PREHRAMBENO-BIOTEHNOLOŠKI FAKULTET

Laboratorij za organsku kemiju

ZBIRKA ZADATAKA IZ ORGANSKE KEMIJE

INTERNA SKRIPTA

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Zagreb, 2018.

Recenzenti

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Ova interna skripta napisana je prema nastavnom programu predmeta Organska kemija na osnovu odabranih poglavlja iz knjiga *S. H. Pine, Organska kemija (prijevod I. Bregovec i V. Rapić), Školska knjiga, Zagreb, 1994., L. G. Wade, Organska kemija (prijevod O. Kronja, V. Rapić i I. Bregovec), Školska knjiga, Zagreb, 2017*. i *V. Rapić, Nomenklatura organskih spojeva, III. Izmijenjeno izdanje, Školska knjiga, Zagreb, 2004*. Namijenjena je studentima 1. godine Prehrambeno-biotehnološkog fakulteta kao pomoć pri svladavanju gradiva.

Izv. prof. dr. sc. Lidija Barišić

Sadržaj

1. Nomenklatura i svojstva organskih spojeva

Imenovanje organskih spojeva provodi se prema preporukama Međunarodne unije za čistu i primijenjenu kemiju (IUPAC).

Pravila za imenovanje alkana

1. Izbor glavnog lanca → lanac s najvećim brojem C-atoma

↓

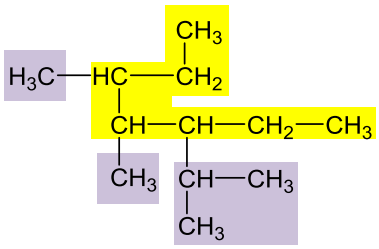
više lanaca jednake duljine → glavni lanac sadrži više bočnih lanaca (alkila)!

2. Numeriranje glavnog lanca → alkilima se dodjeljuju što manji brojevi

↓

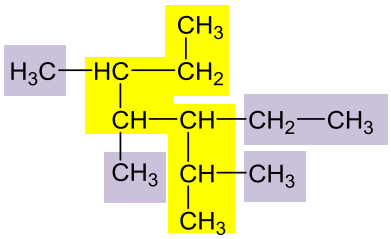
simetrično supstituirani alkani – abecedni kriterij!

Primjer:



pogrešno

(sedmeročlani glavni lanac, četiri supstituenta)



ispravno

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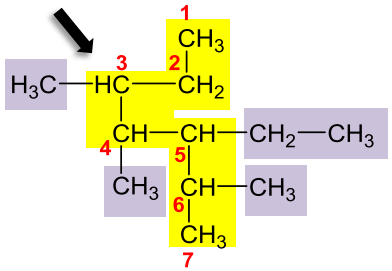

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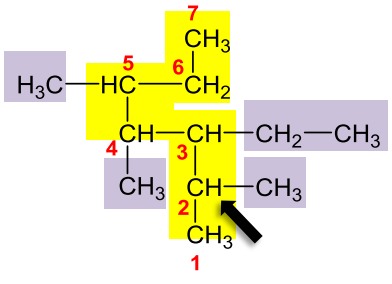
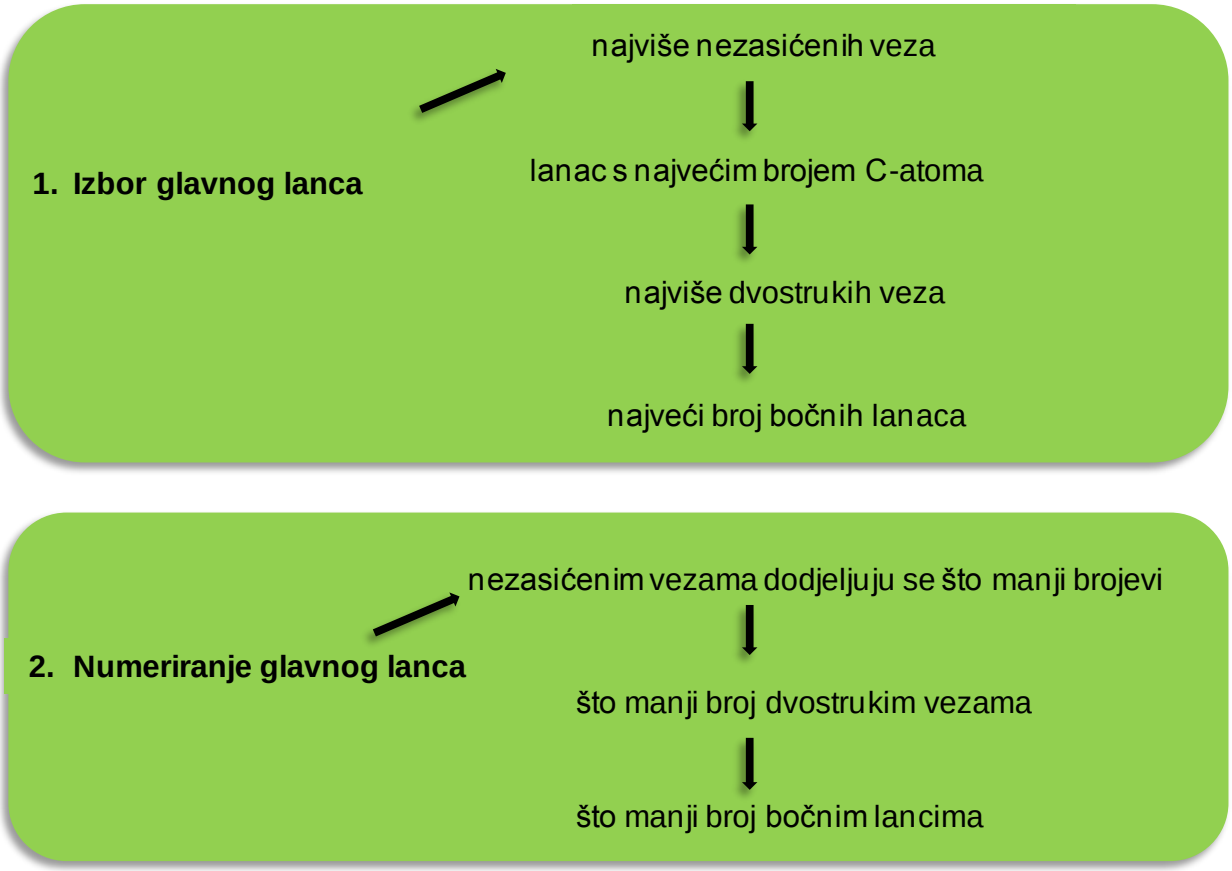
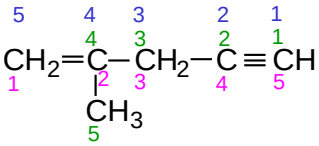


3-etil-2,4,5-trimetilheptan

Pravila za imenovanje alkena i alkina



Primjer:



Ispravno: 2-metilpent-1-en-4-in

Pogrešno: 4-metilpentan-4-en-1-in

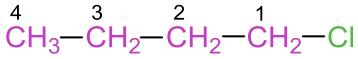
Pravila za imenovanje spojeva s karakterističnim skupinama

Spojevi koji sadrže karakteristične skupine navedene u tablici 1. imenuju se prema supstitucijskoj nomenklaturi tako da se imena karakterističnih skupina navode abecednim redoslijedom u prefiksu imena spoja.

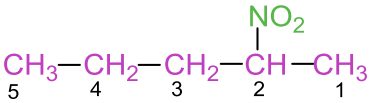
Tablica 1. Karakteristične skupine koje se prema supstitucijskoj nomenklaturi navode u prefisku imena

Karakteristična skupina	Prefiks
–Br	brom-
– F	fluor-
– I	jod-
– Cl	klor-
– NO	nitrozo-
– NO_2	nitro-

Primjer:



1-klorbutan



2-nitropentan

Imenovanje spojeva s karakterističnim skupinama navedenima u tablici 2. započinje određivanjem glavne skupine koja se navodi u sufiksu imena.

1. Izbor glavne skupine

molekula sadrži više karakterističnih skupina

↓

glavna skupina je ona koja je bliža početku tablice (sve ostale karakteristične skupine skupa sa supstituentima navode se abecednim redoslijedom kao prefiksi)

2. Određivanje osnovnog spoja

osnovni spoj mora sadržavati glavnu skupinu (ili veći broj glavnih skupina)

↓

ako dva ili više dijelova molekule sadrže jednak broj glavnih skupina, osnovni spoj se određuje prema „seniornosti" (kao kod alkana)

3. Numeriranje glavnog lanca

→ glavna funkcijska skupina (sufiks)

↓

višestruke veze

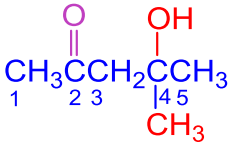
↓

prefiksi

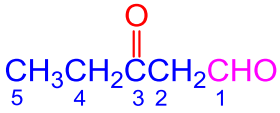
Tablica 2. Karakteristične skupine razvrstane prema opadajućim prioritetima

Vrsta spoja	Formula	Prefiks	Sufiks
karboksilne kiseline	$-CO_2H$ $-(C)O_2H$	karboksi- –	-karboksilna kiselina -ska kiselina
sulfonske kiseline	$-SO_3H$	sulfo-	-sulfonska kiselina
esteri	$-CO_2R$ $-(C)O_2R$	R-oksikarbonil- –	R...-karboksilat R...-oat
acil-halogenidi	–COHal –(C)OHal	halogenkarbonil- –	-karbonil-halogenid -oil-halogenid
amidi	$-CONH_2$ $-(C)ONH_2$	-karbamoil- –	-karboksamid -amid
aldehidi	–CHO –(C)HO	formil- okso-	-karbaldehid -al
ketoni	(C)=O	okso-	-on
alkoholi	–OH	hidroksi-	-ol

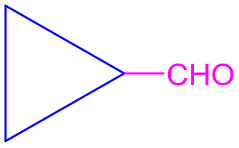
Primjeri:



4-hidroksi-4-metilpentan-2-on



3-oksopentan-1-al

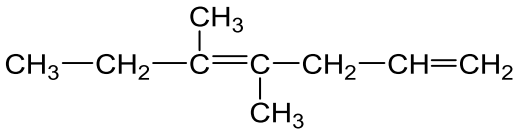


ciklopropankarbaldehid

Zadaci

1.1. Imenujte prikazane organske spojeve:

(a)



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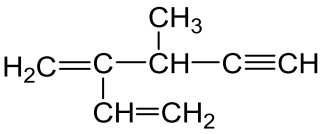
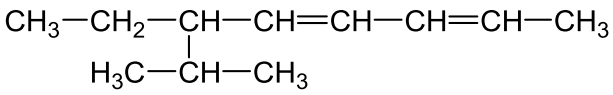


(c)



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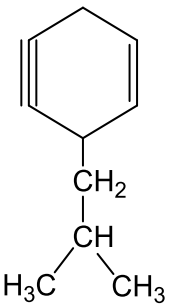

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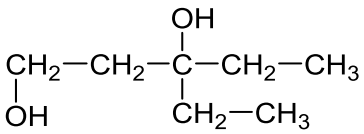

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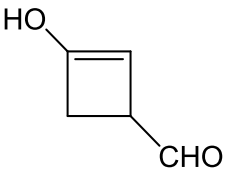

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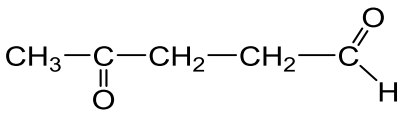

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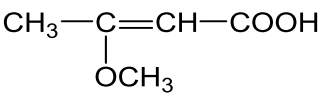

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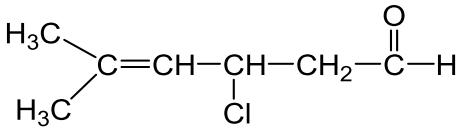

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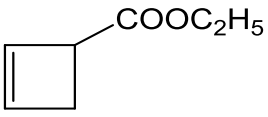

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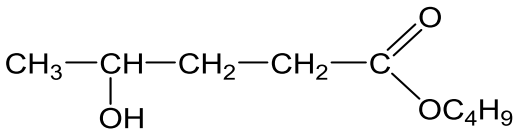

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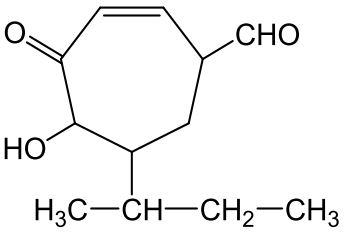
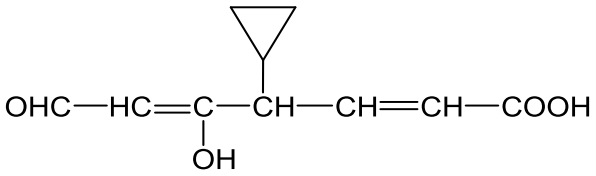
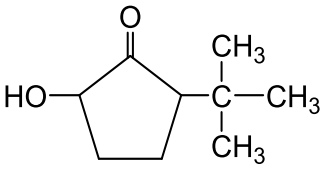


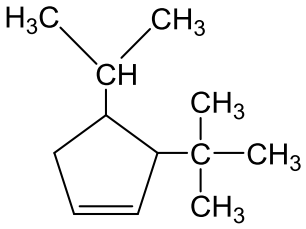
(m)



(n)

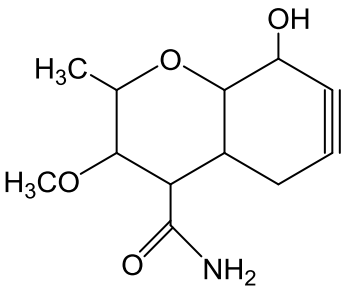


(o)



1.2. Označite funkcijske skupine i navedite kojim vrstama organskih spojeva pripadaju.

(a)



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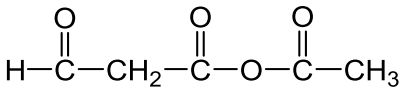
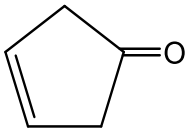


1.3. Označite vrstu hibridizacije atomâ u prikazanim molekulama:

(a)



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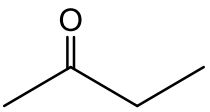

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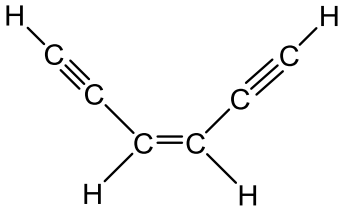
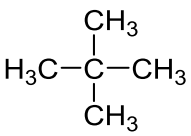


1.4. Prikažite hibridne orbitale u molekuli metil-prop-2-enoata.

1.5. Poredajte prikazane spojeve prema rastućoj temperaturi vrelišta i objasnite svoj odabir.

(a)



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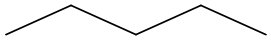
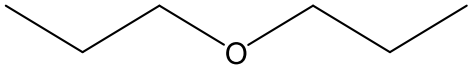
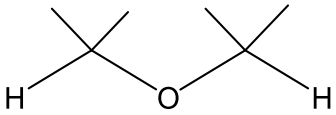
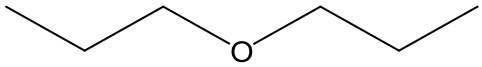
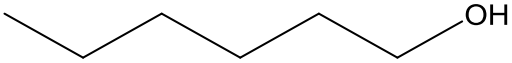
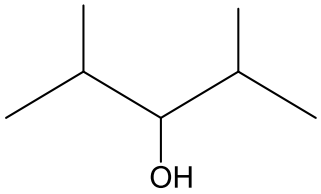
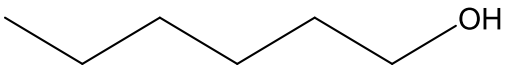


(c) $CH_3—CH_2—O—CH_2—CH_3$ (d) $CH_3—CH_2—O—H$

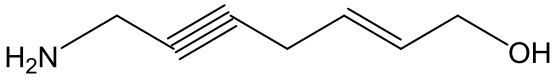
1.6. U prikazanim parovima molekula označite član koji ima višu temperaturu vrelišta i objasnite svoj odabir.

(a)  ili 

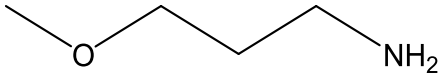
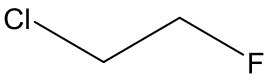
(b)  ili 

(c)  ili 

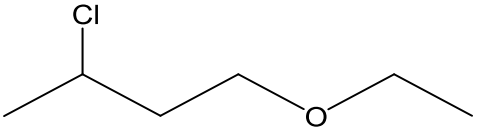
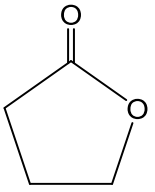
1.7. Navedite ukupan broj $\sigma-$ i $\pi-$veza u prikazanoj molekuli.

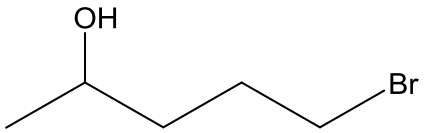


1.8. Označite najelektronegativniji element u prikazanim molekulama.

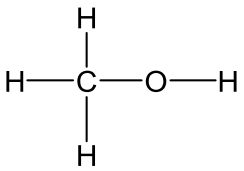
(a)  (b)  (c) $H_3C—Li$

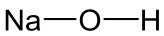
1.9. Označite parcijalno pozitivno nabijene ugljikove atome u prikazanim molekulama

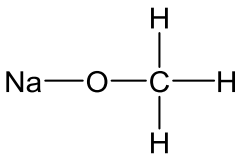
(a)  (b) 

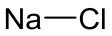
(c) 

1.10. Označite ionske i kovalentne veze u prikazanim molekulama.

(a) 

(b) 

(c) 

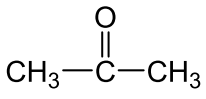
(d) 

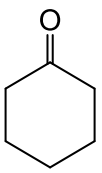
1.11. U prikazanim parovima molekula označite član topljiviji u vodi i objasnite svoj odabir.

