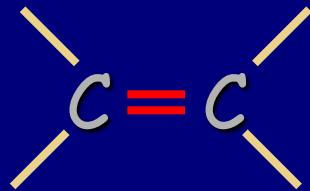


Poglavlje 11: Alkeni



Dvostruka
veza

Nomenklatura:

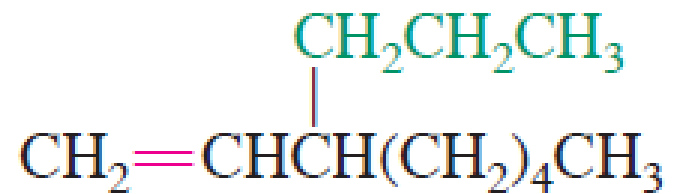
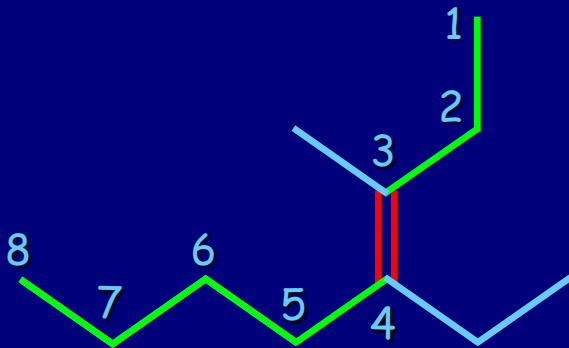
Završetak - an → - en

Primer: Eten, propen, buten, ...

Pravila:

1. Naći najduži niz koji sadrži oba C_{sp^2} atoma.

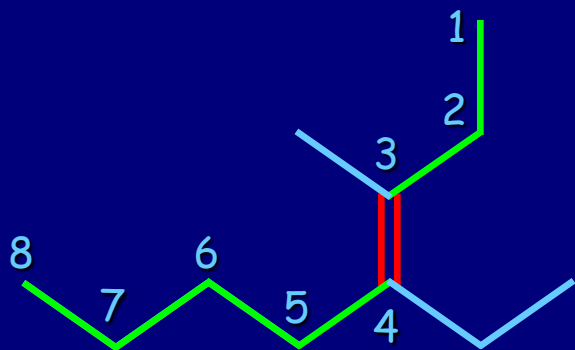
okten



propilokten

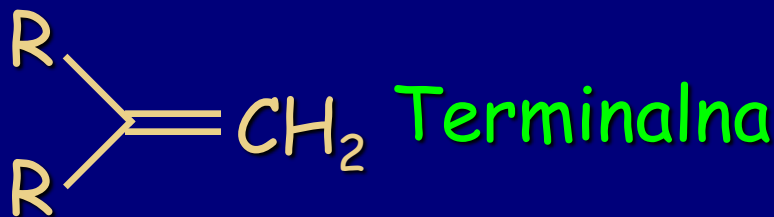
(nije derivat heksena
niti nonana)

2. Mesto dvostruke veze označiti brojem polazeći s najbližeg kraja dvostruke veze



3-okten (samo se prvi od dva C_{sp^2} numeriše)

Položaj dvostruke veze



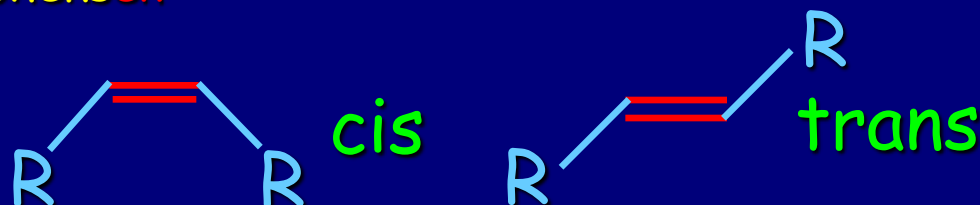
3. Kao prefikse dodati supstituente i numerisati njihov položaj 4-etil-3-metil-3-okten

4. Cikloalkeni



$C^1=C^2$ po definiciji

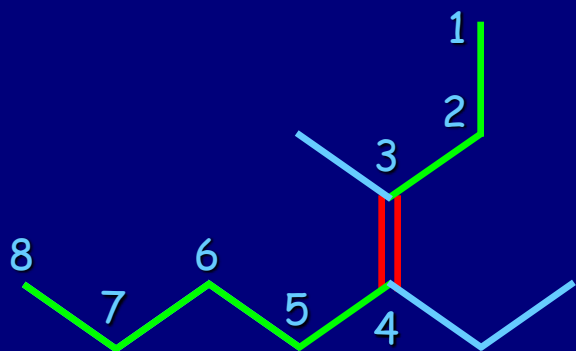
5. Stereoizomeri:



cis/trans nomenklatura za 1,2-disupstituisane alkene.

6. Za tri- i tetrasupstituisane alkene: *E*, *Z*

Primena pravila za određivanje prioriteta kao kod određivanja R, S konfiguracije, za svaki sp^2 -ugljenik posebno.

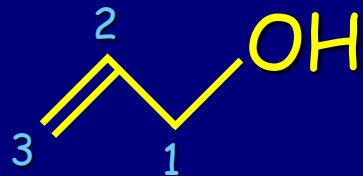


Na suprotnim stranama: *E*
Sa iste strane: *Z*

E-4-etil-3metil-3-okten

Prioritet dvostruke veze

7. $-\text{OH}$ ($-\text{SH}$) $>$ $-\text{en}$

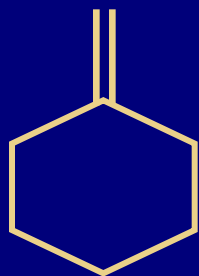


2-Propen-1-ol

8. Supstituenti: Alkenil $\text{CH}_2=\text{CH}-$ Etenil (vinil)

$\text{CH}_2=\text{CH}-\text{CH}_2-$ 2-Propenil (alil)

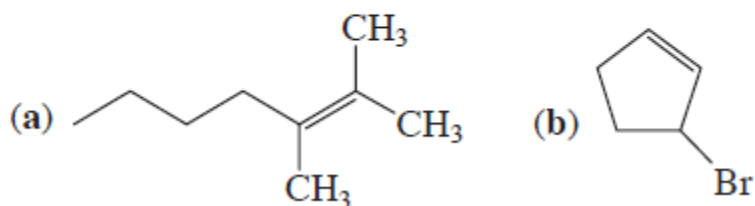
9. Egzociklični alkeni: Alkilidencikloalkani



Metilidencikloheksan
(metilencikloheksan)

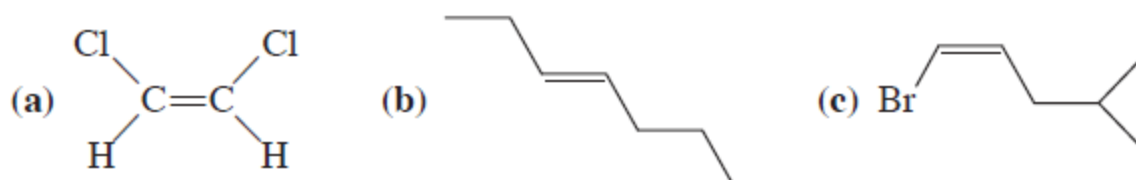
Vežba 11-1

Imenujte sledeća dva alkena.



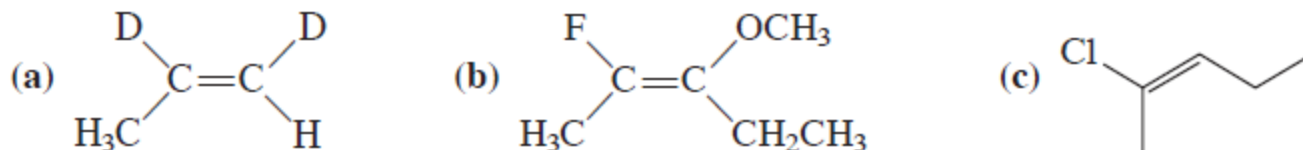
Vežba 11-2

Imenujte sledeća tri alkena.



Vežba 11-3

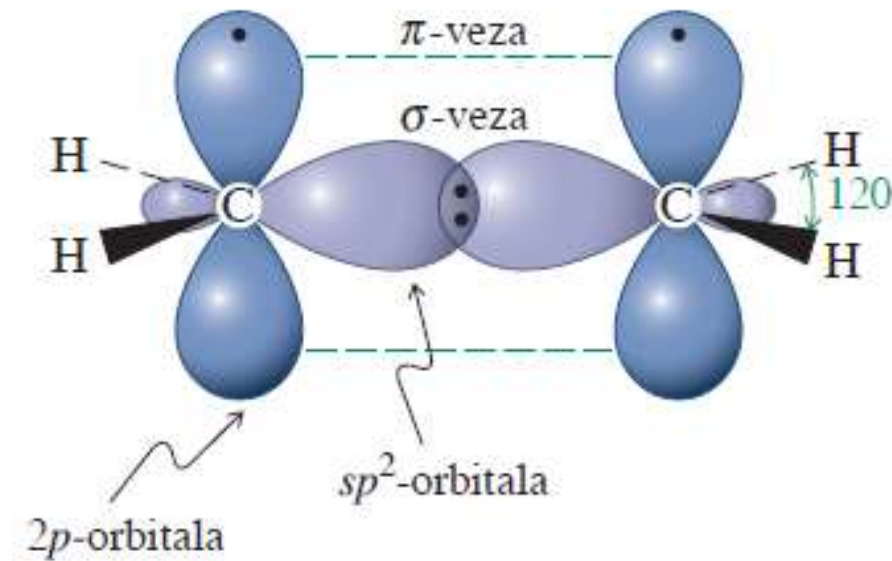
Imenujte sledeća tri alkena.



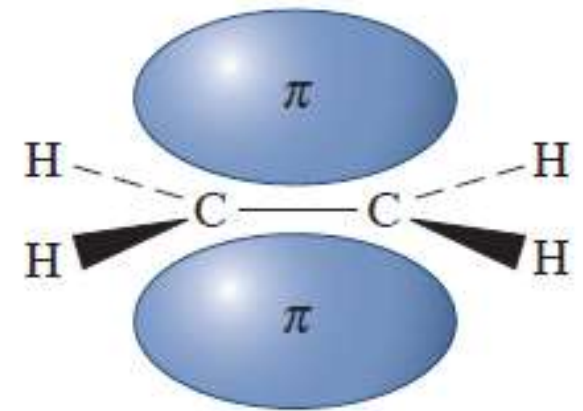
Vežba 11-4

Nacrtajte strukture datih molekula. (a) *trans*-3-penten-1-ol; (b) 3-cikloheksenol.

Struktura dvostruke veze

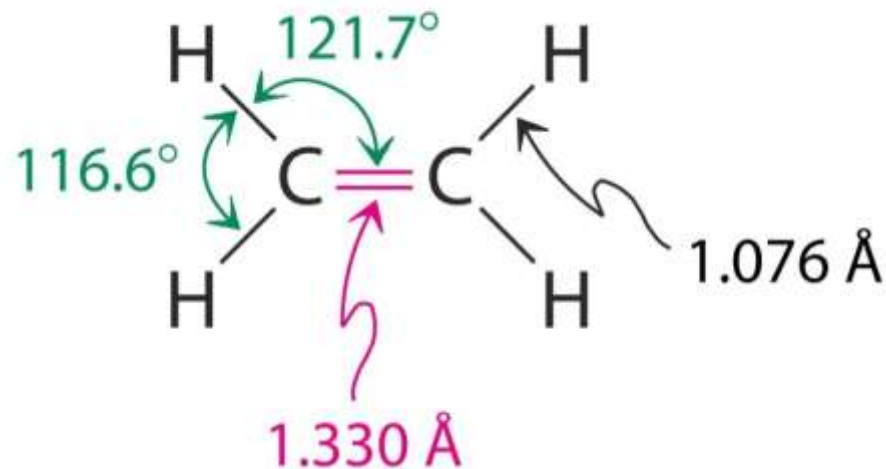


A

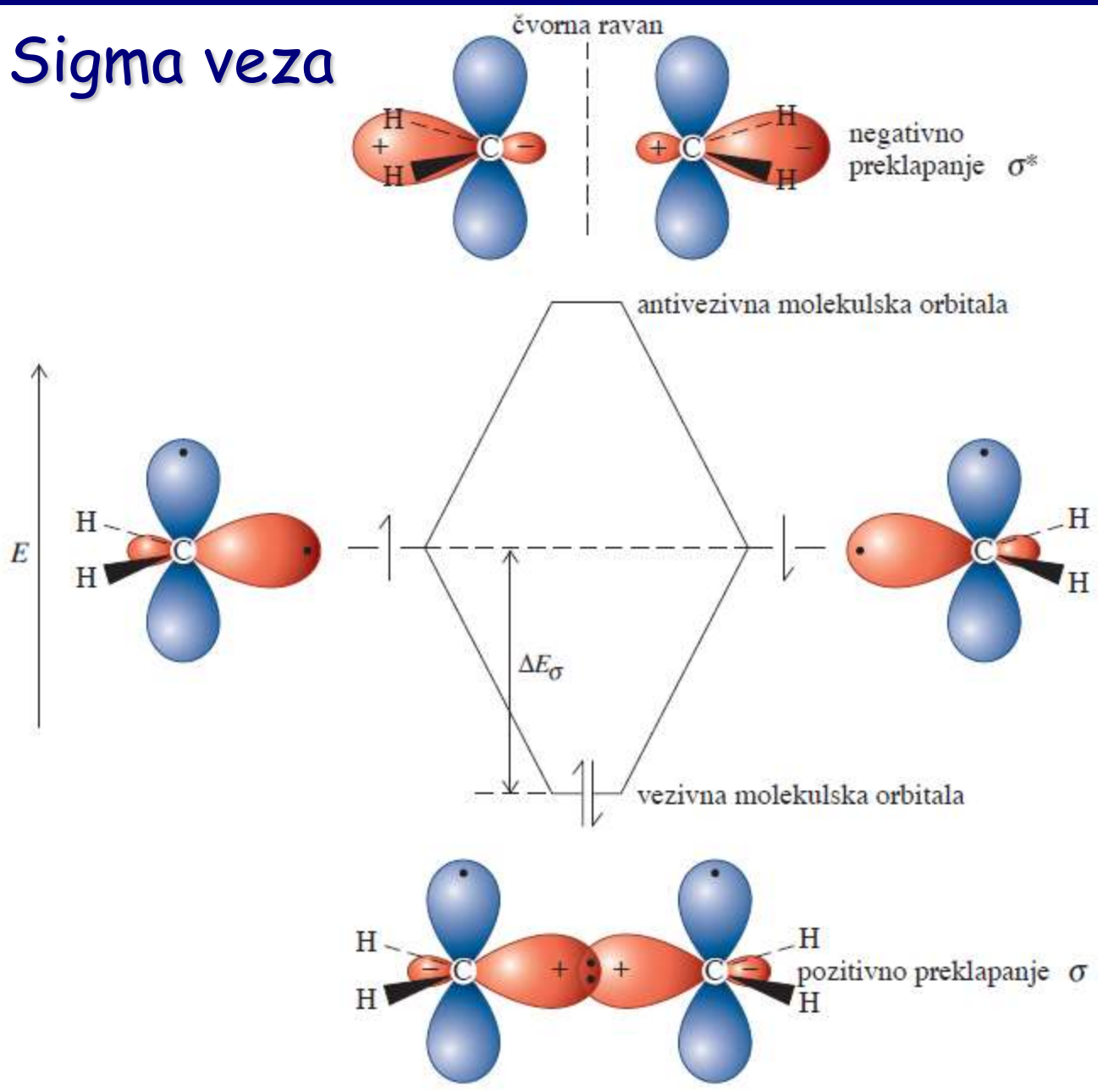


"Elektron-bogata"

