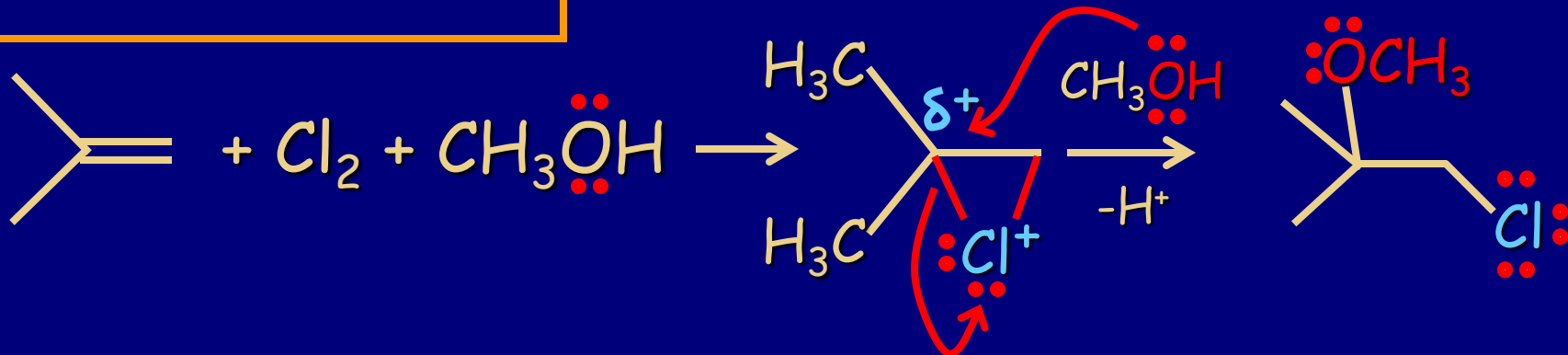


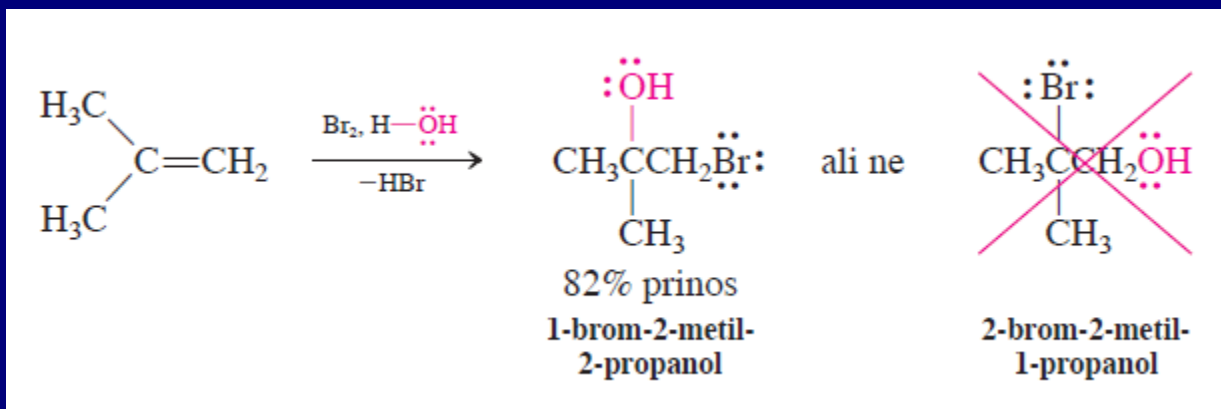
Opšti karakter elektrofilne adicije

Halonijum ioni mogu reagovati sa različitim Nu

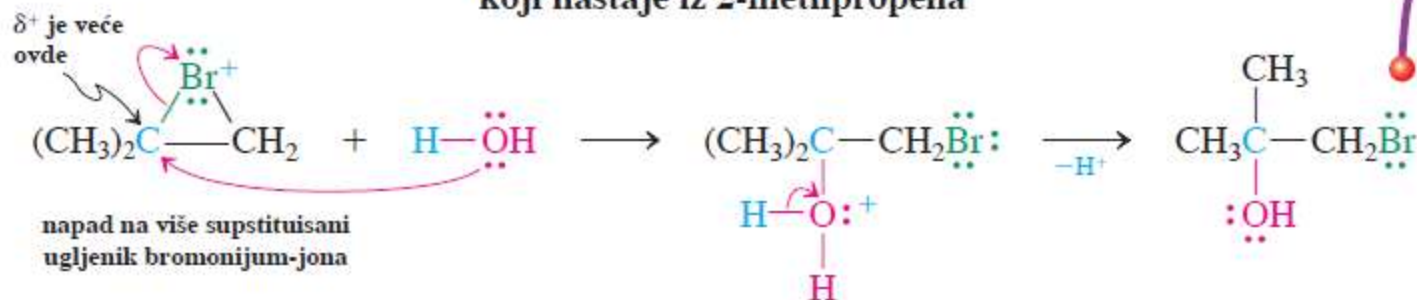


ili $\text{X}_2, \text{ROH} \rightarrow$ haloetri
(anti adicija +
Markovnikov-ljevo pravili)



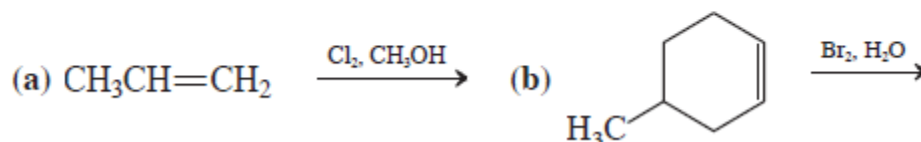


Regioselektivno otvaranje bromonijum-jona koji nastaje iz 2-metilpropena



Vežba 12-11

Šta su proizvodi datih reakcija?



Vežba 12-13

Koji je dobar prekursor za dobijanje racemske smese (2*R*,3*R*)- i (2*S*,3*S*)-2-brom-3-metoksipentana? Koje biste druge izomerne proizvode mogli očekivati na osnovu predloženih reakcija?

TABELA 12-2

Reagensi A-B koji se adiraju na alkene elektrofilnim napadom



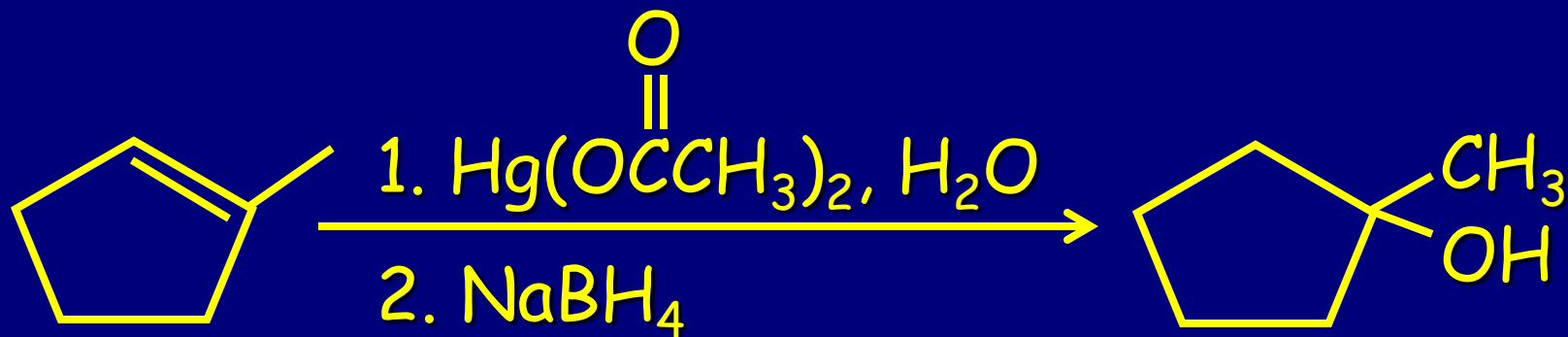
Ime	Struktura	Proizvod adicije na 2-metilpropen
brom-hlorid	$:\ddot{\text{Br}}-\ddot{\text{Cl}}:$	$:\ddot{\text{Br}}\text{CH}_2\text{C}(\text{CH}_3)_2$ $:\ddot{\text{Cl}}:$
cijanogen-bromid	$:\ddot{\text{Br}}-\text{CN}:$	$:\ddot{\text{Br}}\text{CH}_2\text{C}(\text{CH}_3)_2$ $\text{CN}:$
jod-hlorid	$:\ddot{\text{I}}-\ddot{\text{Cl}}:$	$:\ddot{\text{I}}\text{CH}_2\text{C}(\text{CH}_3)_2$ $:\ddot{\text{Cl}}:$
sulfenil-hlorid	$\text{R}\ddot{\text{S}}-\ddot{\text{Cl}}:$	$\text{R}\ddot{\text{S}}\text{CH}_2\text{C}(\text{CH}_3)_2$ $:\ddot{\text{Cl}}:$
živine soli	$\text{XHg}-\text{X}^a \text{H}\ddot{\text{O}}\text{H}$	$\text{XHgCH}_2\text{C}(\text{CH}_3)_2$ $:\ddot{\text{O}}\text{H}$

^aOvde X označava acetat.

Sintetički korisna reakcija:
oksimerkurovanje-demerkurovanje

Oksimerkurovanje - demerkurovanje

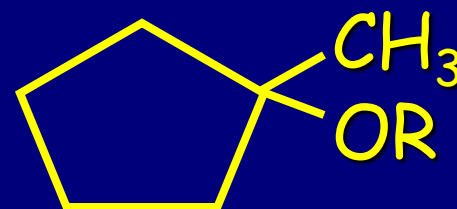
Markovnikov-ljeva hidratacija bez karbokatjona



ili



2. ROH: dobijanje etara

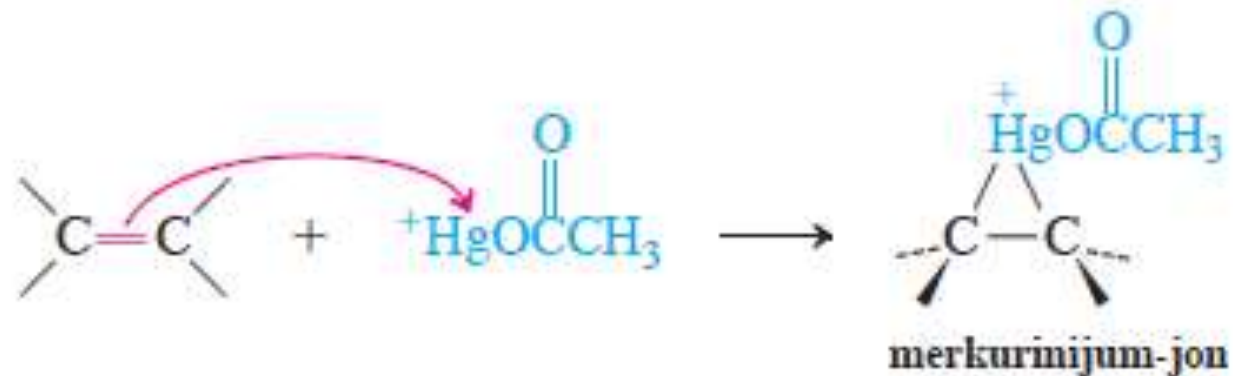


Mehanizam oksimerkurovanja-demerkurovanja

FAZA 1. Disocijacija

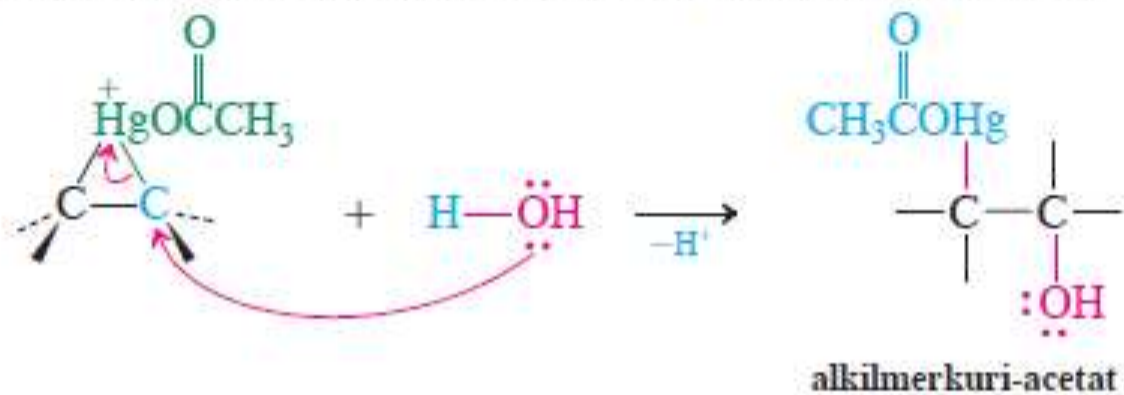


FAZA 2. Elektrofилni napad

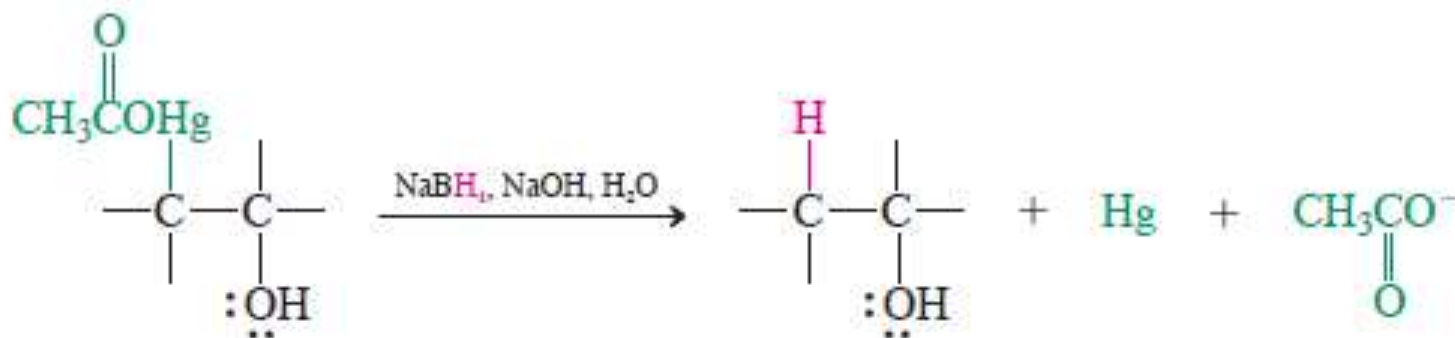


Mehanizam oksimerkurovanja-demerkurovanja

FAZA 3. Nukleofilno otvaranje (Markovnikov-ljeva regioselektivnost)



FAZA 4. Redukcija



Hidroborovanje - oksidacija

anti-Markovnikov-ljeva hidratacija

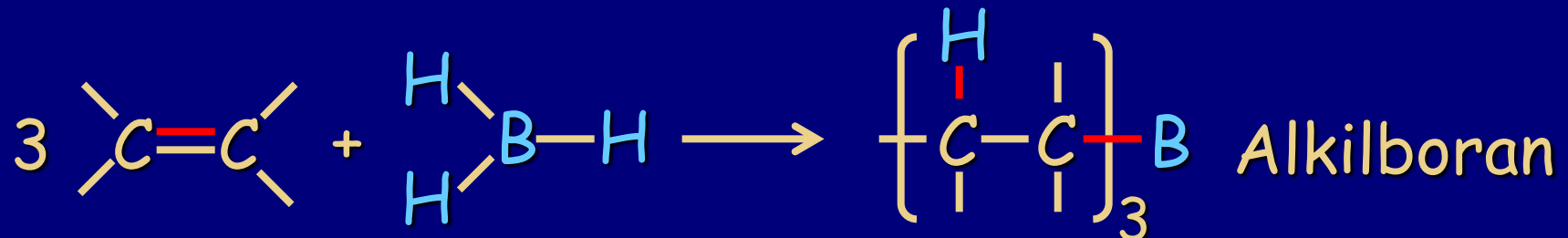


Ključna reakcija: adicija >B-H na π -veze.