(a) $CH_3—CH_2—O—CH_2—CH_3$ ili $CH_3CH_2CH_2CH_3$

(b) $CH_3CH_2NHCH_3$ ili $CH_3CH_2CH_3$

(c) CH_3OH ili $CH_3(CH_2)_4CH_3$

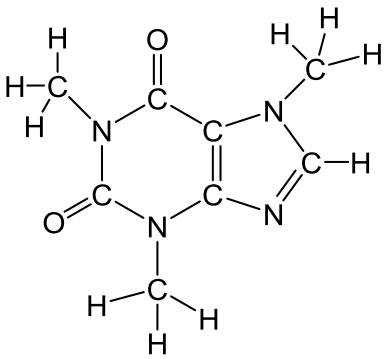
(d) 

ili 

1.12. Označite spojeve čije se molekule mogu međusobno mogu povezivati vodikovim vezama.

CH_3CH_2O CH_2O C_2H_4 CH_3OCH_3

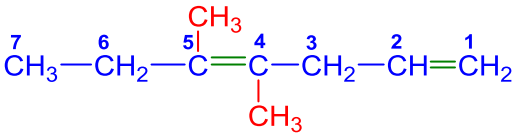
1.13. Označite nevezne elektrone u molekuli kafeina.



Rješenja

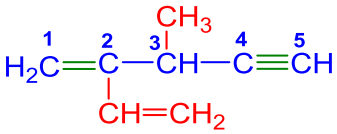
1.1. .

(a)



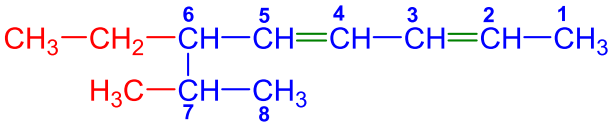
4,5-dimetilhepta-1,4-dien

(b)



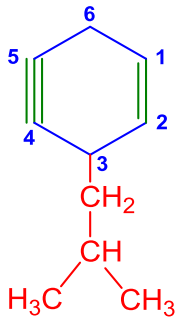
3-metil-2-vinilpent-1-en-4-in

(c)



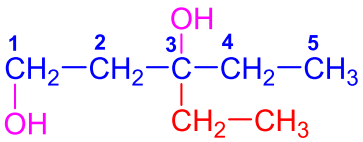
6-etil-7-metilokta-2,4-dien

(d)



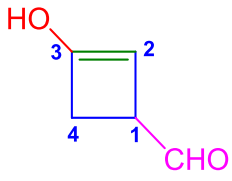
3-izobutilcikloheks-1-en-4-in

(e)



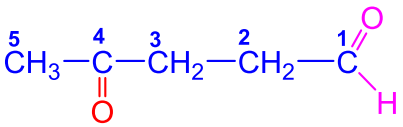
3-etilpentan-1,3-diol

(f)



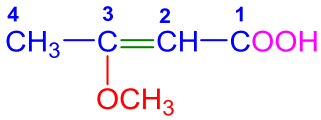
3-hidroksiciklobut-2-en-1-karbaldehid

(g)



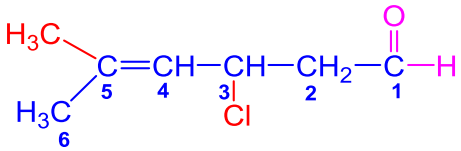
4-oksopentan-1-al

(h)



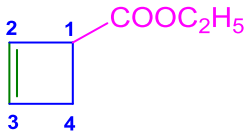
3-metoksibut-2-enska kiselina

(i)



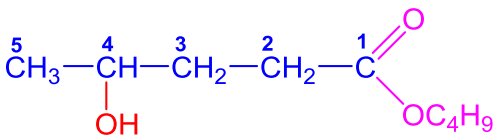
3-klor-5-metilheks-4-en-1-al

(j)



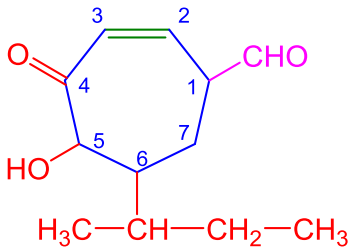
etil-ciklobut-2-en-1-karboksilat

(k)



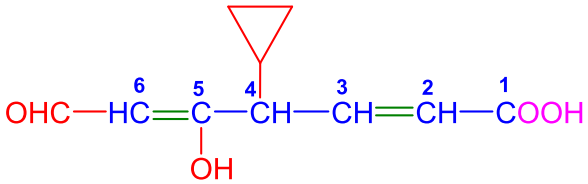
butil-4-hidroksipentanoat

(l)



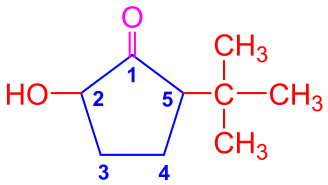
6-*sec*-butil-5-hidroksi-4-oksociklohept-2-en-1-karbaldehid

(m)



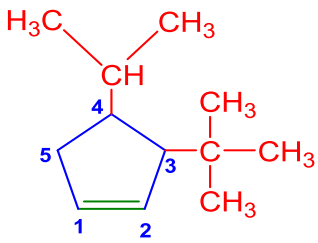
4-ciklopropil-6-formil-5-hidroksiheksa-2,5-dienska kiselina

(n)



5-*tert*-butil-2-hidroksiciklopentan-1-on

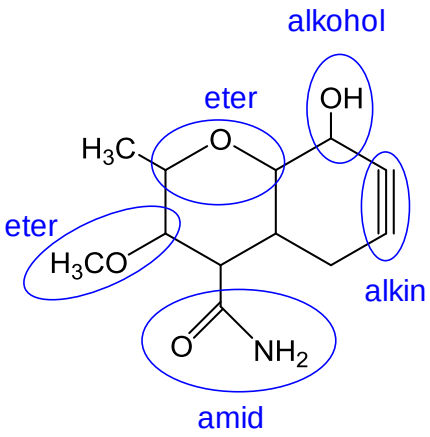
(o)



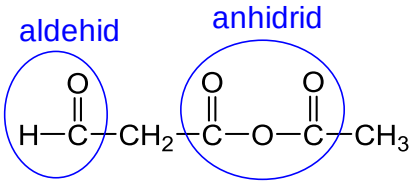
3-*tert*-butil-4-izopropilciklopent-1-en

1.2.

(a)

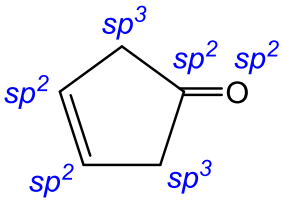


(b)

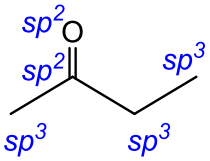


1.3.

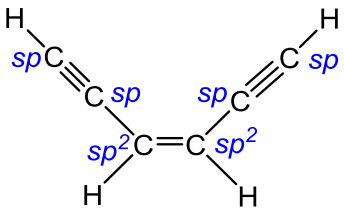
(a)



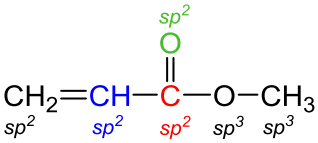
(b)

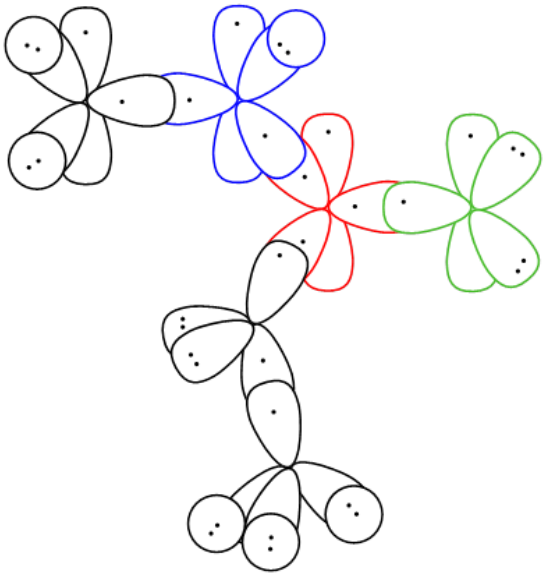


(c)



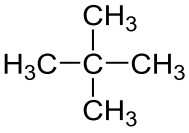
1.4.





1.5.

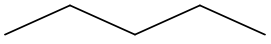
(a)



Razgranati alkan ⇒

slabije Londonove sile

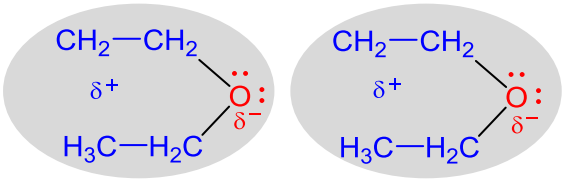
(b)



Nerazgranati alkan ⇒

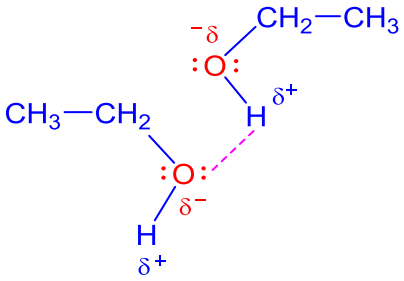
jače Londonove sile

(c) $CH_3—CH_2—O—CH_2—CH_3$



Dipol-dipol interakcije

(d) $CH_3–CH_2–O–H$



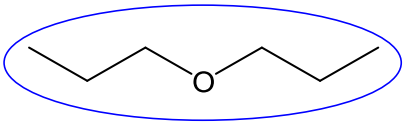
Vodikove veze

(a) (b) (c) (d)

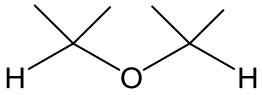
t_v

1.6.

(a)

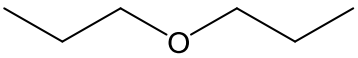


ili

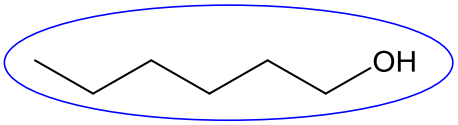


Nerazgranati eter ⇒ jače privlačne sile (dipol-dipol interakcije)

(b)

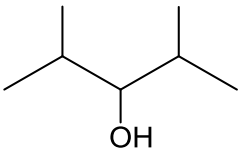


ili



Alkoholi imaju višu temperaturu vrelišta jer se povezuju vodikovim vezama, jačim međumolekulskim interakcijama u odnosu na dipol-dipol inetrakcije kojima se međusobno povezuju eteri.

(c)



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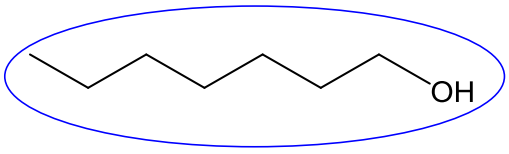
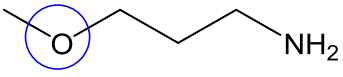


Nerazgranati alkohol ⇒ jače privlačne sile (vodikove veze).

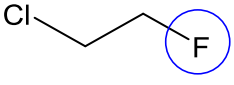
1.7. 11 σ-veza i 3 π-veze.

1.8.

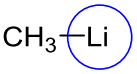
(a)



(b)

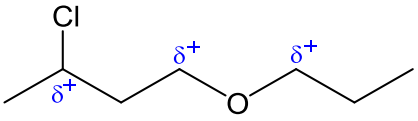


(c)

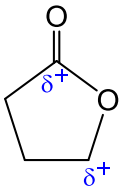


1.9.

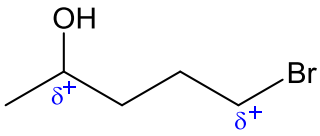
(a)



(b)

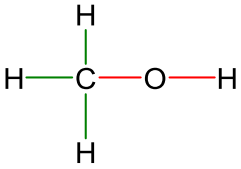


(c)

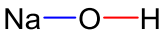


1.10.

(a)

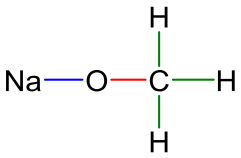


(b)



Jonska veza
Polarna kovalentna veza
Nepolarna kovalentna veza

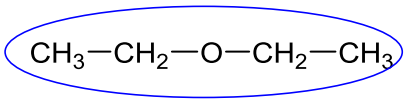
(c)



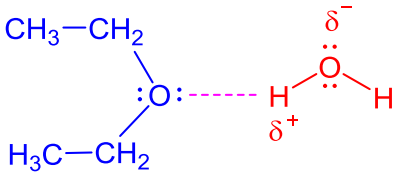
(d)

1.11.

(a)



ili $CH_3CH_2CH_2CH_3$

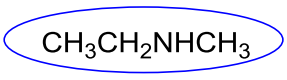


$CH_3CH_2CH_2CH_3$

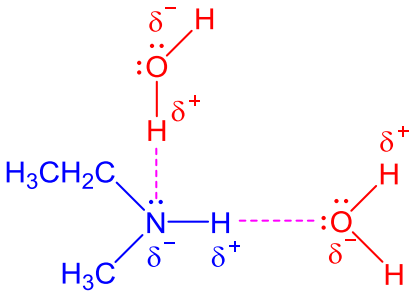
Eter je akceptor vodikove veze.

Alkan nije niti akceptor niti donor vodikove veze.

(b)



ili $CH_3CH_2CH_3$

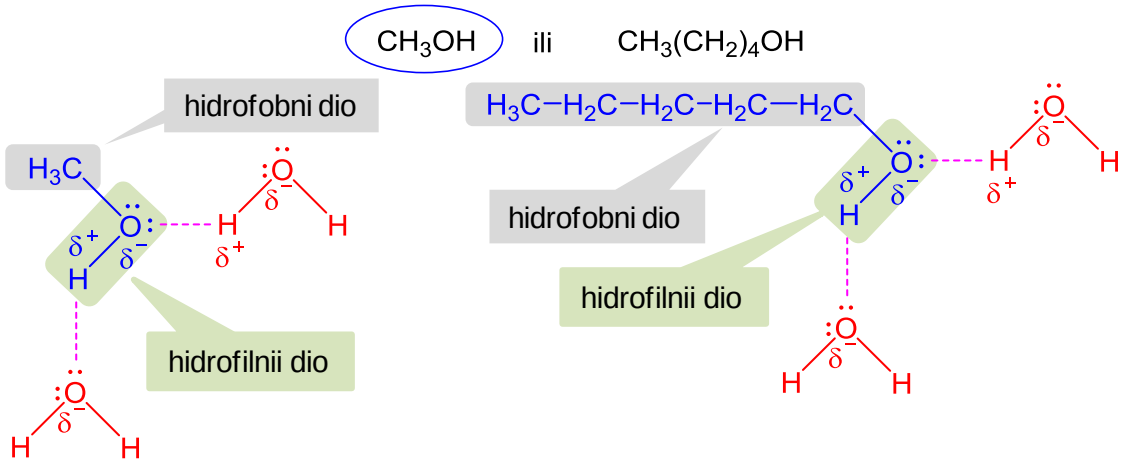


$CH_3CH_2CH_3$

2° amin je i akceptor i donor vodikove veze.

Alkan nije niti akceptor niti donor vodikove veze.

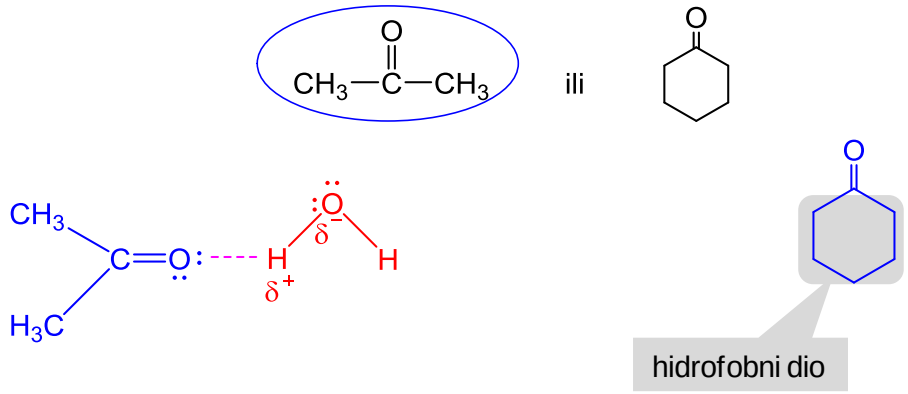
(c)



Alkoholi su akceptori i donori vodikove veze.

Alkoholi većih molekulskih masa ne miješaju se s vodom zbog prevladavajućeg hidrofobnog karaktera velike alkilne skupine.