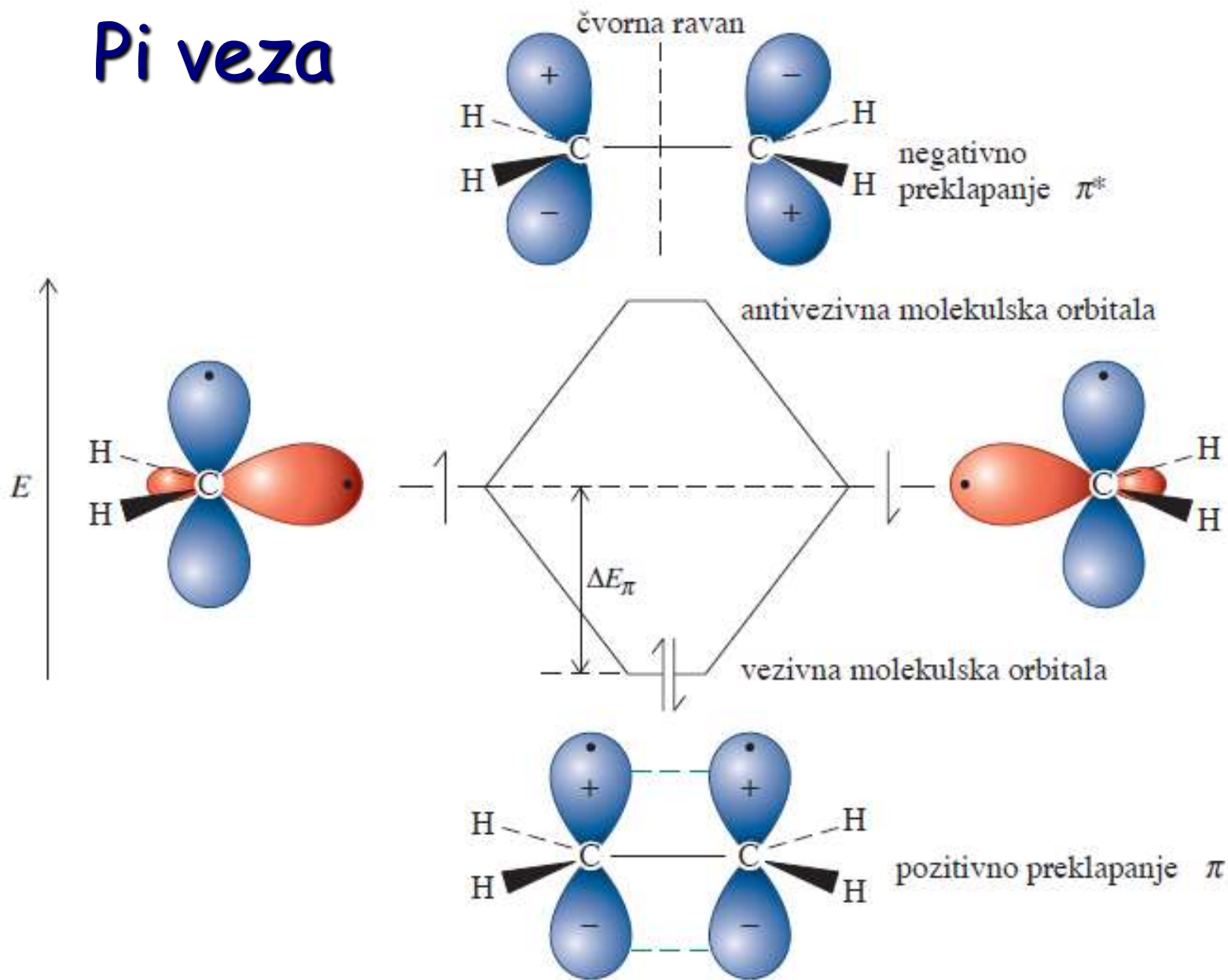
B



Sigma veza

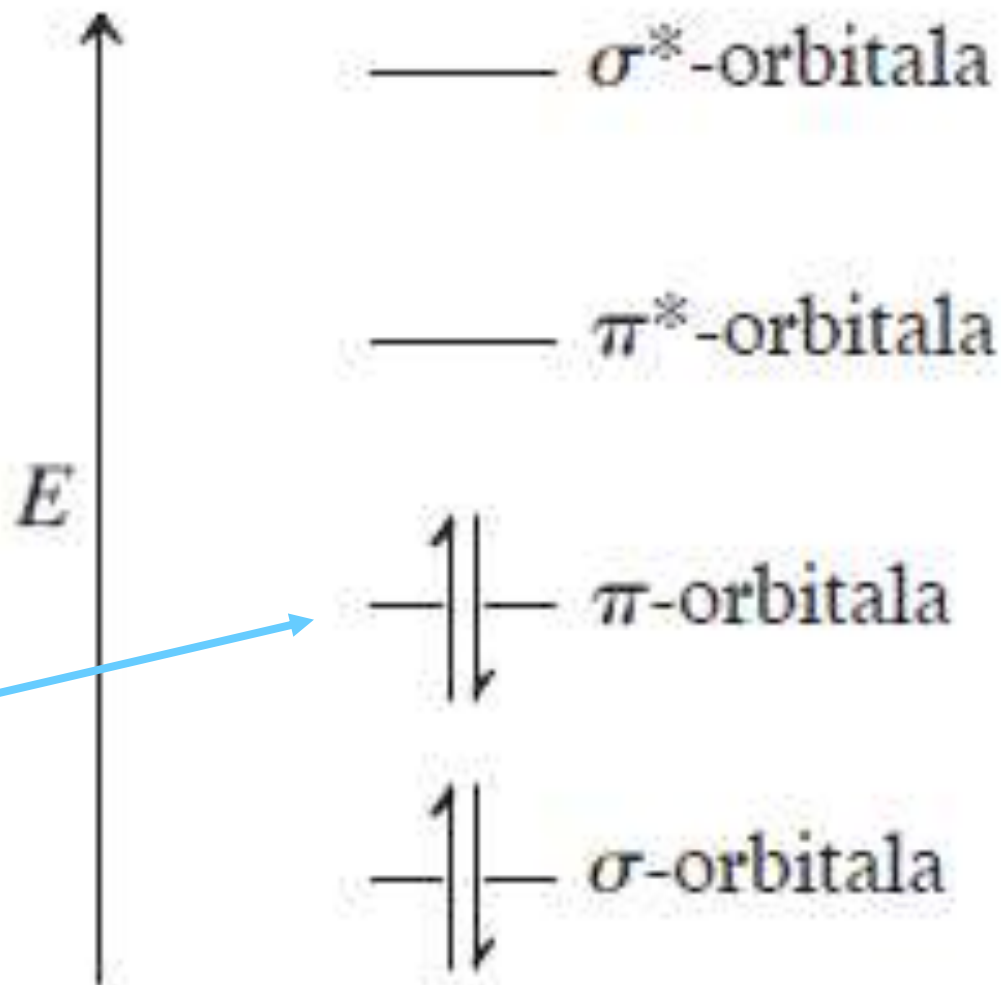


Pi veza



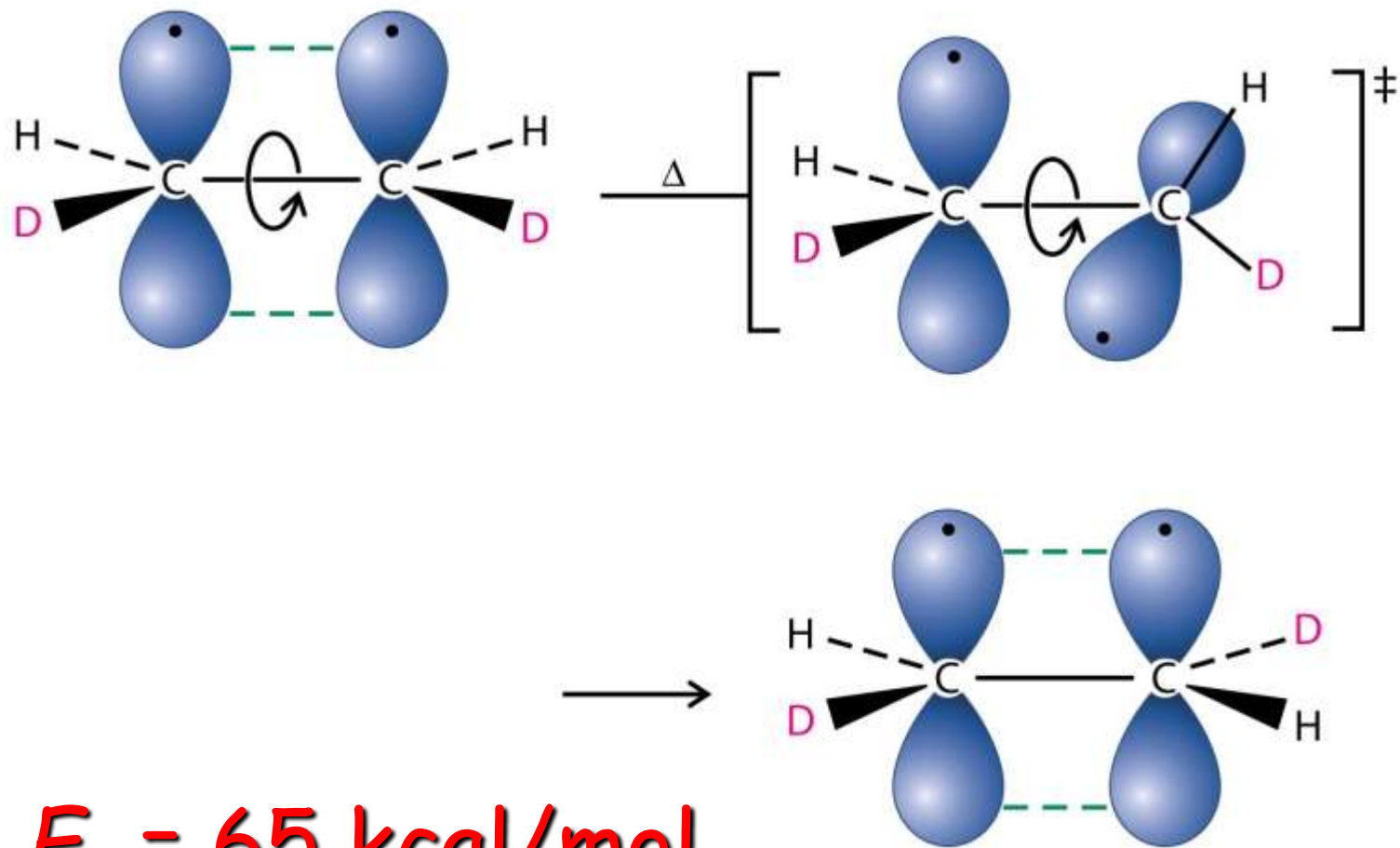
Energije orbitala

π Veza je relativno slaba



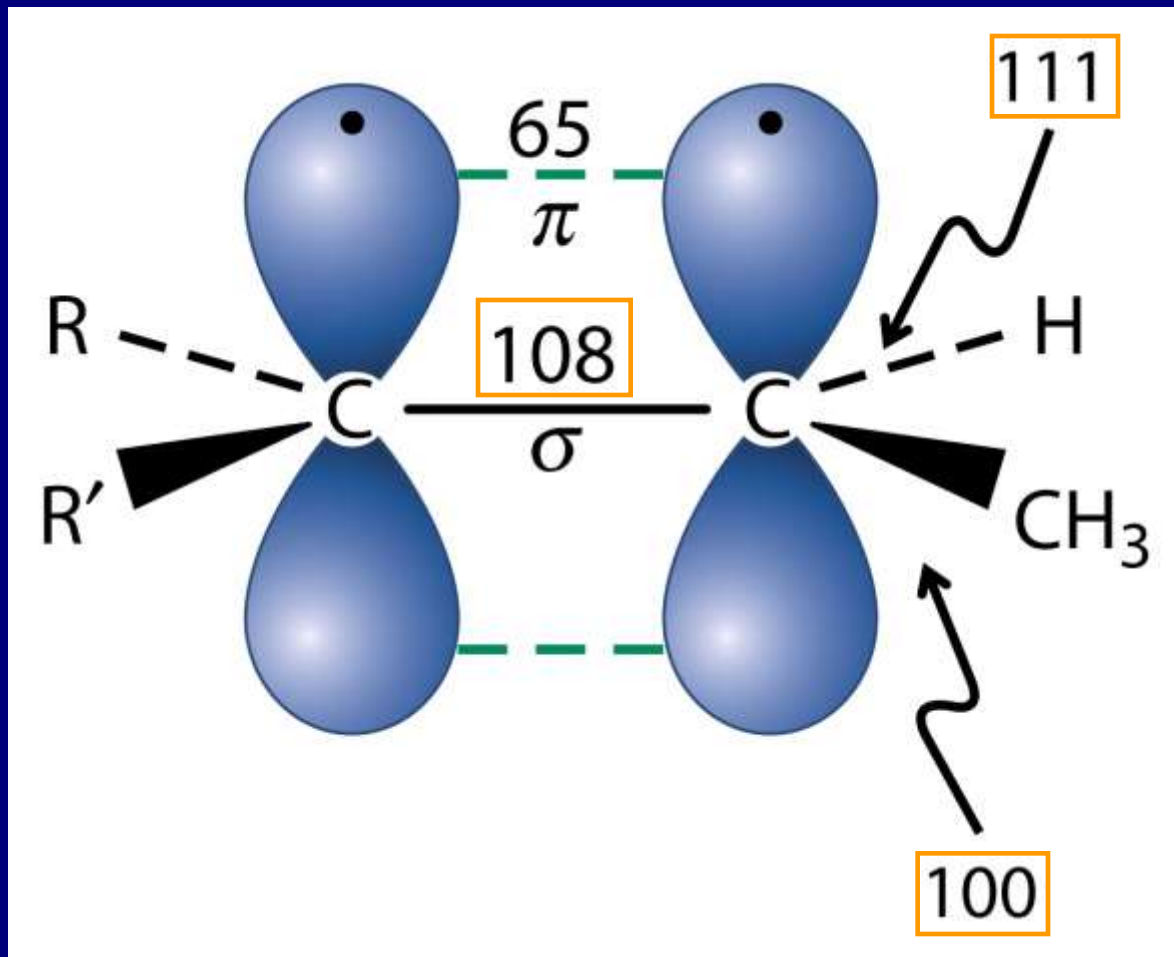
antivezivne orbitale: π^* , σ^*
vezivne orbitale: π , σ

Koliko je jaka π veza?

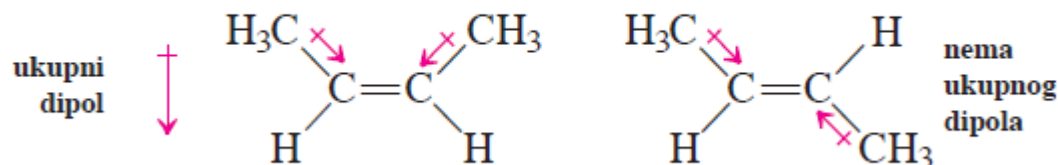


$E_a = 65 \text{ kcal/mol}$

Jačina veza (kcal/mol)



Polarizacija kod alkena



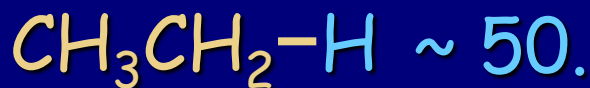
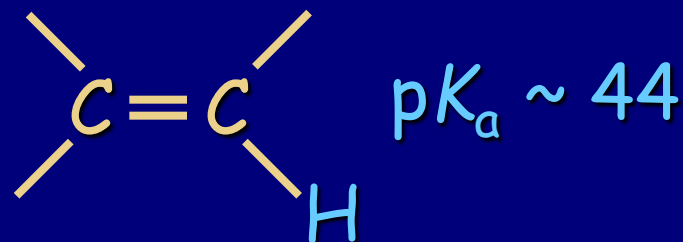
Tačke ključanja alkena su slične odgovarajućima alkanima

TABELA 11-1

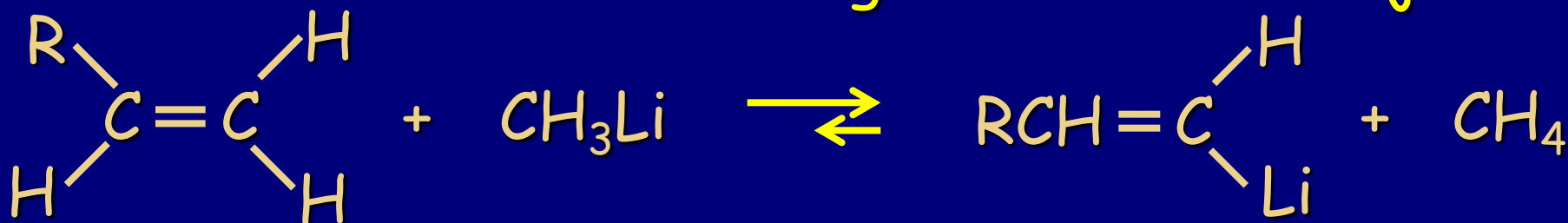
Poređenje tački topljenja alkena i alkana

Jedinjenje	Tačka topljenja (°C)
butan	-138
<i>trans</i> -2-buten	-106
<i>cis</i> -2-buten	-139
pentan	-130
<i>trans</i> -2-penten	-135
<i>cis</i> -2-penten	-180
heksan	-95
<i>trans</i> -2-heksen	-133
<i>cis</i> -2-heksen	-141
<i>trans</i> -3-heksen	-115
<i>cis</i> -3-heksen	-138

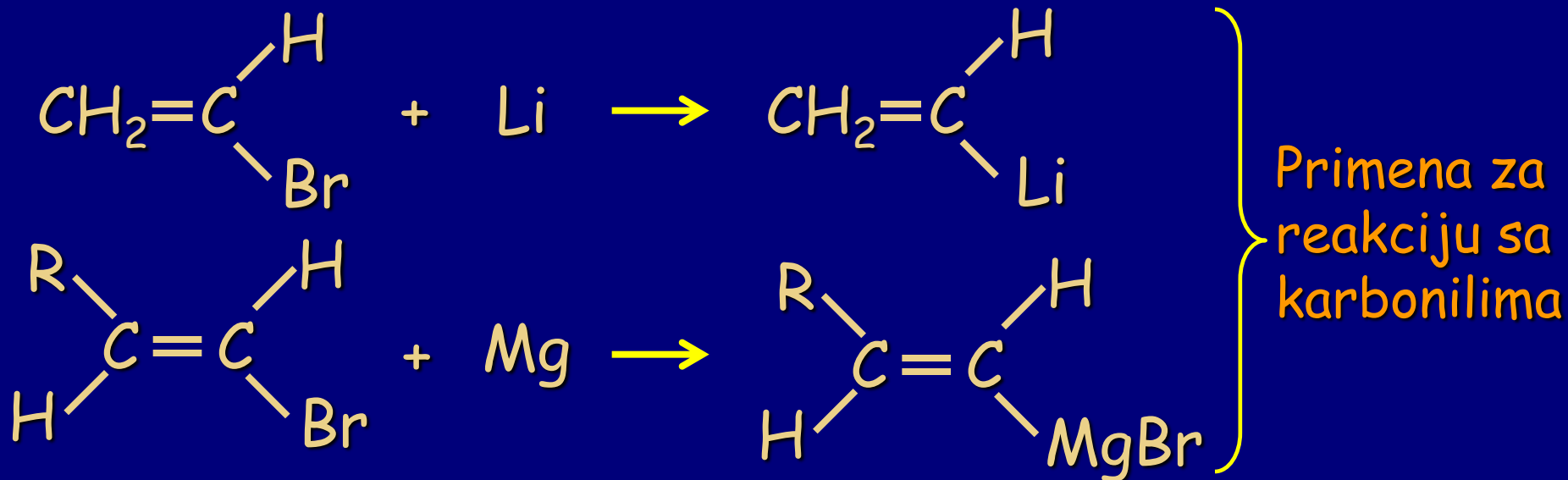
Kiselost: Alkenil vodonici su „kisel“



Zato je alkenil-anjon moguće dobiti reakcijom:

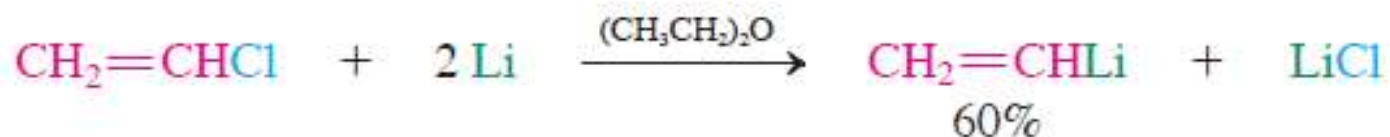


Problemi: Regio-, stereoselektivnost. Bolji način:



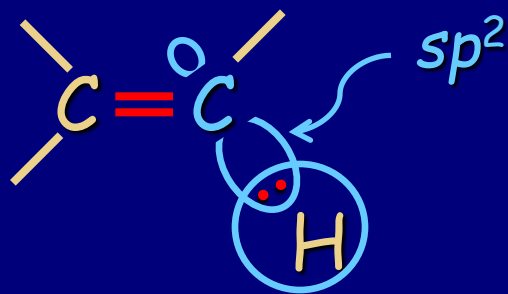
Vežba 11-6

Etenilitijum (vinilitijum) obično se ne dobija direktnim deprotonovanjem etena, već iz hloretena (vinil-hlorida) (odeljak 8-7)



Dejstvom propanona (acetona) na etenilitijum, posle obrade reakcije vodom, dobija se bezbojna tečnost u prinosu od 74%. Predložite strukturu proizvoda

Zašto su alkenil vodonici kiseli?