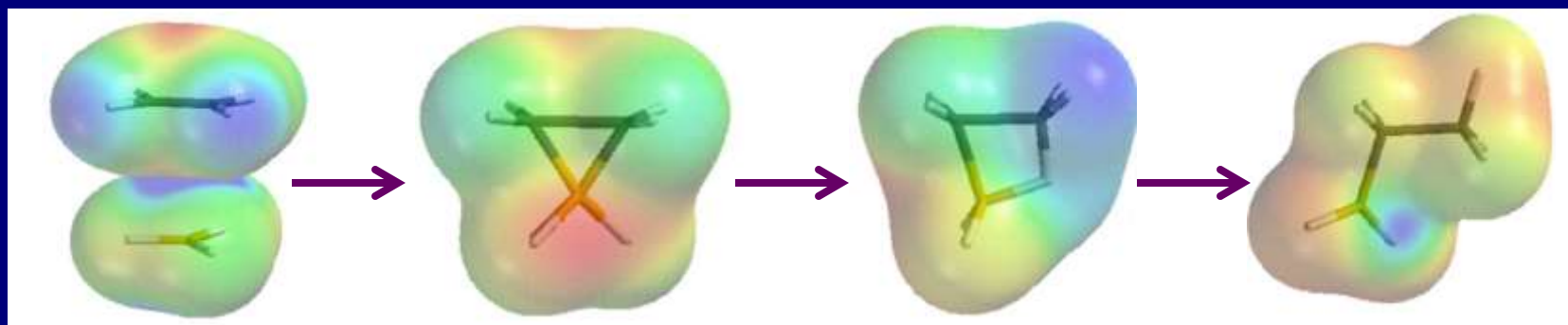
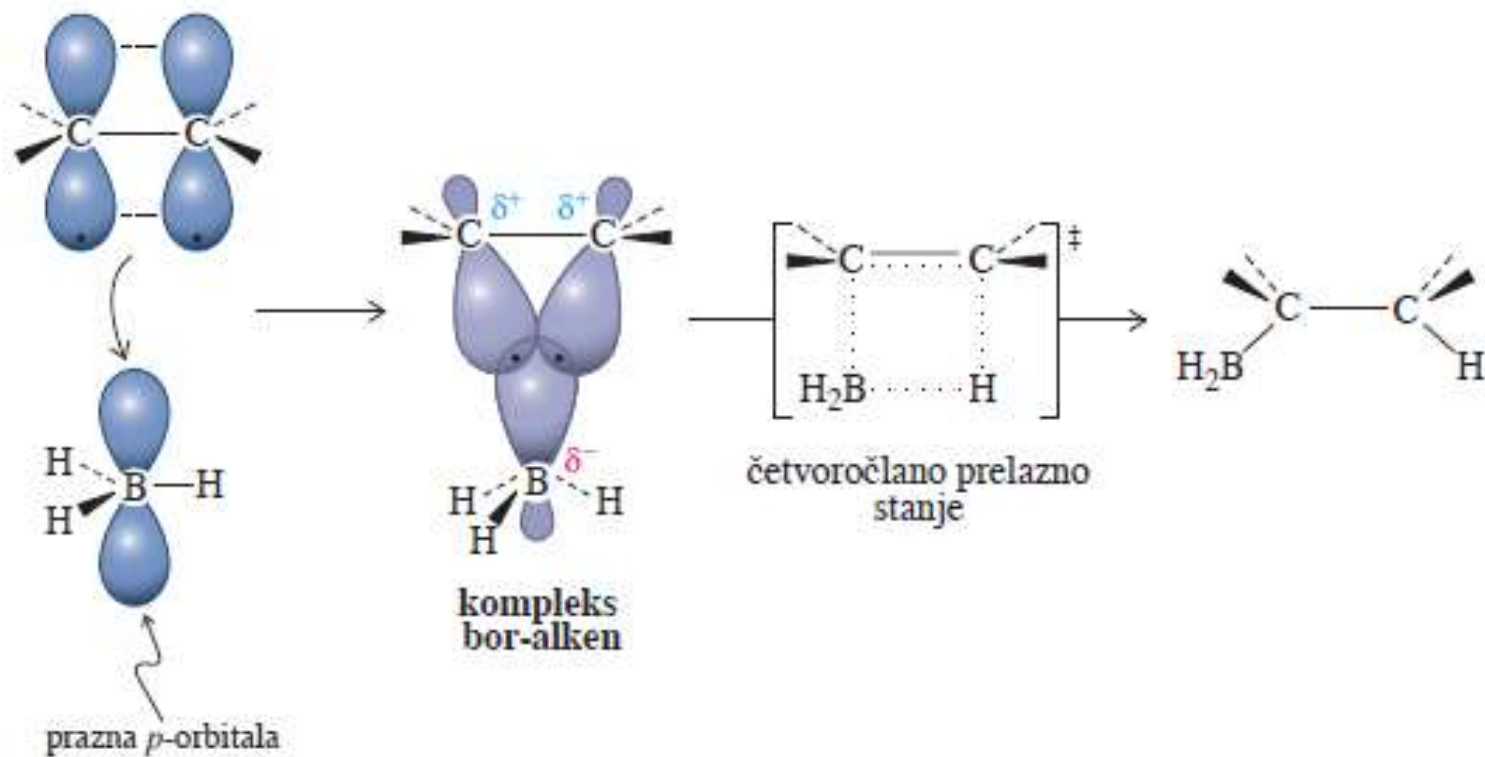
Boran, BH_3 , postoji kao dimer



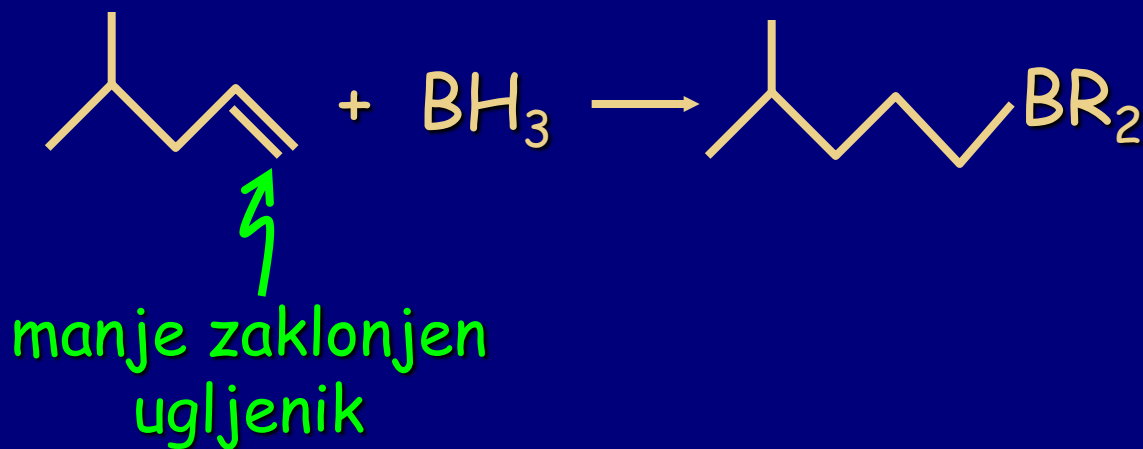
Sve tri B-H veze reaguju:



Mehanizam hidroborovanja

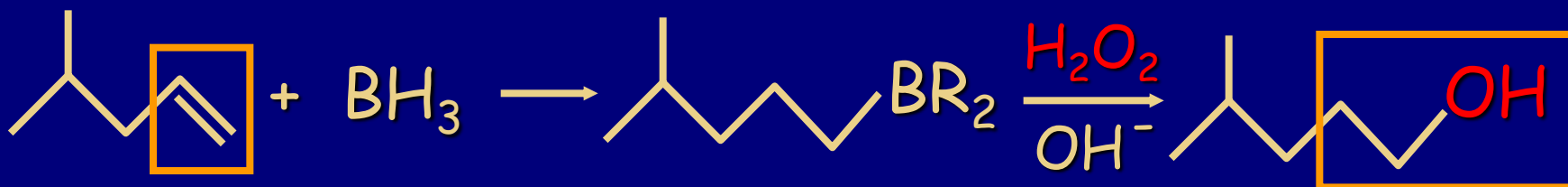


Hidroborovanje je regioselektivno:
Sterni činioci kontrolišu adiciju B-H

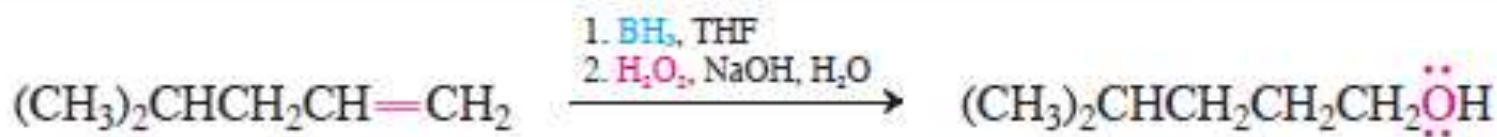
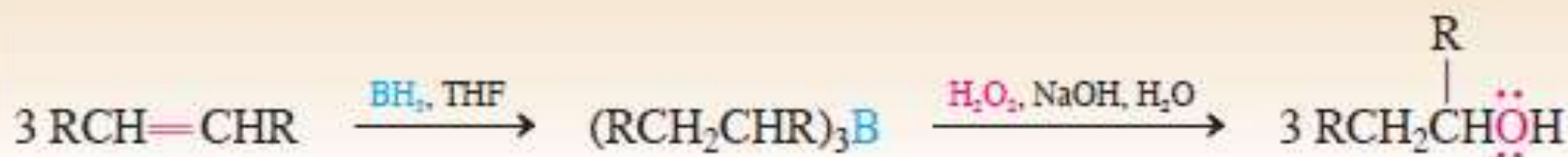


Primena hidroborovanja?

Oksidacijom alkilborana dobijaju se alkoholi!!!



Sekvenca reakcije hidroborovanje-oksidacija

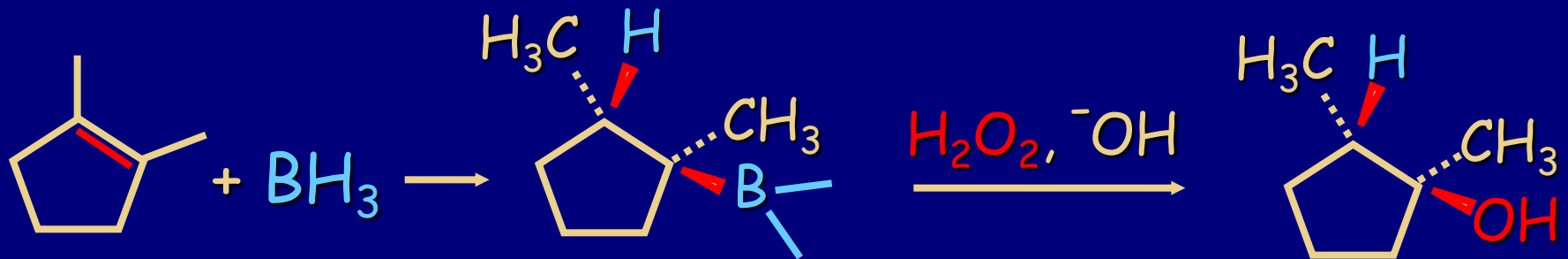


4-metil-1-penten

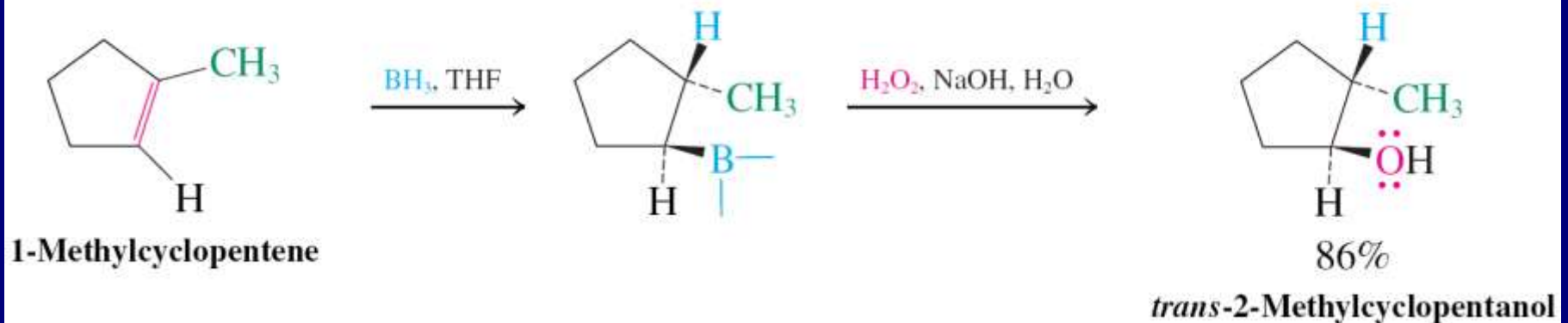
80%

4-metil-1-pentanol

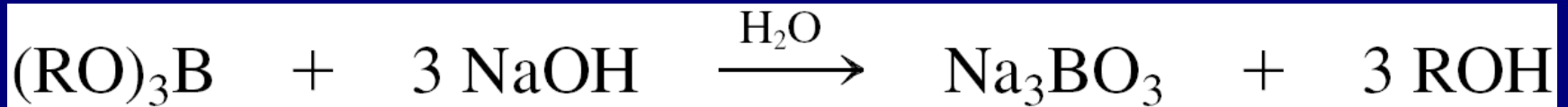
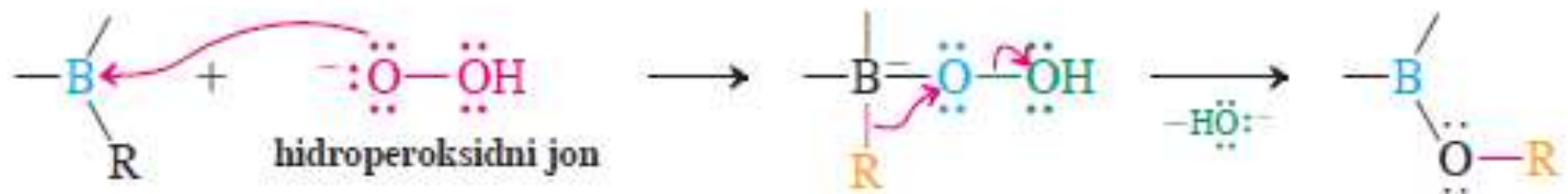
Hidrobtorovanje je stereospecifično: sin adicija B—H