(d)



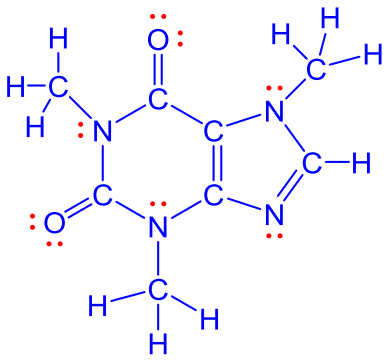
Ketoni su akceptori vodikove veze.

Ketoni većih molekulskih masa ne miješaju se s vodom zbog prevladavajućeg hidrofobnog karaktera ugljikovodičnog dijela molekule.

1.12.

CH_3NH_2 C_3H_8 NH_3 C_2H_2

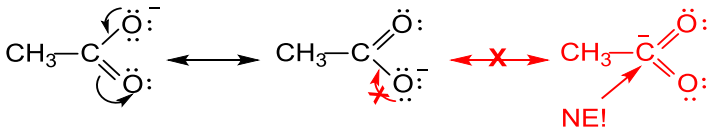
1.13.



2. Rezonancija. Kiselo-bazne reakcije

Strukture nekih molekula moguće je prikazati pomoću više Lewisovih struktura. Takve se strukture nazivaju **rezonancijskim strukturama** ili **rezonancijskim oblicima**. Rezonancijske strukture ne prikazuju različite spojeve, već predstavljaju različite prikaze ISTOG spoja. Rezonancijske strukture ne prelaze jedna u drugu!

I. Sve rezonancijske strukture moraju biti ispravne Lewisove strukture (oktet!).



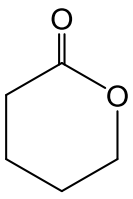
II. **Jedina razlika među rezonancijskim strukturama jest položaj njihovih π i neveznih elektrona**. Jezgre atoma se ne pomiču niti se mijenjaju vezni kutovi. Sve rezonancijske strukture imaju jednak ukupni naboj.

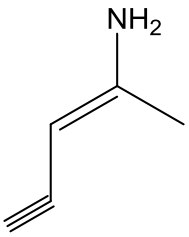
III. **Rezonanciji najviše doprinosi struktura najmanje energije**. Takve strukture imaju (*i*) atome s elektronskim oktetima, (*ii*) što veći broj veza i (*iii*) što je moguće manje odijeljenih naboja. Najstabilnije rezonancijske strukture imaju negativni naboj na elektronegativnim atomima (O, S i N).

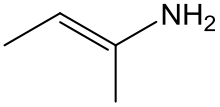
IV. **Delokalizacija naboja preko dvaju ili više atoma stabilizira ion** u usporedbi s oblicima u kojima je naboj lokaliziran.

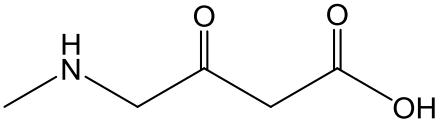
Zadaci

2.1. Prikažite rezonancijske strukture molekula (a) do (d). Označite strukture koje najviše pridonose rezonancijskom hibridu.

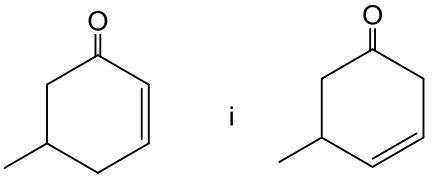
(a) 

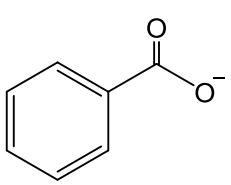
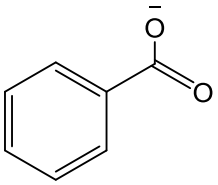
(b) 

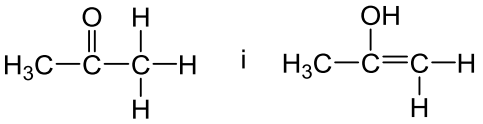
(c) 

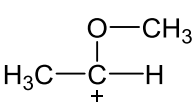
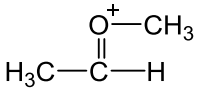
(d) 

2.2. Navedite jesu li molekule u prikazanim parovima predstavljaju različite spojeve ili rezonancijske strukture istog spoja.

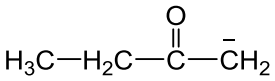
(a)  i

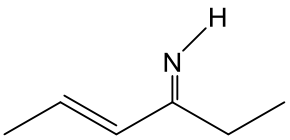
(b)  i 

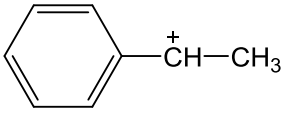
(c) 

(d)  i 

2.3. Prikažite rezonancijske strukture sljedećih molekula i označite one koje najviše doprinose rezonancijskom hibridu.

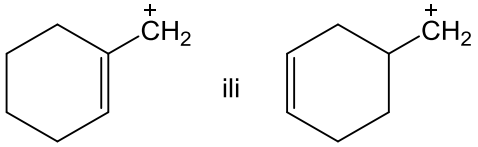
(a) 

(b) 

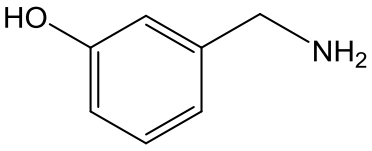
(c) 

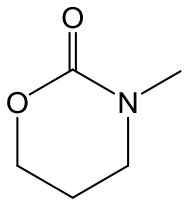
2.4. Označite stabilniji kation u prikazanim parovima.

(a) 

(b) 

2.5. U prikazanim molekulama označite nevezne elektronske parove i objasnite radi li se o lokaliziranim ili delokaliziranim elektronima. Označite hibridizaciju atoma s neveznim elektronskim parovima.

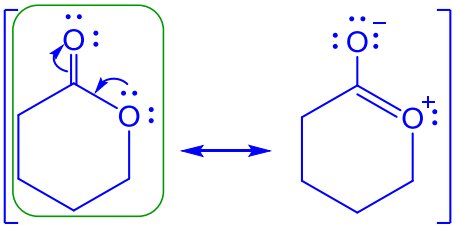
(a) 

(b) 

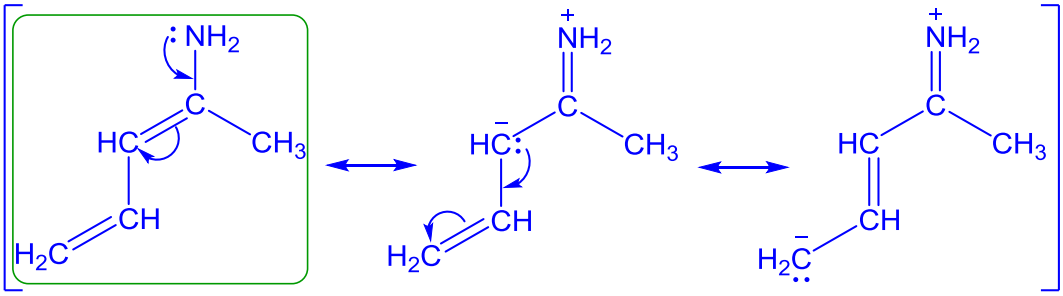
Rješenja

2.1.

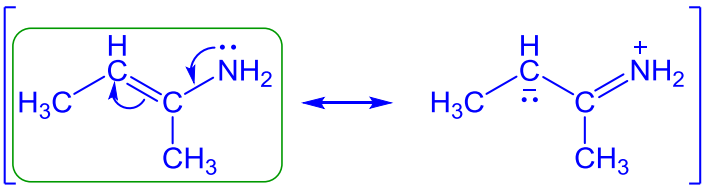
(a)



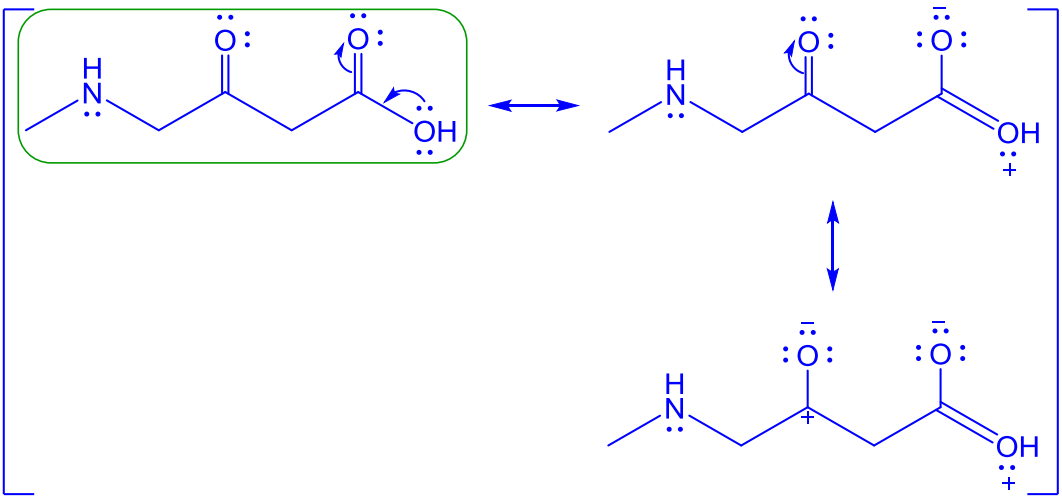
(b)



(c)



(d)



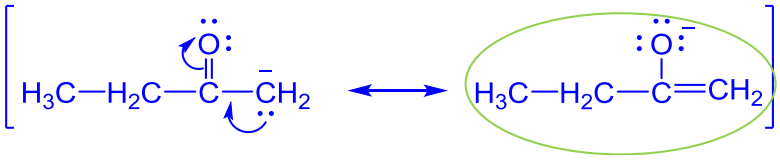
2.2.

(a) različiti spojevi (b) rezonancijske strukture istog spoja

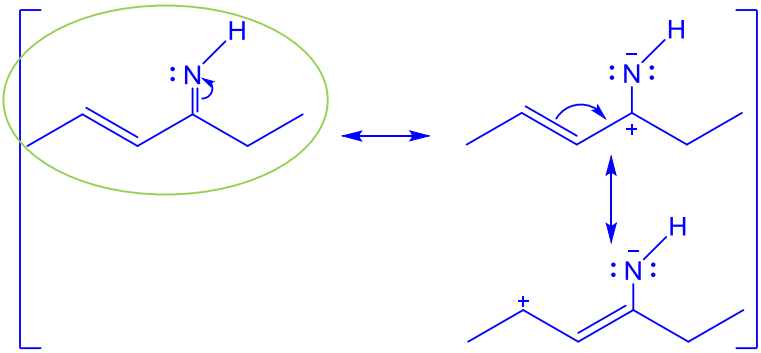
(c) različiti spojevi (d) rezonancijske strukture istog spoja

2.3.

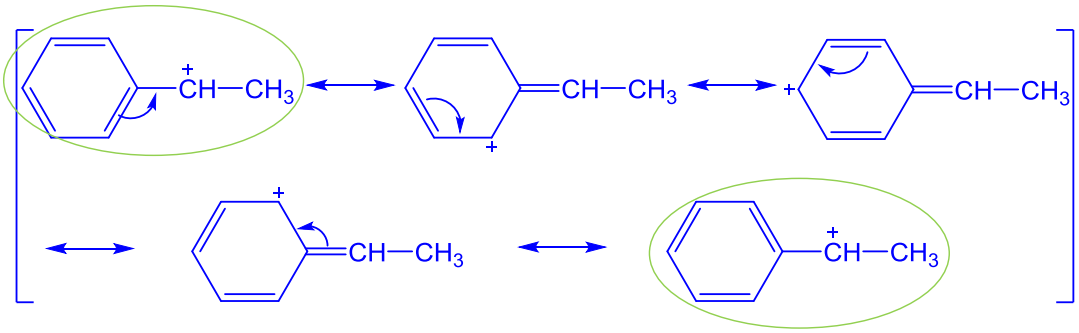
(a)



(b)

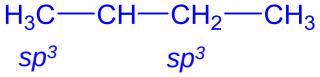


(c)

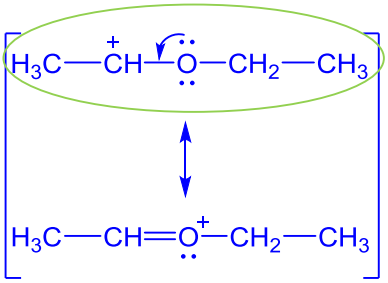


2.4.

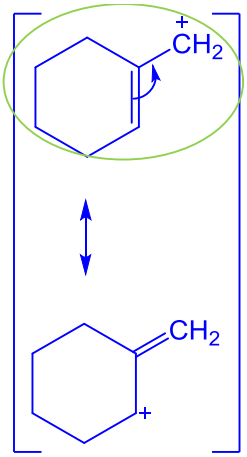
(a)



ili



(b)



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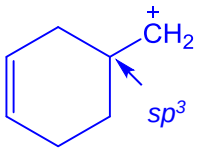
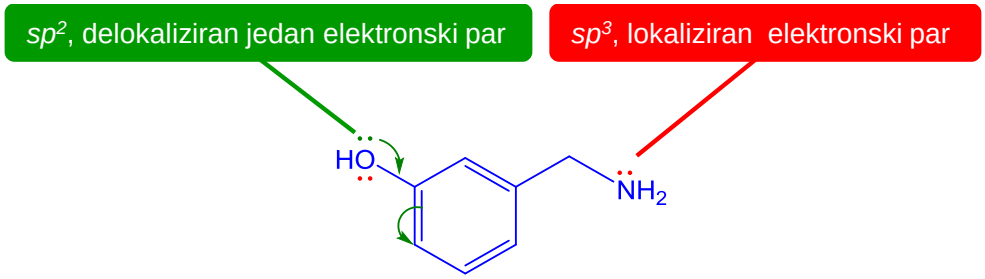
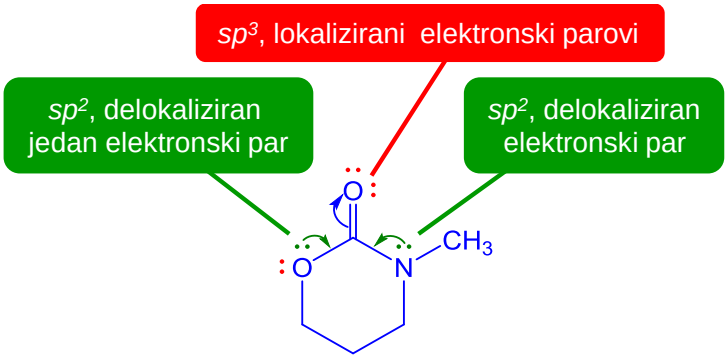


2.5.

(a)



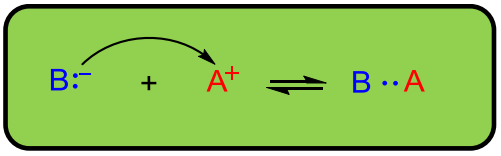
(b)



Kiselo-bazne reakcije

Lewisove baze su kemijske vrste koje **mogu donirati elektrone** drugoj jezgri pri čemu nastaje nova veza (**nukleofili,** "vole nukleus").

Lewisove kiseline mogu **prihvatiti te elektronske parove** da bi stvorile nove veze (**elektrofili**, "vole elektrone").

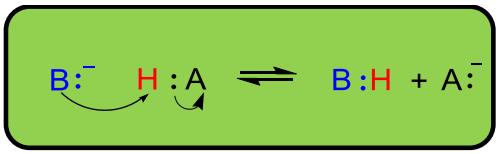


baza: elektron-donor (BED)

kiselina: elektron-akceptor (KEA)

Brønsted-Lowryjeva kiselina je bilo koja kemijska vrsta koja može **dati proton.**

Brønsted-Lowryjeva baza je bilo koja kemijska vrsta koja može **primiti proton**.



baza: proton-akceptor (BPA)

kiselina: proton-donor (KPD)

Zadaci

2.6. Razvrstajte prikazane kemijske vrste prema rastućoj kiselosti:

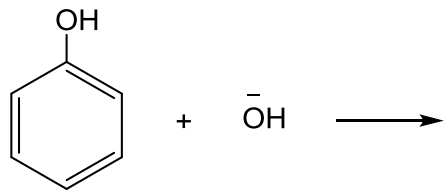
HF NH_3 CH_3OH CH_3COOH H_3O^+

2.7. Razvrstajte prikazane kemijske vrste prema rastućoj bazičnosti.

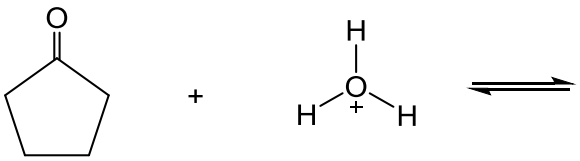
CH_3O^- H_2O CH_3COO^- NH_2^-

2.8. Dovršite prikazane kiselo-bazne reakcije. Označite kiseline, baze, konjugirane kiseline i konjugirane baze.

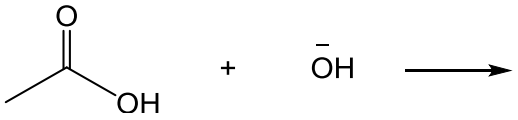
(a)



(b)



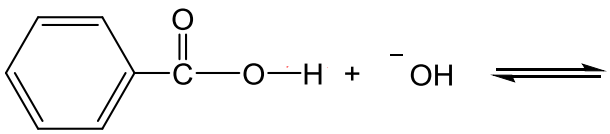
(c)



2.9. Prikažite produkte kiselo-baznih reakcija.

(a) H_2SO_4 + CH_3COO^- ⇌

(b)



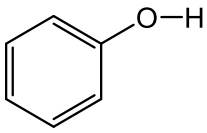
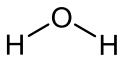
(c) $H_2O + NH_3 \rightleftharpoons$

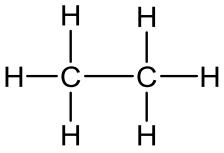
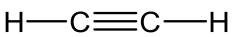
(d) $CH_3COOH + CH_3\bar{O} \rightleftharpoons$

(e) $HCOOH + NH(CH_3)_2 \rightleftharpoons$

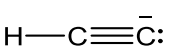
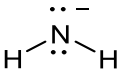
(f) $\overset{+}{N}H(CH_3)_3 + \bar{O}H \rightleftharpoons$

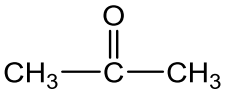
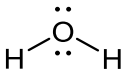
2.10. U prikazanim parovima označite kiseliji spoj i objasnite svoj odabir.