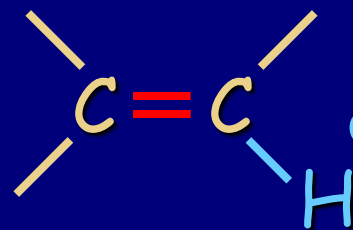


sp^2 ugljenik je 33% s karaktera, dok je sp^3 ugljenik samo sa 25% s karakterom

Ukupan efekat:

slabo e-privlačne osobine sp^2 ugljenika

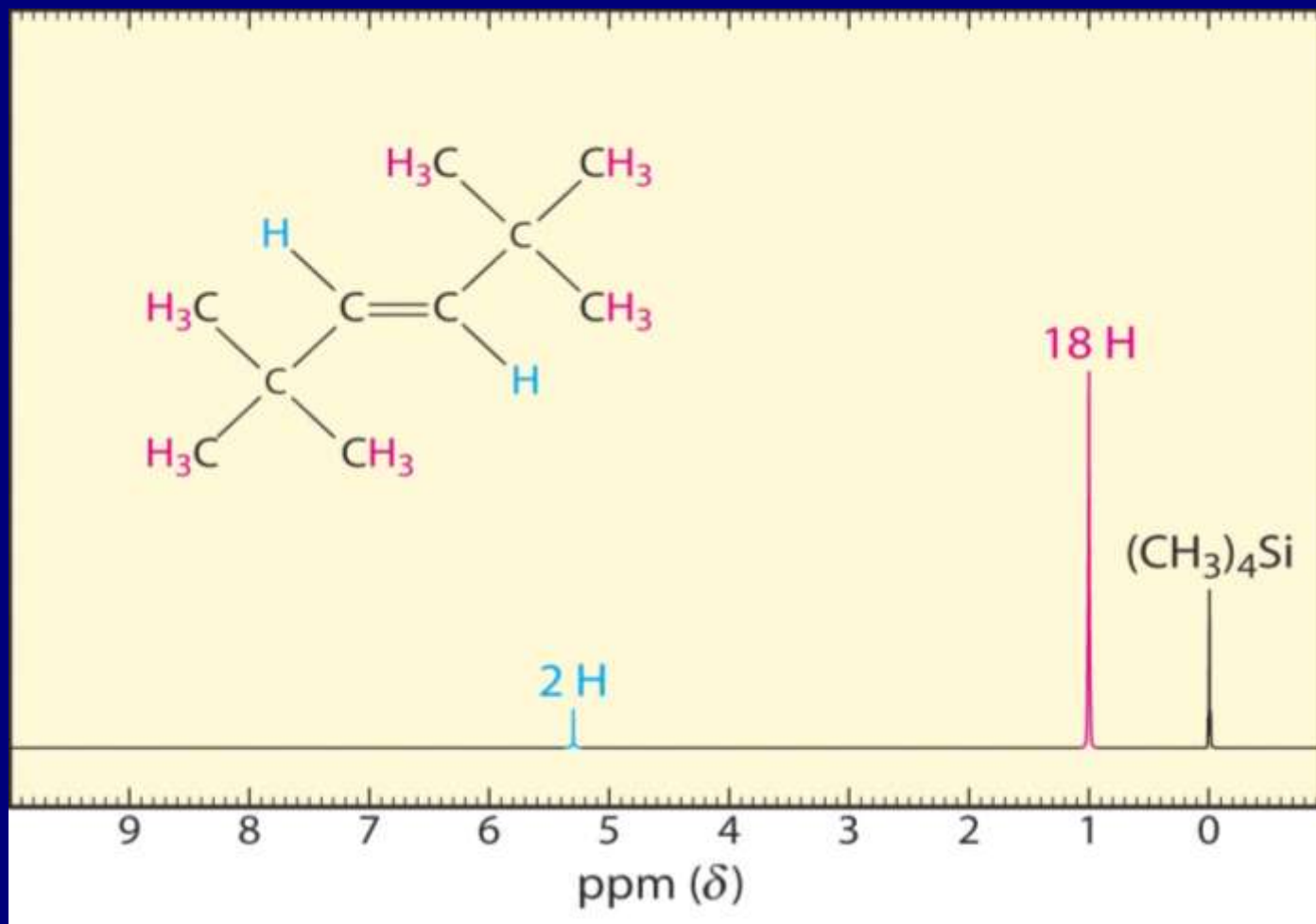
$^1\text{H NMR}$

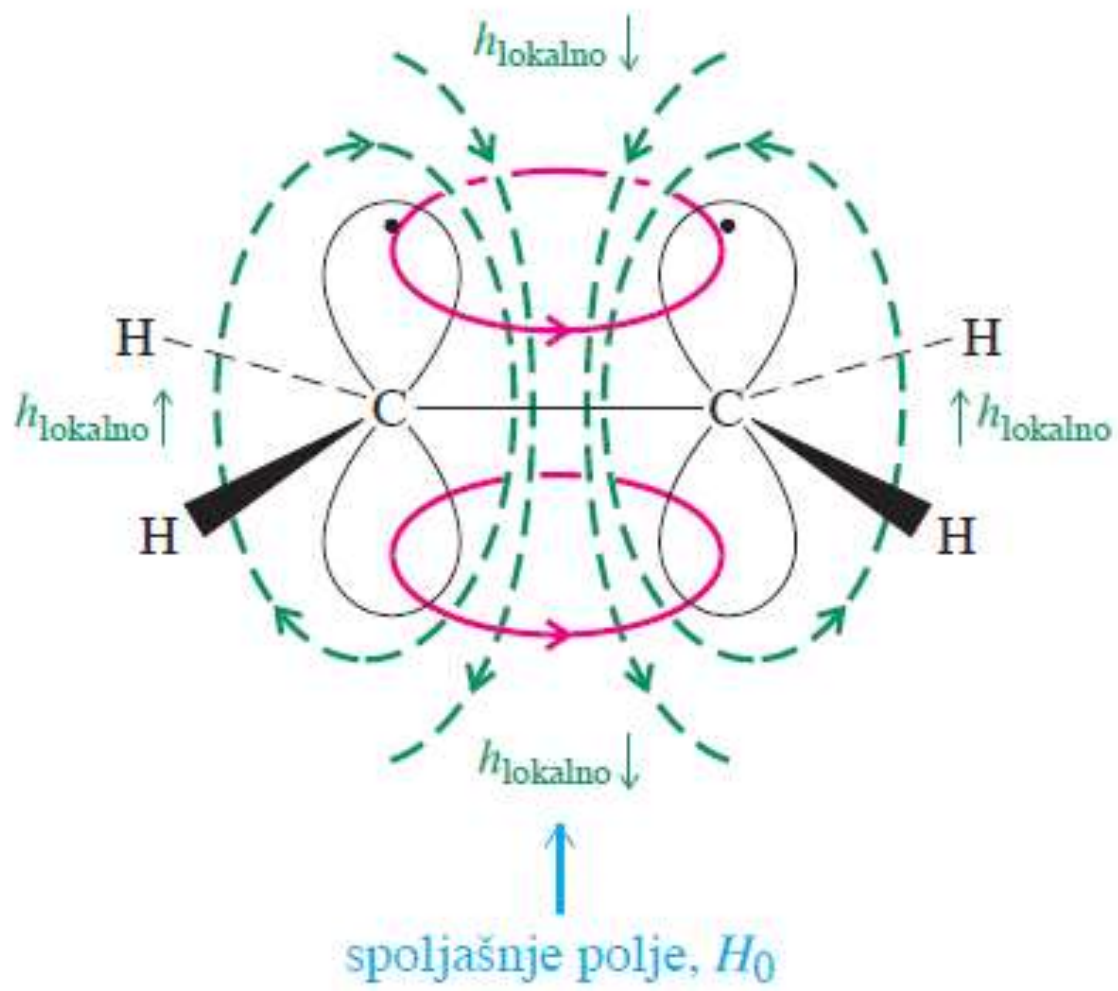


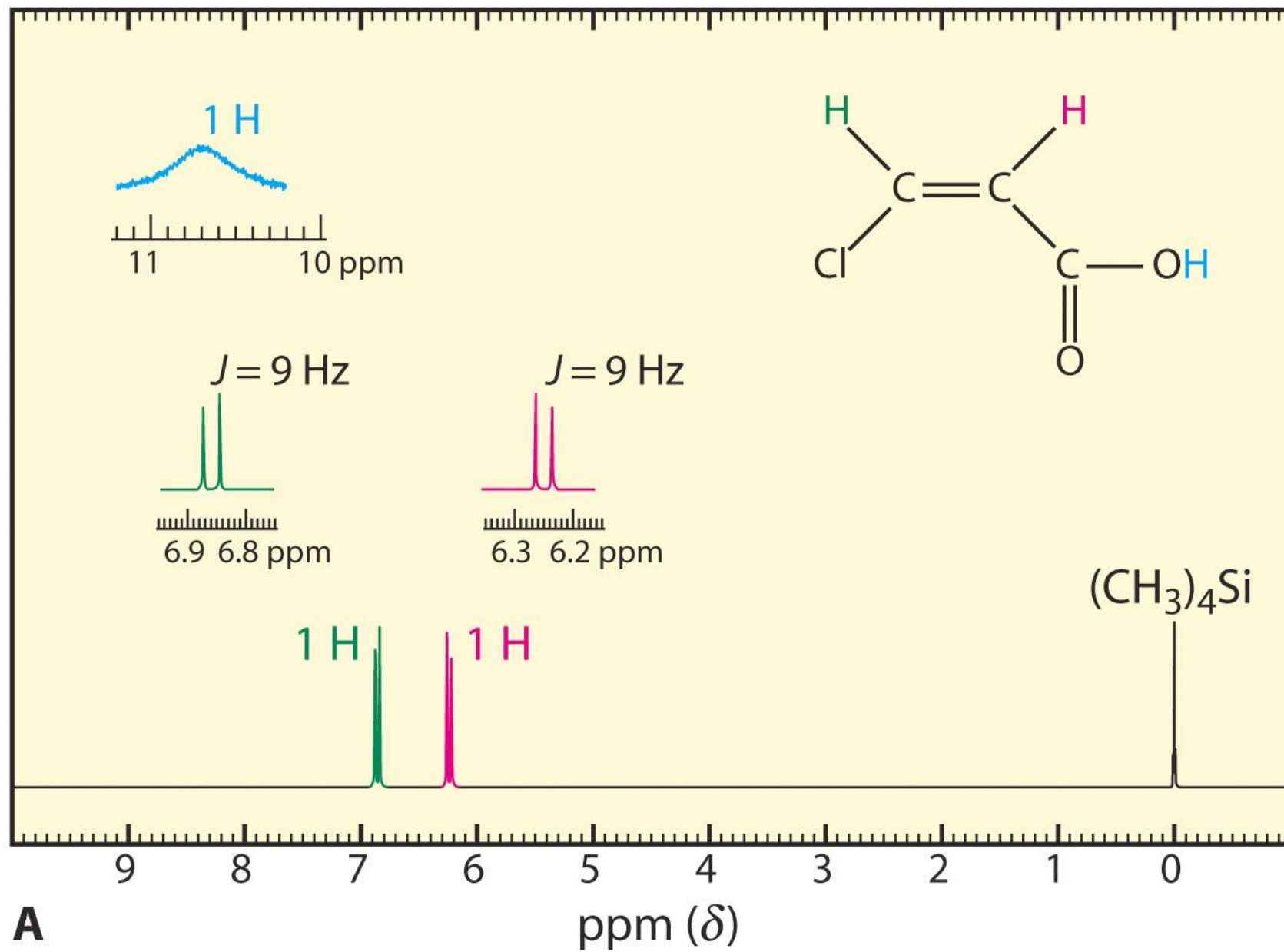
$\delta \sim 4.5-6$ ppm: nezaklonjeni!

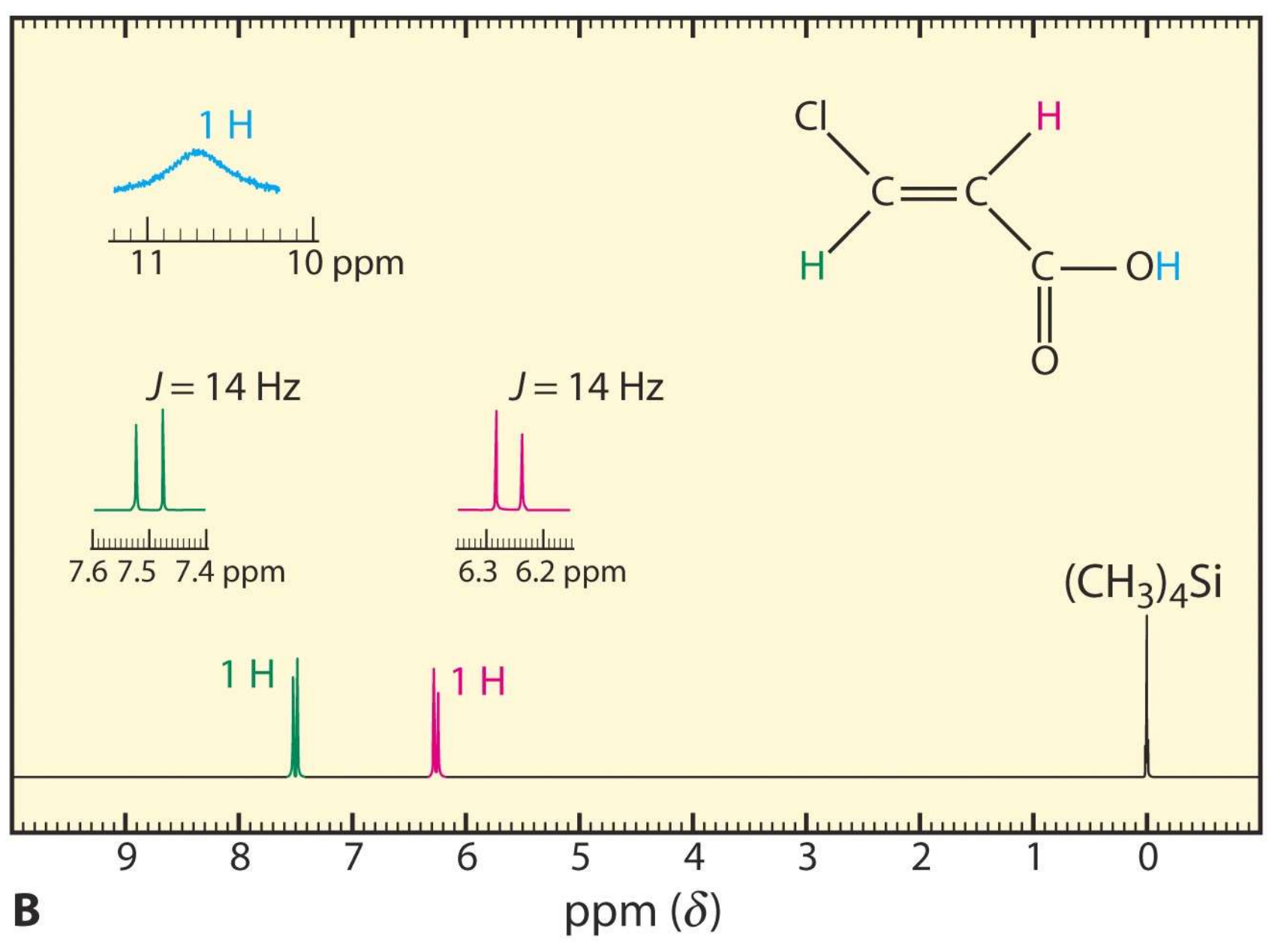
Terminalni alkeni: 4.6-5.0

Unutrašnji alkeni: 5.2-5.7





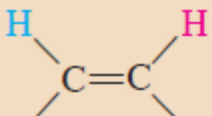
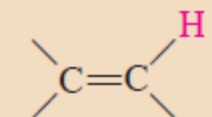
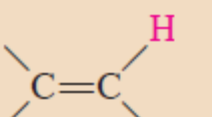
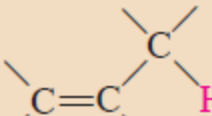
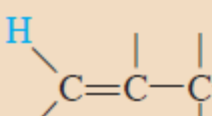
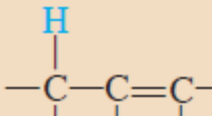


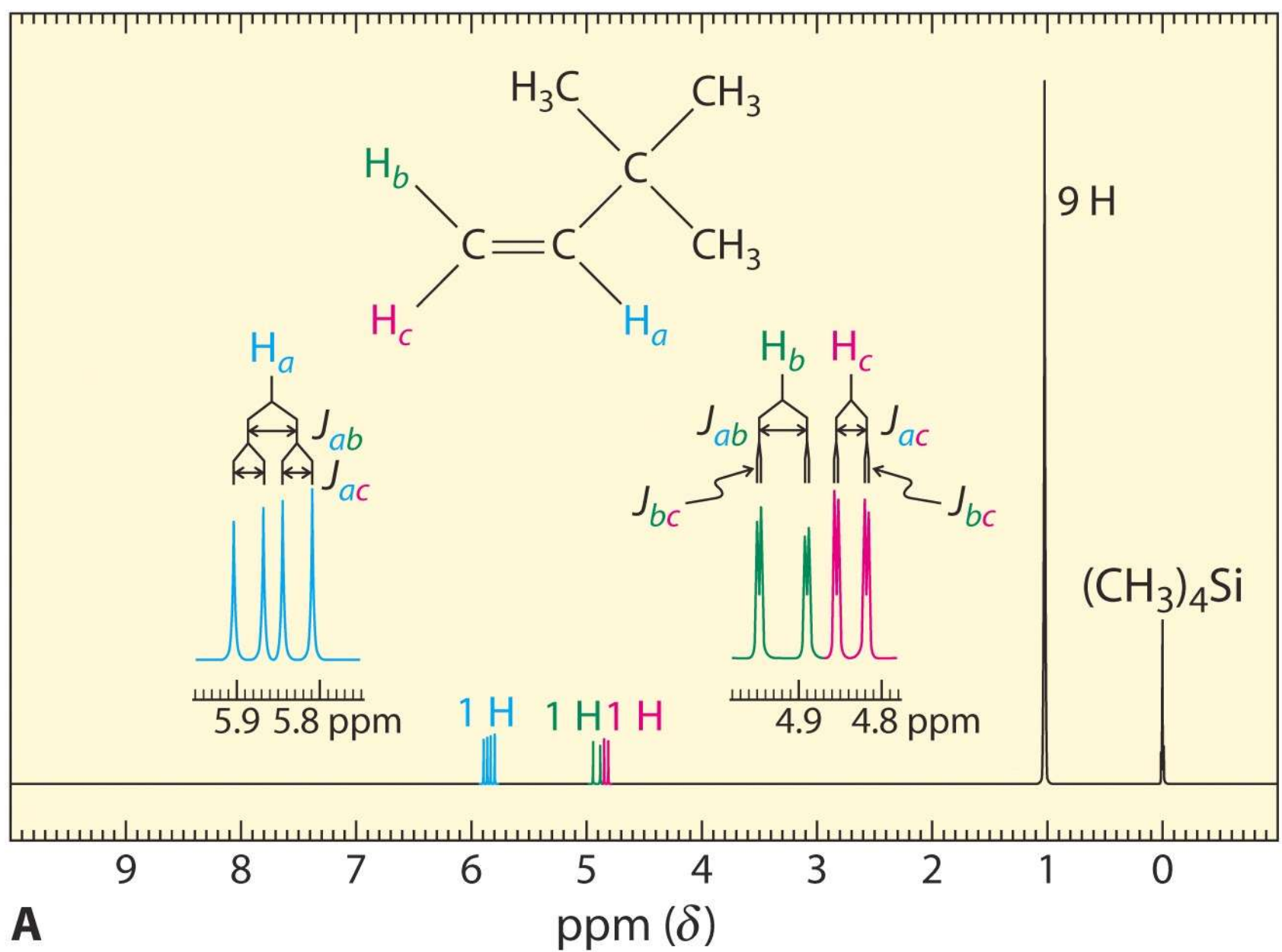


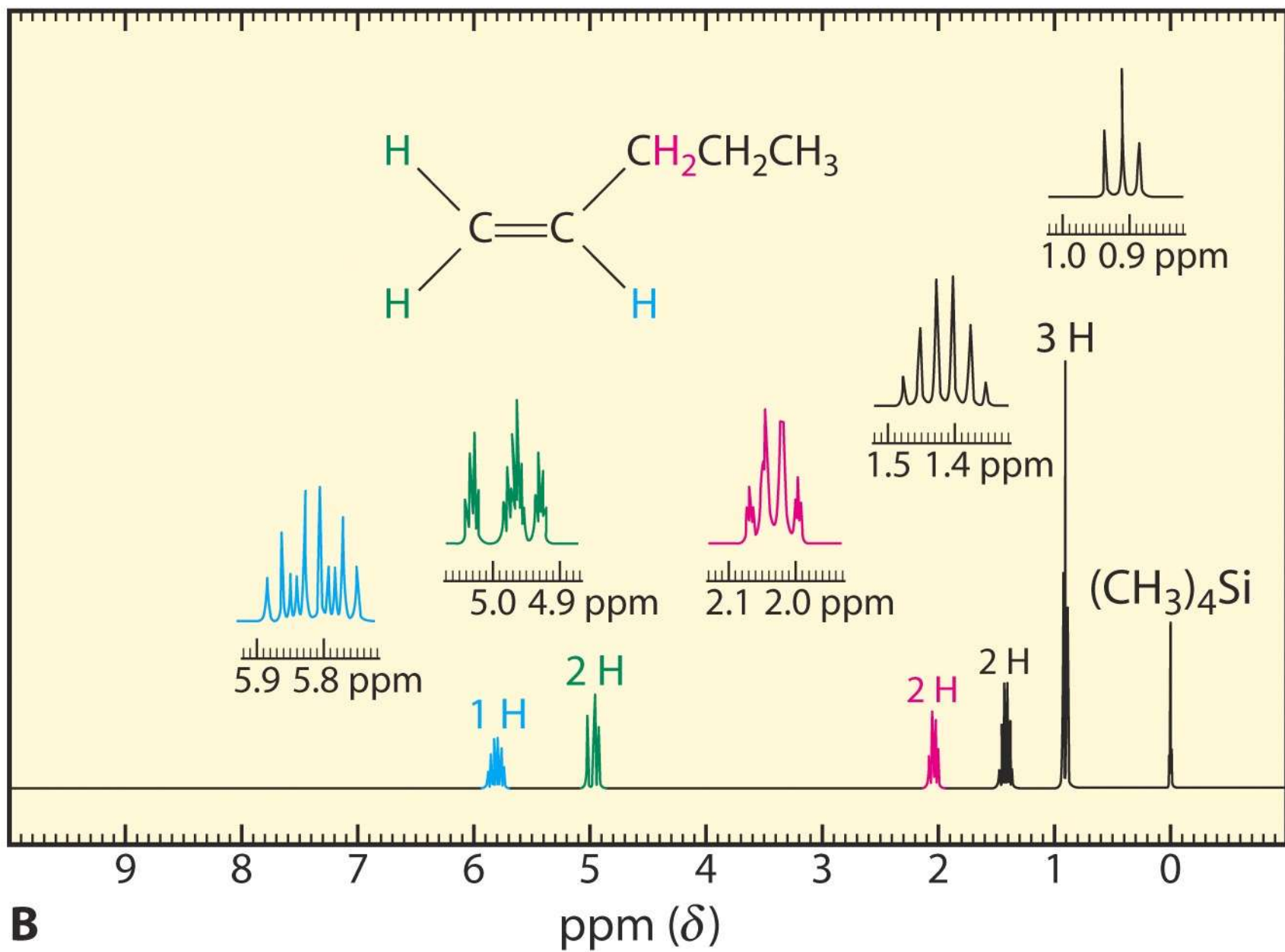
B

TABLE 11-2

Konstante sprežanja na dvostrukoj vezi

Vrsta sprežanja	Ime	<i>J</i> (Hz)	
		Interval	Tipično
	vicinalno, cis	6–14	10
	vicinalno, trans	11–18	16
	geminalno	0–3	2
	nema	4–10	6
	alilno, (1,3)-cis ili -trans	0,5–3,0	2
	(1,4)- ili daljinsko	0,0–1,6	1