A Stereospecific and Regioselective Alcohol Synthesis by Hydroboration–Oxidation

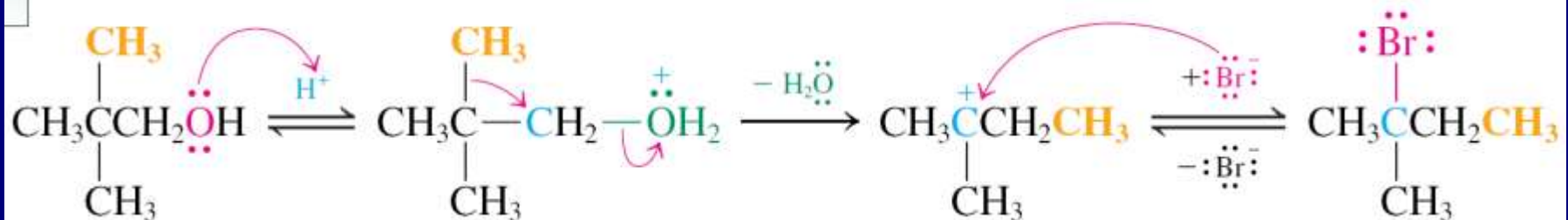


Mehanizam oksidacije alkilborana



Sličnost sa premeštanjem alkil-grupa?

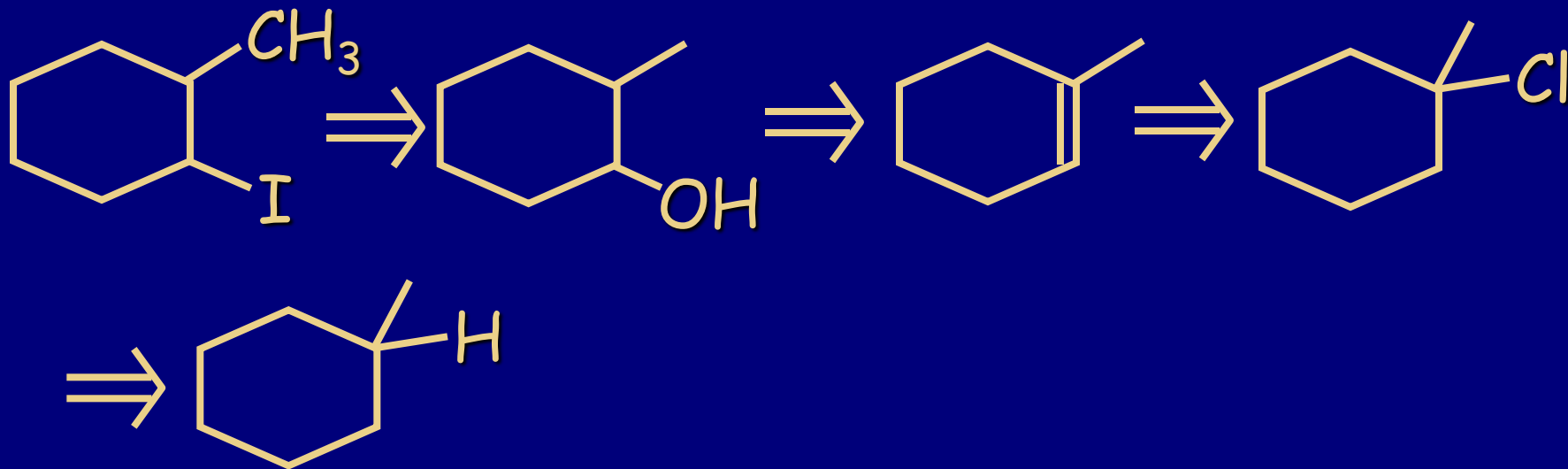
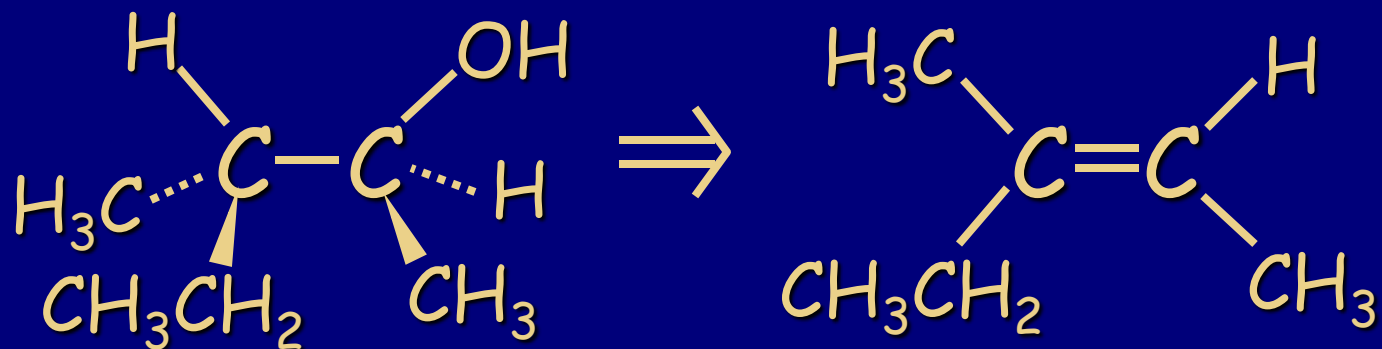
Mechanism of Concerted Alkyl Shift



Vežba 12-15

Napišite proizvode sekvence reakcija hidroborovanje-oksidacija (a) propena i (b) (*E*)-3-metil-2-pentena. Naznačite jasno stereochemiju.

Primena u sintezi retrosinteza:

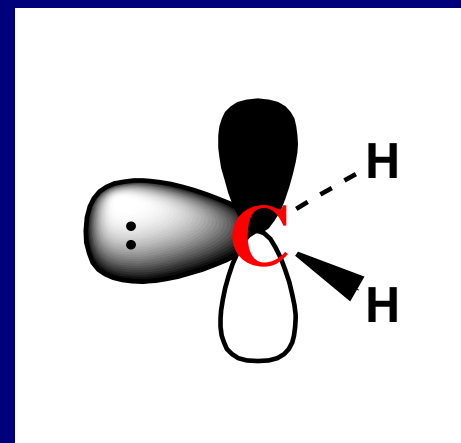


Elektrofilna adicija karbena Sinteze ciklopropana

karbeni,

$:CR_2$, vrste sa 6-elektrona,
prvi član je metilen $:CH_2$.

Možemo zamisliti da nastaje
deprotonovanjem karbokatjona:

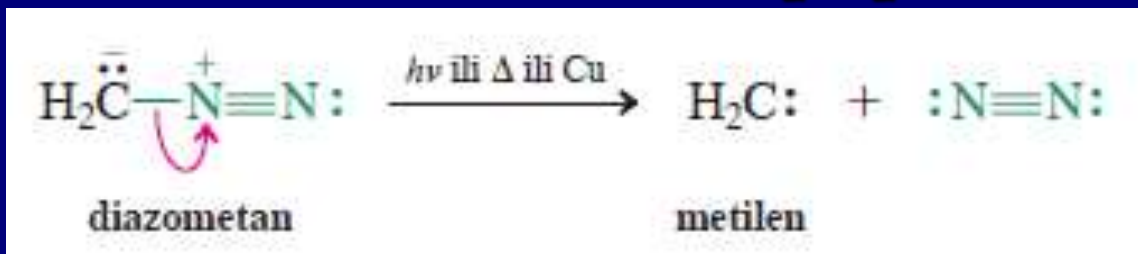


Metilene

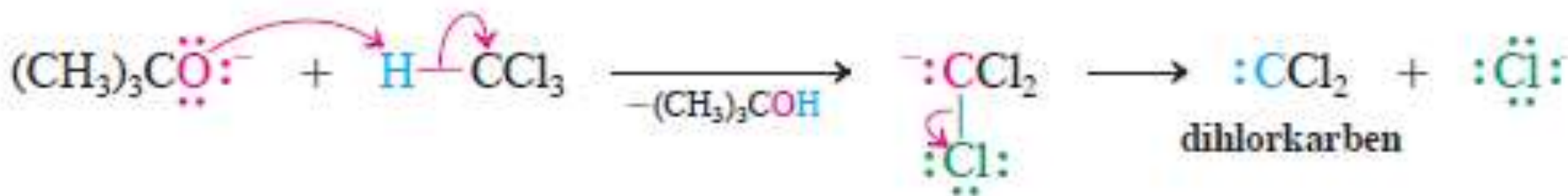
Karbeni su elektron-deficitarni, ponašaju se
prema alkenima kao elektrofilni.

Dobijanje

a. Metilen iz diazometana CH_2N_2



b. Dihlorkarben iz hloroforma



c. Simmons-Smith-ov reagens

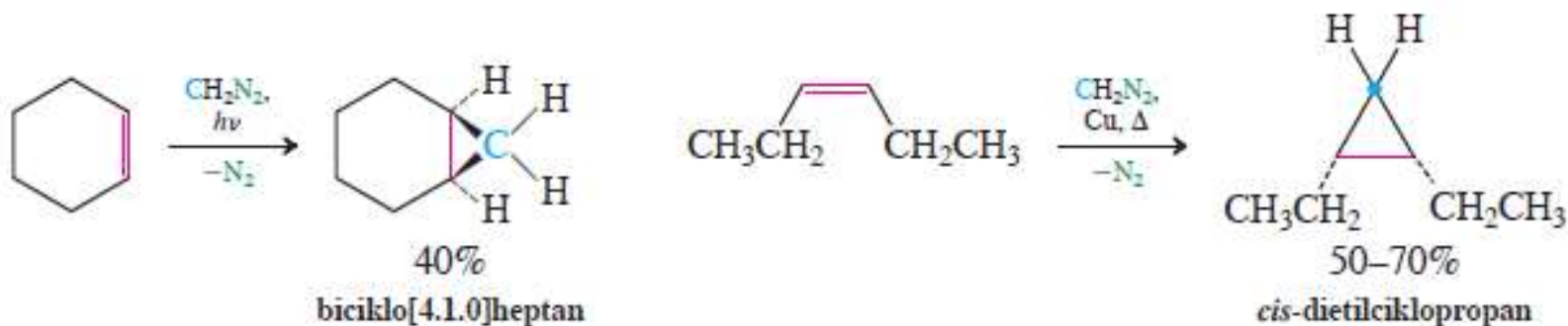


Karbeni uzimaju dva π elektrona iz alkena i formiraju ciklopropane

Karbeni uzimaju dva π elektrona iz alkena i formiraju ciklopropane

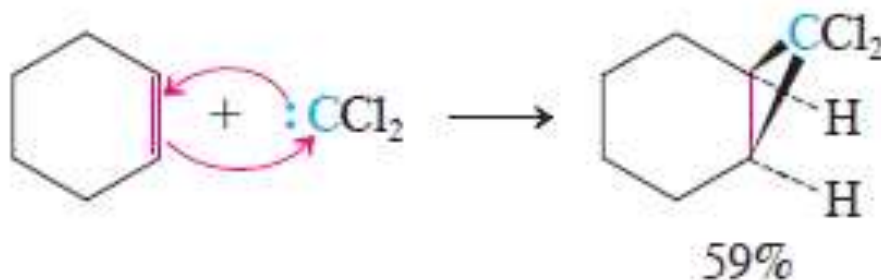
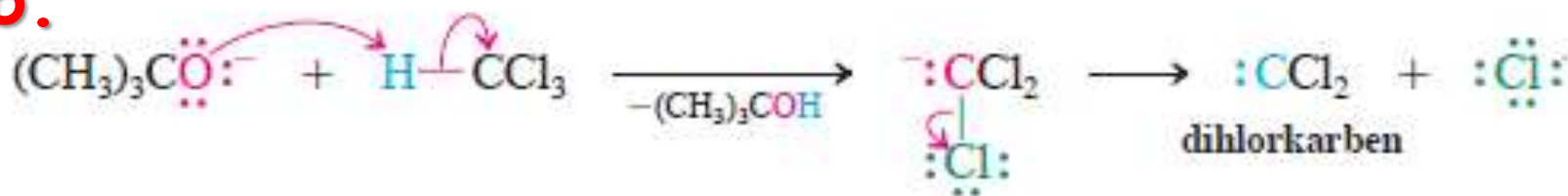
a.