(a)  ili 

(b)  ili 

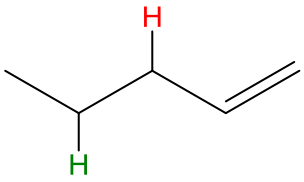
2.11. U prikazanim parovima označite jače baze i objasnite svoj odabir..

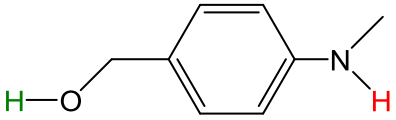
(a)  ili 

(b)  ili 

(c) Cl^- ili $\bar{O}H$

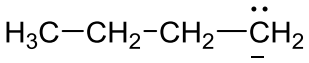
2.12. Objasnite koji je od dvaju označenih protona kiseliji.

(a) 

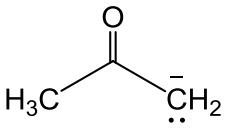
(b) 

2.13. Nacrtajte konjugirane kiseline prikazanih baza.

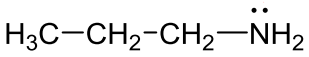
(a)



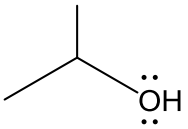
(b)



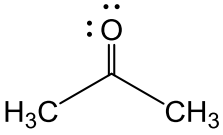
(c)



(d)

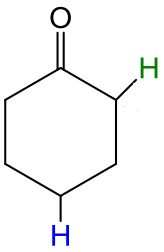


(e)

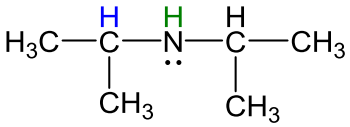


2.14. Nacrtajte konjugirane baze prikazanih kiselina.

(a)

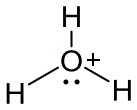


(b)

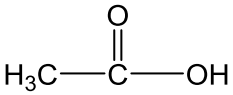


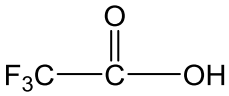
(c)

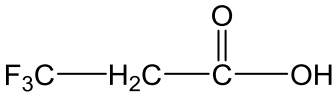
(d)

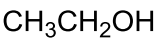


2.15. Razvrstajte prema jakosti prikazane kiseline. Objasnite.



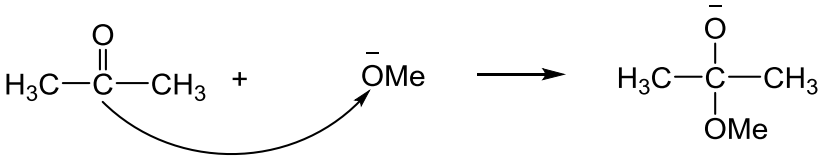




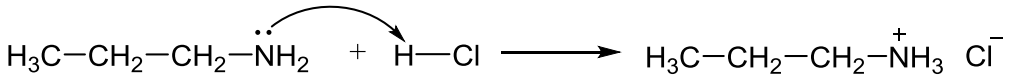


2.16. Uočite pogreške u prikazanim mehanizmima i predložite korekcije.

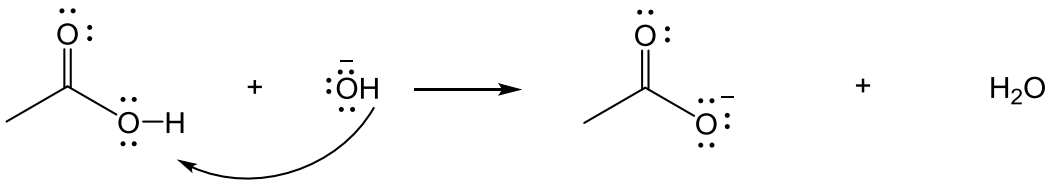
(a)



(b)

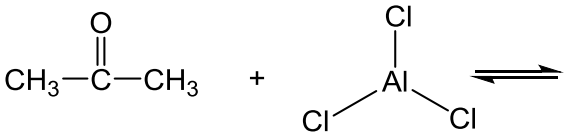


(c)

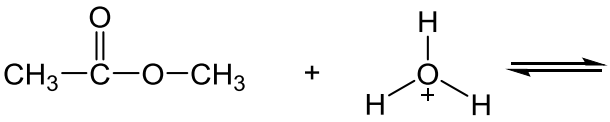


2.17. Napišite produkte prikazanih kiselo-baznih reakcija. Označite Lewisove kiseline i baze.

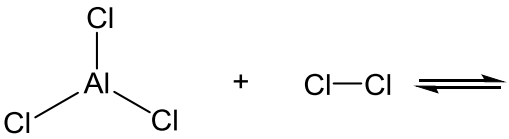
(a)



(b)



(c)



2.18. Naznačite ravnotežni položaj prikazanih kiselo-baznih reakcija.

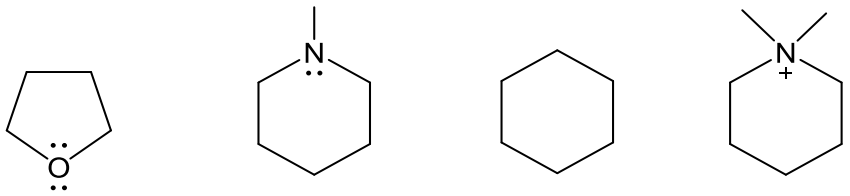
(a) $CH_3{-}OH + \bar{O}H \rightleftharpoons CH_3{-}\bar{O} + H_2O$

(b) $CH_2{=}CH{-}OH + \bar{O}H \rightleftharpoons CH_2{=}CH{-}\bar{O} + H_2O$

(c) $H{-}I + H_2O \rightleftharpoons I^- + H_3O^+$

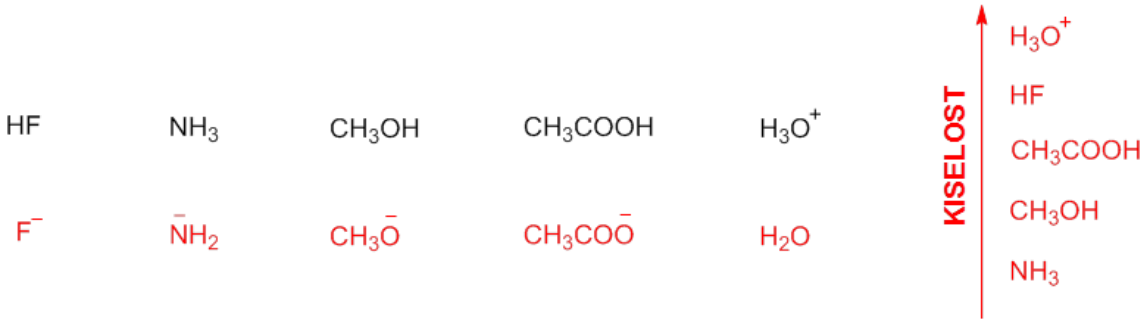
(d) $HC{\equiv}CH + \bar{N}H_2 \rightleftharpoons HC{\equiv}\bar{C} + NH_3$

2.19. Zaokružite Lewisove baze među prikazanim spojevima.

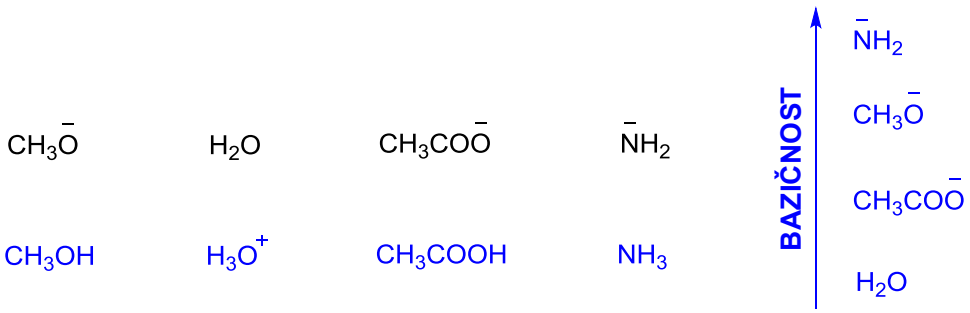


Rješenja

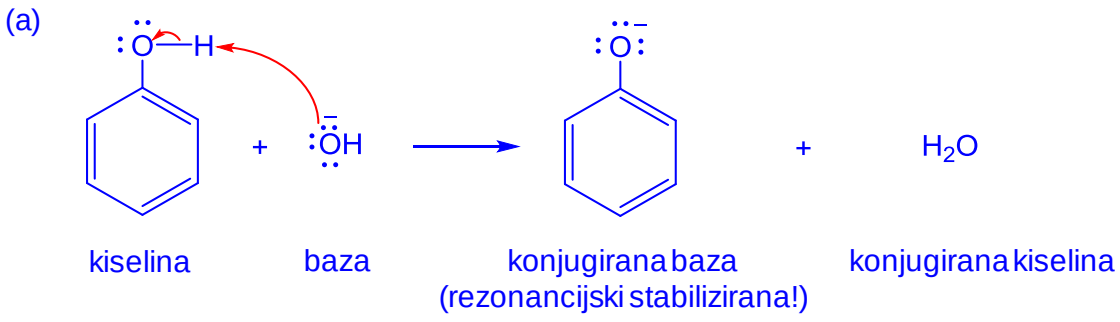
2.6.



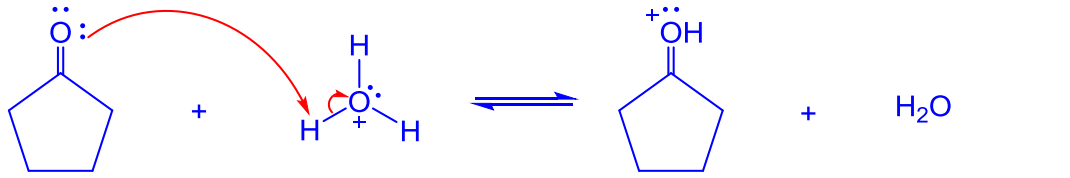
2.7.



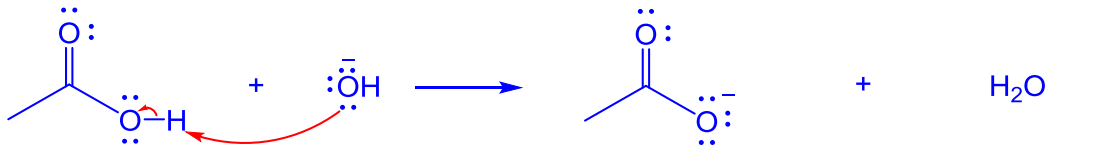
2.8.



(b)

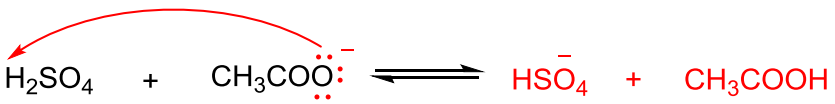

baza
kiselina
konjugirana kiselina
konjugirana baza

(c)

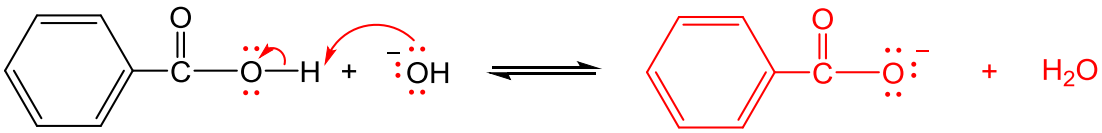

kiselina
baza
konjugirana baza
(rezonancijski stabilizirana!)
konjugirana kiselina

2.9.

(a)

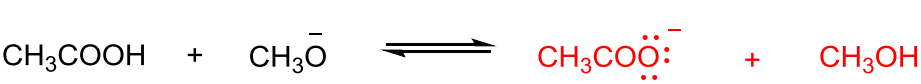


(b)

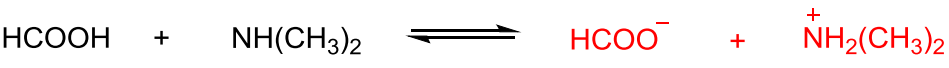


(c)

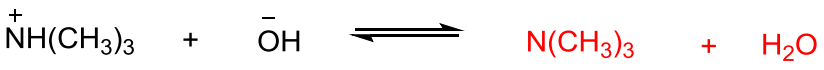
(d)



(e)

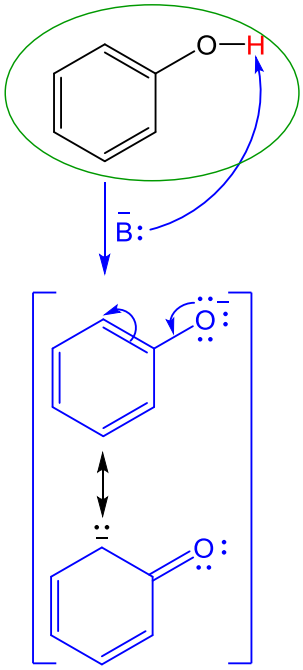


(f)

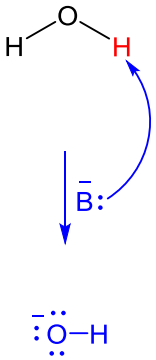


2.10.

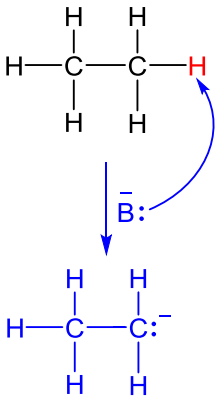
(a)



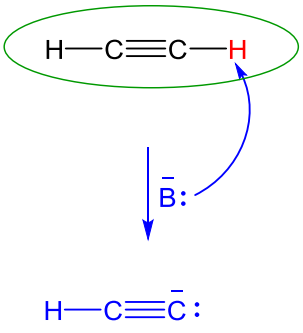
rezonancijski stabilizirana konjugirana baza



(b)



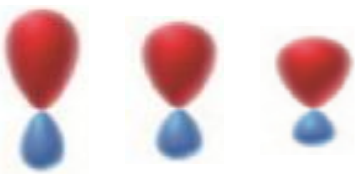
*sp*³-hibridizacija



sp-hibridizacija

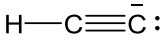
prevladava *s*-karakter ⇒ elektroni su bliže jezgri ⇒ slabija konjugirana baza ⇒ jača kiselina

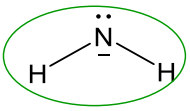
2.11.



sp³ sp² sp

(a)



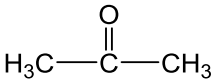


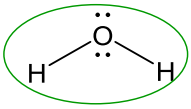
sp-hibridizacija

sp^3-hibridizacija

prevladava *s*-karakter ⇒ elektroni su bliže jezgri
⇒ slabija stabilnija konjugirana baza

(b)



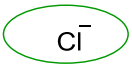


sp2-hibridizacija

sp^3-hibridizacija

prevladava *s*-karakter ⇒ elektroni su bliže jezgri
⇒ slabija stabilnija konjugirana baza

(c)

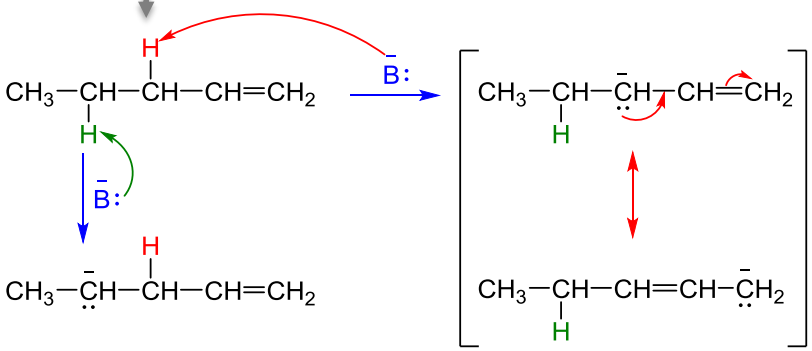


klor je elektronegativniji ⇒ njegova jezgra jače privlači elektrone
⇒ slabija stabilnija konjugirana baza