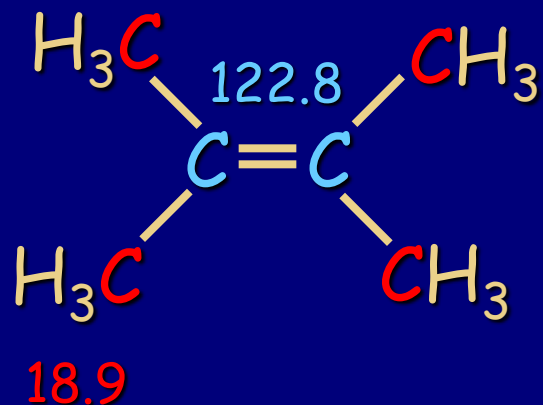


B

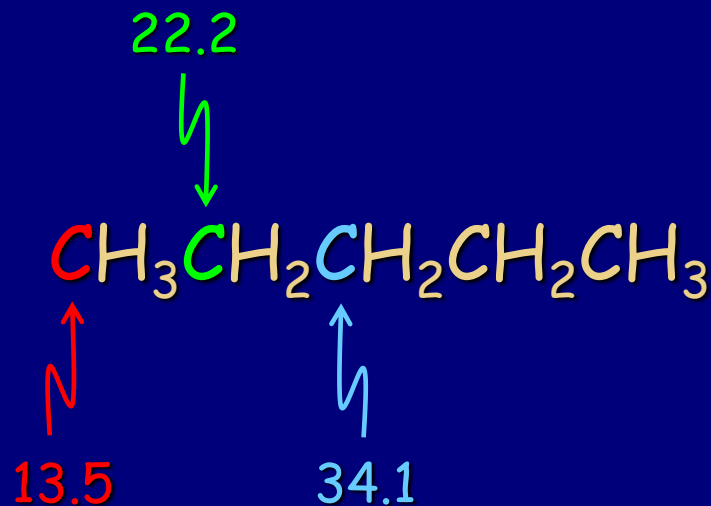
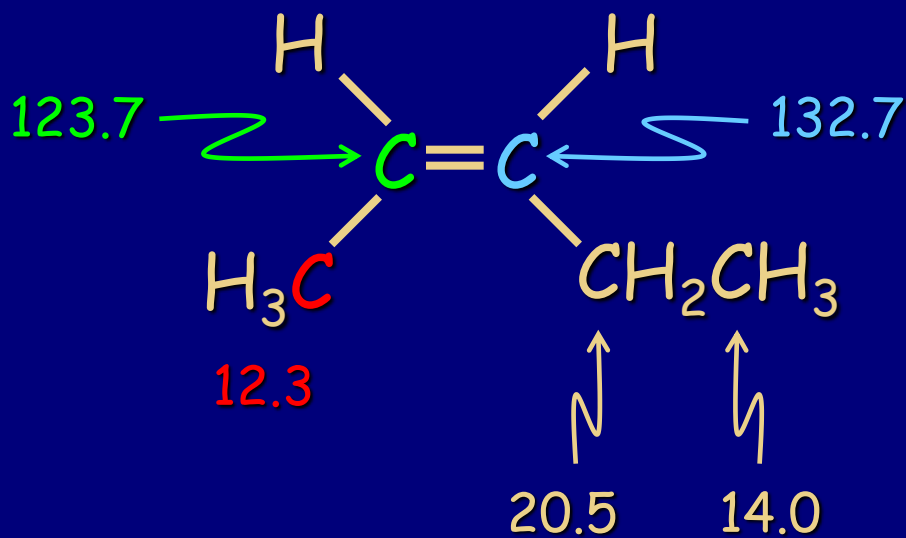
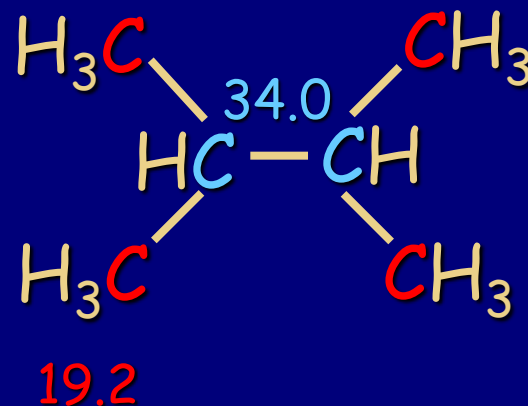
^{13}C NMR C_{sp^2} nezaklonjeni

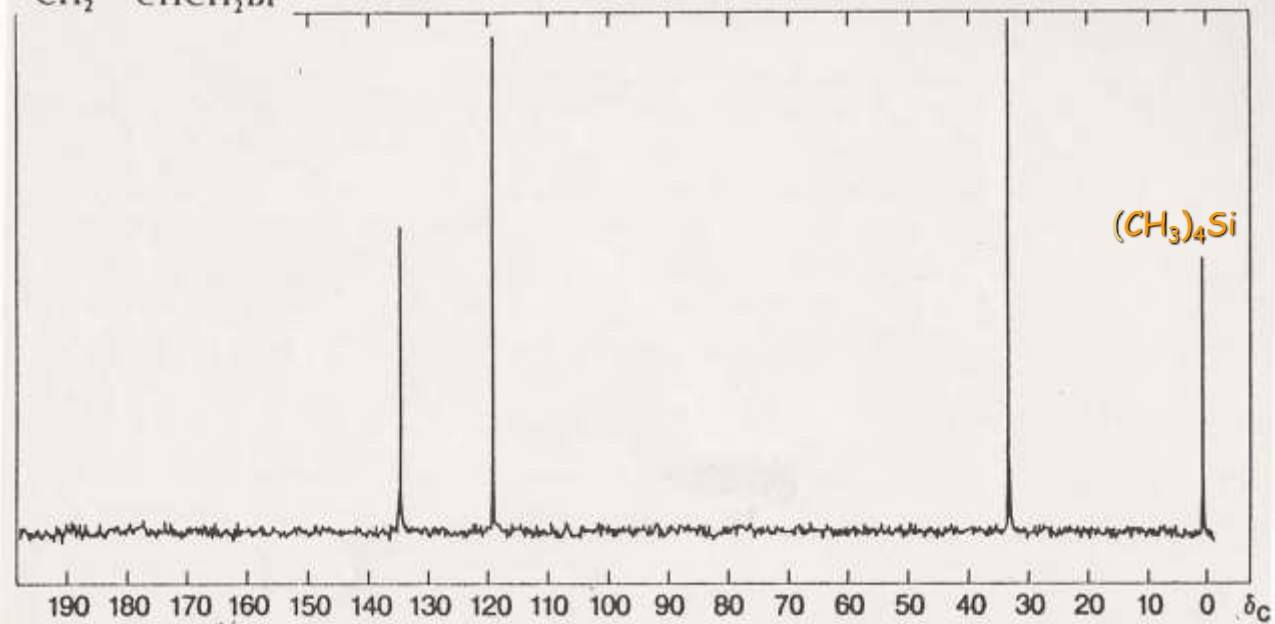
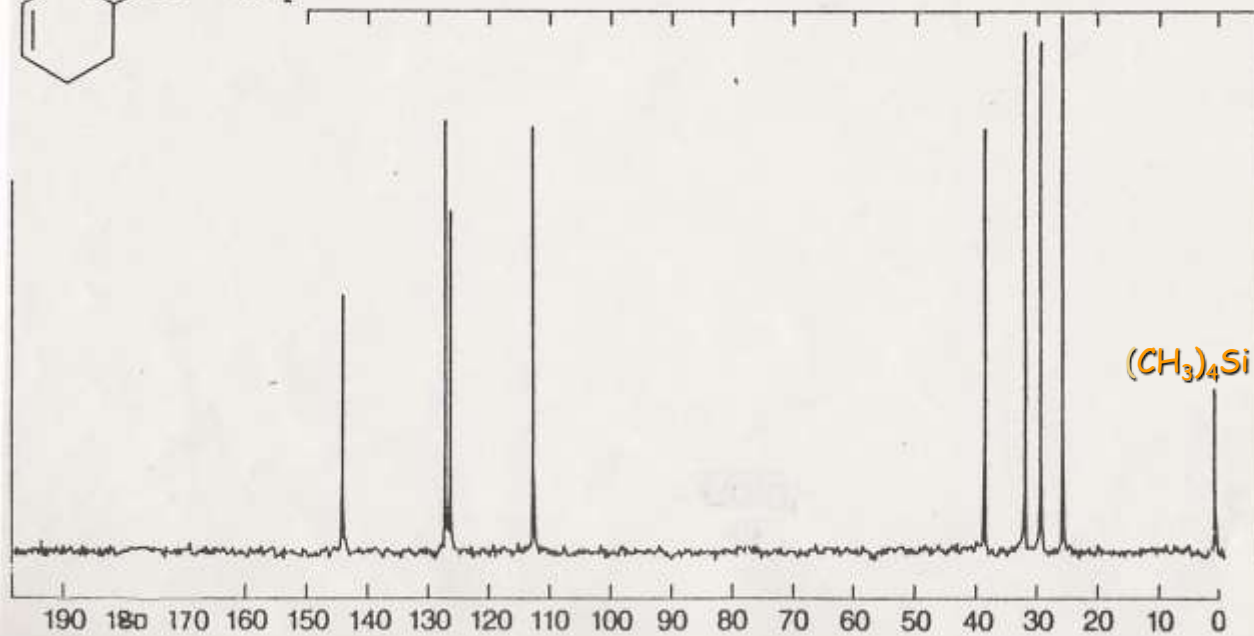
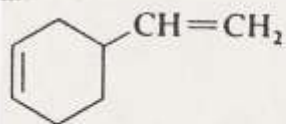
$\delta = 110 - 150$ ppm "leva strana" spektra

Alkeni

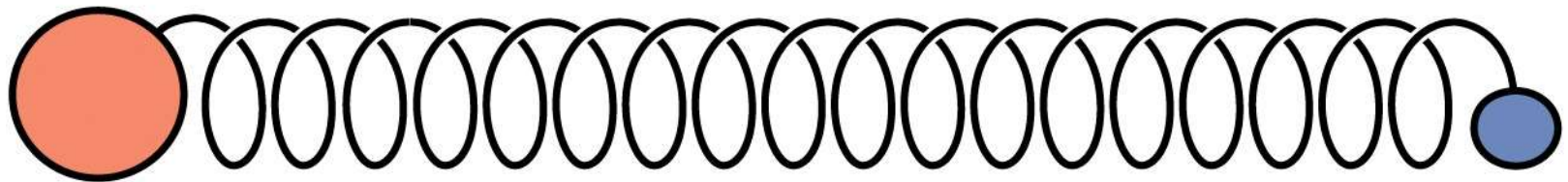


Alkani





Vibracije u molekulima: Infracrvena (IC) Spektroskopija



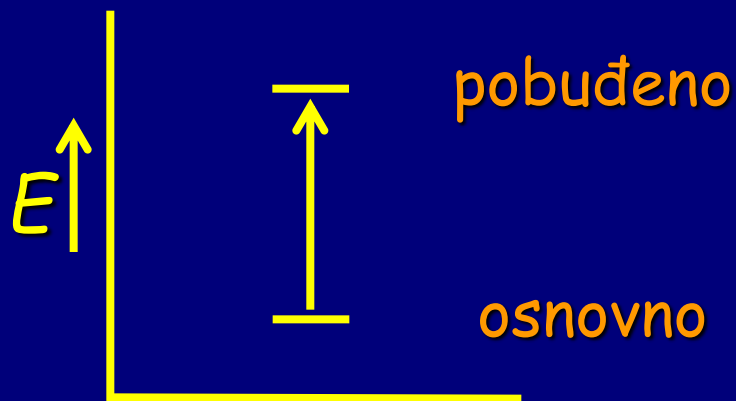
A



B

Frequency (ν)

Apsorpcija infracrvene svetlosti prouzrokuje molekulske vibracije

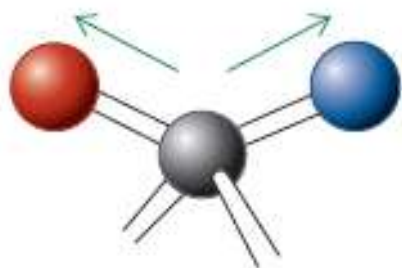


$$\Delta E = h\nu \sim 1-10 \text{ kcal mol}^{-1}$$

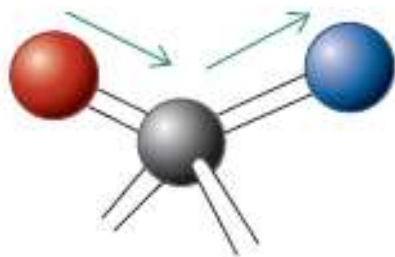
$$\lambda \text{ ili } 1/\lambda = \tilde{\nu} \text{ "talasni broj"}$$

$$\text{opseg: } 600-4000 \text{ cm}^{-1}$$

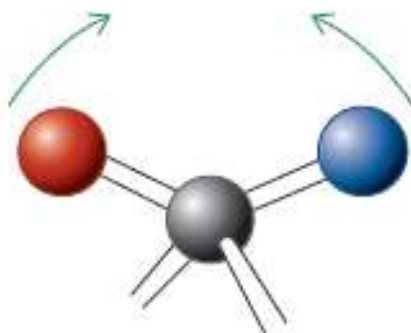
Različite vrste vibracija



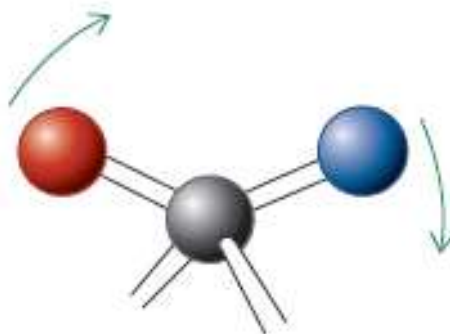
simetrične valencione vibracije (oba spoljašnja atoma vibriraju od i prema centru)



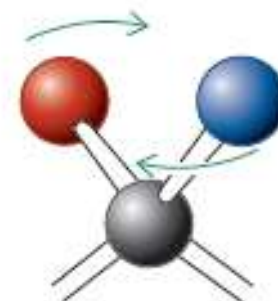
asimetrične valencione vibracije (jedan atom vibrira prema centru, a drugi od centra)



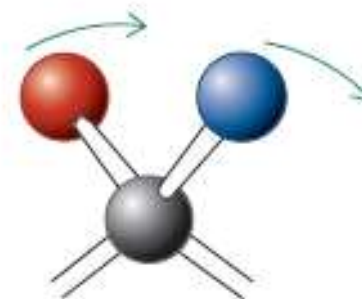
simetrične deformacione vibracije u ravni (seckanje)



asimetrične deformacione vibracije u ravni (klackanje)



simetrične deformacione vibracije van ravni (uvrtanje)



asimetrične deformacione vibracije van ravni (klanjanje)