Adicija metilena na dvostruke veze

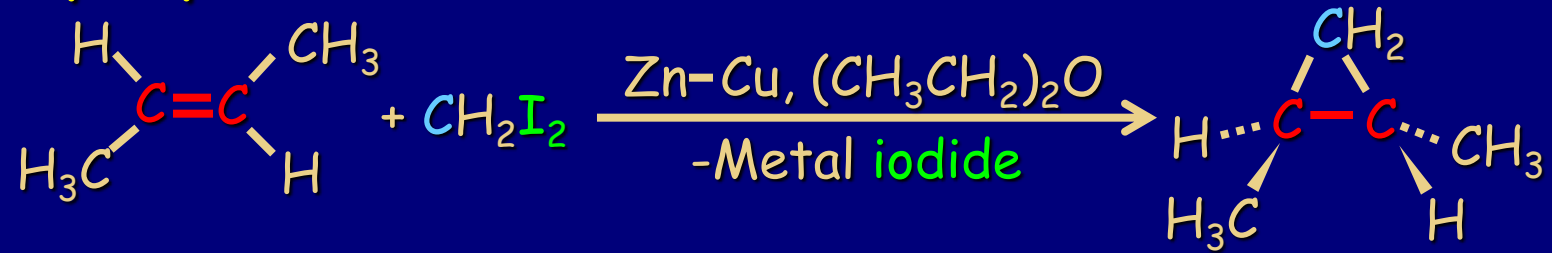


Dobijanje dihlorkarbena iz hloroforma i njegova reakcija sa cikloheksenom

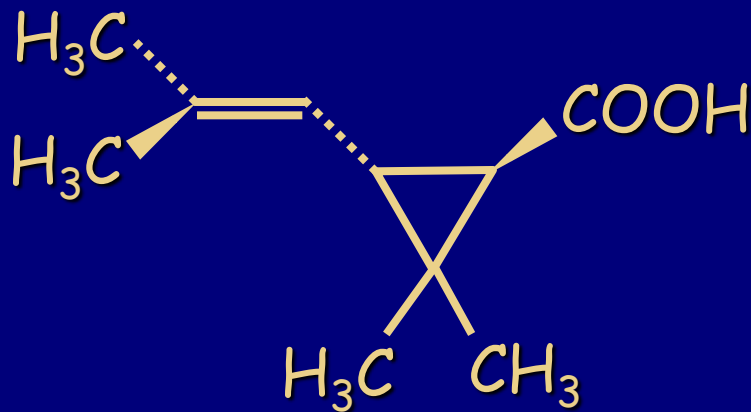
b.



c. Simmons-Smith-ov reagens za dobijanje ciklopropana

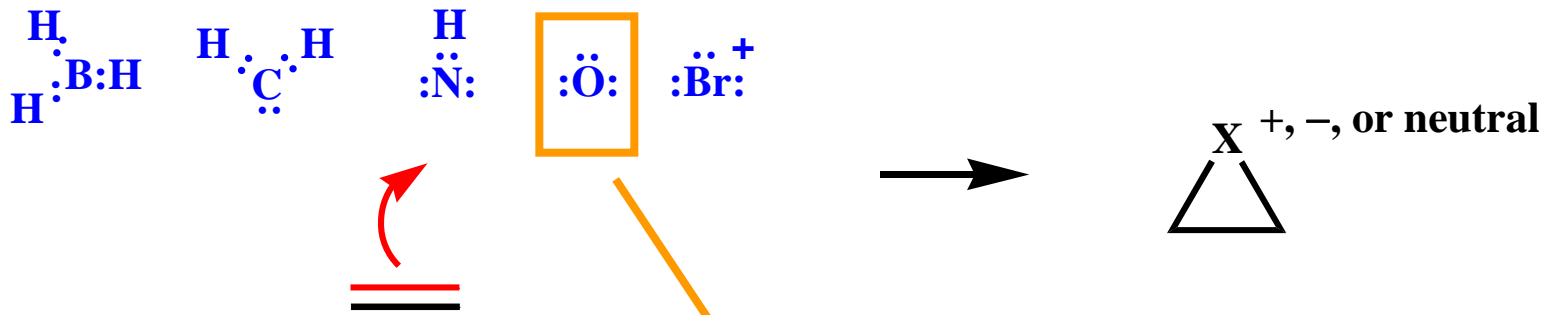


Ciklopropani-prirodni proizvodi:



(+)- hrizantemna kiselina
(protiv insekata);
rodonačelnik piretroida.
US : 1.5 milijarda \$!!

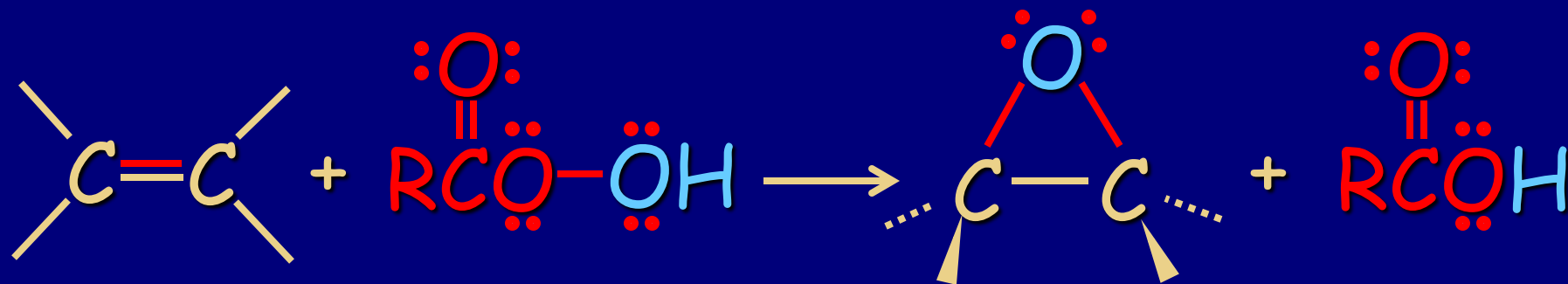
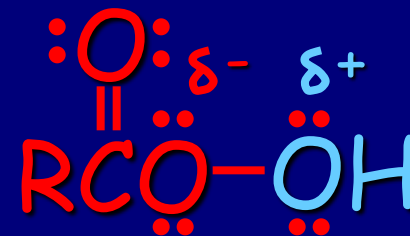
Adicija vrsta sa šest elektrona na π -vezu



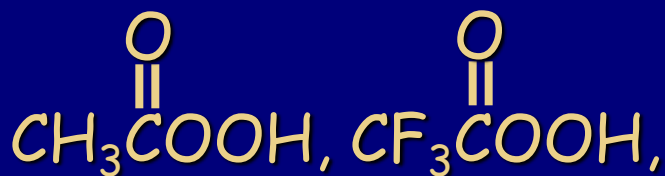
Oksidacija?

EPOKSIDACIJA

Oksidacija alkena
peroksidkarboksilnim kiselinama

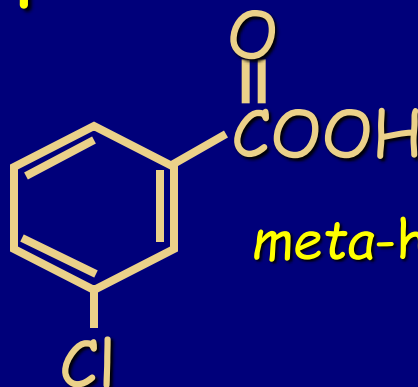


Najčešće korišćene peroksidkarboksilne kiseline



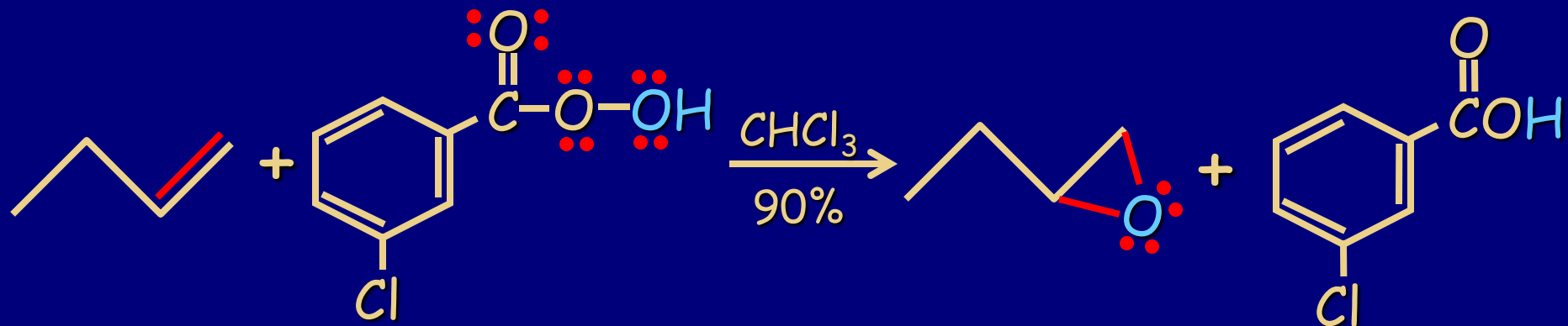
Persirćetna
kiselina

Trifluor-
persirćetna
kiselina

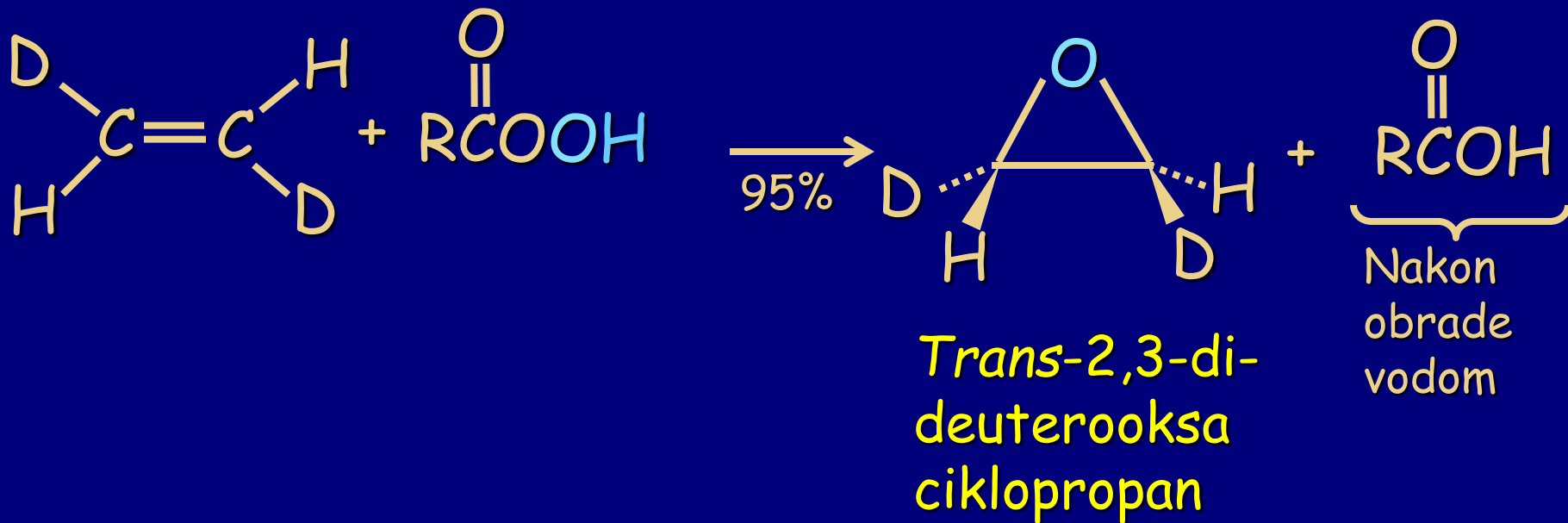


meta-hlorperbenzoeva kiselina

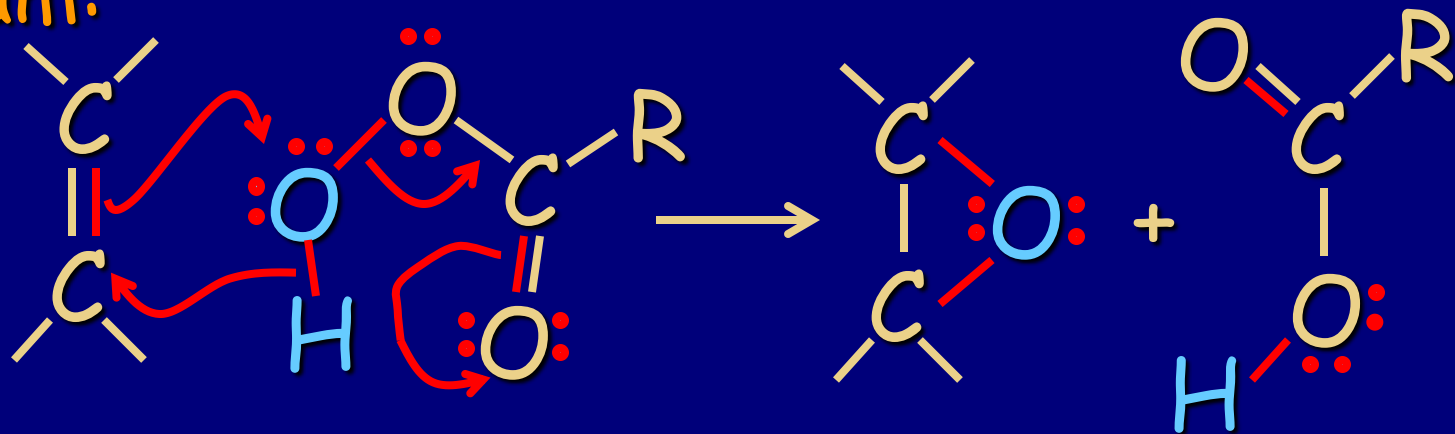
"MCPBA"