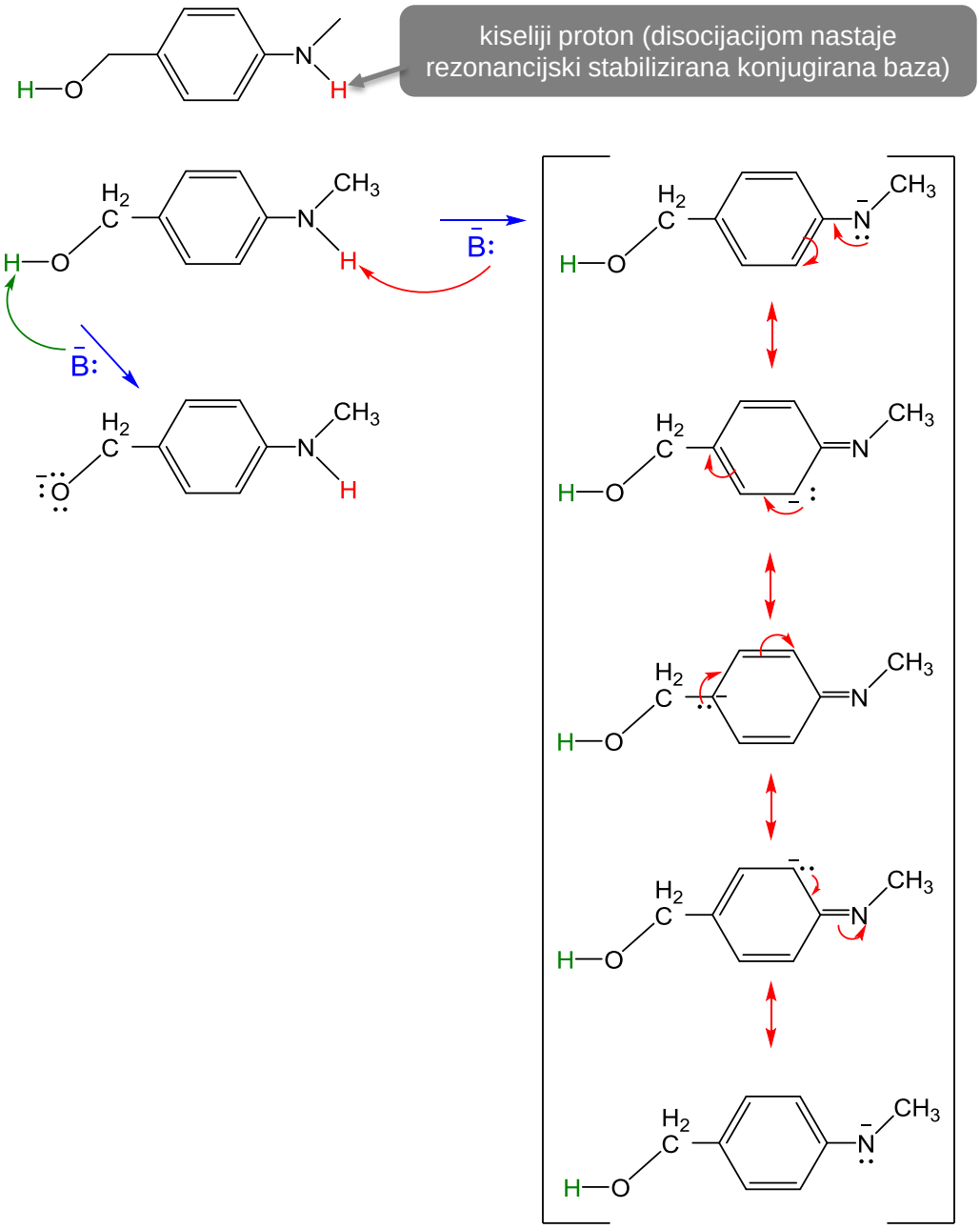
2.12.

(a)

kiseliji proton (disocijacijom nastaje rezonancijski stabilizirana konjugirana baza)



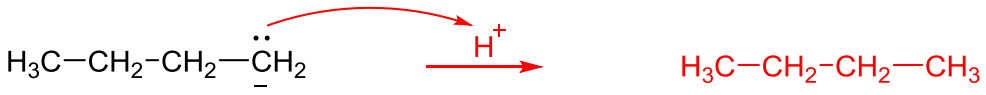
(b)



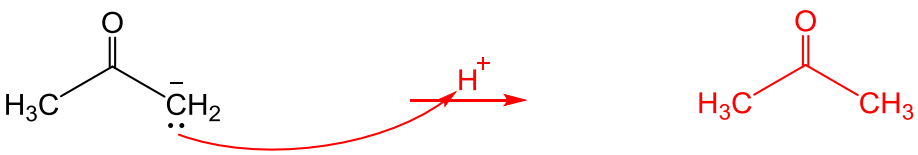
2.13.

Baza **Konjugirana kiselina**

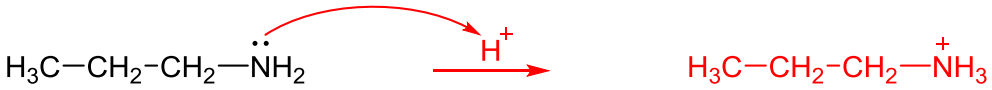
(a)



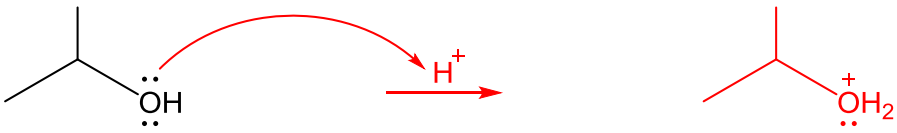
(b)



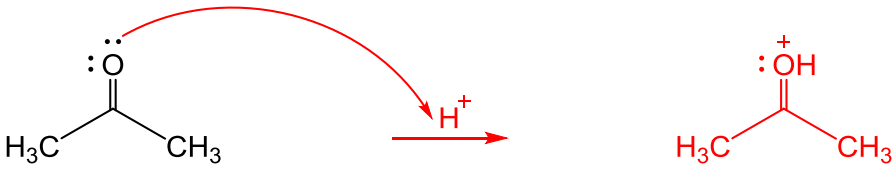
(c)



(d)



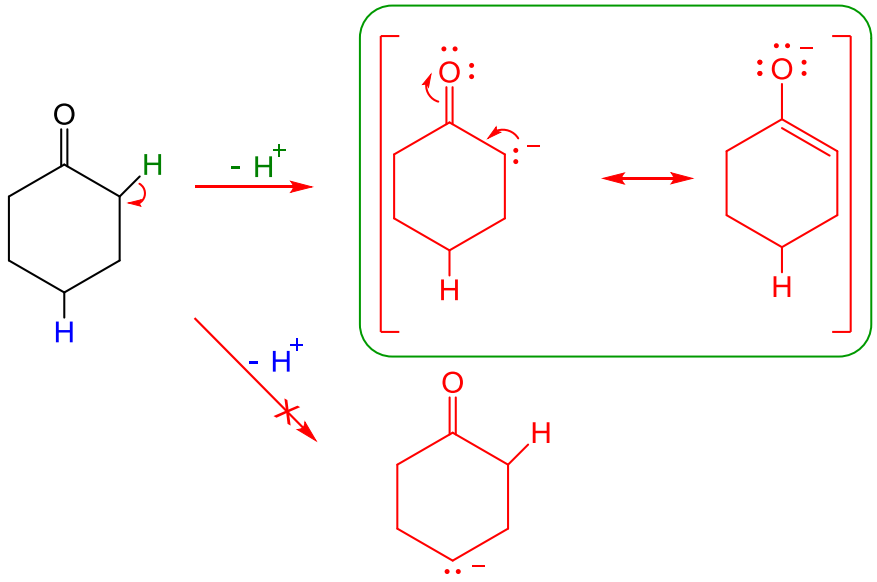
(e)



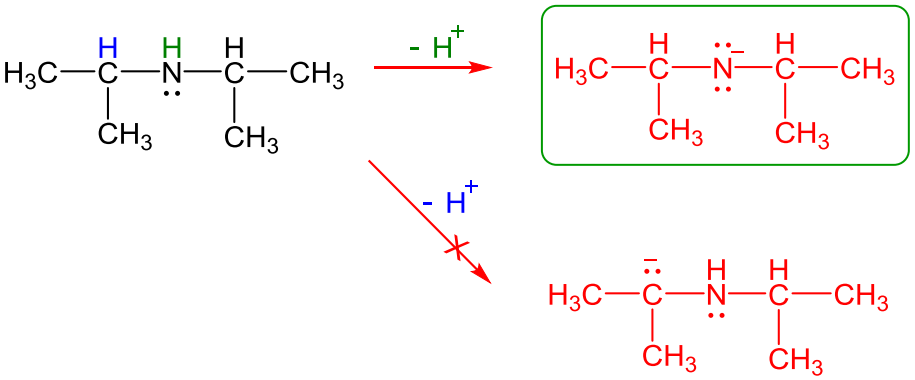
2.14.

Kiselina **Konjugirana baza**

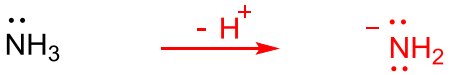
(a)



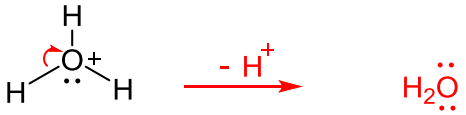
(b)



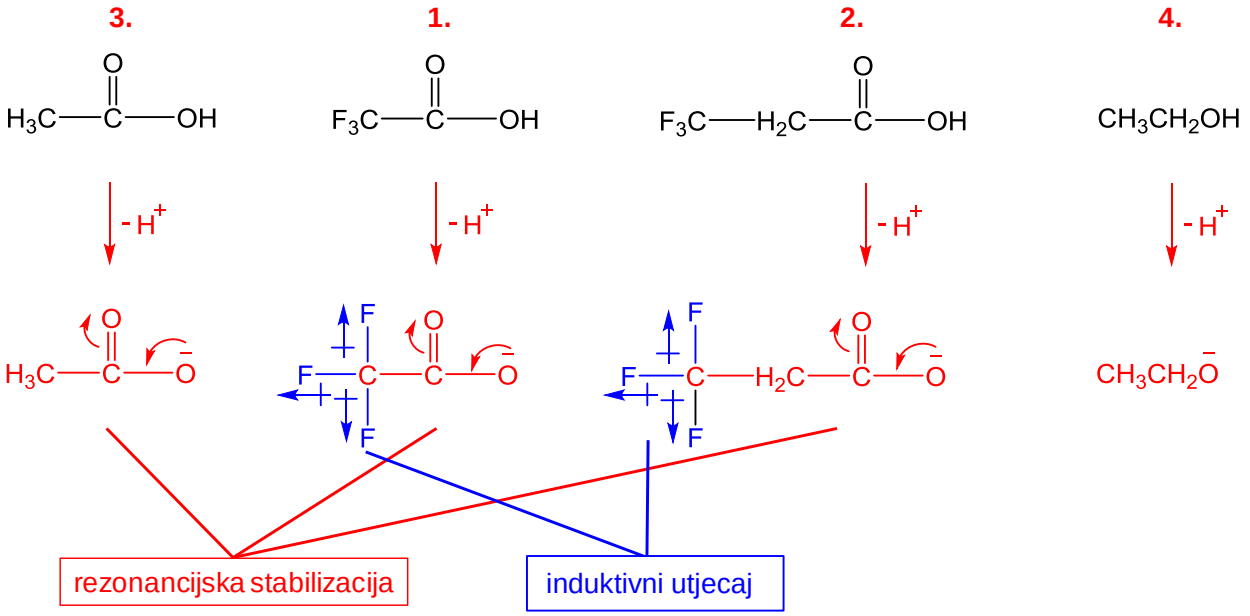
(c)


NH3
- H+
NH2

(d)

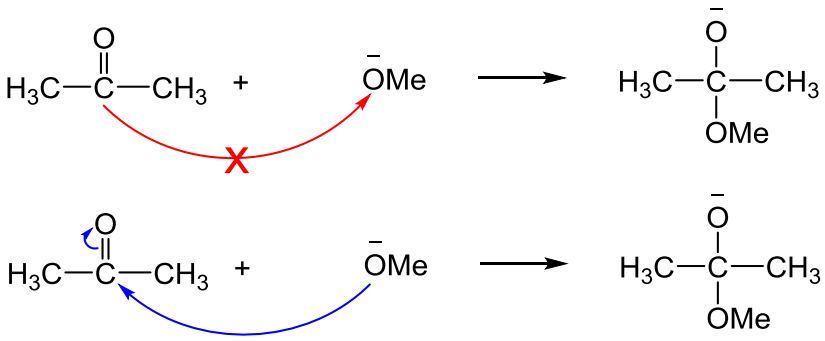

H
O+
H
H
- H+
H2O

2.15.

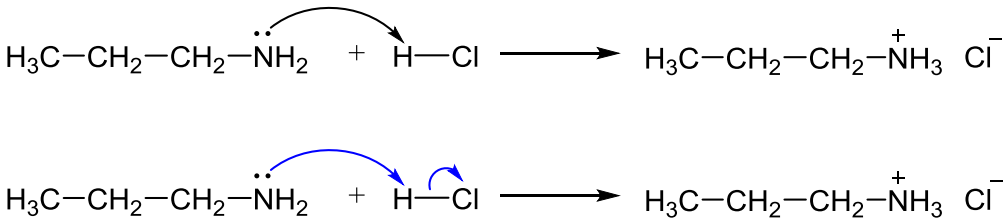

3.
1.
2.
4.
H3C—C—OH
F3C—C—OH
F3C—H2C—C—OH
CH3CH2OH
- H+
CH3CH2O
rezonancijska stabilizacija
induktivni utjecaj

2.16.

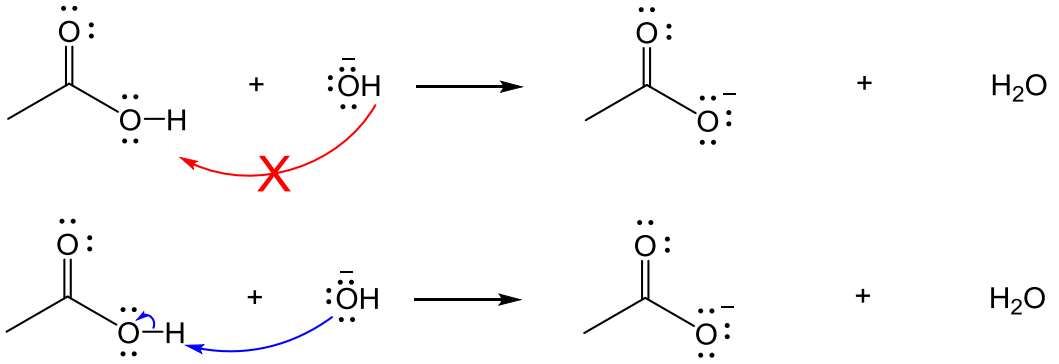
(a)


H3C—C—CH3
+
OMe
H3C—C(O)(OMe)—CH3

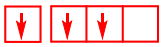
(b)


H3C—CH2—CH2—NH2
+
H—Cl
H3C—CH2—CH2—NH3 Cl

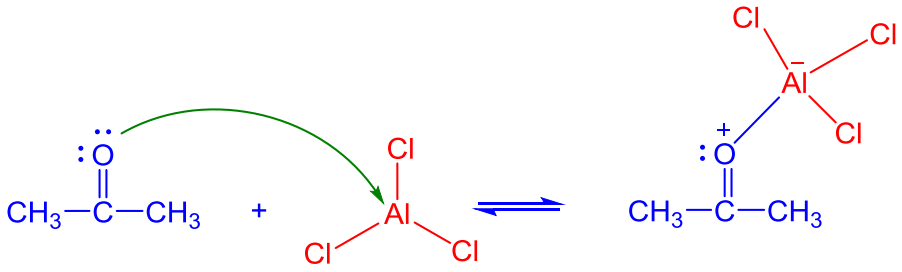
(c)



2.17.

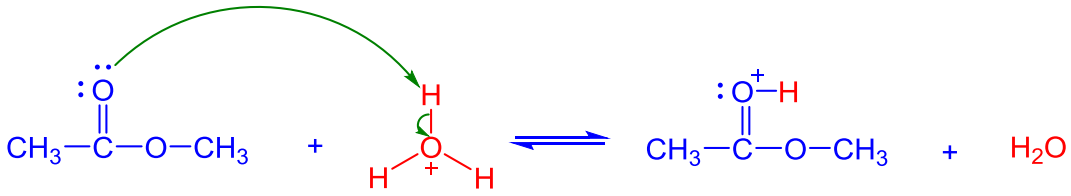
^{13}Al $3s^2\ 3p^1$  Lewisova kiselina (elektron-akceptor)

(a)



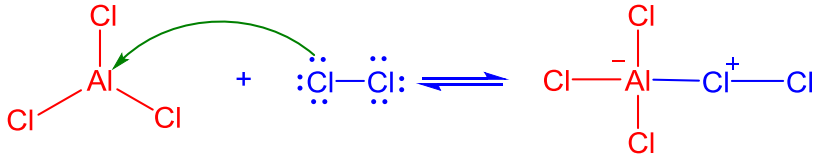
Lewisova baza Lewisova kiselina

(b)



Lewisova baza Lewisova kiselina

(c)



Lewisova kiselina Lewisova baza

2.18.