IC Spektrometar

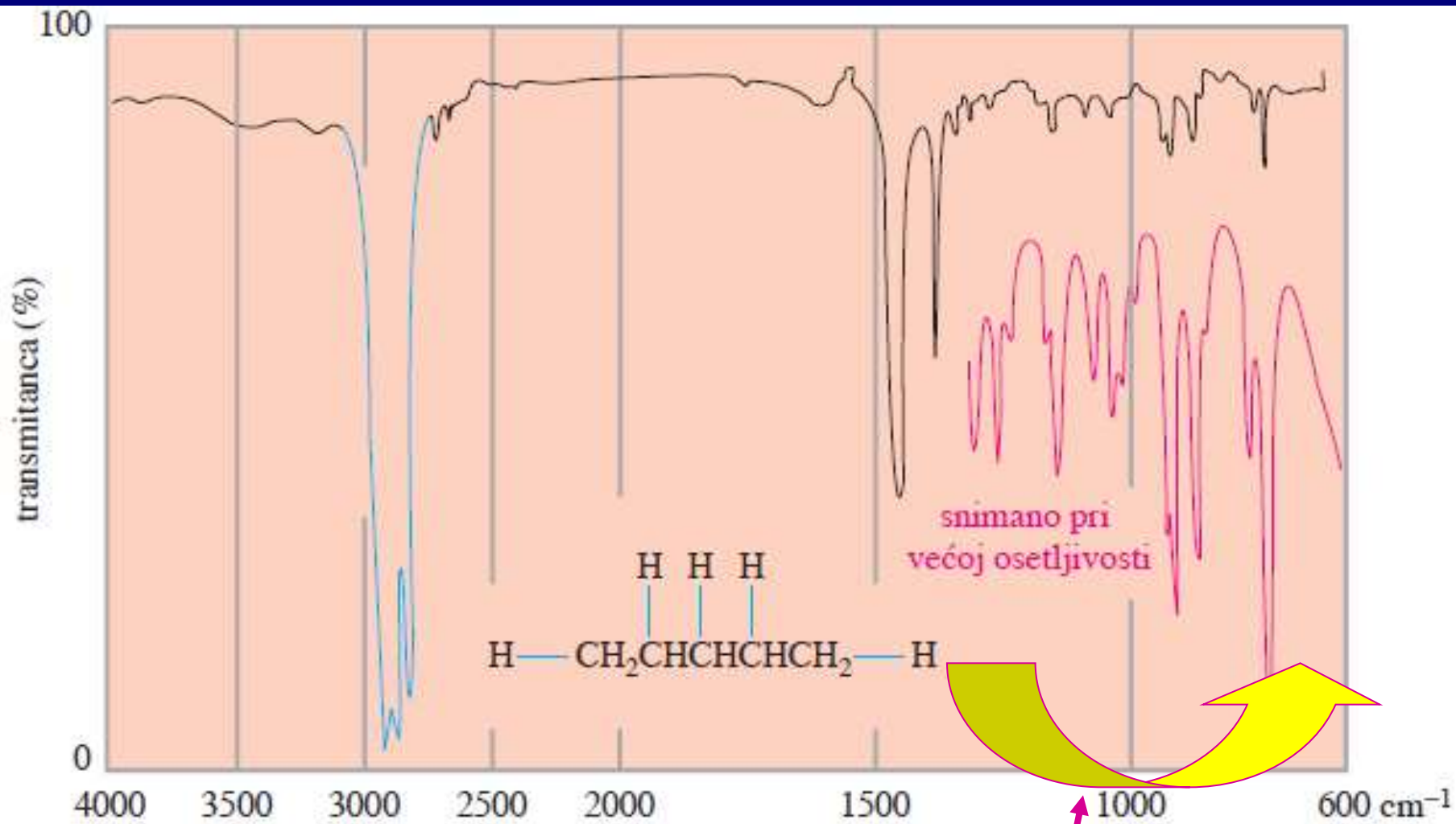


Funkcionalne grupe imaju karakteristične infracrvene apsorpcije

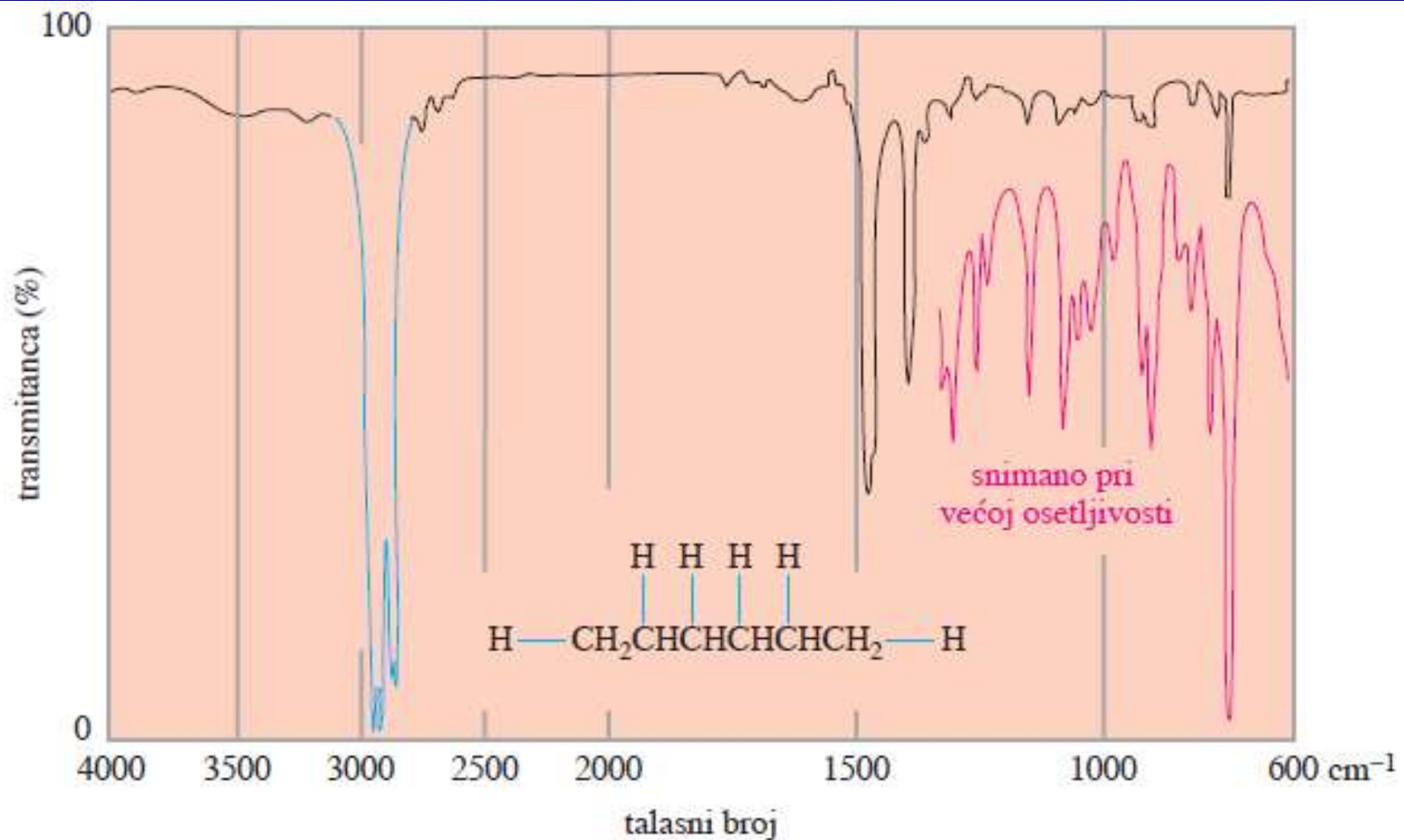
TABELA 11-4

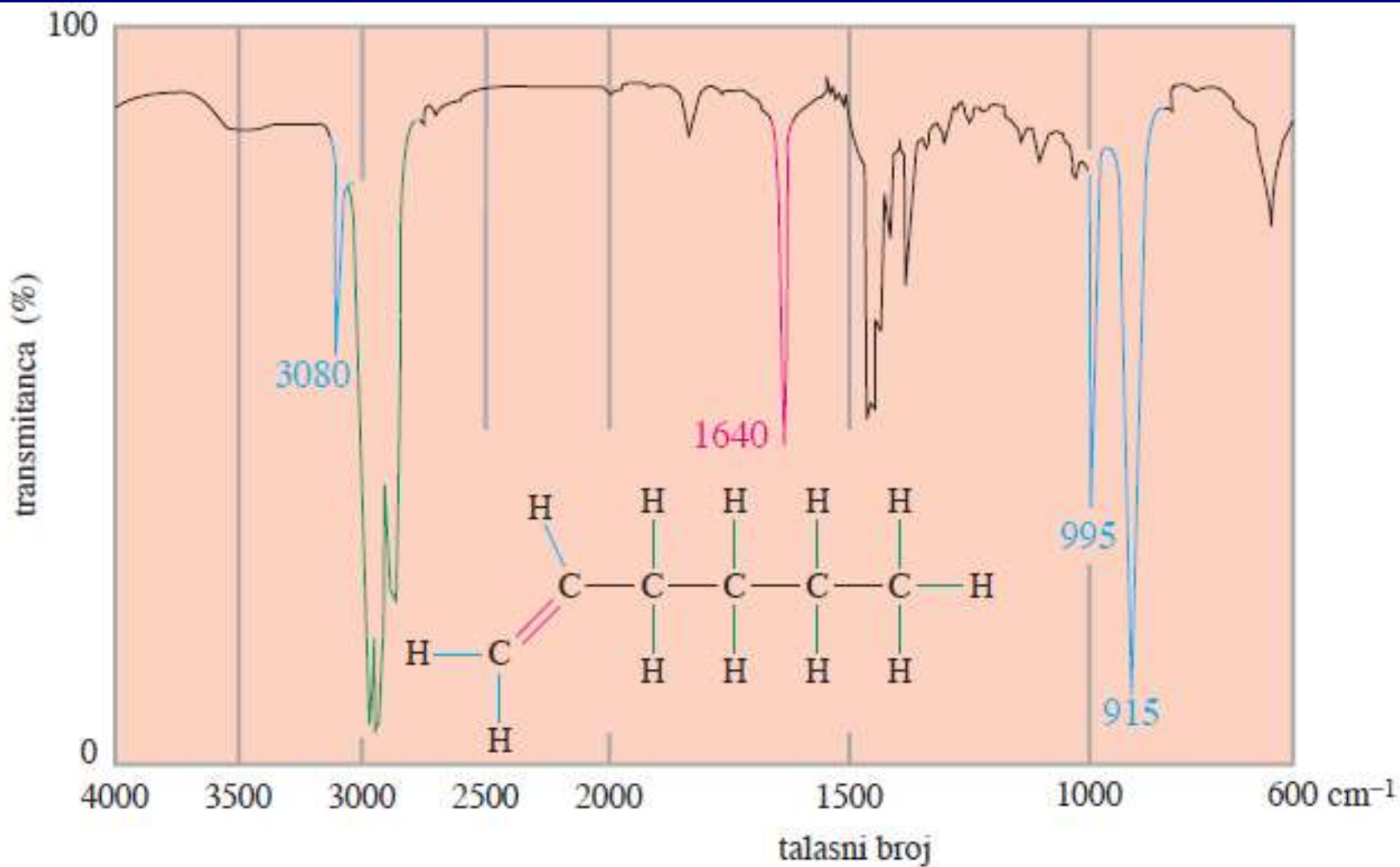
Karakteristične infracrvene oblasti valencionih vibracija organskih molekula

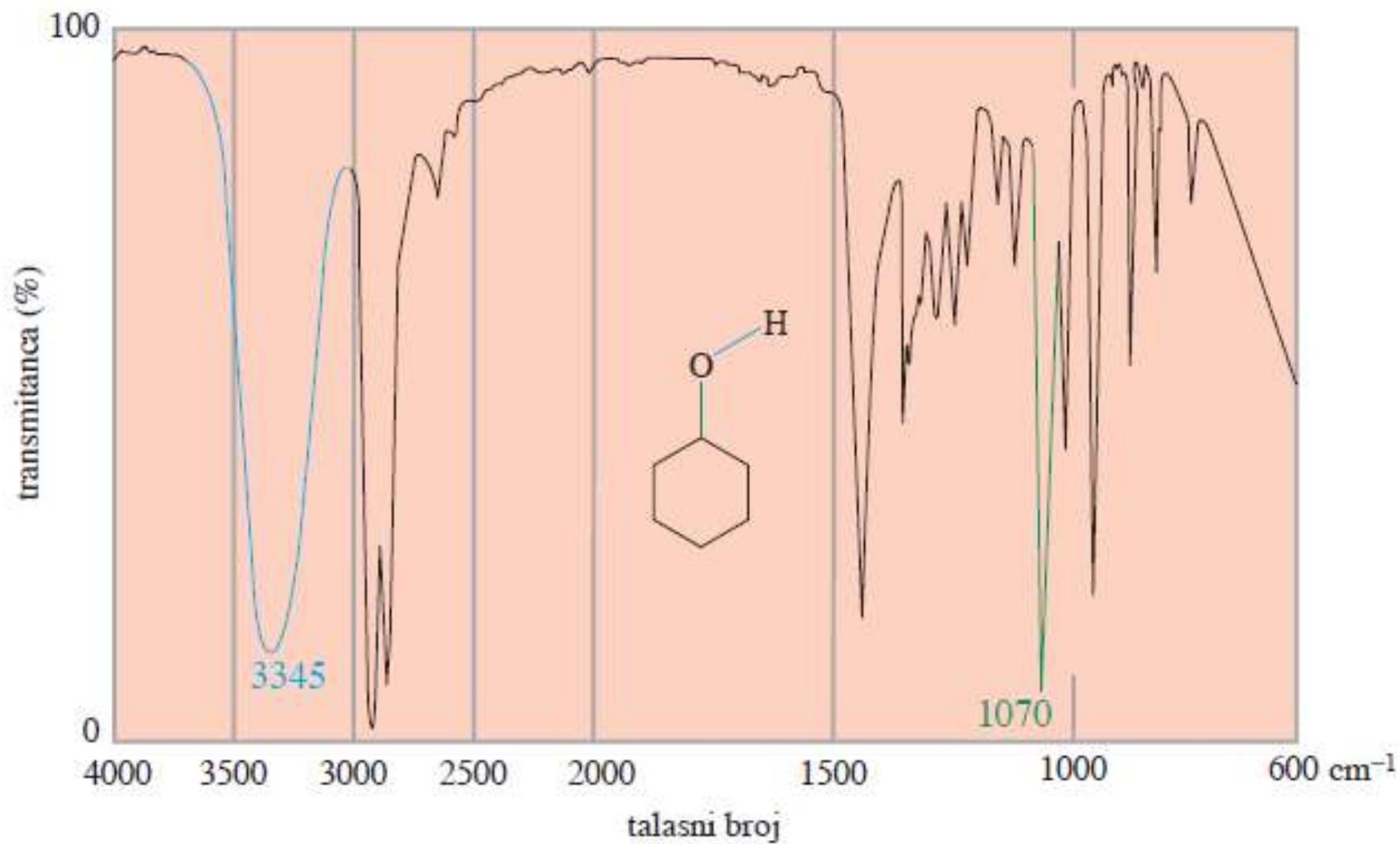
Veza ili funkcionalna grupa	$\tilde{\nu}$ (cm ⁻¹)	Veza ili funkcionalna grupa	$\tilde{\nu}$ (cm ⁻¹)
RO—H (alkoholi)	3200–3650	RC≡N (nitrili)	2220–2260
$\begin{array}{c} \text{O} \\ \\ \text{RCO—H} \end{array}$ (karboksilne kiseline)	2500–3300	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{RCH, RCR}' \end{array}$ (aldehidi, ketoni)	1690–1750
R ₂ N—H (amini)	3250–3500	$\begin{array}{c} \text{O} \\ \\ \text{RCOR}' \end{array}$ (estri)	1735–1750
RC≡C—H (alkini)	3260–3330	$\begin{array}{c} \text{O} \\ \\ \text{RCOH} \end{array}$ (karboksilne kiseline)	1710–1760
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$ (alkeni)	3050–3150	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$ (alkeni)	1620–1680
$\begin{array}{c} \\ \text{—C—H} \\ \end{array}$ (alkani)	2840–3000	$\begin{array}{c} \\ \text{RC—OR}' \\ \end{array}$ (alkoholi, etri)	1000–1260
RC≡CH (alkini)	2100–2260		



Oblast: otisak prsta

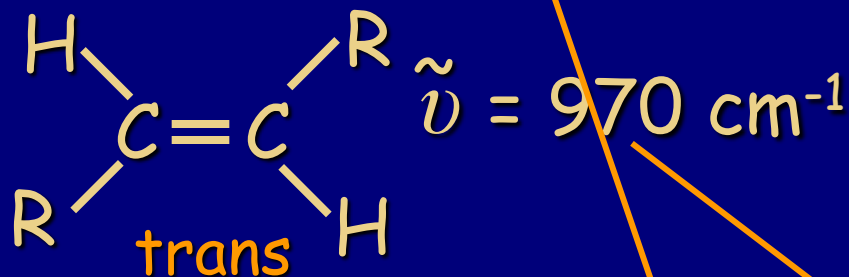




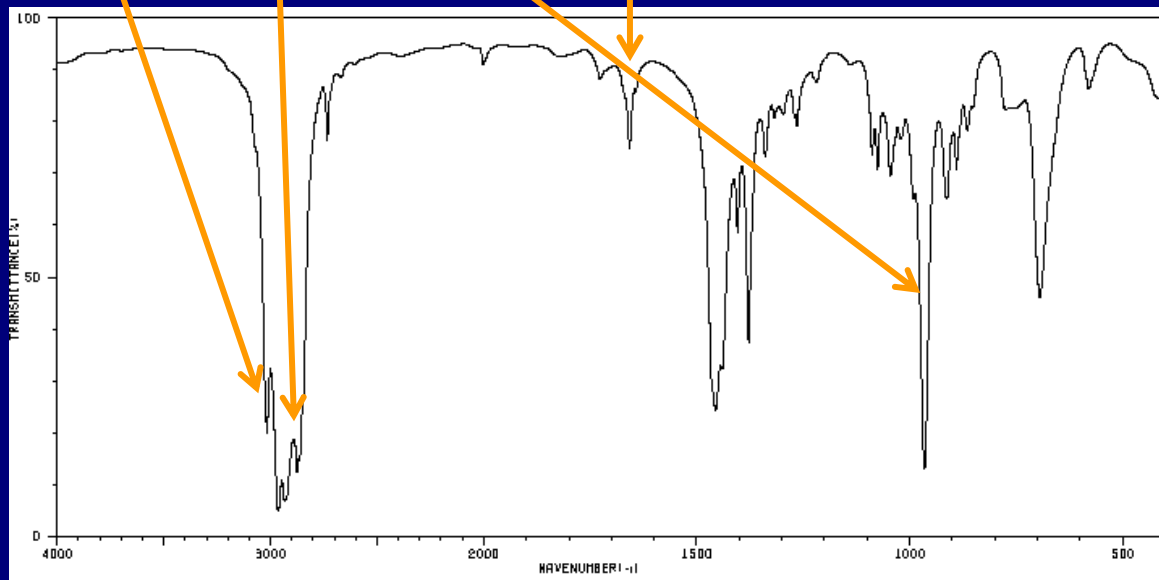
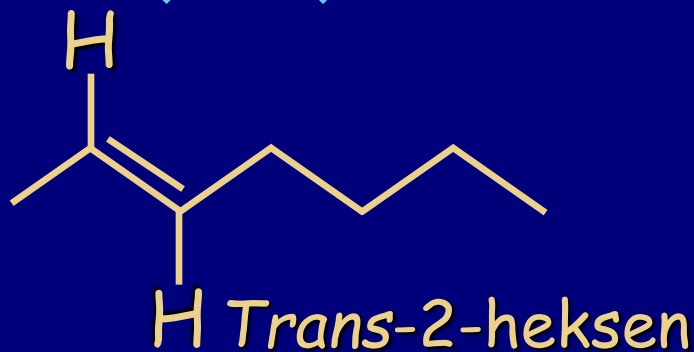
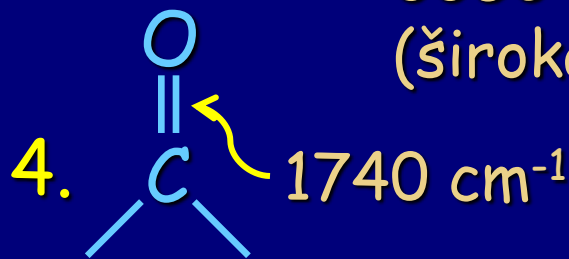


Korisno: 1. Alkyl $\tilde{\nu}_{C-H} = 2900\text{cm}^{-1}$

2. Alkeni $\tilde{\nu}_{Csp^2-H} = 3080\text{ cm}^{-1}$, $\tilde{\nu}_{C=C} = 1640\text{ cm}^{-1}$,



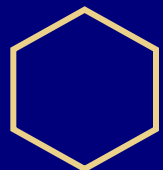
3. R-O-H 3350 cm^{-1}
(široka)



Stepen nezasićenja-pomoć pri određivanj strukture molekula

Molekulska formula nam govori koliko prstenova i/ili π veza je prisutno u molekulu. Polazi se od opšte formule zasićenih acikličnih alkana: C_nH_{2n+2} .






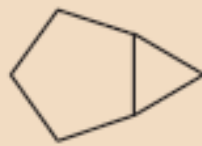


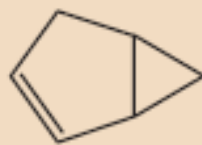
Primer:



Potrebno je odrediti odstupanje od molekulske formule C_nH_{2n+2} (po 2H). Svaki prsten ili dvostruka veza ima za 2H, trostruka veza za 4H manje od C_nH_{2n+2} .

TABELA 11-5

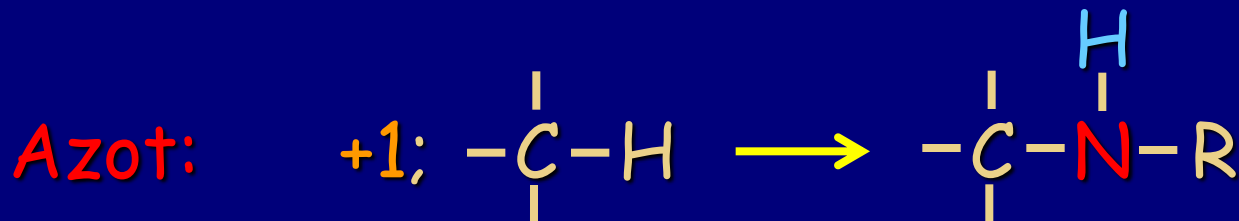
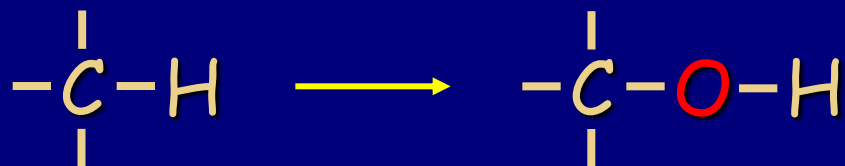
Stepen nezasićenja kao ključ rešenja strukture

Formula	Primeri struktura	Stepen nezasićenja
C_6H_{14}		0
C_6H_{12}	 ;  (jedna π -veza) (jedan prsten)	1
C_6H_{10}	 ;  ;  (dve π veze) (jedna π veza + jedan prsten) (dva prstena)	2
C_6H_8	 ;  ;  (tri π -veze) (dve π -veze + jedan prsten) (jedna π -veza + dva prstena)	3

Uticaj heteroatoma na bruto formulu C_nH_{2n+2}

Zavisno od valence elemenata:

S, O ne utiču (still $C_nH_{2n+2} + S_x$ or O_y)



Postupak:

1. Broj H atoma potrebnih za zasićenje:

$H_{zas} = 2n_C + 2 - n_X + n_N$ n_X broj atoma halogena; $n_N =$ "number of"

2. $H_{stvarno}$ -stvarni broj atoma vodonika u datoj molekulskoj formuli

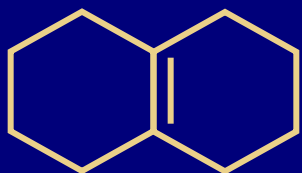
3. Stepen nezasićenja: $(H_{zas} - H_{stvarno})/2$

Primeri:



$$1. H_{zas} = (2 \times 10) + 2 = 22$$

$$2. \text{Stepen nezasićenja: } (22 - 16) / 2 = 3$$



ili

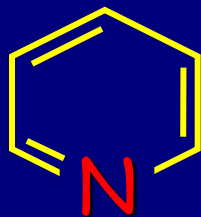


itd.



$$1. H_{zas} = 10 + 2 + 1 = 13$$

$$2. (13 - 5) / 2 = 4 \text{ stepena nezasićenja:}$$



ili



ili?