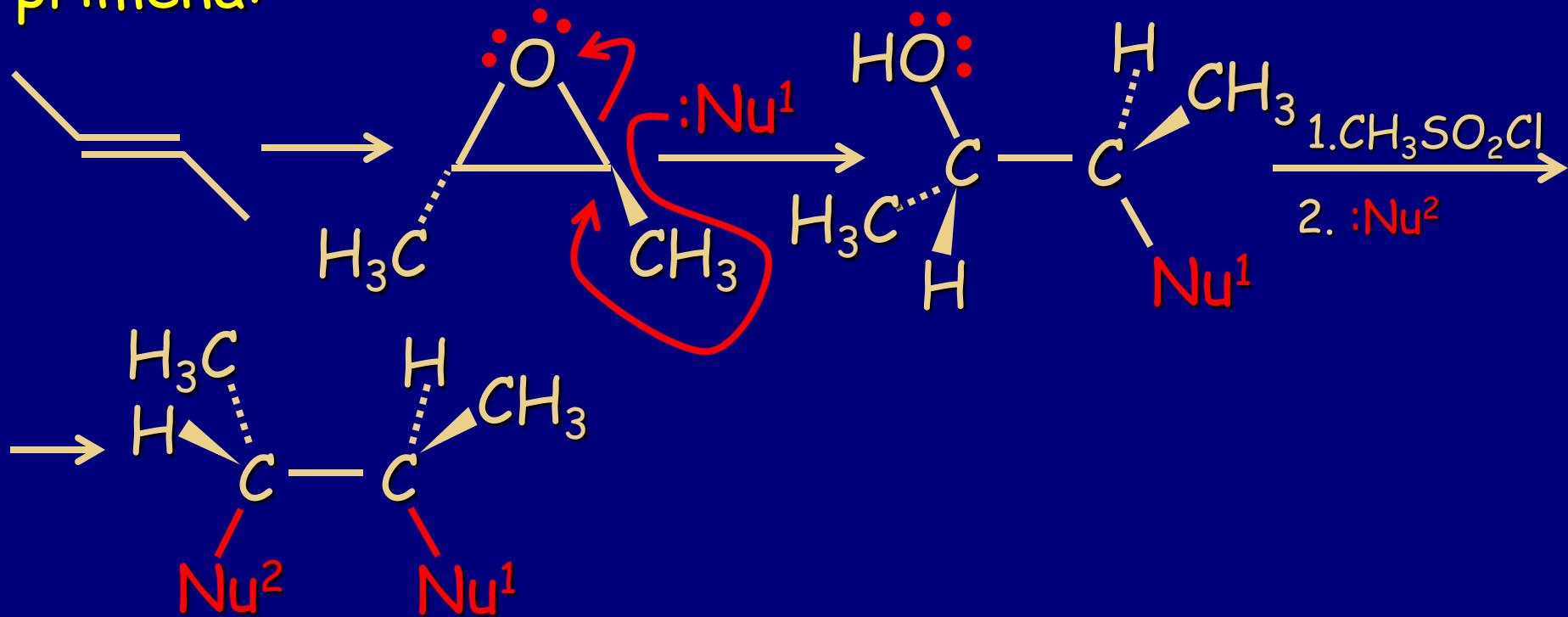
Stereospecifična sin adicija



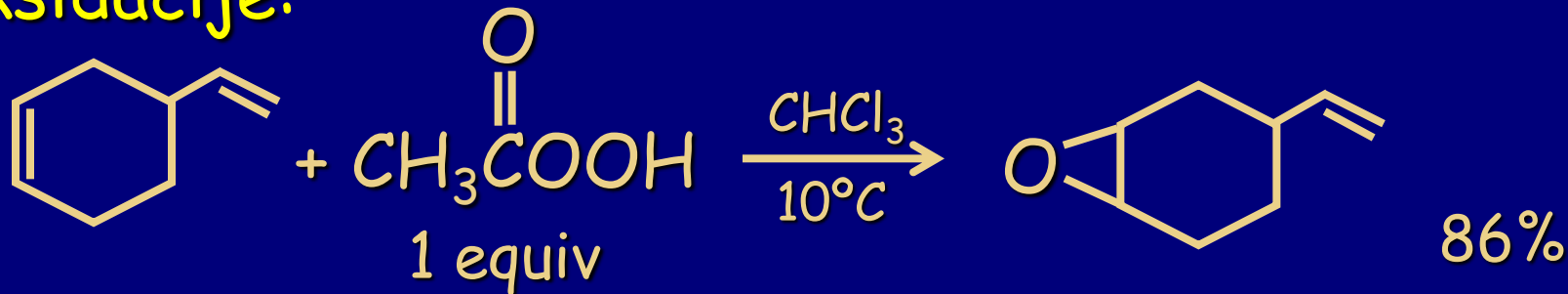
Mehanizam:



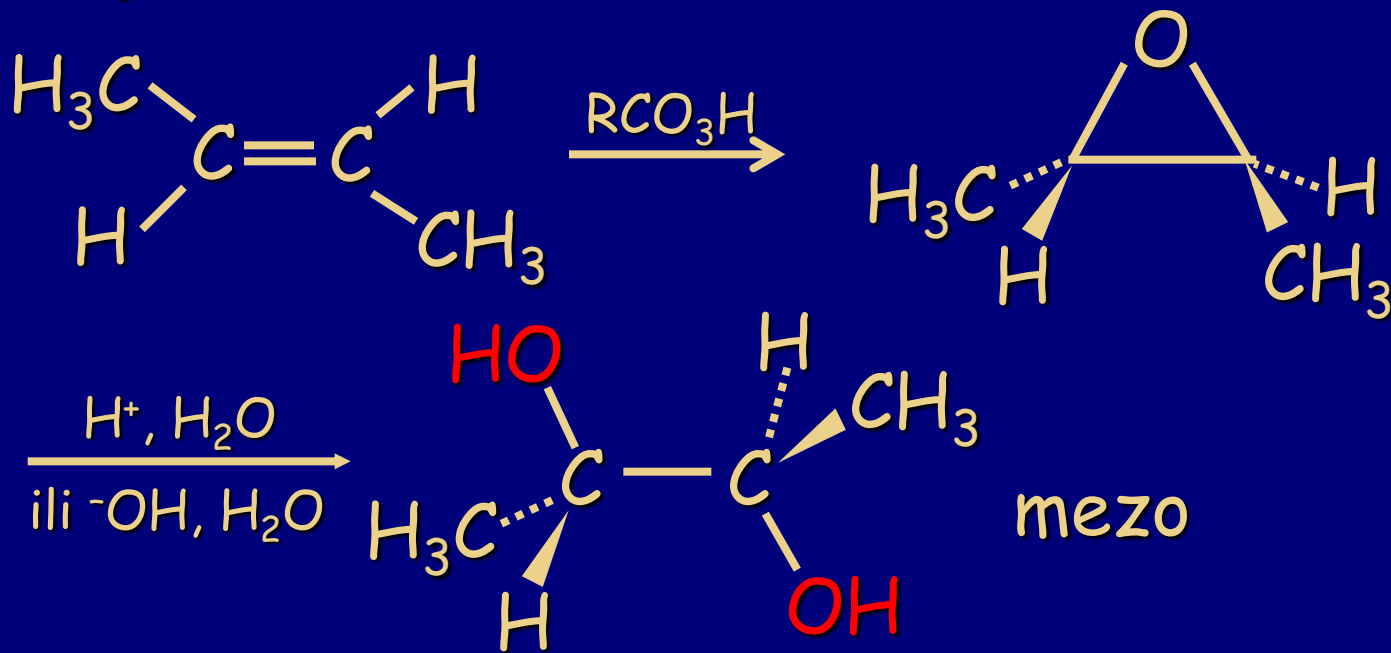
primena:



Reaktivnost alkena prema perkiselinama povećava se sa alkil-supstitucijom, što omogućava selektivne oksidacije:

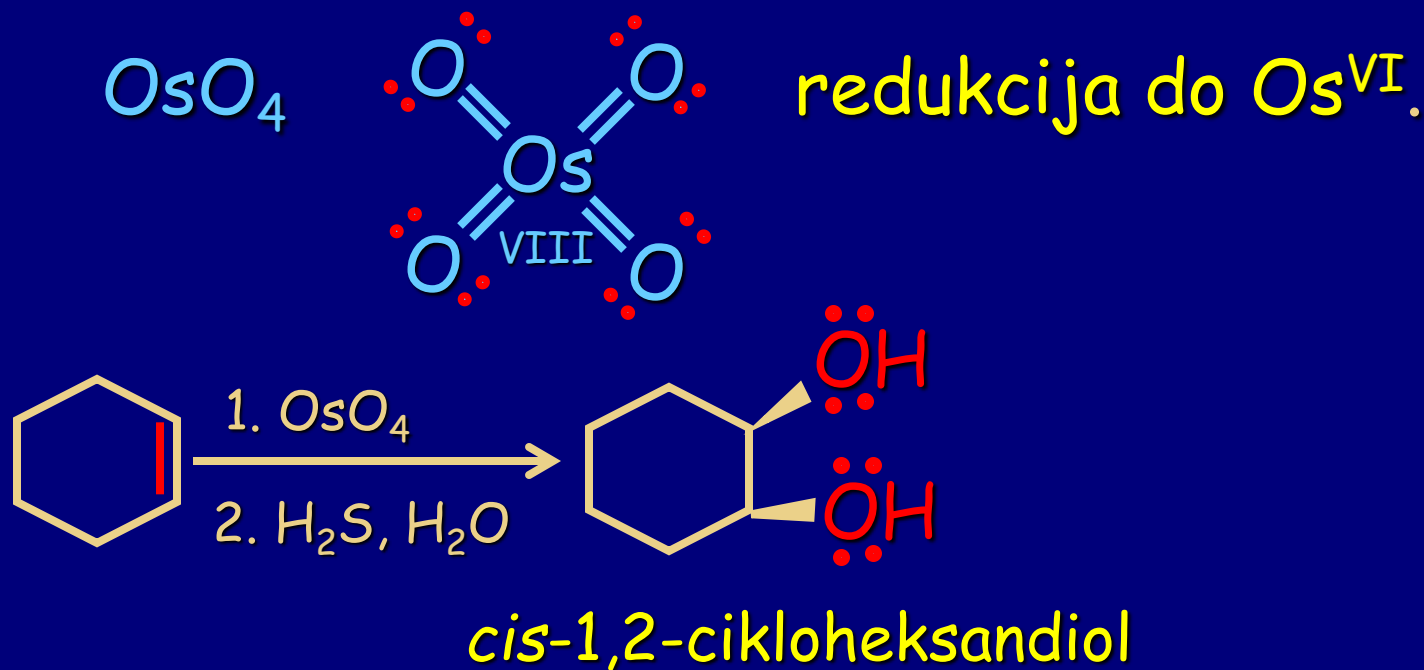


Ukupan rezultat sekvence oksidacije hidrolize anti-dihidroksilovanje alkena:



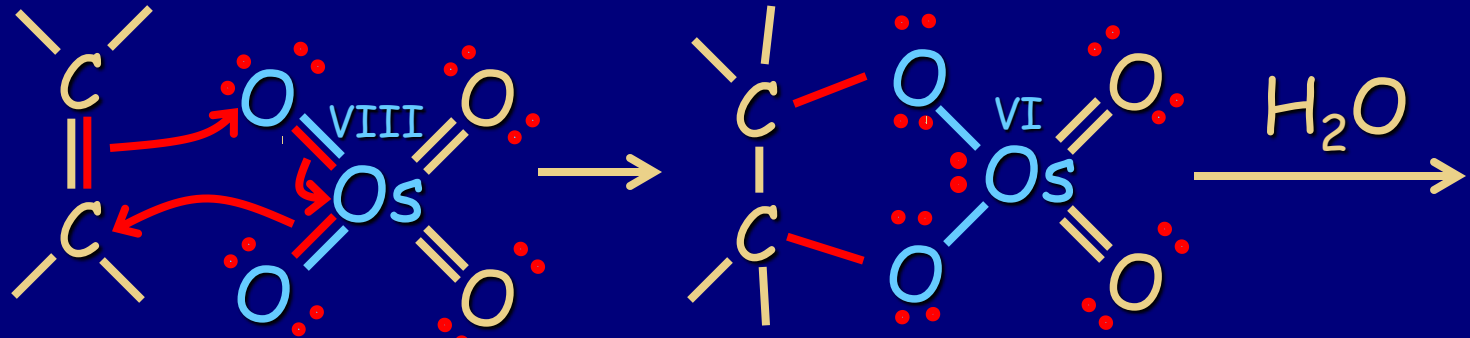
Vicinalno sin-dihidroksilovanje

Reagensi : KMnO_4 , $^- \text{OH}$, ali je bolje sa:



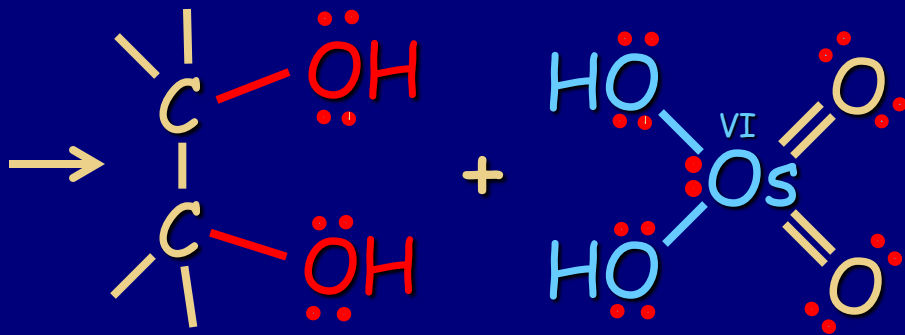
Komplementarna stereohemija anti-dihidroksilaciji

Mehanizam:

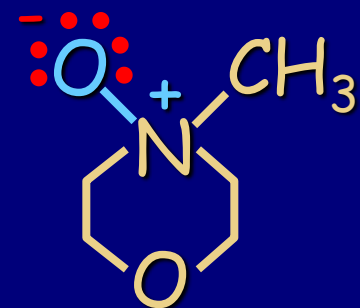


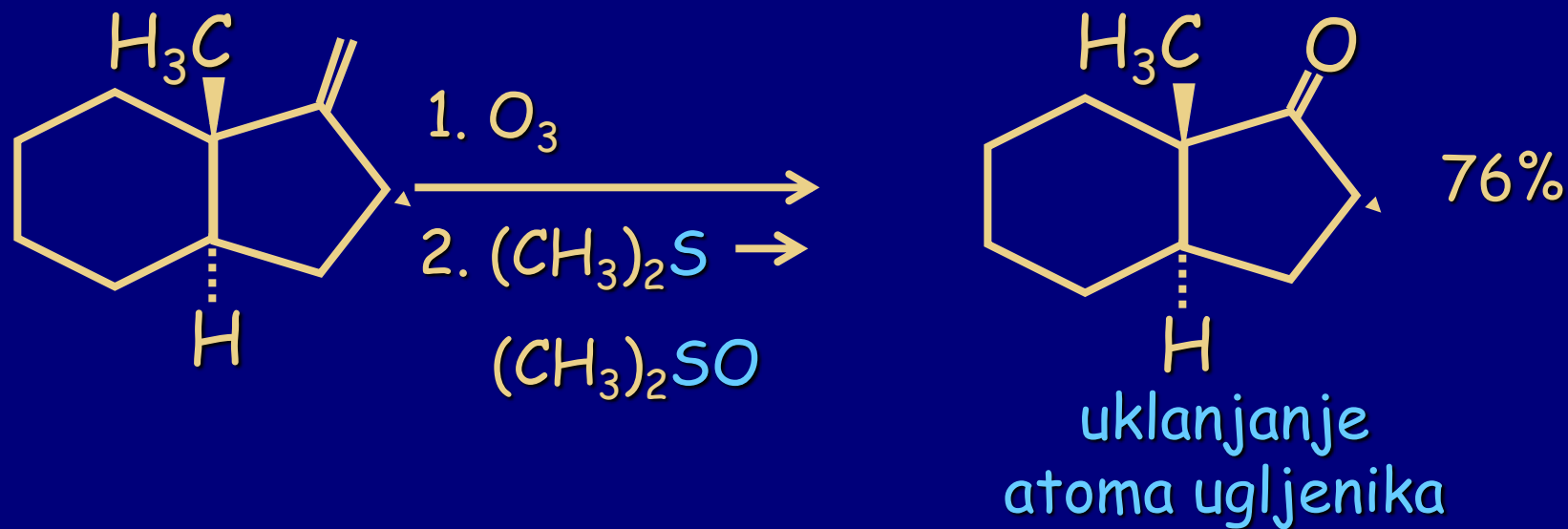
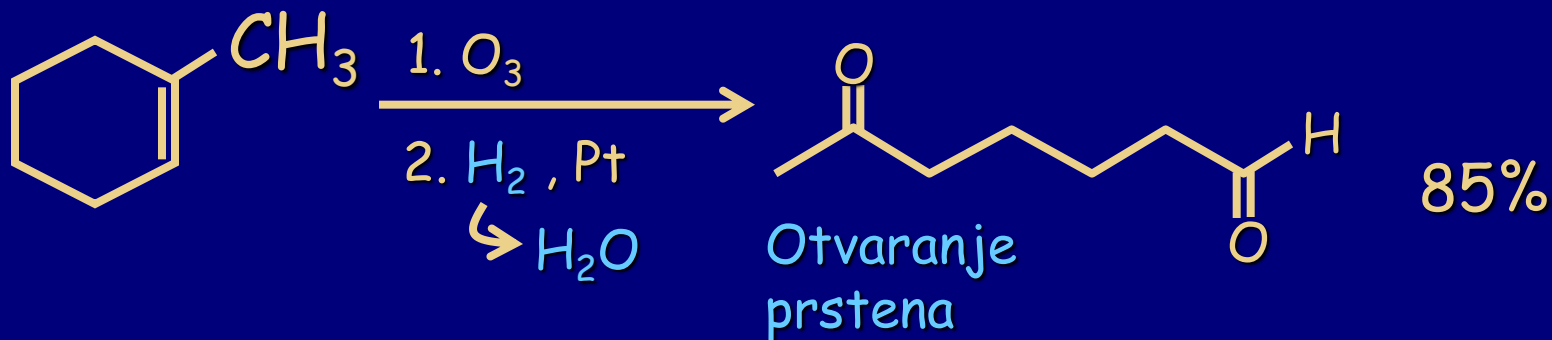
Šesto-elektronsko TS

Osmatni estar



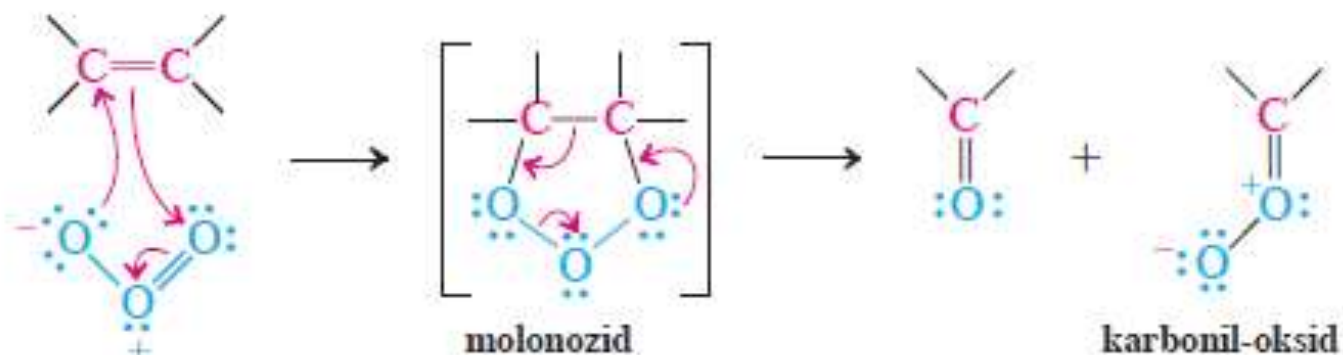
Zbog toga što je OsO₄ skup i vrlo toksičan, on se veoma često koristi u katalitičkim količinama, a u stehiometrijskim količinama koristi se drugo oksidaciono sredstvo, koje ima ulogu da vrši ponovnu oksidaciju redukovanog osmijuma



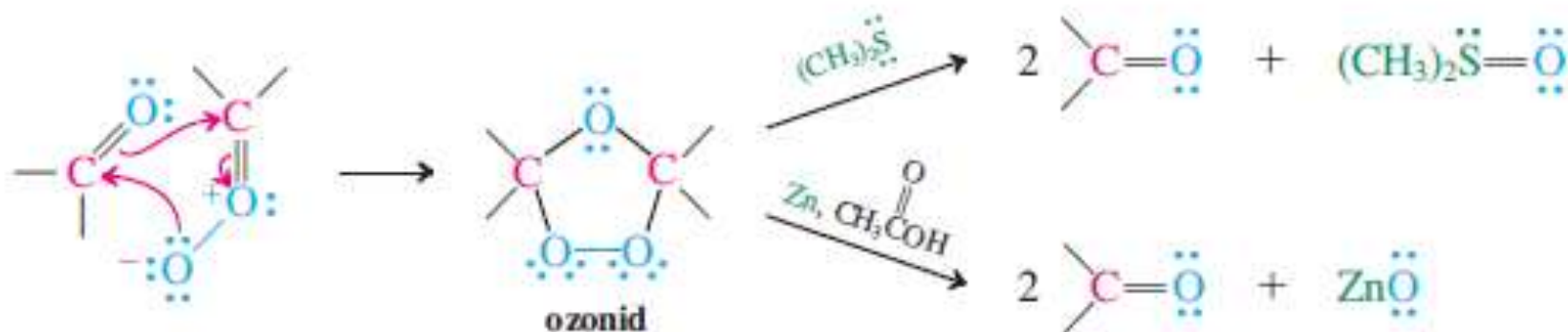


Mehanizam ozonolize

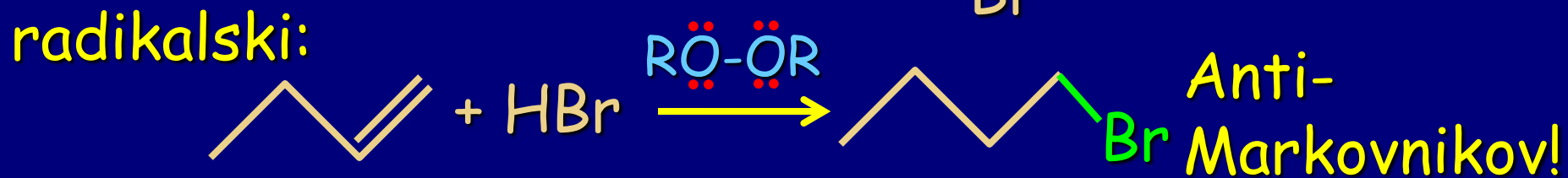
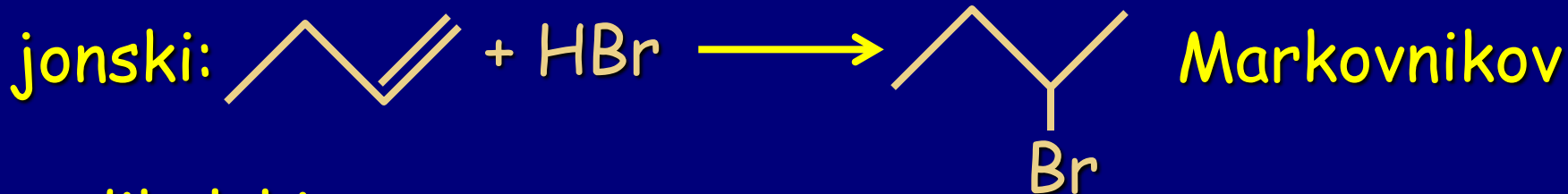
FAZA 1. Nastajanje i raskidanje molonozida



FAZA 2. Nastajanje i redukcija ozonida

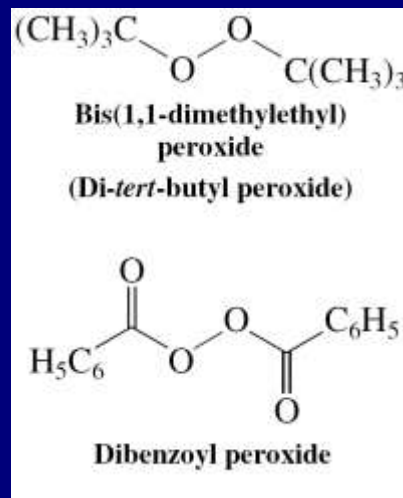


Radikalske adicije hidrobromovanje alkena



Dva potpuno različita mehanizma!!!!

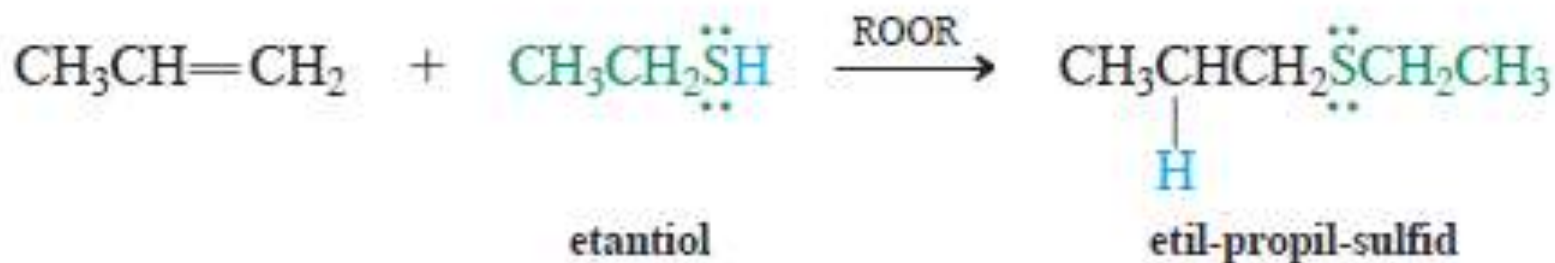
Peroksidi kao
radikalni inicijatori



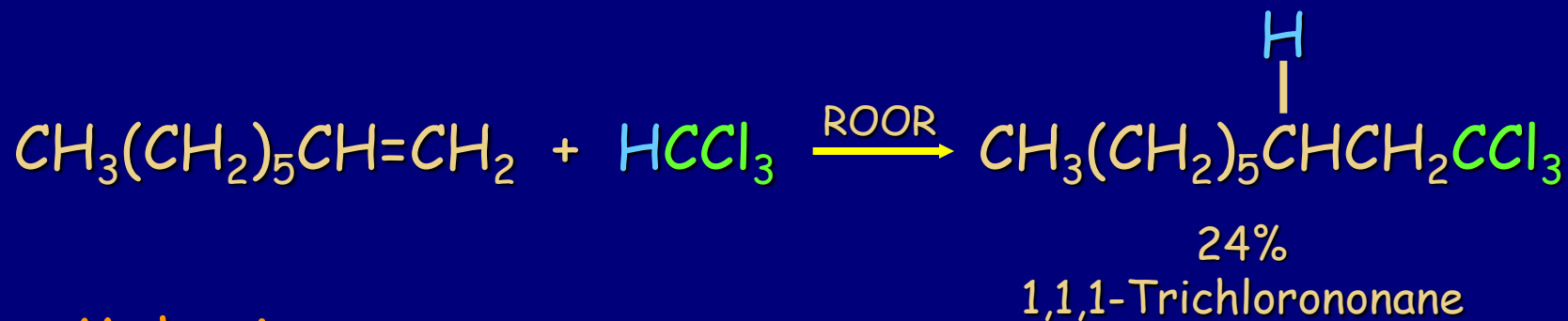
HCl i HI zbog nepovoljne kinetike ne daju anti-Markovnikov-ljeve adicione proizvode, jer je jedna od faza propagacije endotermna. adicija HCl i HI se vrši isključivo jonskim mehanizmom.

Tioli uspešno podležu anti-Markovnikov-ljevoj adiciji na alkene

Radikalske adicije tiola na alkene



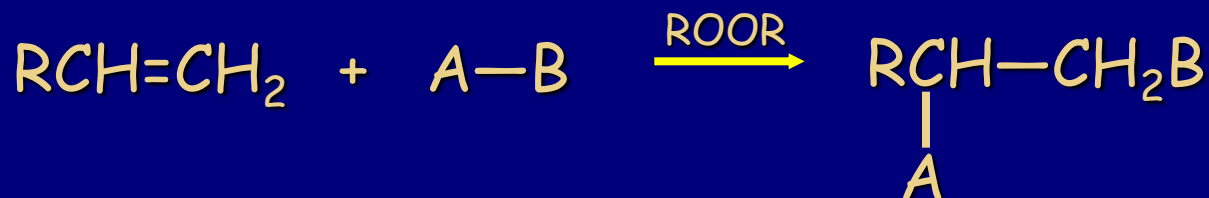
Adicija hloroforma



Mehanizam:

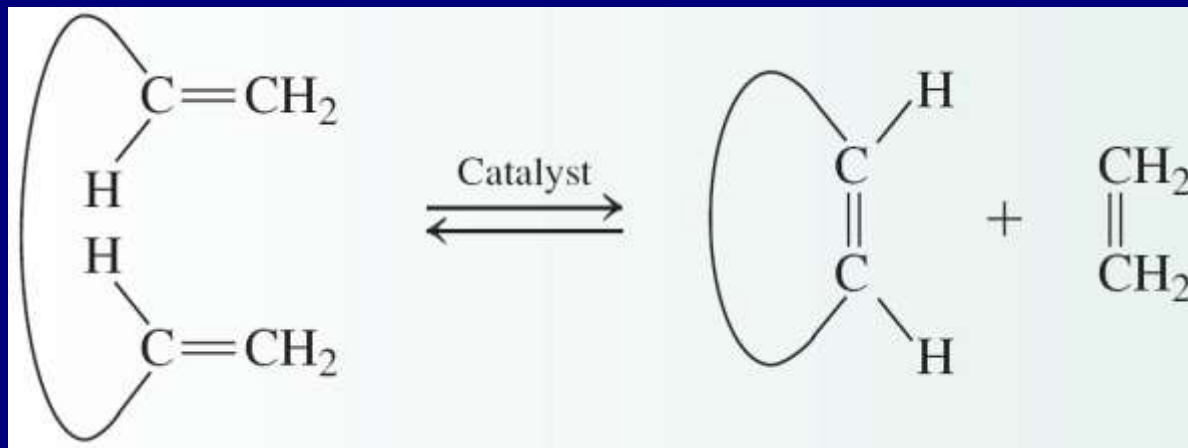
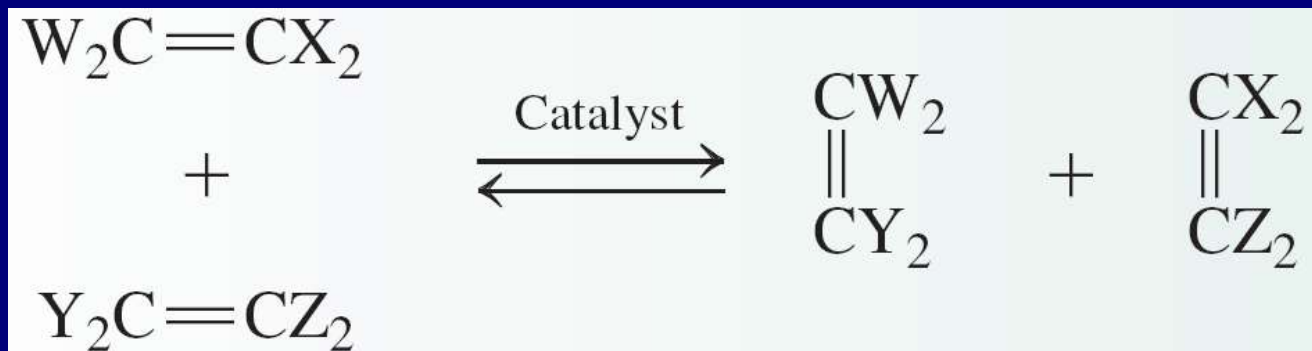


Generalno:



Nobel-ova nagrada za hemiju 2005

Metateza alkena:



Chauvin, Schrock, Grubbs

Polimerizacija alkena

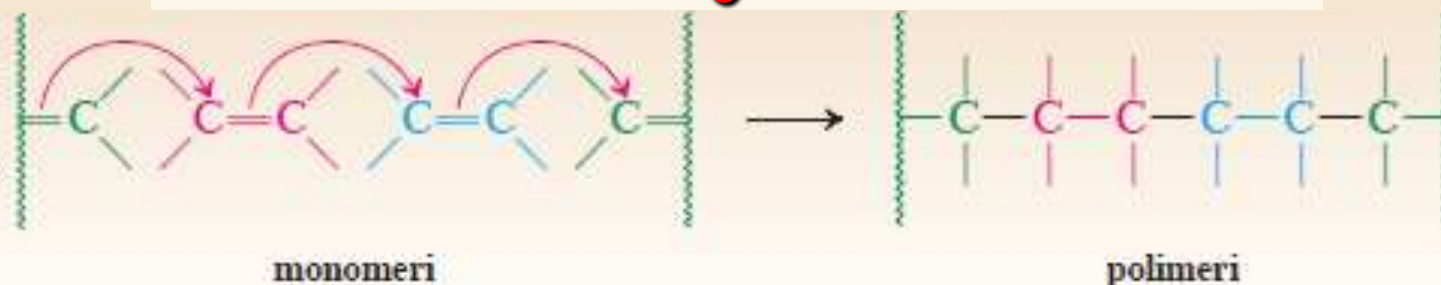
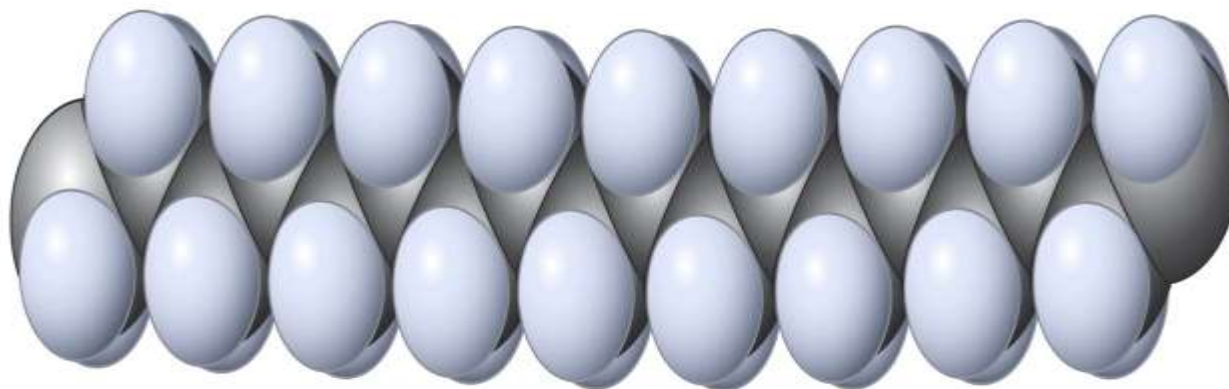
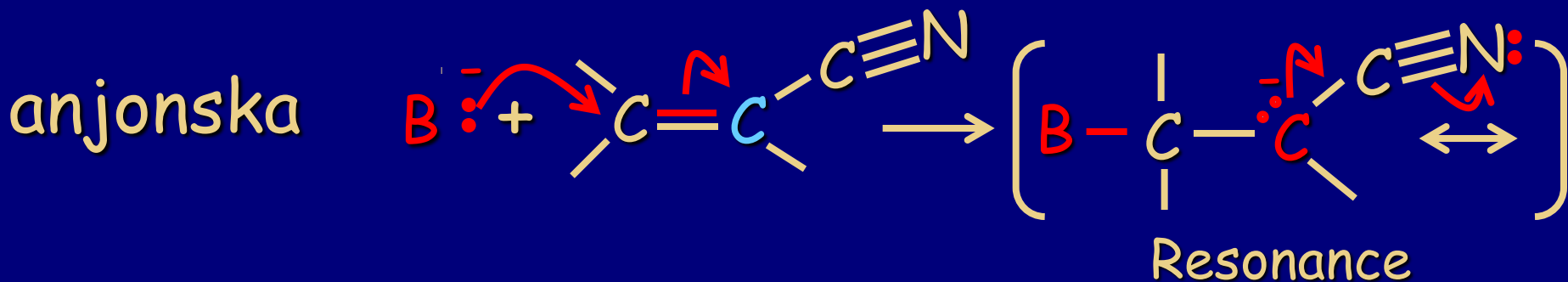
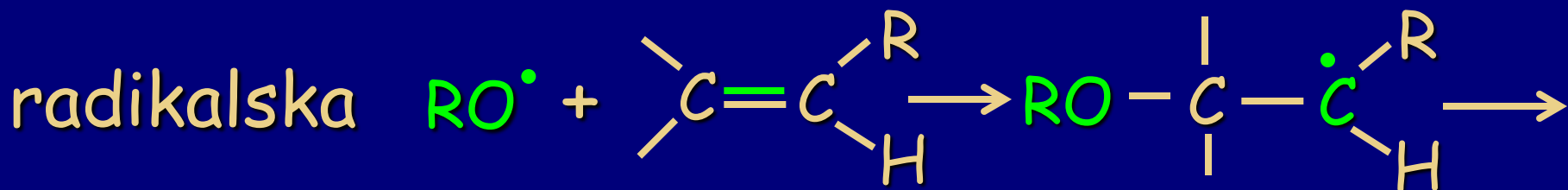
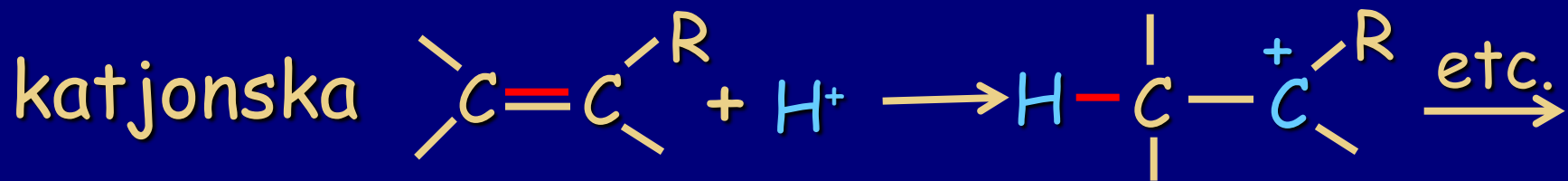


TABELA 12-3

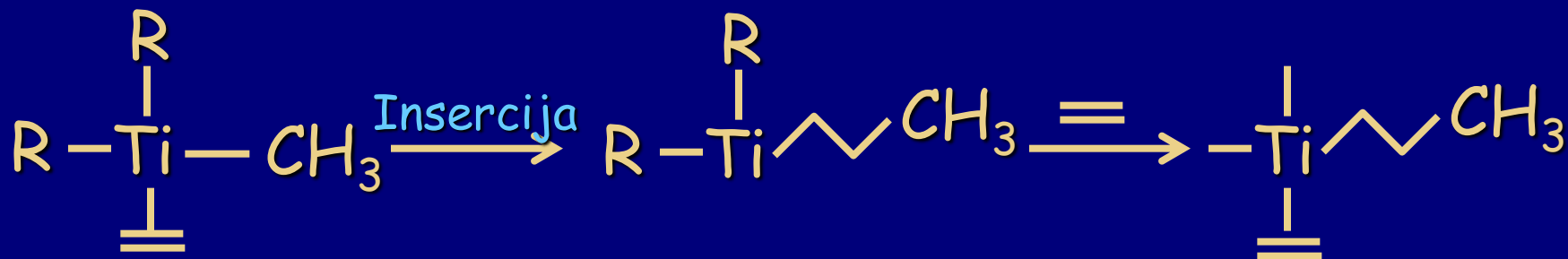
Uobičajeni polimeri i njihovi monomeri

Monomer	Struktura	Polimer (uobičajeno ime)	Struktura	Primena
eten	$\text{H}_2\text{C}=\text{CH}_2$	polietilen	$-(\text{CH}_2\text{CH}_2)_n-$	čuvanje hrane, posude





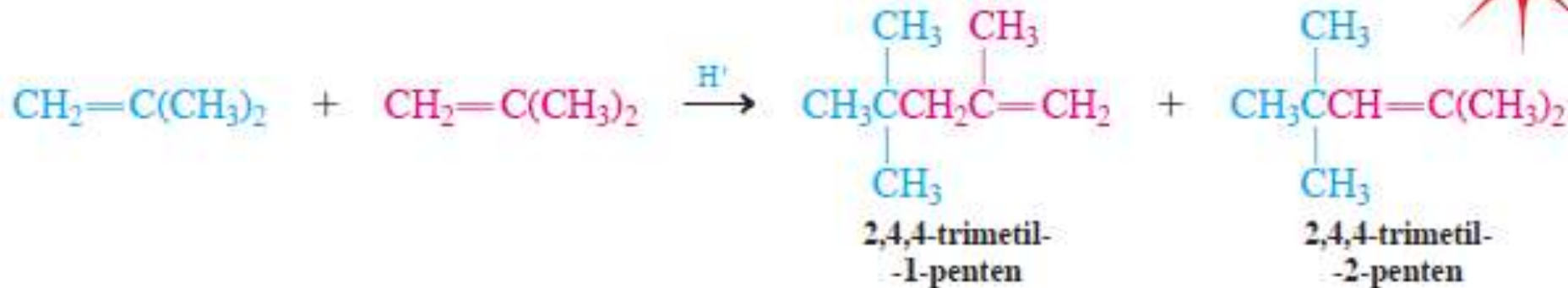
Metali (Ti, Zr, lanthanidi): Ziegler-Natta;
mehanizam preko organometala



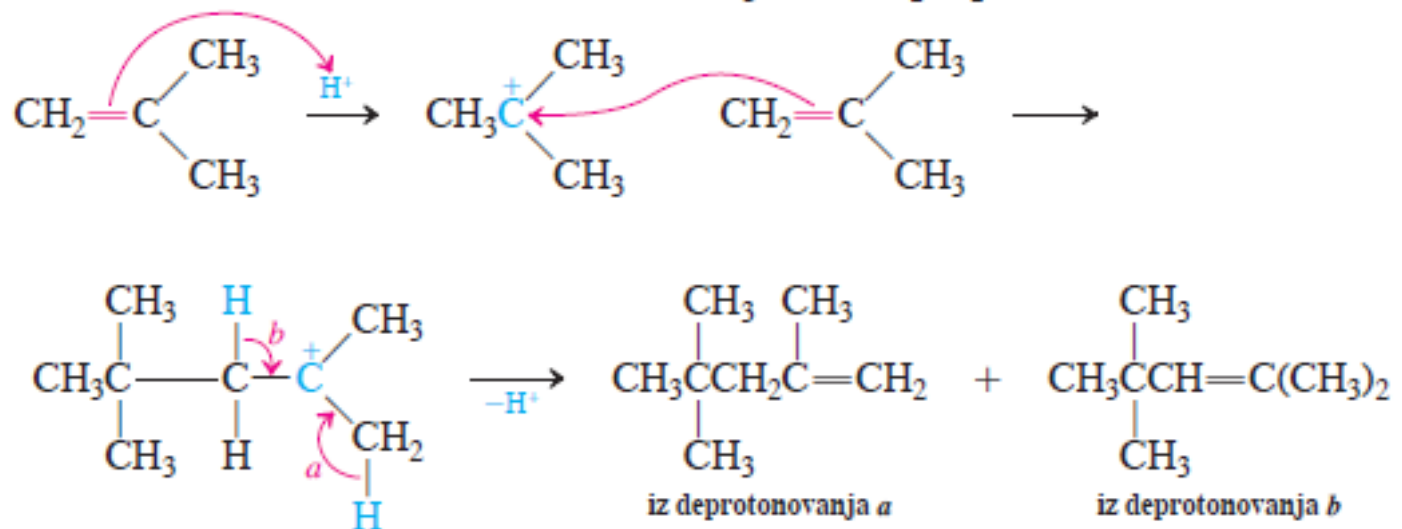
Kiselo-katalizovana reakcija

Reakcija preko karbokatjona.