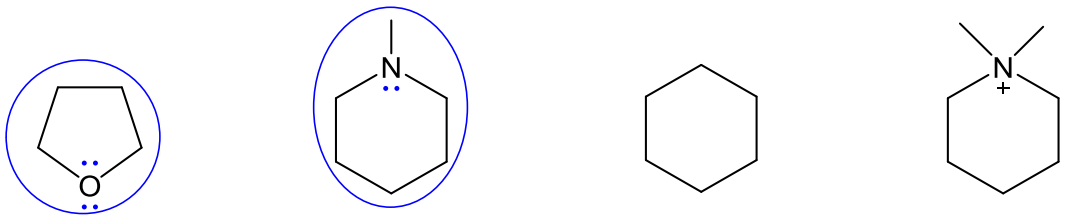
(a) $CH_3{-}OH + \bar{O}H \rightleftharpoons CH_3{-}\bar{O} + H_2O$

(b) $CH_2{=}CH{-}OH + \bar{O}H \rightleftharpoons CH_2{=}CH{-}\bar{O} + H_2O$

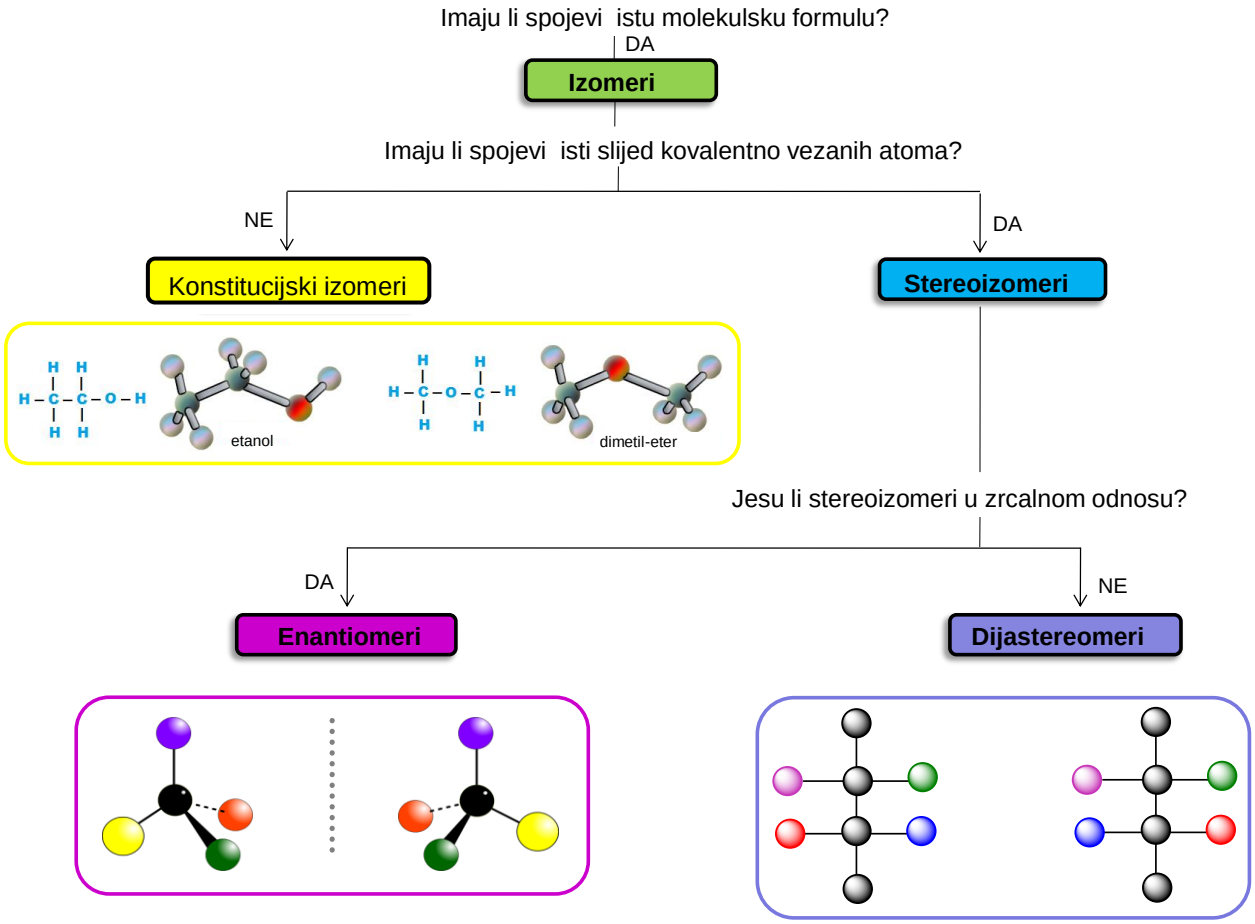
(c) $H{-}I + H_2O \rightleftharpoons I^- + H_3O^+$

(d) $HC{\equiv}CH + \bar{N}H_2 \rightleftharpoons HC{\equiv}\bar{C} + NH_3$

2.19. Zaokružite Lewisove baze među prikazanim spojevima.



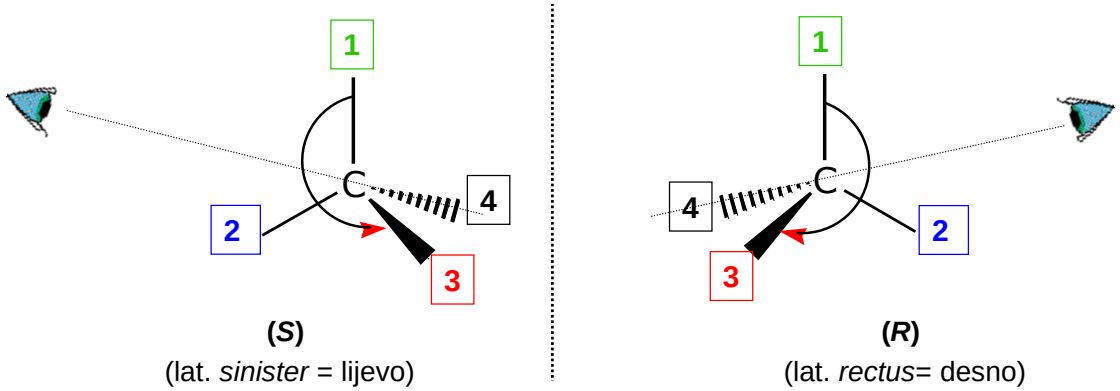
3. Stereokemija



Cahn-Ingold-Prelogova konvencija predstavlja najšire prihvaćen sustav za obilježavanje konfiguracija kiralnih središta. Postupak određivanja konfiguracije uključuje nekoliko koraka:

1. Identifikacija četiriju atoma izravno vezanih za kiralni centar.
2. Dodijeljivanje prioriteta svakom atomu prema njegovom atomskom broju [atom najvišeg atomskog broja poprima najviši prioritet (1), dok najmanji atomski broj poprima najniži prioritet (4)].
3. Ako su atomi izravno vezani na kiralni centar (atomi 1. pojasa) jednaki, uspoređuju se atomi koji su na njih neposredno vezani (atomi 2. pojasa), itd.
4. Dvostruke i trostruke veze promatramo kao veze s odvojenim atomima (cijepanje I udvostručavanje).

Skupinu najnižeg prioriteta usmjerava se od sebe, a molekula se promatra duž veze između kiralnog centra i skupine najnižeg prioriteta. Ukoliko slijed 1-2-3- prati smjer kazaljke na satu, asimetrični ugljikov atom dobiva oznaku (*R*). U suprotnom se dodjeljuje oznaka (*S).*



(*S*)
(lat. *sinister* = lijevo)

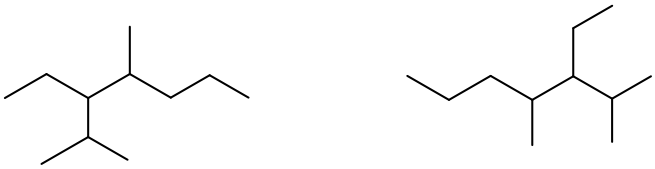
(*R*)
(lat. *rectus*= desno)

Zadaci

3.1. Navedite jesu li članovi u prikazanim parovima konstitucijski izomeri ili je riječ o istim spojevima.

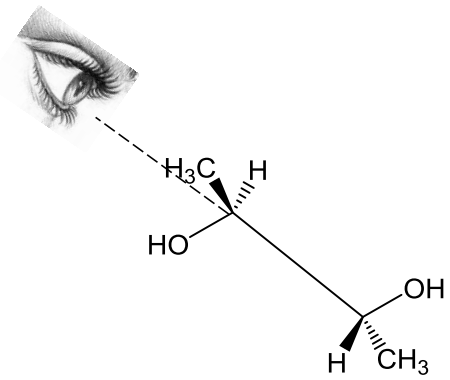
(a) 

(b) 

(c) 

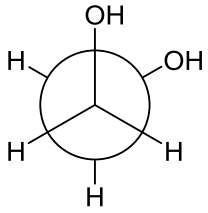
3.2. Klinastom, perspektivnom i Newmanovom projekcijskom formulom prikažite najstabilniju konformaciju pentana gledajući kroz vezu C_2–C_3.

3.3. Nacrtajte Newmanovom formulom trodimenzijsku strukturu prikazanog spoja.

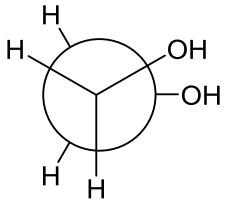


3.4. Razvrstajte prikazane konformacije prema rastućoj energiji.

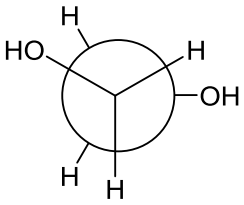
(a)



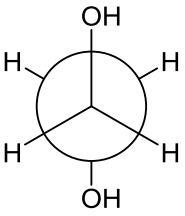
(b)



(c)



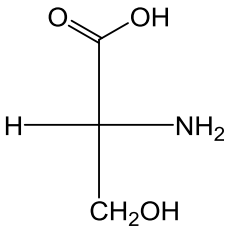
(d)



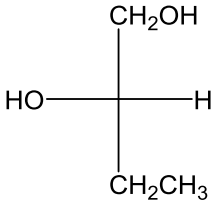
3.5. Nacrtajte četiri konstitucijska izomera molekulske formule C_4H_9Br i označite kiralne centre.

3.6. Odredite konfiguraciju kiralnih centara u prikazanim molekulama.

(a)

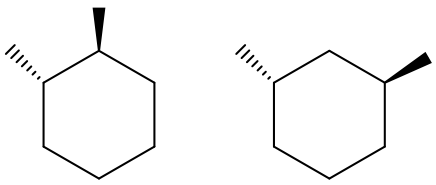


(b)

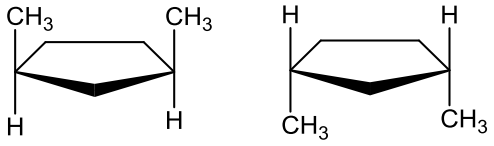


3.7. Za članove u prikazanim parovima označite radi li se o identičnim spojevima, konstitucijskim izomerima, stereoizomerima ili spojevima koji nisu u izomernom odnosu.

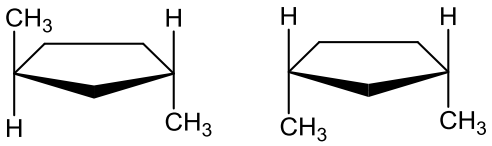
(a)



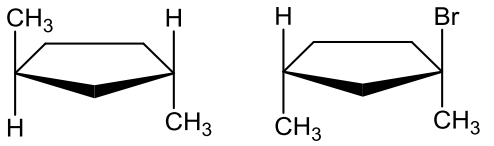
(b)

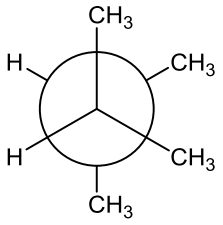


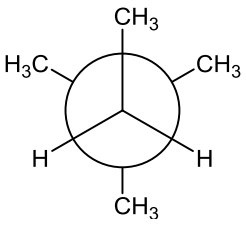
(c)

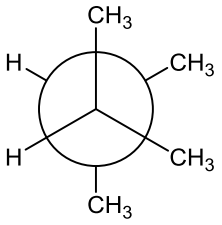


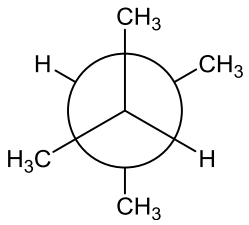
(d)



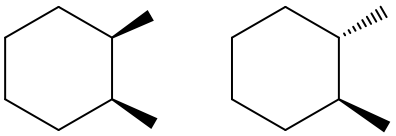
(e) 

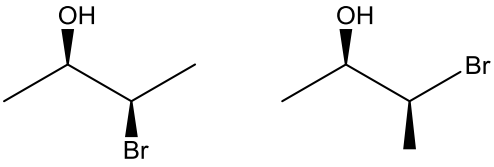


(f) 

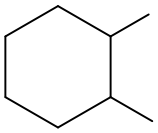


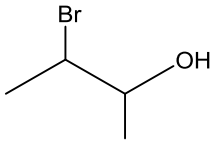
3.8. Navedite jesu li prikazani parovi molekula u enantiomernom ili dijastereomernom odnosu.

(a) 

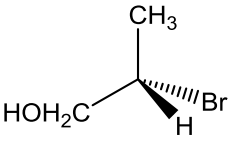
(b) 

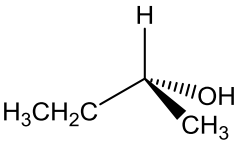
3.9. Nacrtajte sve moguće stereoizomere prikazanih molekula.

(a) 

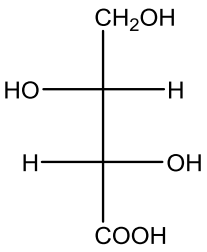
(b) 

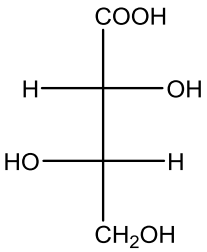
3.10. Odredite konfiguraciju kiralnih centara u prikazanim molekulama.

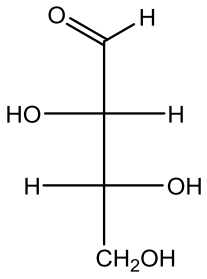
(a) 

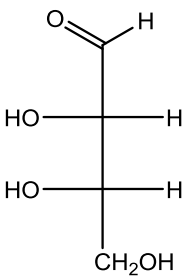
(b) 

3.11. Označite u kakvom su odnosu prikazani parovi. Odredite konfiguraciju kiralnih centara molekula prikazanih pod (a).

(a) 



(b) 

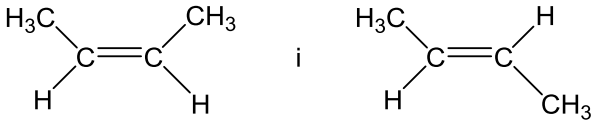


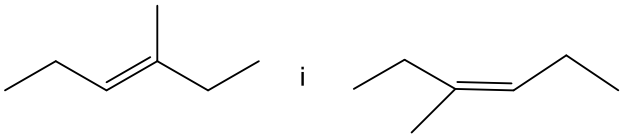
3.12. Koje od prikazanih molekula pokazuju *cis-trans* izomeriju? Prikažite *cis* i *trans* izomere.

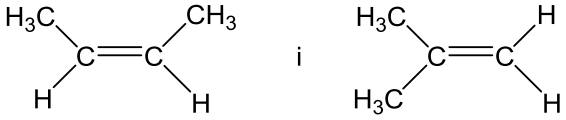
(a) $H_3C—CH=CH—CH_3$ (b) $H_3C—C\equiv C—CH_3$ (c) $CH_2=C—(CH_3)_2$

3.13. U kakvom su odnosu (isti, *cis-trans* izomeri, konstitucijski izomeri, različiti) članovi u prikazanim parovima?

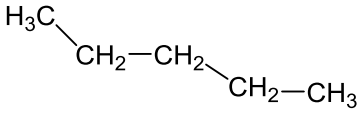
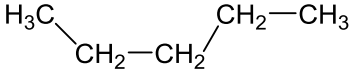
(a) $CH_3CH_2CH_2CH_3$ i $(CH_3)_3CH$

(b)  i

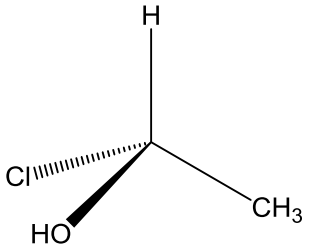
(c)  i

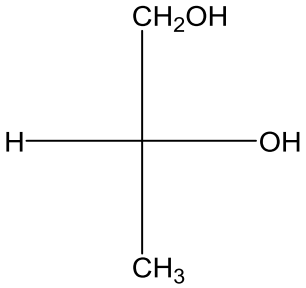
(d)  i

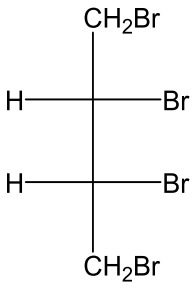
(e) $H_2C{=}CH{-}CH_2Cl$ i $ClHC{=}CH{-}CH_3$

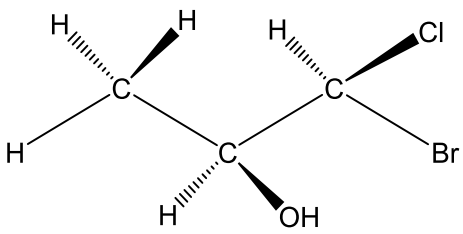
(f)  i 

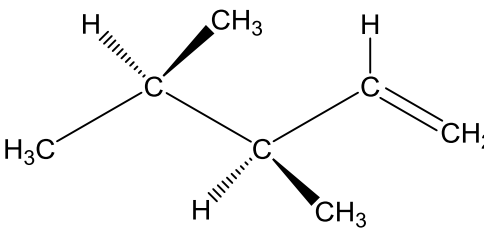
3.14. U prikazanim strukturama označite kiralne atome i odredite njihovu konfiguraciju. Označite strukture kao kiralne ili akiralne.