Piridin

Problem

C_3HN : koliki je stepen nezasićenja?

$$H_{zas} = 2n_C + 2 - n_X + n_N$$

Stepen nezasićenje: $(H_{zas} - H_{stvarno})/2$

- A. 2
- B. 3
- C. 4

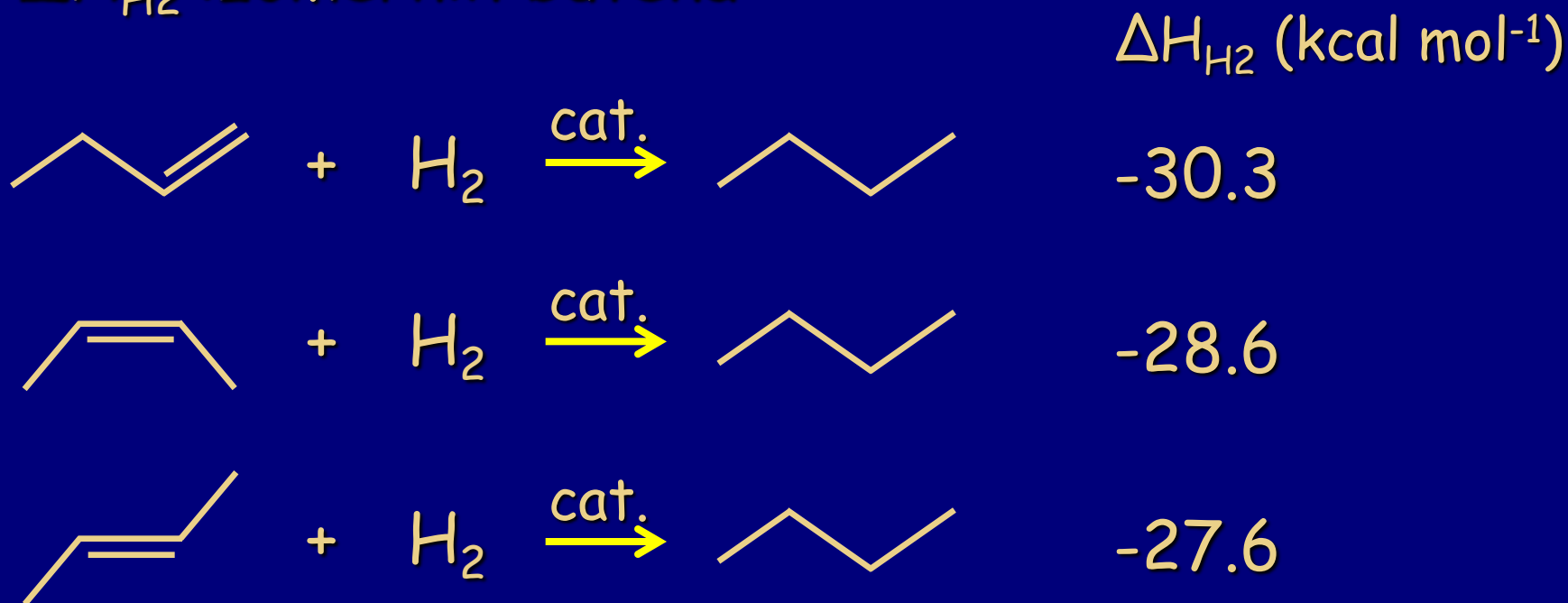
Vežba 11-10

Izračunajte stepen nezasićenja naznačen svakom od navedenih molekulskih formula.

(a) C_5H_{10} ; (b) $C_9H_{12}O$; (c) C_8H_7ClO ; (d) $C_8H_{15}N$; (e) $C_4H_8Br_2$.

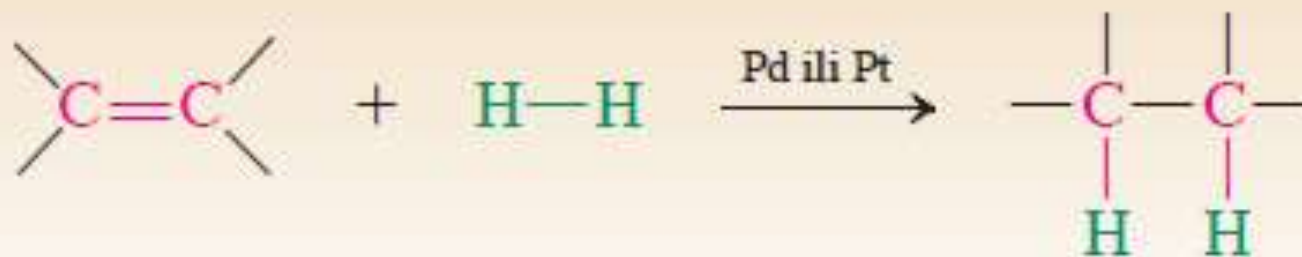
Relativna stabilnost alkena

Merenje toplote hidrogenizacije za izomere-
 ΔH_{H_2} izomernih butena:



Stabilnost: unutrašnji > terminalni , trans > cis

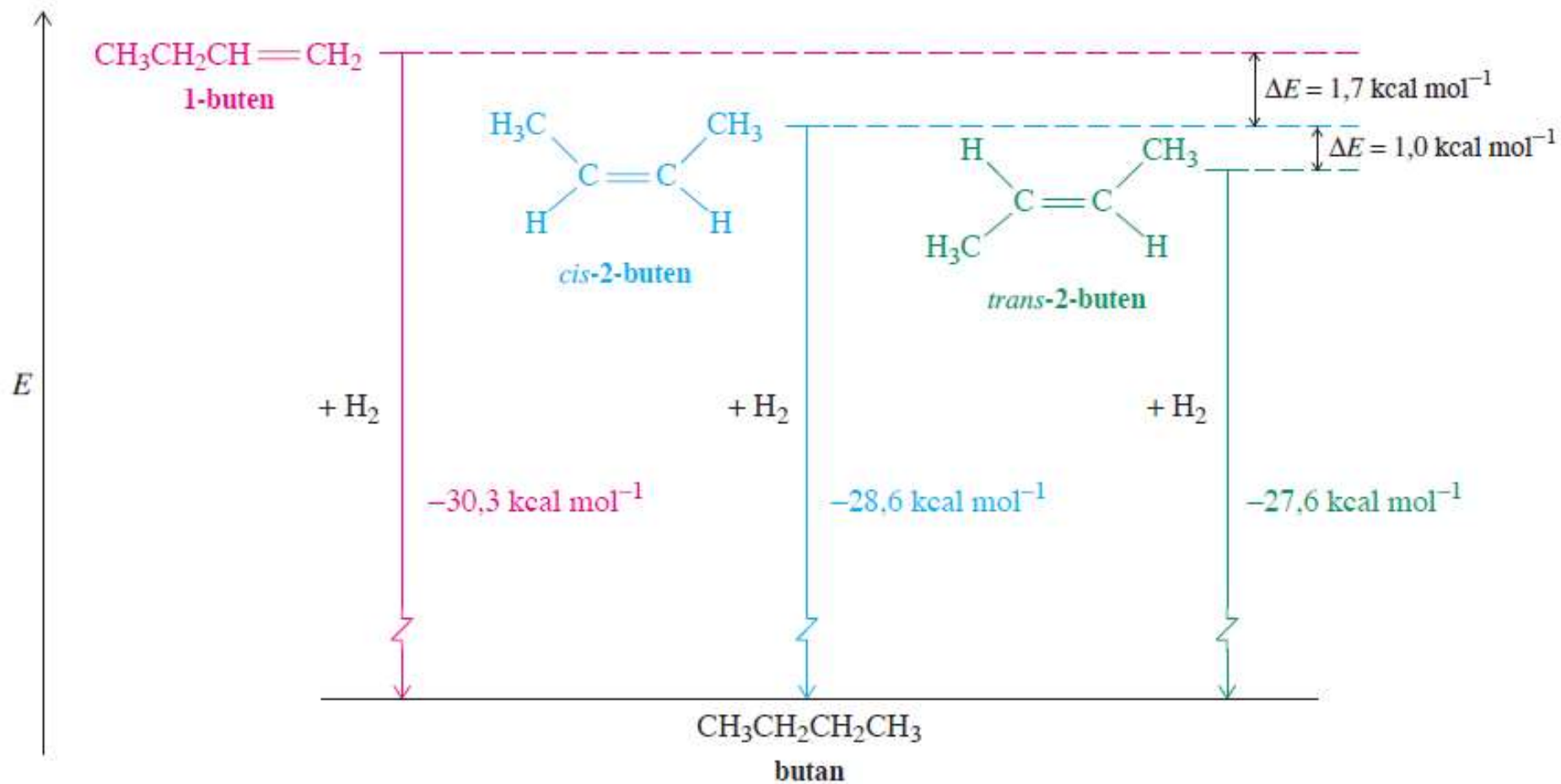
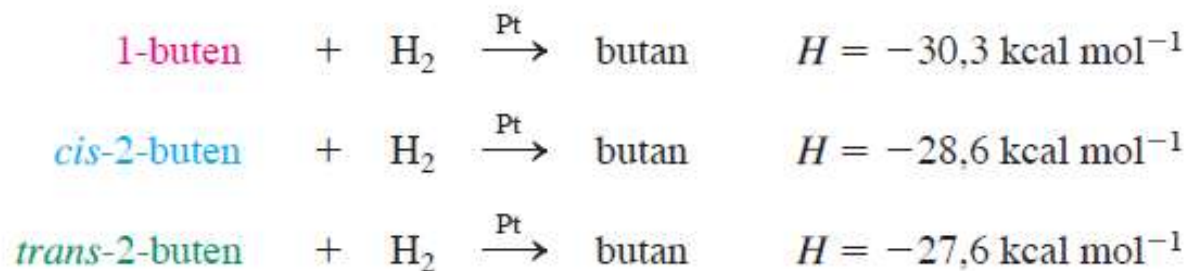
Hidrogenizacija alkena



$H \sim -30 \text{ kcal mol}^{-1}$

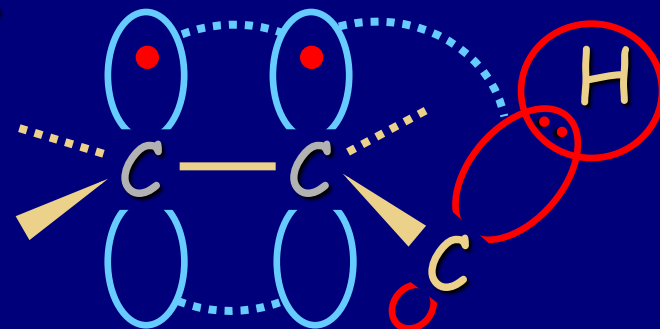
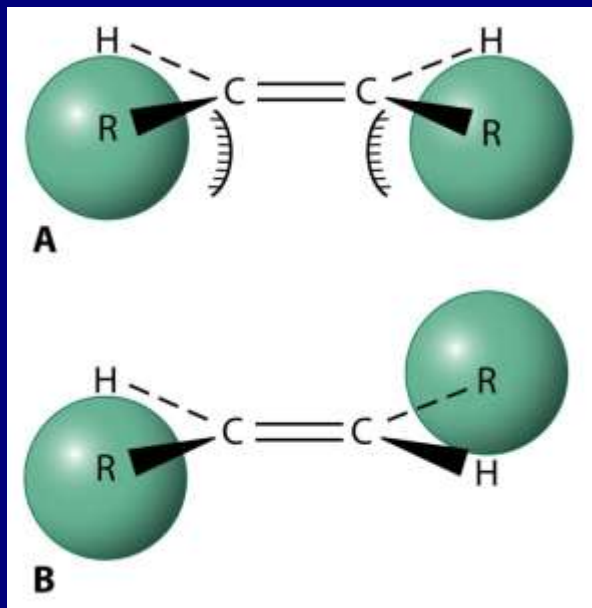


Molekuli masti u buteru i čvrstom margarinu imaju visok stepen zasićenja, dok molekuli u biljnim uljima imaju veliki udeo *cis*-alkena. Delimičnom hidrogenizacijom biljnih ulja dobija se mekani margarin.



Razlog? 1. Hiperkonjugacija:

2. Sterno nagomilavanje (napon)



Cis je manje stabilan od trans zbog Sternog nagomilavanja

Relativna stabilnost alkena:

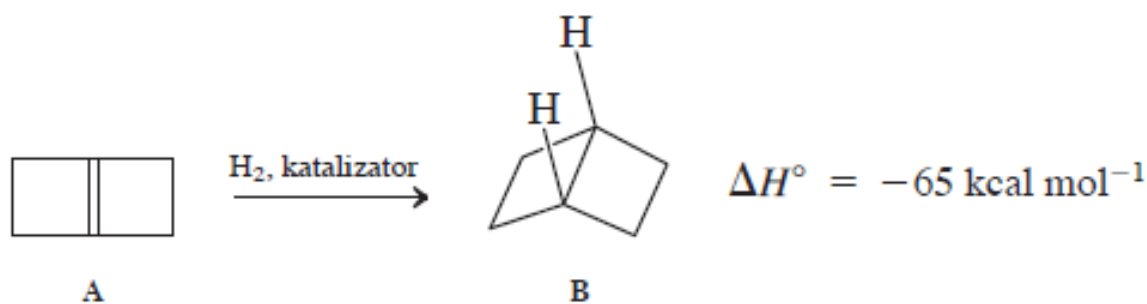


Vežba 11-12

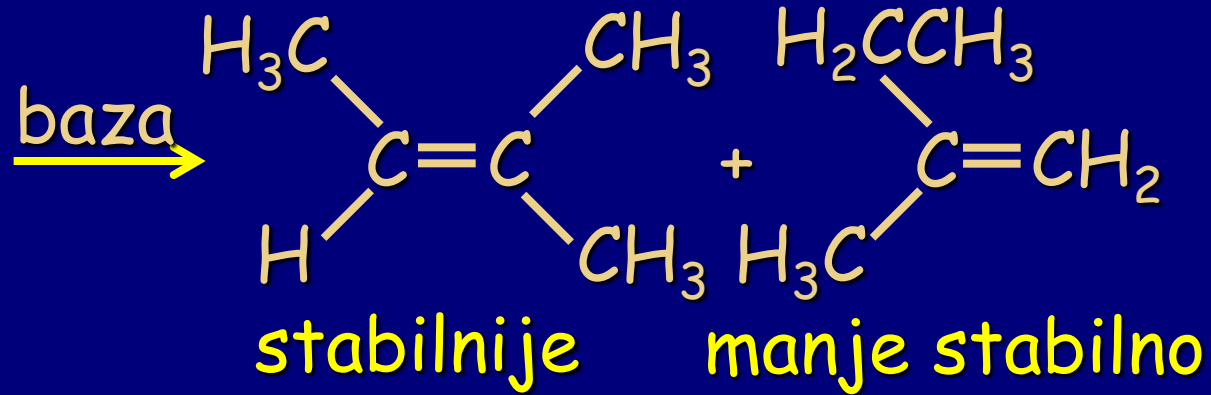
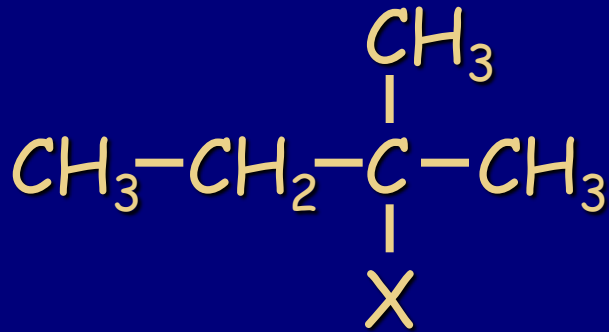
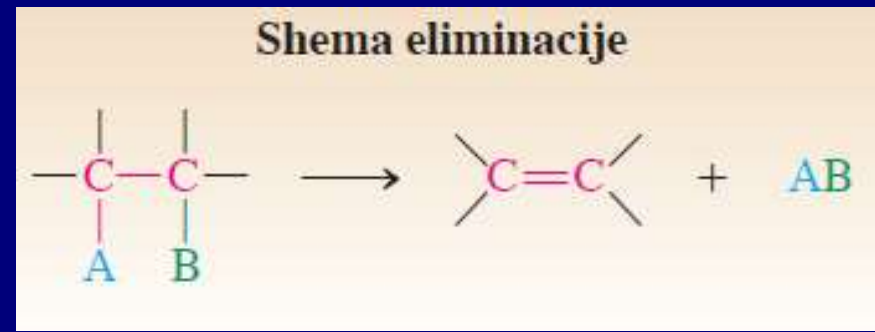
Poređajte dvostruke veze po redosledu stabilnosti prema hidrogenizaciji (poređajte ΔH° hidrogenizacije): 2,3-dimetil-2-buten, *cis*-3-heksen, *trans*-4-okten i 1-heksen.

Vežba 11-13

Ustanovljeno je da se alken A hidrogenizuje u B uz oslobađanje energije od 65 kcal mol^{-1} , više od dvostruke vrednosti za hidrogenizaciju prikazanu na slici 11-18. Objasnite.