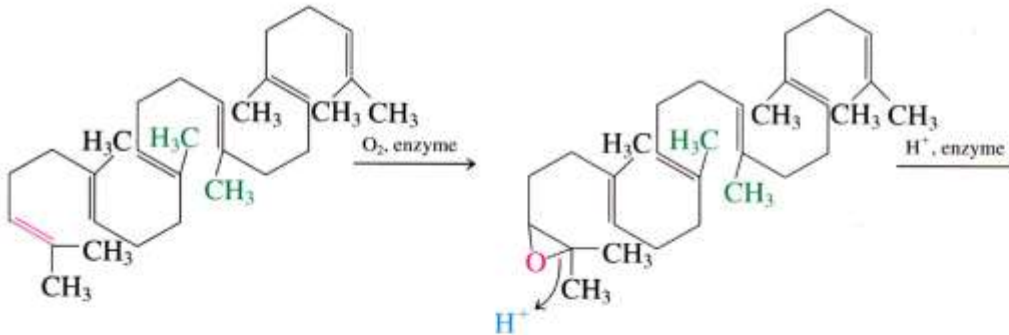
Dimerizacija 2-metilpropena



Mehanizam dimerizacije 2-metilpropena

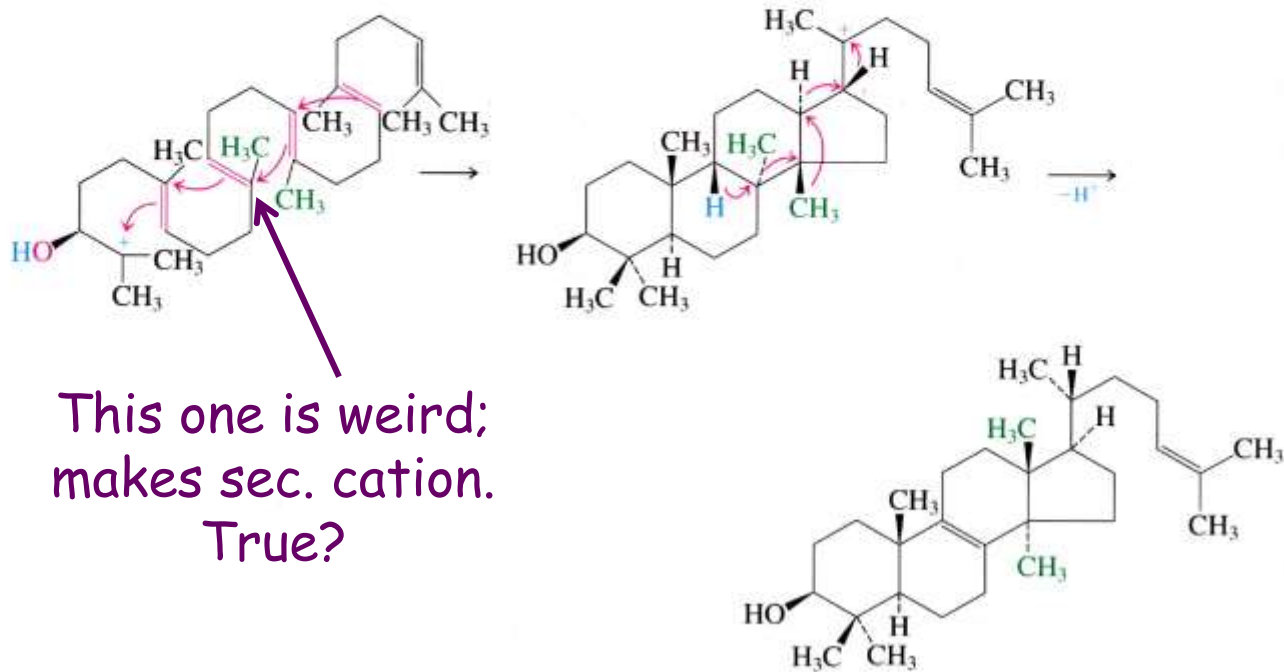


Kontrolisana oligomerizacija u prirodi: kiselo-katalizovana sinteza steroida (postupna)



Squalene

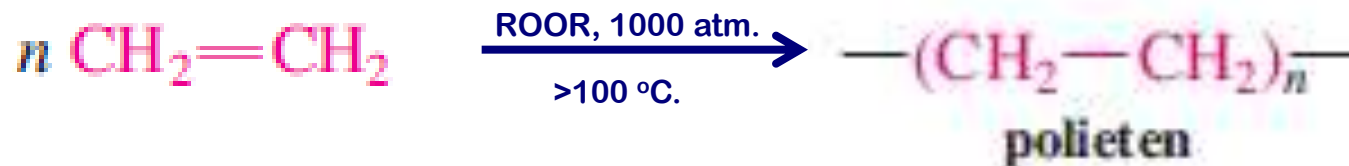
Squalene oxide



This one is weird;
makes sec. cation.
True?

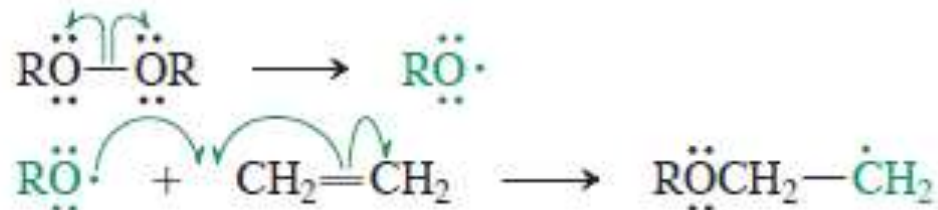
Lanosterol

Radikalska polimerizacija

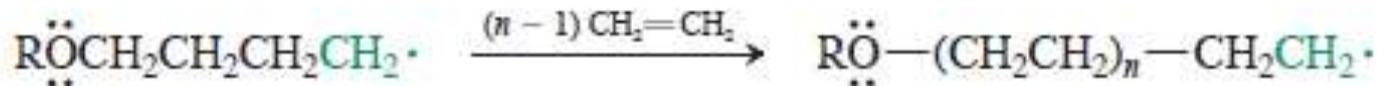
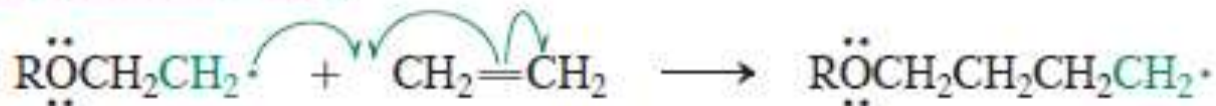


Mehanizam radikalske polimerizacije etena

FAZA INICIRANJA



FAZA PROPAGACIJE



Anjonska polimerizacija

Anjonska polimerizacija superlepka (metil α -cijanoakrilat)

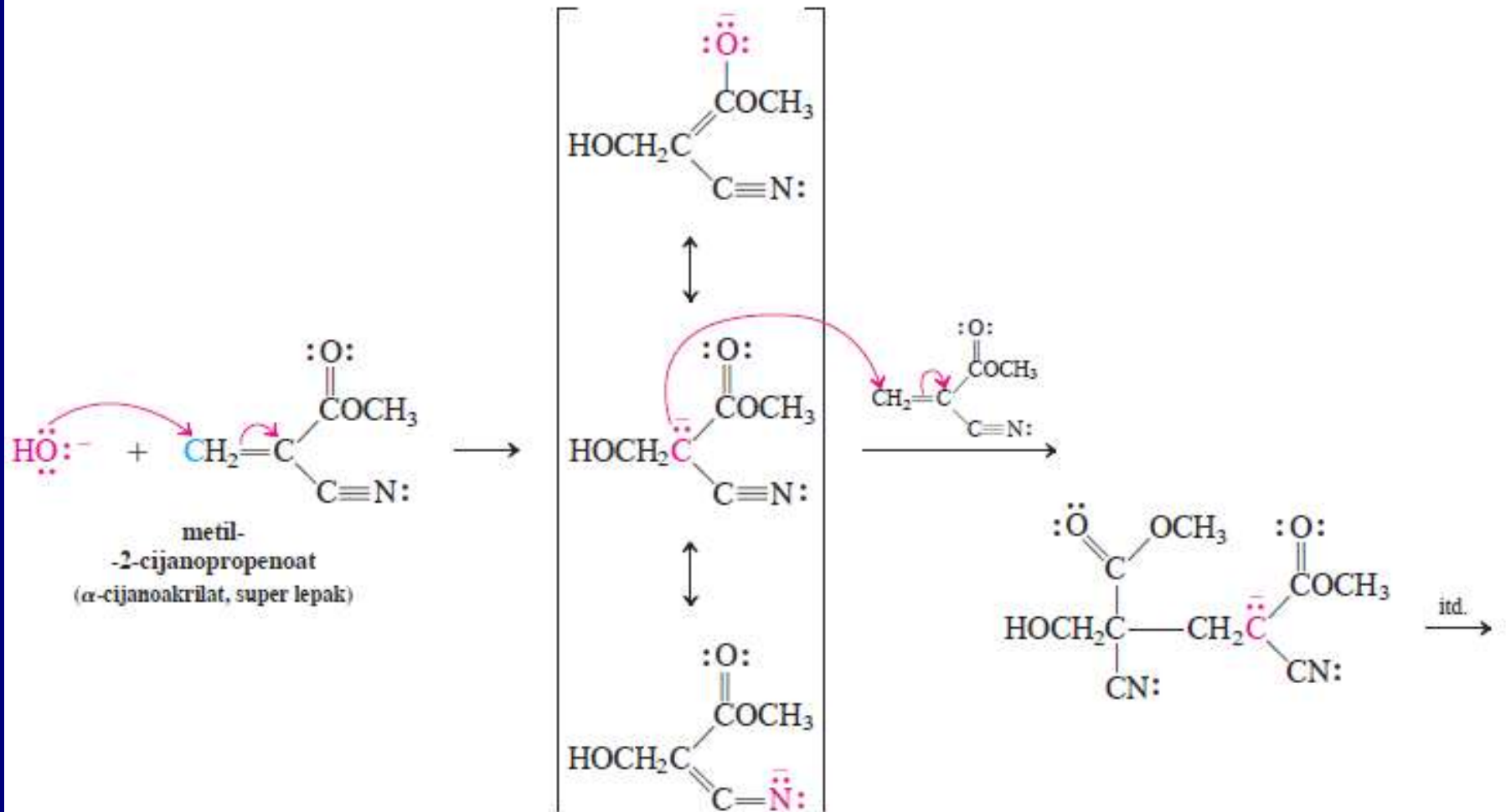
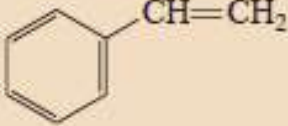



TABELA 12-3

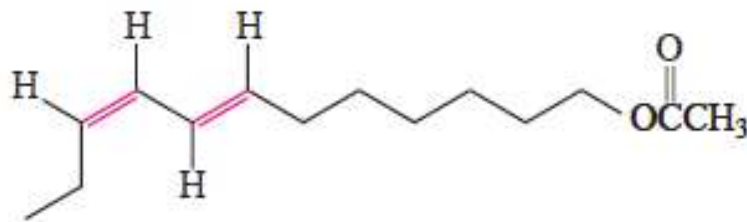
Uobičajeni polimeri i njihovi monomeri

Monomer	Struktura	Polimer (uobičajeno ime)	Struktura	Primena
eten	$\text{H}_2\text{C}=\text{CH}_2$	polietilen	$-(\text{CH}_2\text{CH}_2)_n-$	čuvanje hrane, posude
hloreten (vinil-hlorid)	$\text{H}_2\text{C}=\text{CHCl}$	poli(vinil-hlorid) (PVC)	$-(\text{CH}_2\text{CH})_n-$ Cl	cevi, vinilne tkanine
tetrafluoretan	$\text{F}_2\text{C}=\text{CF}_2$	teflon	$-(\text{CF}_2\text{CF}_2)_n-$	posude u kome ne zagoreva hrana
etenilbenzen (stiren)		polistiren	$-(\text{CH}_2\text{CH})_n-$ 	penasti materijal za pakovanje
propenonitril (akrilonitril)	$\text{H}_2\text{C}=\text{C}\begin{matrix} \text{H} \\ \text{C}\equiv\text{N} \end{matrix}$	orlon	$-(\text{CH}_2\text{CH})_n-$ CN	odeća, sintetička vlakna
metil 2-metil- propenoat (metil metakrilat)	$\text{H}_2\text{C}=\text{C}\begin{matrix} \text{CH}_3 \\ \text{COCH}_3 \\ \text{O} \end{matrix}$	pleksiglas	$-(\text{CH}_2\text{C})_n-$ CH ₃ CO ₂ CH ₃	providne ploče otporne na udar
2-metilpropen (izobutilen)	$\text{H}_2\text{C}=\text{C}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	elastol	$-(\text{CH}_2\text{C})_n-$ CH ₃ CH ₃	sredstvo za čišćenje naftnih mrlja

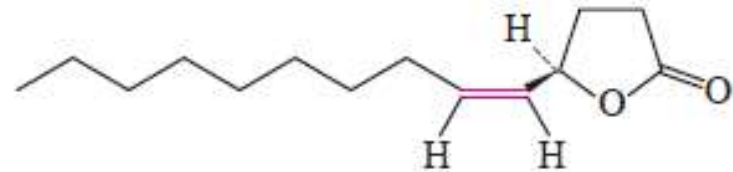
Alkeni u prirodi: feromoni

Feromoni su hemijske supstance koje služe za komunikaciju u okviru vrste. Postoje seksualni feromoni, feromoni za obeležavanje kretanja, feromoni upozoravnja, odbrambeni feromoni

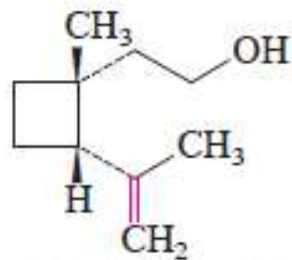
Feromoni insekata



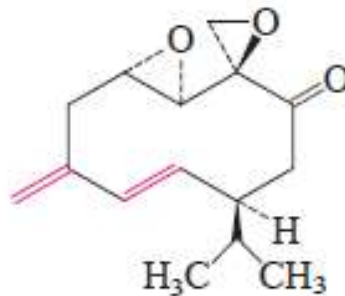
evropskog vinskog moljca



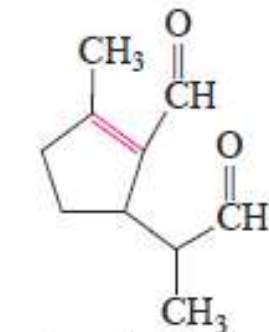
japanske bube



mužjaka loptastog žiška



američke bubašvabe



odbrambeni feromon
larve bube listara