(a) 

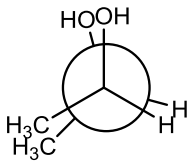
(b) 

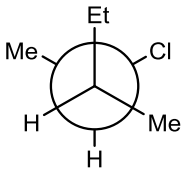
(c) 

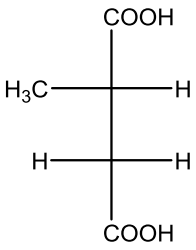
(d) 

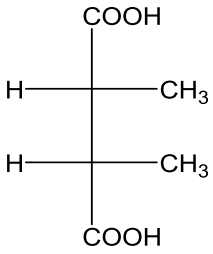
(e) 

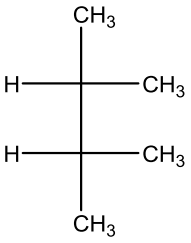
3.15. Objasnite jesu li prikazane molekule optički aktivne.

(a) 

(b) 

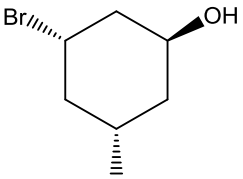
(c) 

(d) 

(e) 

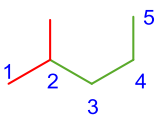
3.16. Fischerovim formulama prikažite: (a)) *meso*-heksan-3,4-diola i (b) (2*R*, 3*S*)-2,3-dibromheksana. Označite kiralne centre, ravnine simetrije, enantiomere i dijastereomere prikazanih struktura. Označite kiralne i akiralne molekule.

3.17. Nacrtajte enantiomer prikazane molekule.



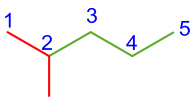
Rješenja

3.1.

(a) 

C_6H_{14}

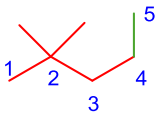
2-metilpentan



C_6H_{14}

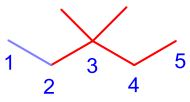
2-metilpentan

ISTI SPOJEVI

(b) 

C_7H_{16}

2,2-dimetilpentan

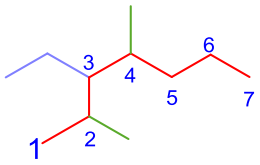


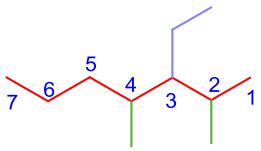
C_7H_{16}

3,3-dimetilpentan

KONSTITUCIJSKI IZOMERI

(c)



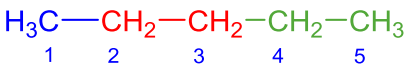


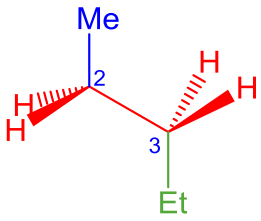
$C_{11}H_{24}$ — 3-etil-2,4-dimetilheptan

$C_{11}H_{24}$ — 3-etil-2,4-dimetilheptan

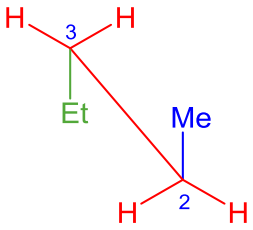
ISTI SPOJEVI

3.2.

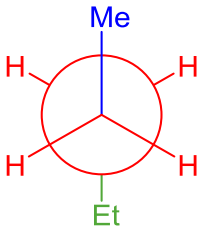




klinasta formula

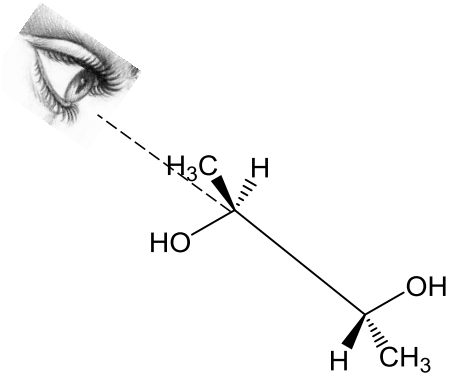


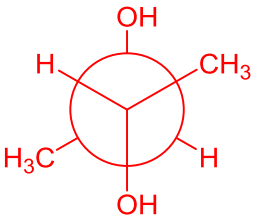
perspektivna formula



Newmanova formula

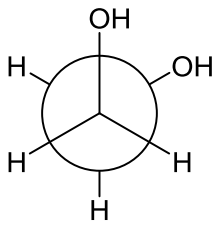
3.3.





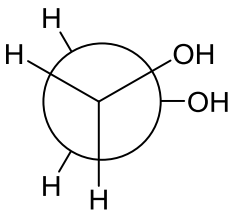
3.4.

(a)



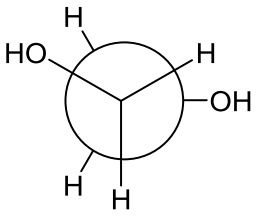
kosa (zvjezdasta) konformacija

(b)



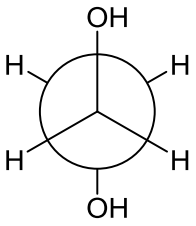
potpuno zasjenjena konformacija

(c)



zasjenjena konformacija

(d)

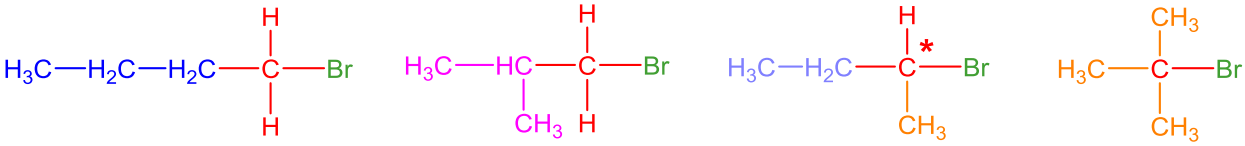


anti-zvjezdasta konformacija

(d) (a) (c) (b)

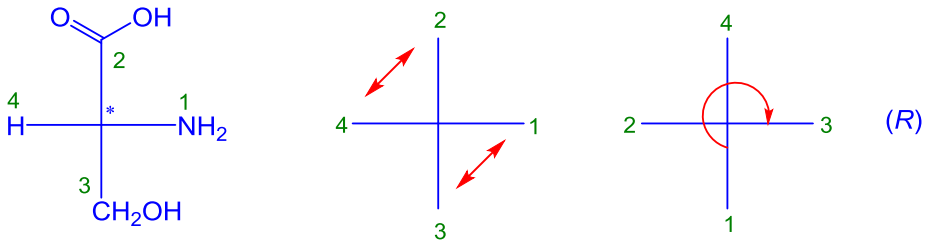
energija

3.5.

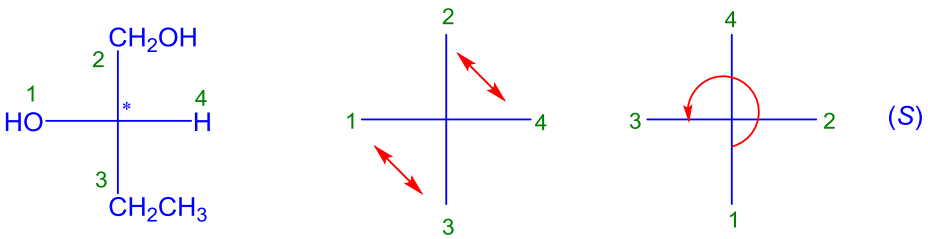


3.6.

(a)

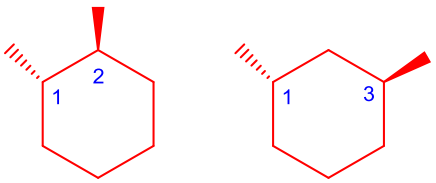


(b)



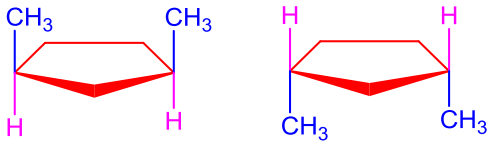
3.7.

(a)



KONSTITUCIJSKI IZOMERI

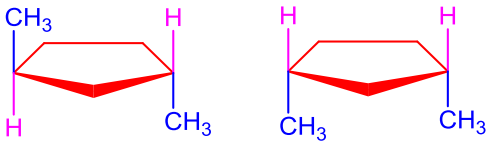
(b)



cis *cis*

ISTI SPOJEVI

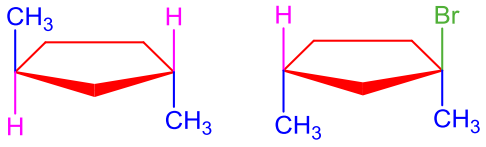
(c)



trans *cis*

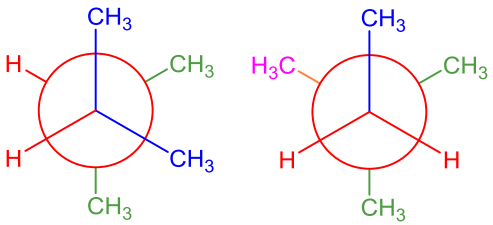
DIJASTEREOMERI

(d)



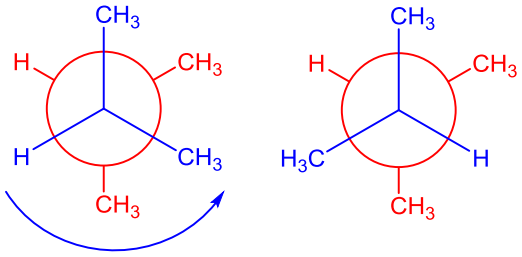
NISU U IZOMERNOM ODNOSU

(e)



KONSTITUCIJSKI IZOMERI

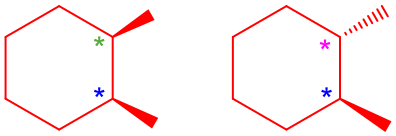
(f)



KONFORMACIJSKI IZOMERI

3.8.

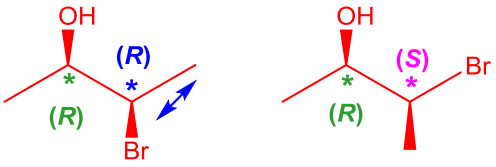
(a)



jednostruka zamjena mijenja konfiguraciju!

DIJASTEREOMERI

(b)

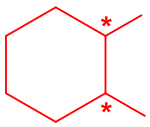


jednostruka zamjena mijenja konfiguraciju!

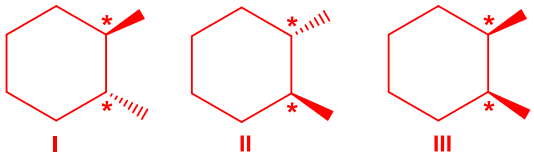
DIJASTEREOMERI

3.9.

(a)

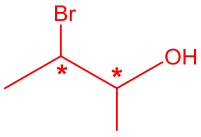


broj mogućih stereoizomera
$2^2 = 4$

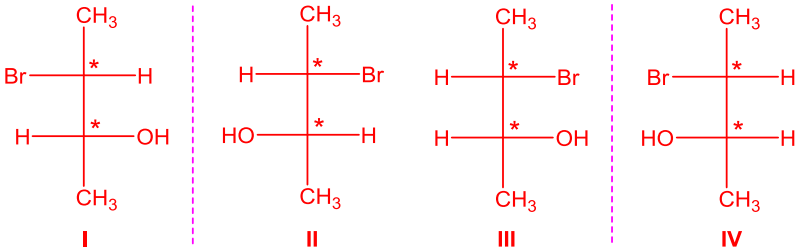


enantiomeri: **I** i **II** (kiralni, optički aktivni)
dijastereomeri: **I** i **III**, **II** i **III**
meso-oblik: **III** (akiralan, optički inaktivan)

(b)



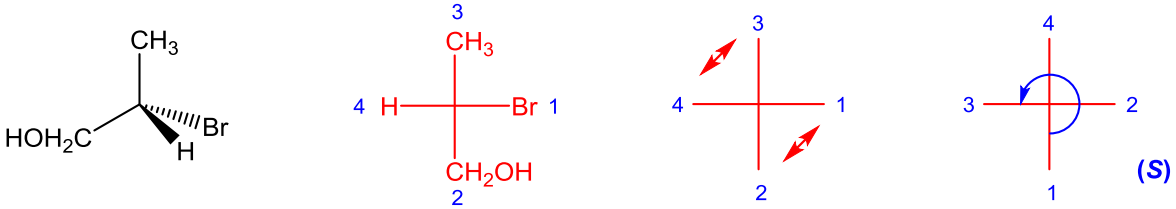
broj mogućih stereoizomera
$2^2 = 4$



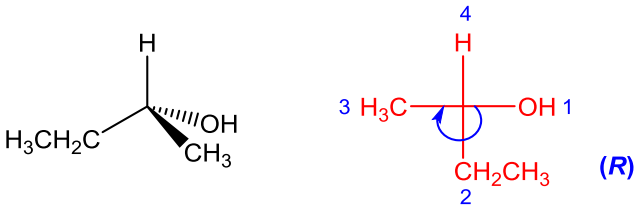
enantiomeri: **I** i **II**, **III** i **IV** (kiralni, optički aktivni)
dijastereomeri: **I** i **III**, **II** i **III**, **I** i **IV**, **II** i **IV**

3.10.

(a)

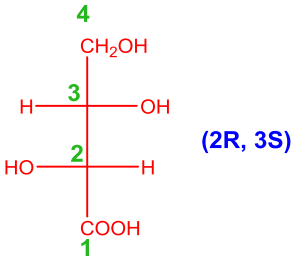


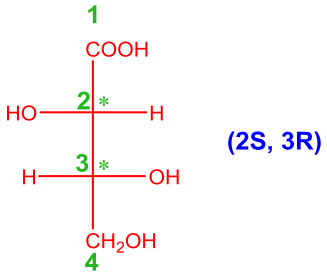
(b)

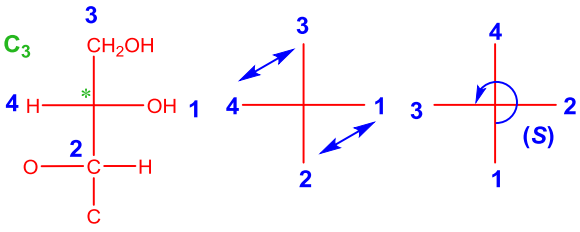


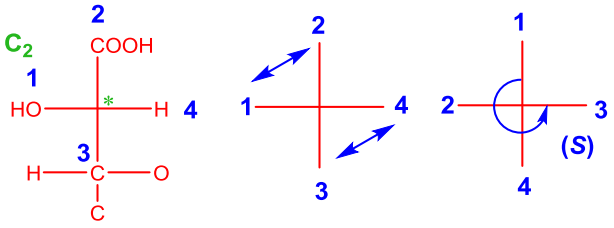
3.11.

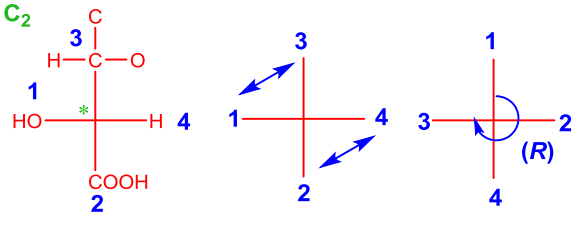
(a)

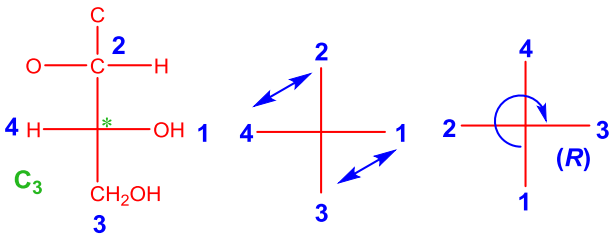






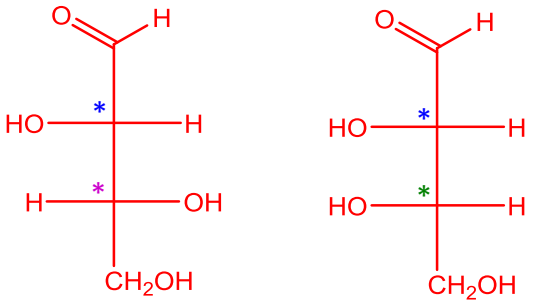






ENANTIOMERI

(b)



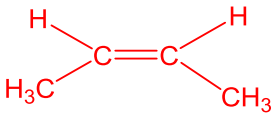
Konfiguracija gornjeg kiralnog centra je nepromijenjena.

Jednostruka zamjena na kiralnom centru mijenja njegovu konfiguraciju

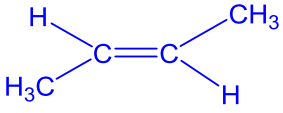
DIJASTEREOMERI

3.12.