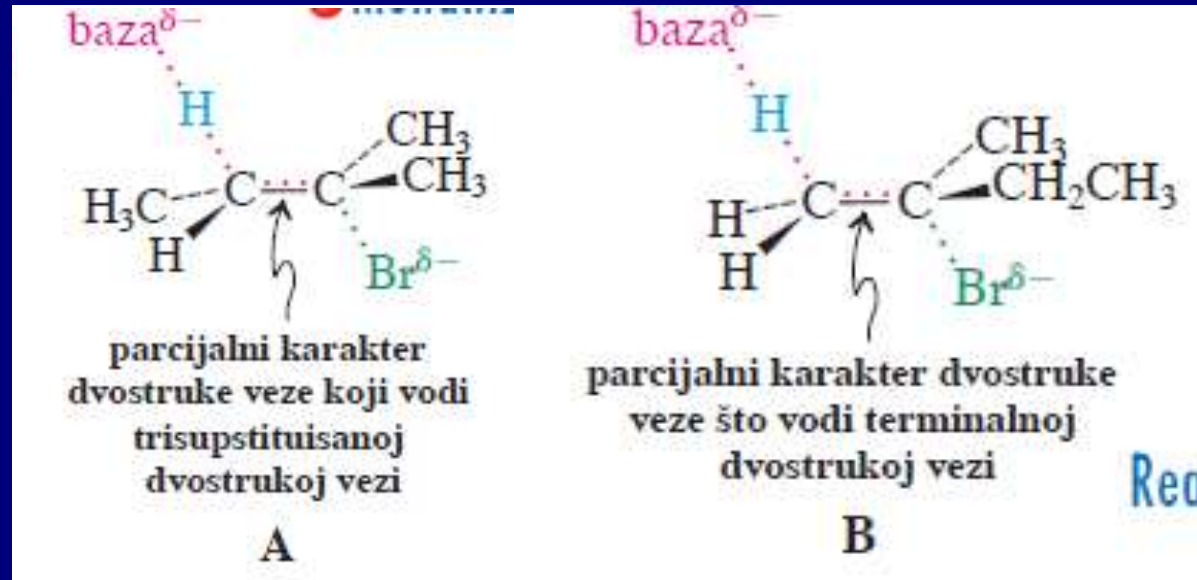


Dobijanje alkena eliminacija

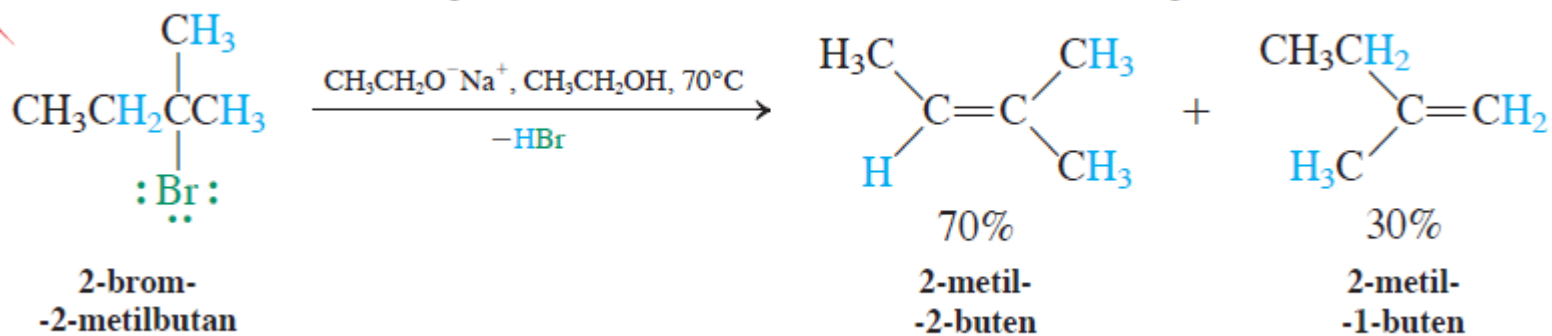


Saytzev-ljevo pravilo

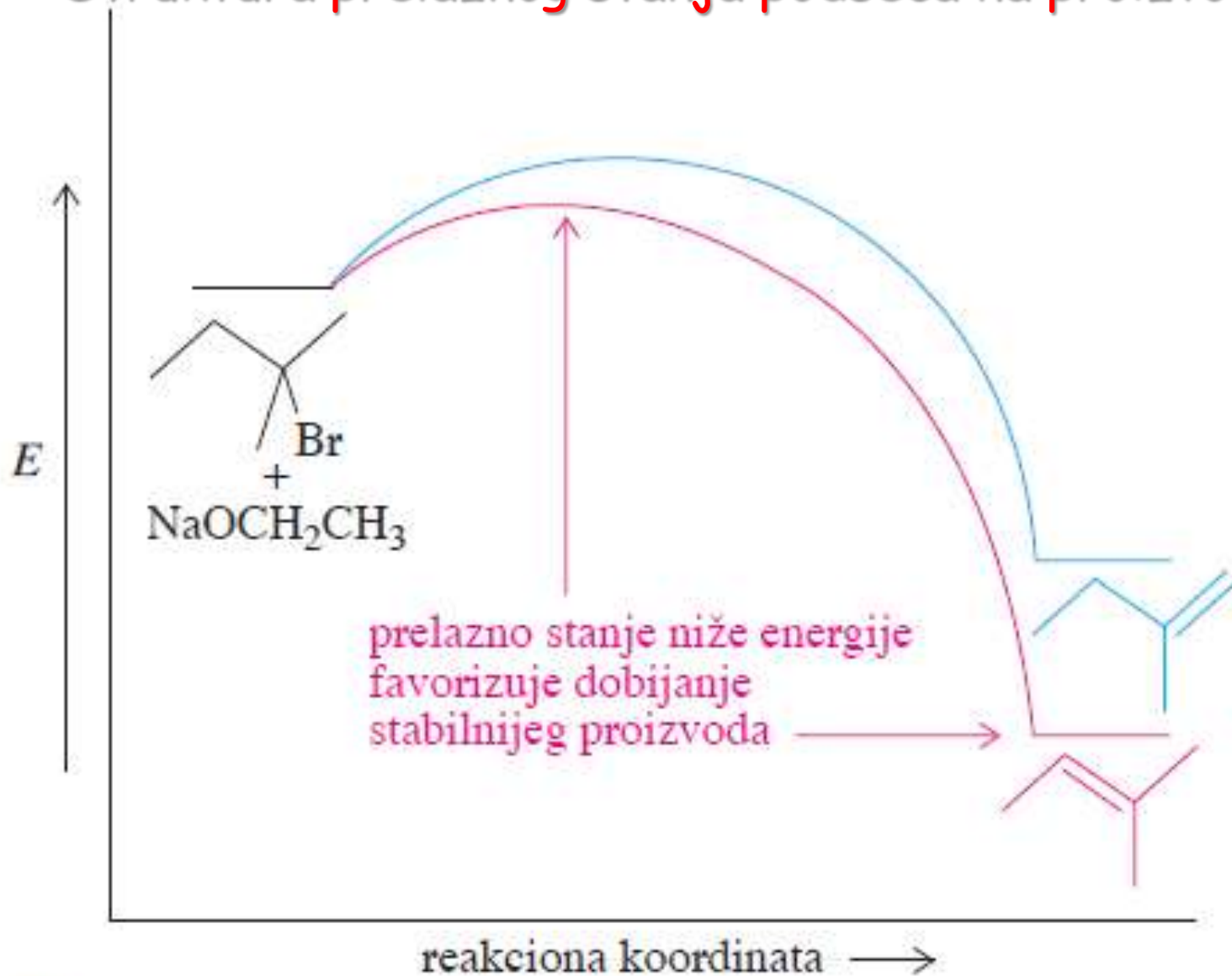
Nastanak više supstituisanog alkena.



E2-reakcija 2-brom-2-metilbutana sa etoksidnim jonom

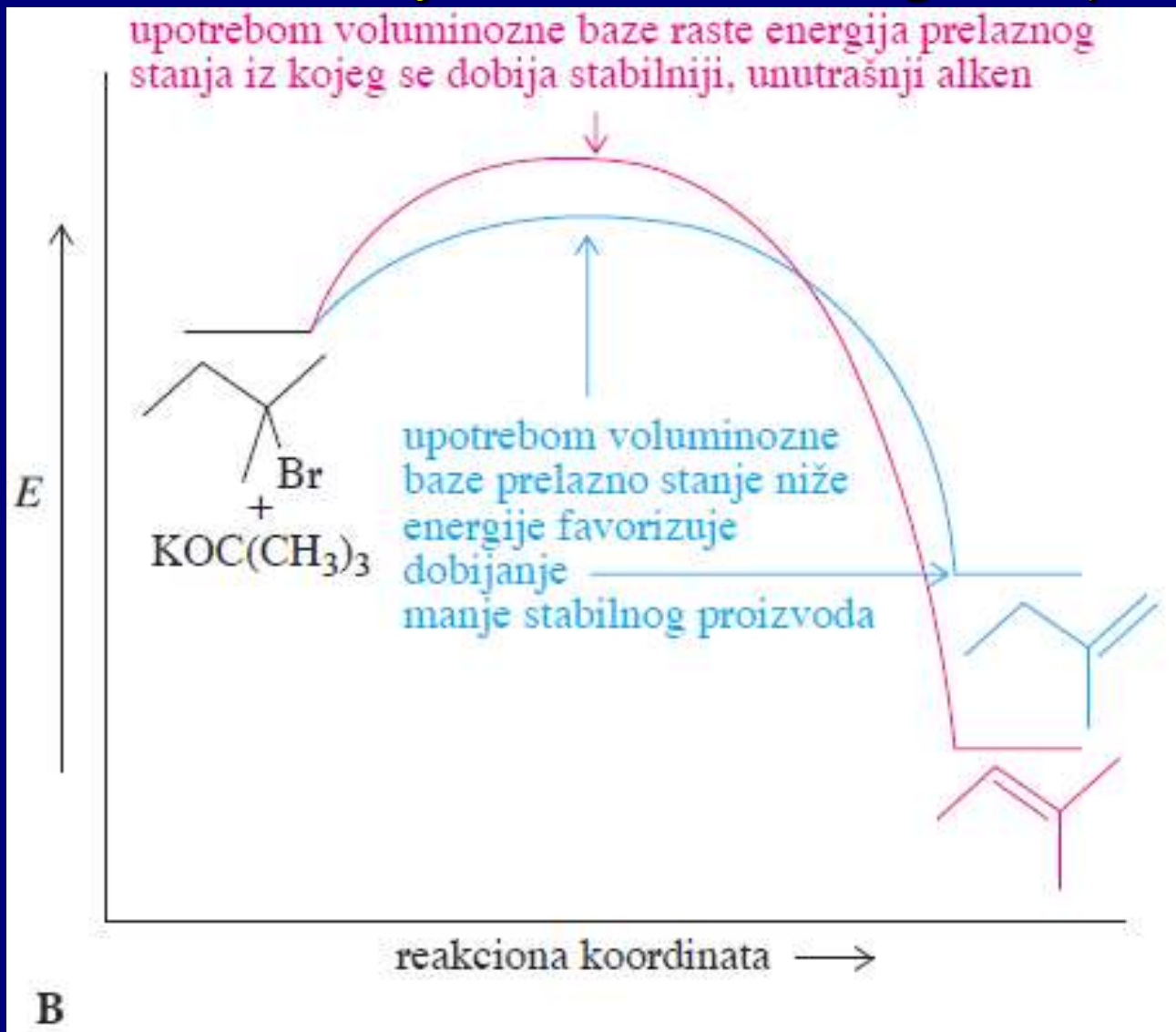


Struktura prelaznog stanja podseća na proizvode



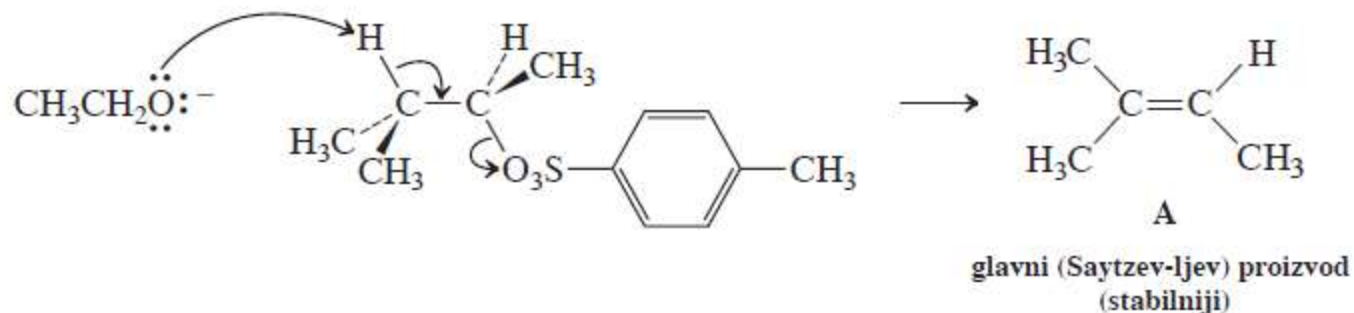
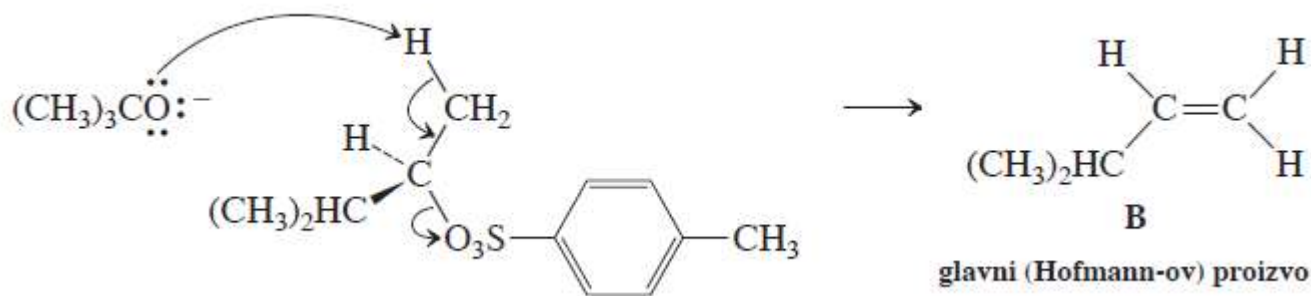
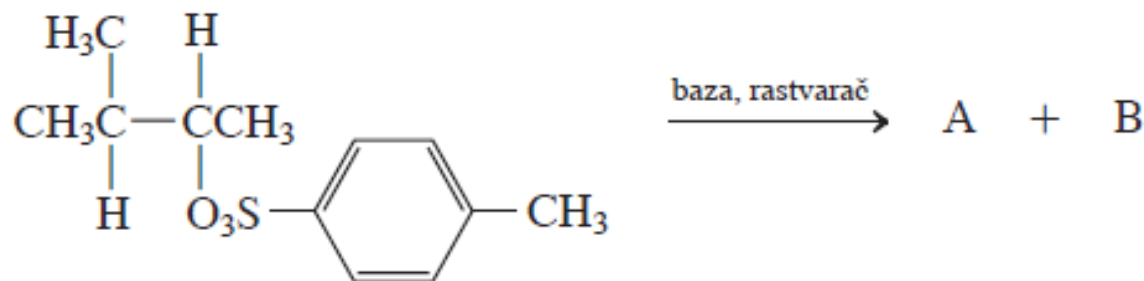
Hofmann-ovo pravilo

Voliminozne baze: manje stabilan alken glavni proizvod

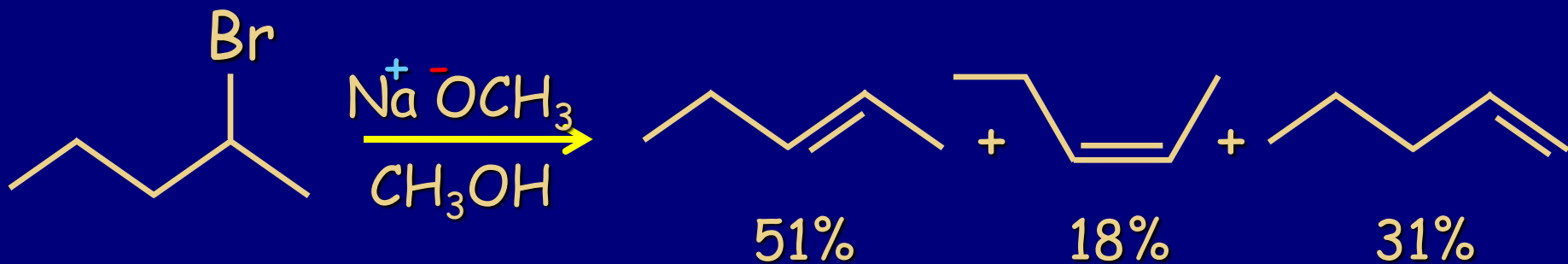


Vežba 11-14

Kada se sledeća reakcija vrši pomoću *tert*-butoksida u 2-metil-2-propanolu (*tert*-butil-alkoholu) dobijaju se dva proizvoda, A i B, u odnosu od 23:77. Kada se vrši pomoću etoksida u etanolu, odnos se menja u 82:18. Šta su A i B, i kako objašnjavate razliku u odnosima proizvoda u ova dva eksperimenta?



U E2 reakcijama trans-proizvodi su više favorizovani u odnosu na cis-proizvode

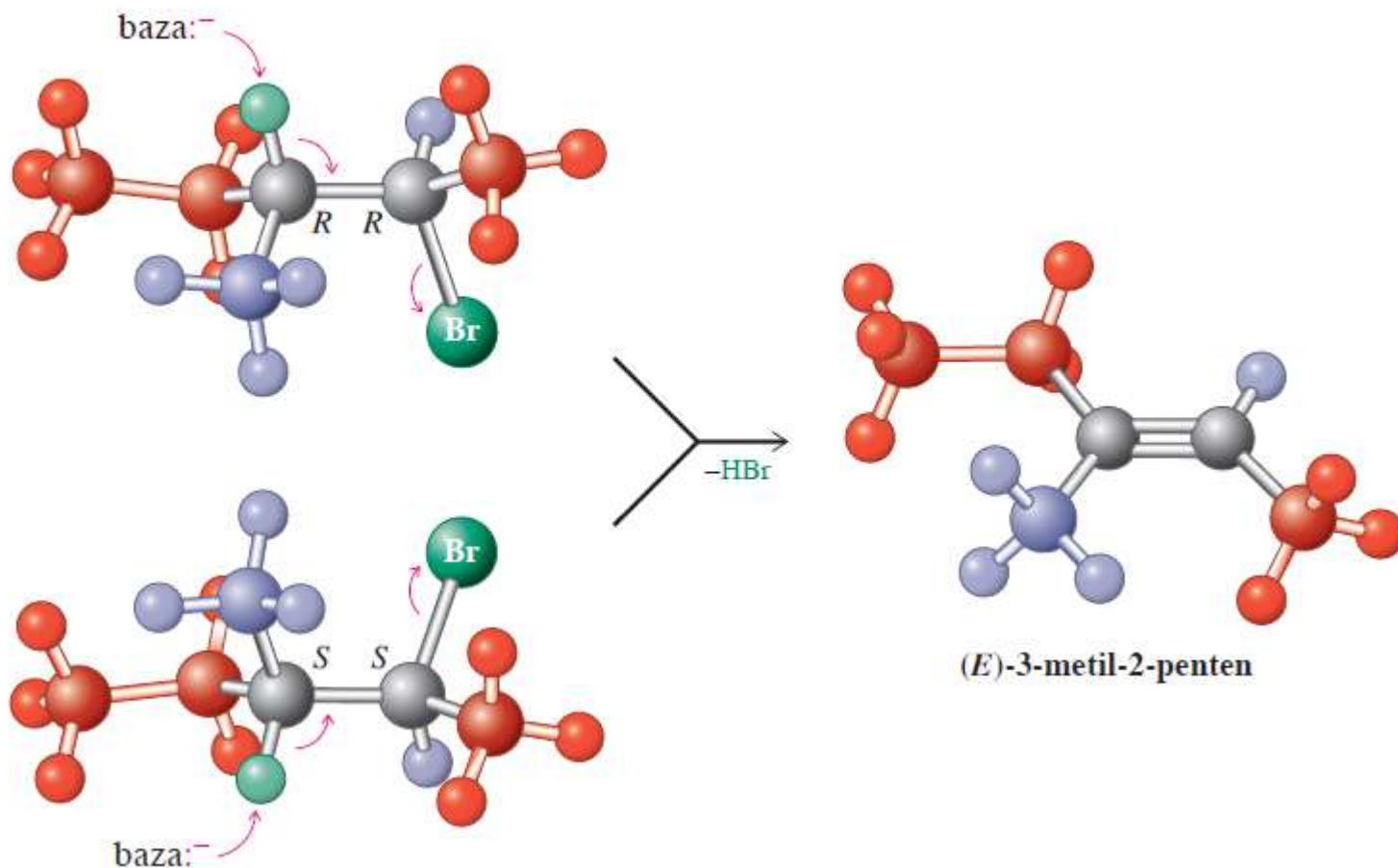


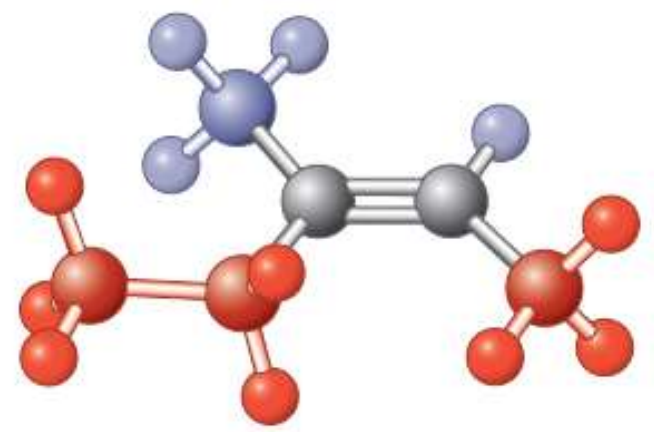
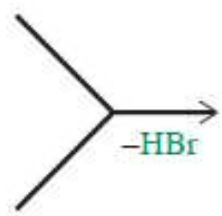
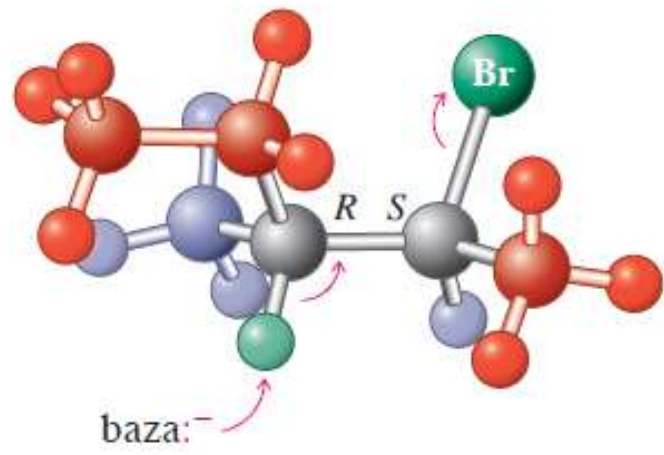
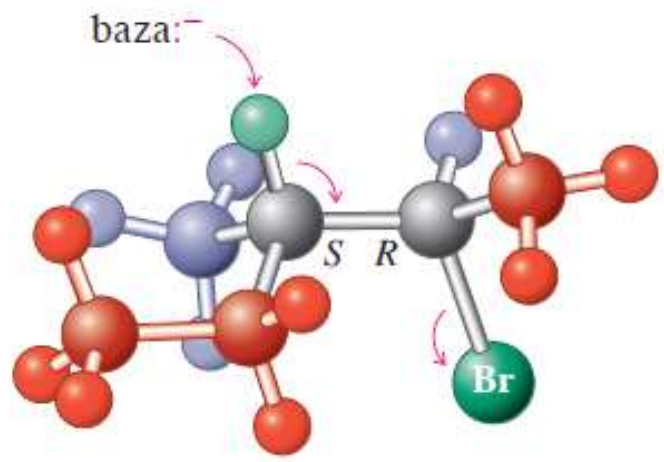
Trans predominira (ne potpuno)

Neki E2 procesi su stereospecifični

Proton koji se eliminiše i odlazeća grupa u anti-položaju

Stereospecifičnost u E2-reakcijama 2-brom-3-metilpentana

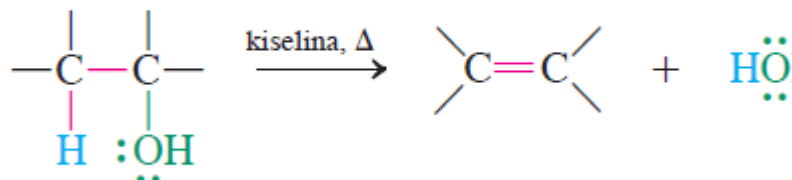




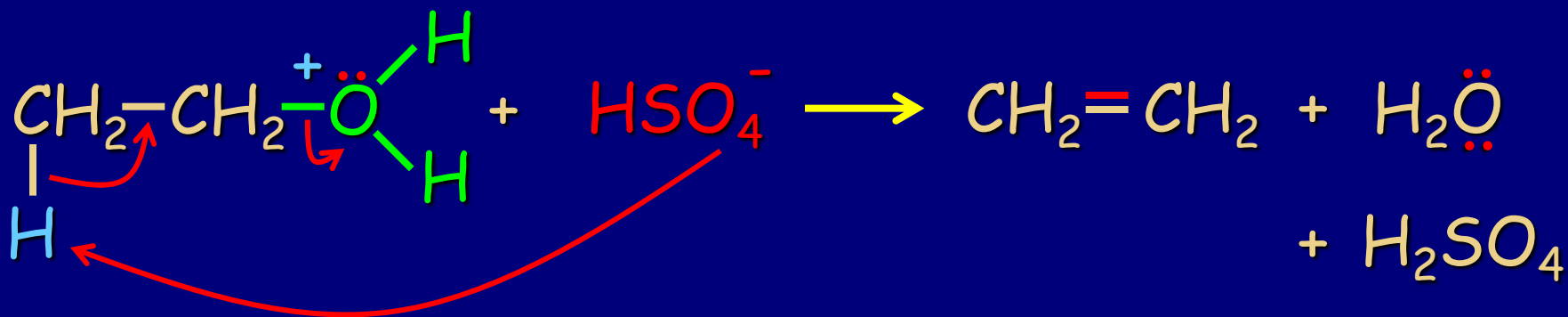
(Z)-3-metil-2-penten

Dobijanje alkena dehidratacijom alkohola

Dehidratacija alkohola katalizovana kiselinom

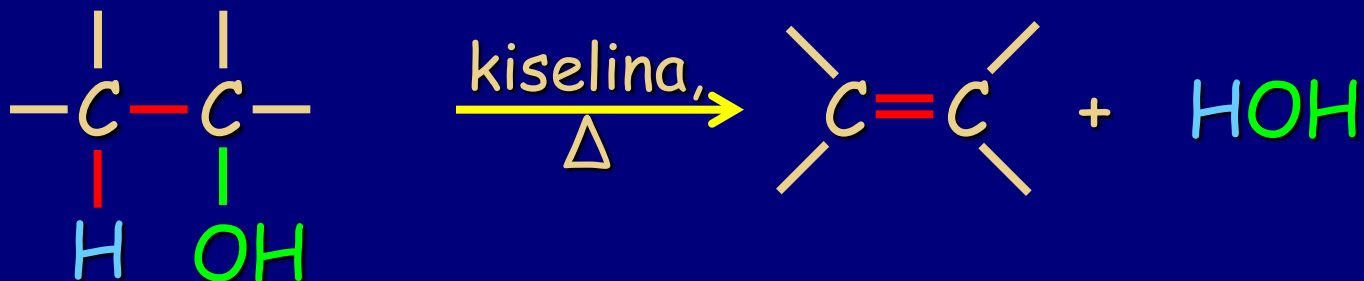


$R_{\text{prim}}-\text{OH} + \text{H}_2\text{SO}_4 \text{ conc.}, E_2, \text{ uz zagrevanje:}$



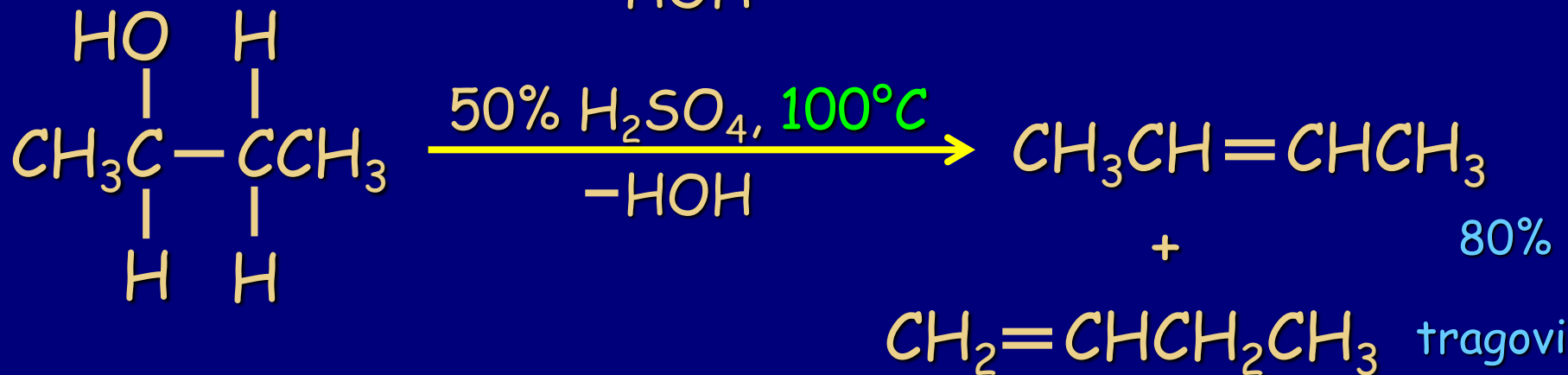
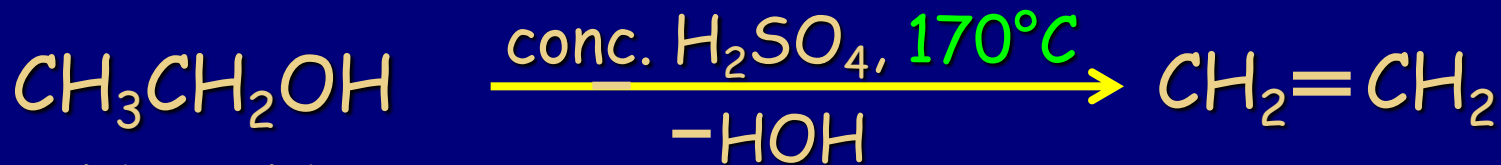
$R_{\text{sec}}, R_{\text{tert}}-\text{OH} : E_1 + \text{premeštanja}$

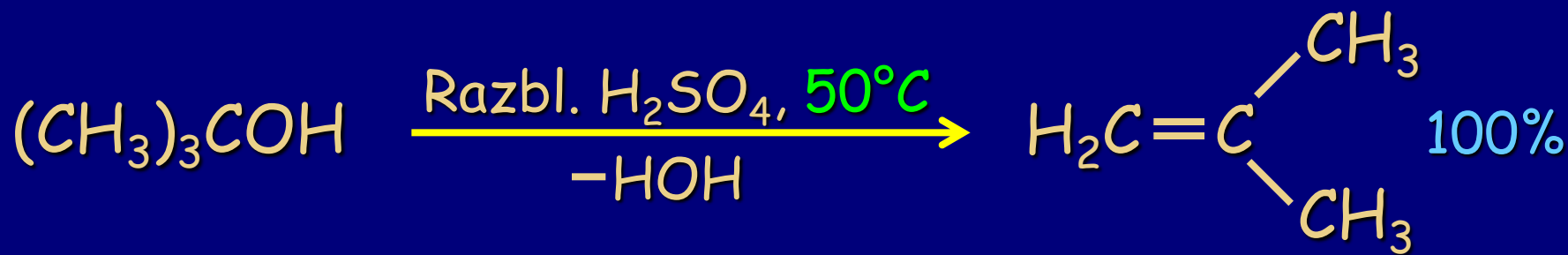
Kiselo-katalizovana dehidratacija alkohola



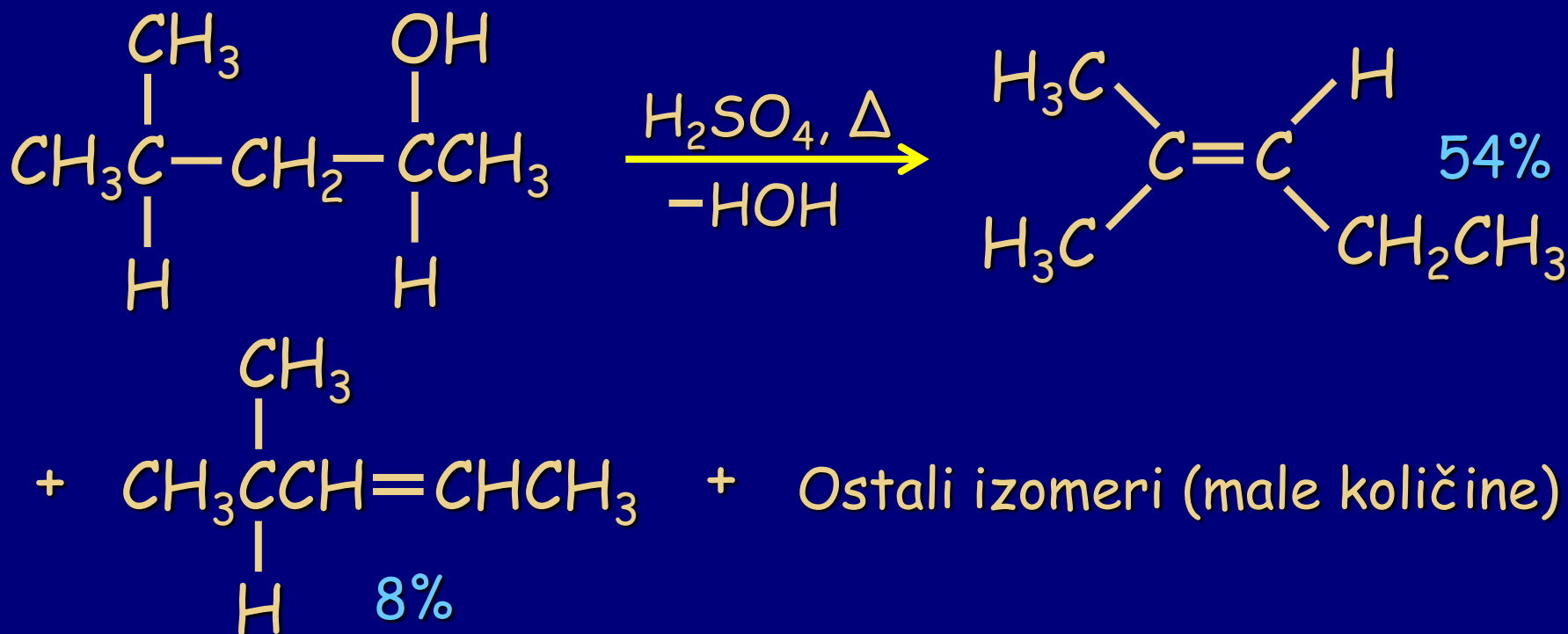
Relativna reaktivnost alkohola (ROH) u reakcijama dehidratacije

R = primarni < sekundarni < tercijsarni





Dehidratacija uz premeštanje

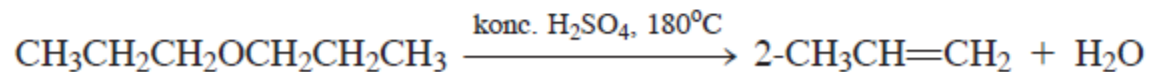


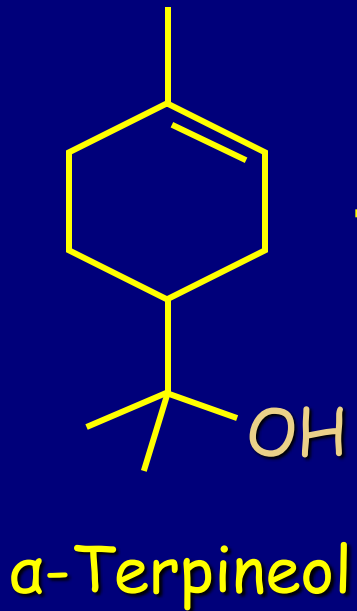
Vežba 11-15

Koji diastereomer 2-brom-3-deuterobutana daje (*E*)-2-deutero-2-buten, a koji diastereomer daje (*Z*)-izomer?

Vežba 11-17

- (a) Predložite mehanizam nastajanja propena tretiranjem 1-propanola vrućom konc. H_2SO_4 .
(b) Propen nastaje i tretiranjem propoksipropana (dipropil-etra) pod istim uslovima (dole).
Objasnite.

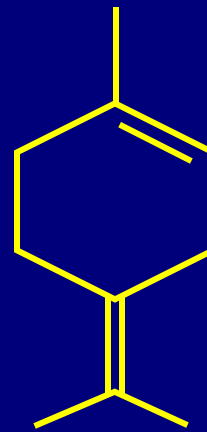




33% H_2SO_4 , 1 h, 100°C

$-H_2O$

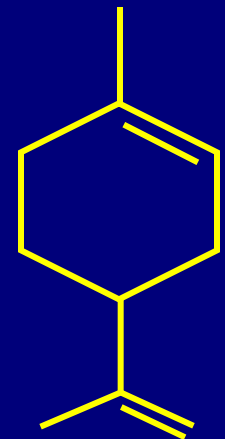
Kiselo-katalizovanom
dehidratacijom se
dobija smesa proizvoda



15%

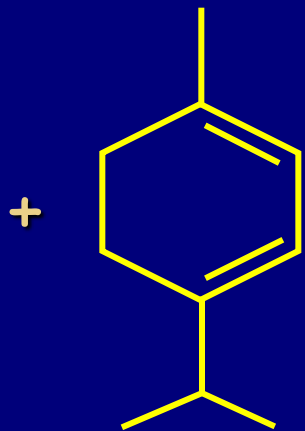
Terpinolen

+



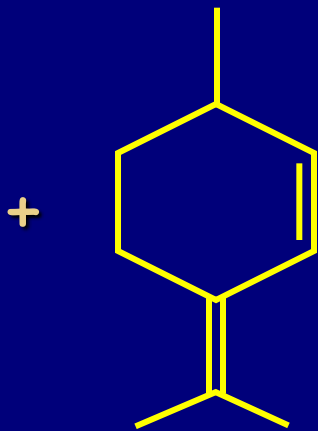
9%

Limonen



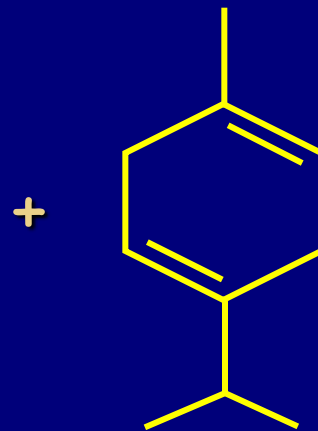
28.5%

α -Terpinen



18.5%

Izoterpinolen



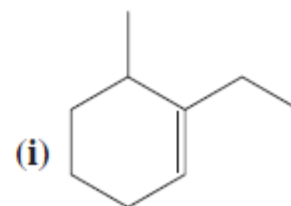
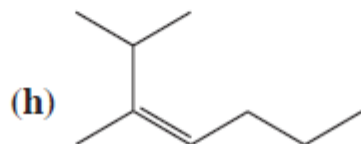
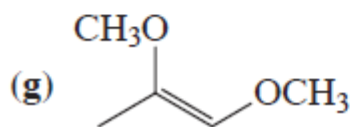
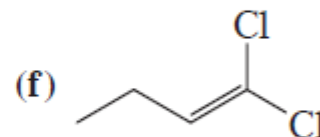
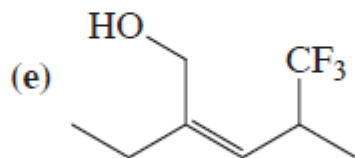
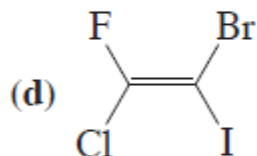
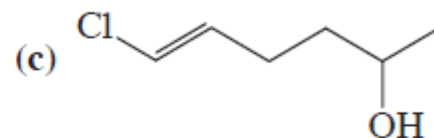
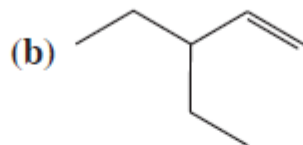
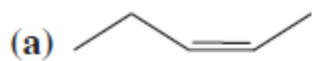
15%

γ -Terpinen

Terpen: mirišljavi
sapun



21. Imenujte sledeće molekule prema IUPAC-ovom sistemu nomenklature.



32. Za svaku od datih struktura odredite molekulsku formulu. Za svaku strukturu na osnovu molekulske formule izračunajte stepen nezasićenja i utvrdite da li se vaš račun podudara sa datim strukturama.