(a)

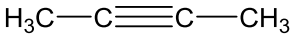


cis



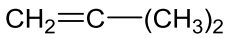
trans

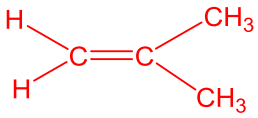
(b)



oko trostruke veze
nema *cis/trans*-izomerije

(c)



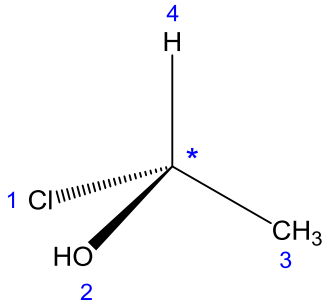


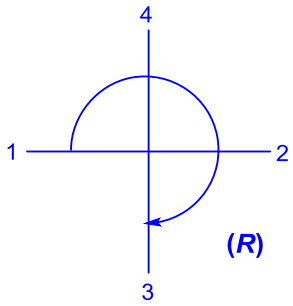
na krajnjim C-atomima vezane iste skupine - nema *cis/trans*-izomerije

3.13. (a) konstitucijski izomeri, (b) *cis/trans* izomeri, (c) *cis/trans* izomeri, (d) konstitucijski izomeri, (e) konstitucijski izomeri, (f) isti spojevi.

3.14.

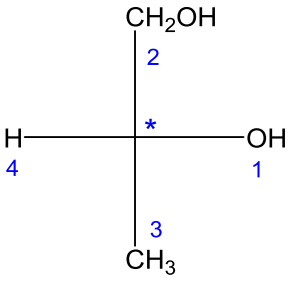
(a)

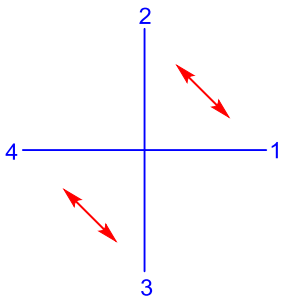


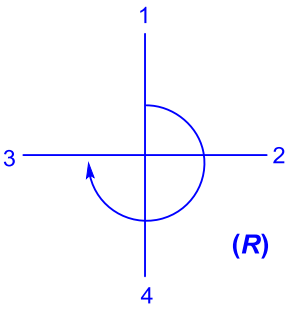


kiralan

(b)

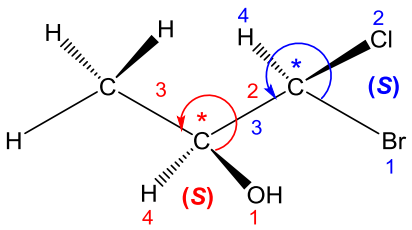






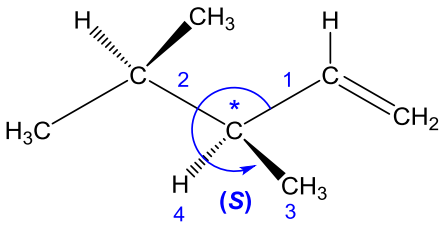
kiralan

(c)



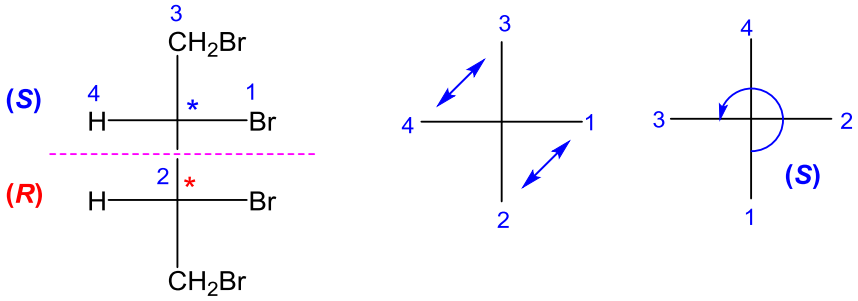
kiralan

(d)



kiralan

(e)

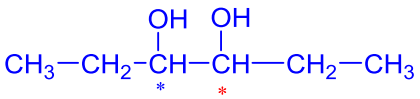


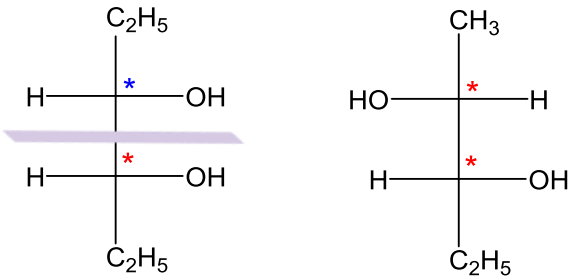
akiralan (*meso*)

3.15. (a) optički inaktivna (dva kiralna centra, ravnina simetrije, *meso*-oblik), (b) optički aktivna (dva kiralna centra, nema ravninu simetrije), (c) optički aktivna (jedan kiralni centar, nema ravninu simetrije), (d) optički inaktivna (dva kiralna centra, ravnina simetrije, *meso*-oblik), (e) optički inaktivna (nema kiralnih centara).

3.16.

(a)





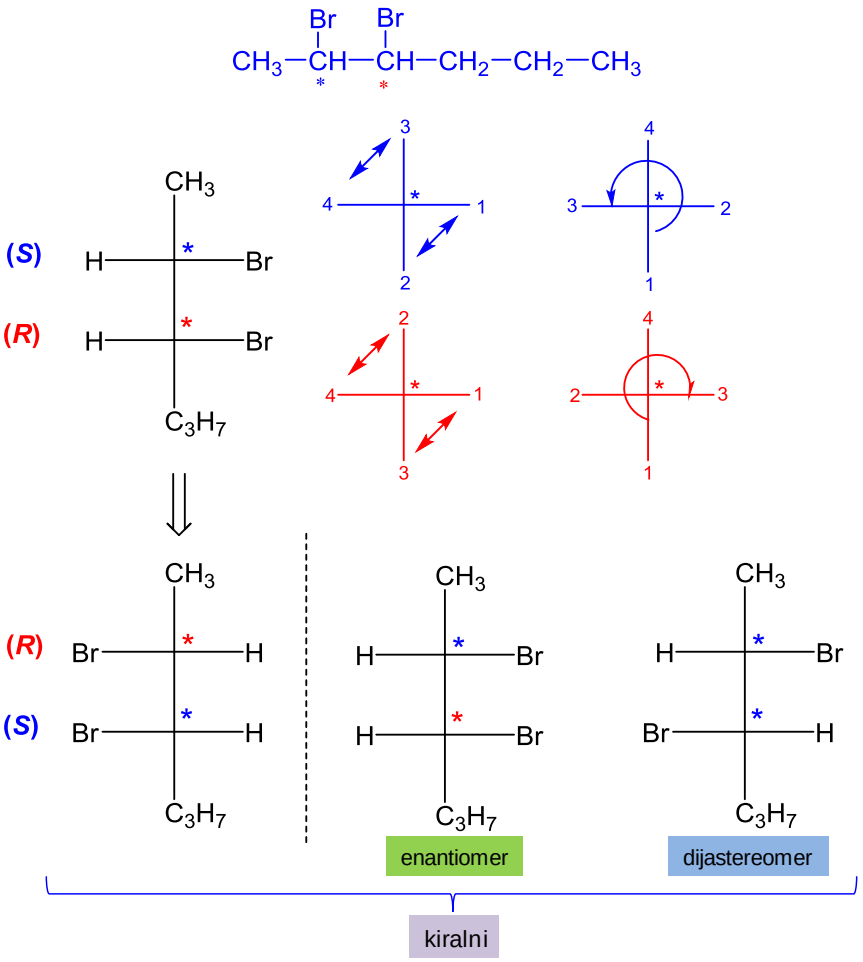
meso

akiralan

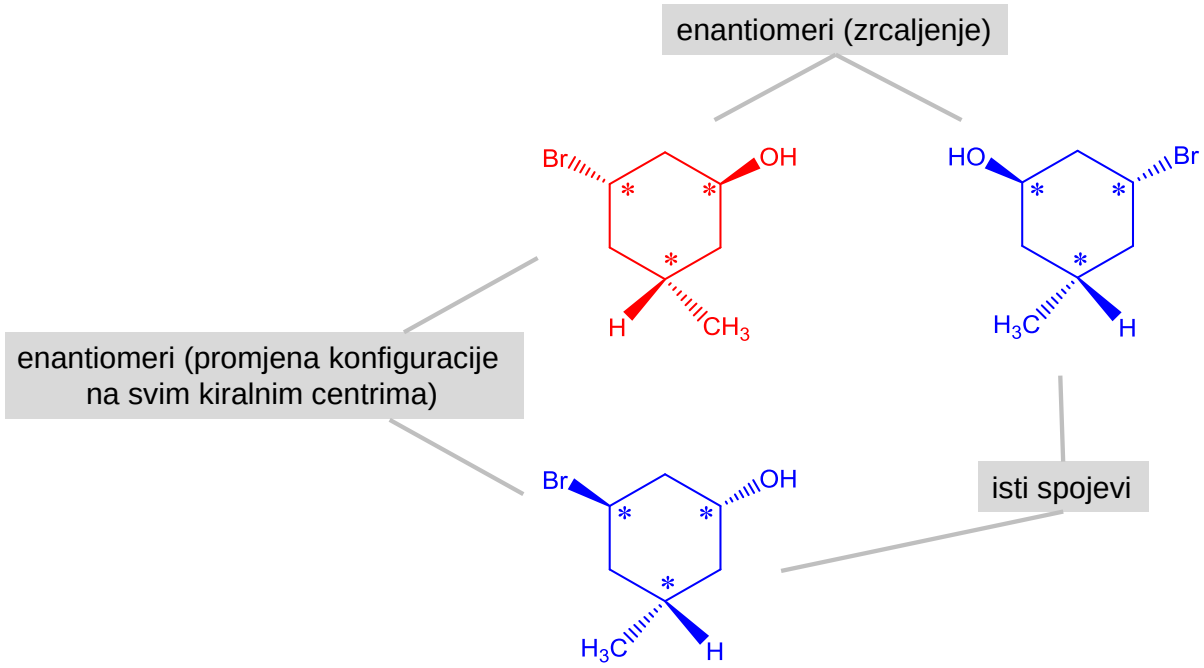
dijastereomer

kiralan

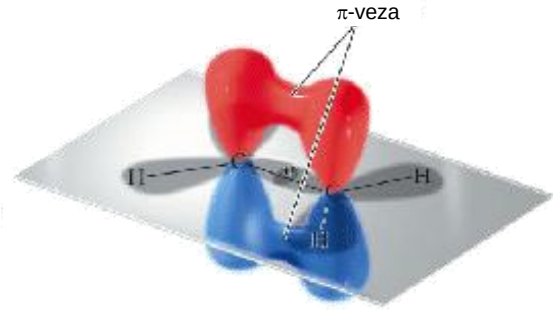
(b)


Br Br
CH3—CH—CH—CH2—CH2—CH3
(S)
(R)
CH3
H
Br
C3H7
(R)
(S)
enantiomer
dijastereomer
kiralni

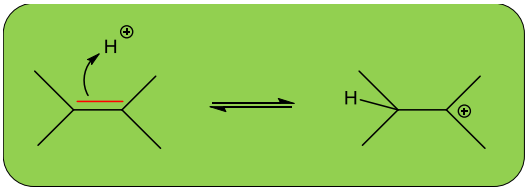
3.17.

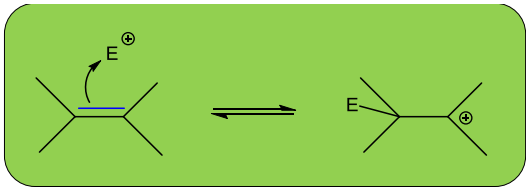

enantiomeri (zrcaljenje)
enantiomeri (promjena konfiguracije na svim kiralnim centrima)
isti spojevi
Br
OH
H
CH3
HO
Br
H3C
H
Br
OH
H3C
H

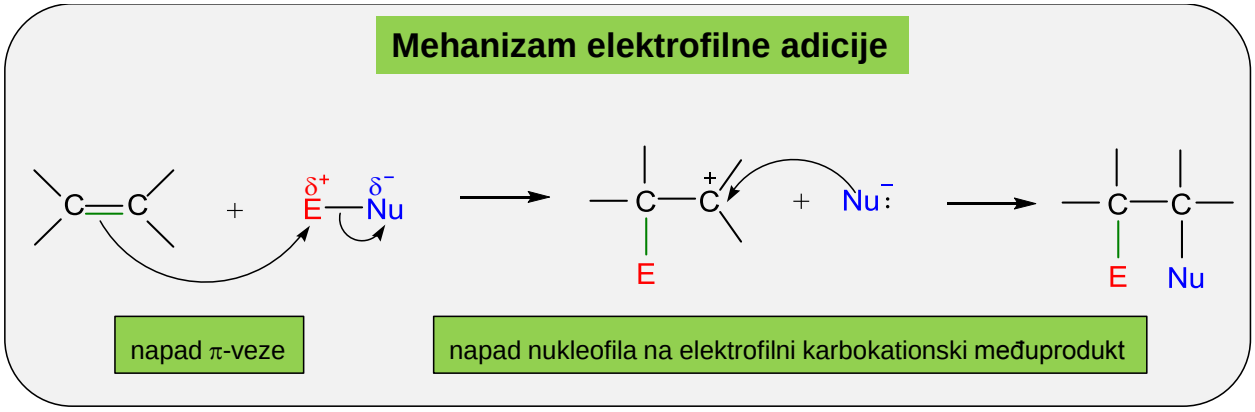
4. Alkeni – elektrofilna adicija



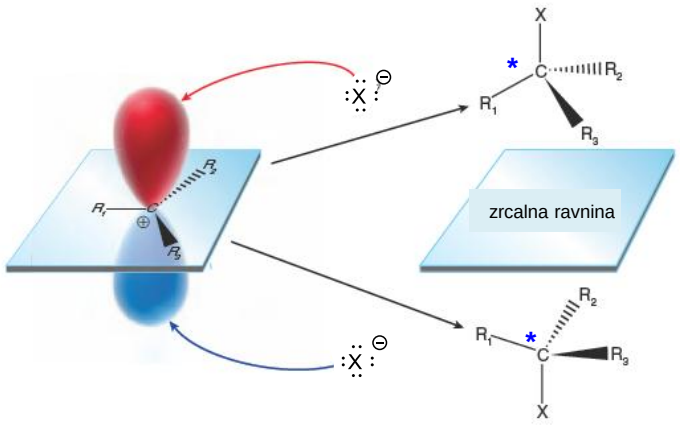
Dvostruka veza u alkenima predstavlja funkcijsku skupinu. π-Veza ima svojstva slabe baze i slabog nukleofila.







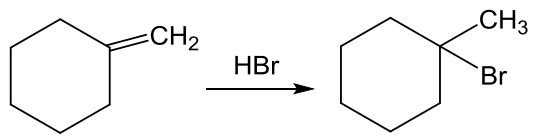
Stereokemijski ishod reakcije: nukleofil napada planarni karbokation s obje strane njegove ravnine s podjednakom vjerojatnošću. Najčešće dolazi do tvorbe dvaju enantiomernih produkata u jednakim količinama – **racemizacija**!



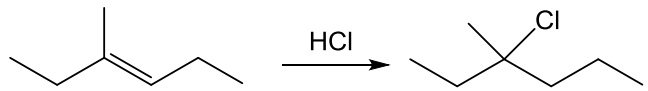
Zadaci

4.1. Predložite reakcijske mehanizme sljedećih pretvorbi.

(a)



(b)

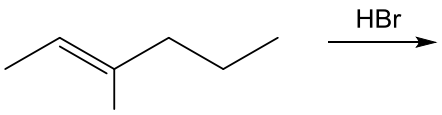


4.2. Predložite pripravu 2-brom-4-metilpentana **(B)** te 1-brom-4-metilpentana **(C)** iz odgovarajućeg alkena **(A)**, uz prikaz odgovarajućih reakcijskih mehanizama.

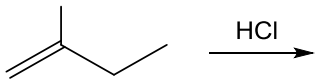
4.3. Prikažite reakciju hidrobromiranja 3-metilbut-2-ena **(A)** kojom se pripravlja sekundarni halogenalkan **B**. Prikažite strukturne formule dvaju konstitucijskih izomerâ halogenalkana **B**.

4.4. Predvidite stereokemijske ishode sljedećih pretvorbi:

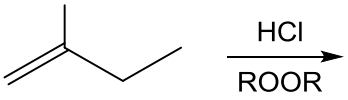
(a)



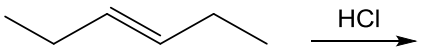
(b)



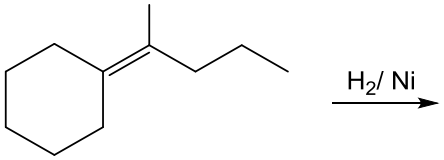
(c)



(d)

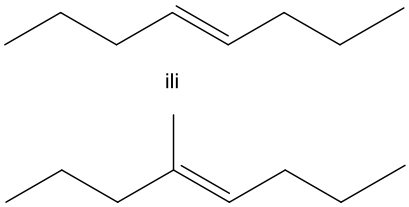


(e)



4.5. U prikazanim parovima označite alken koji je reaktivniji u reakciji kiselo-kataliziranog hidratiranja.

(a)



ili

(b) 2-metilbut-2-en

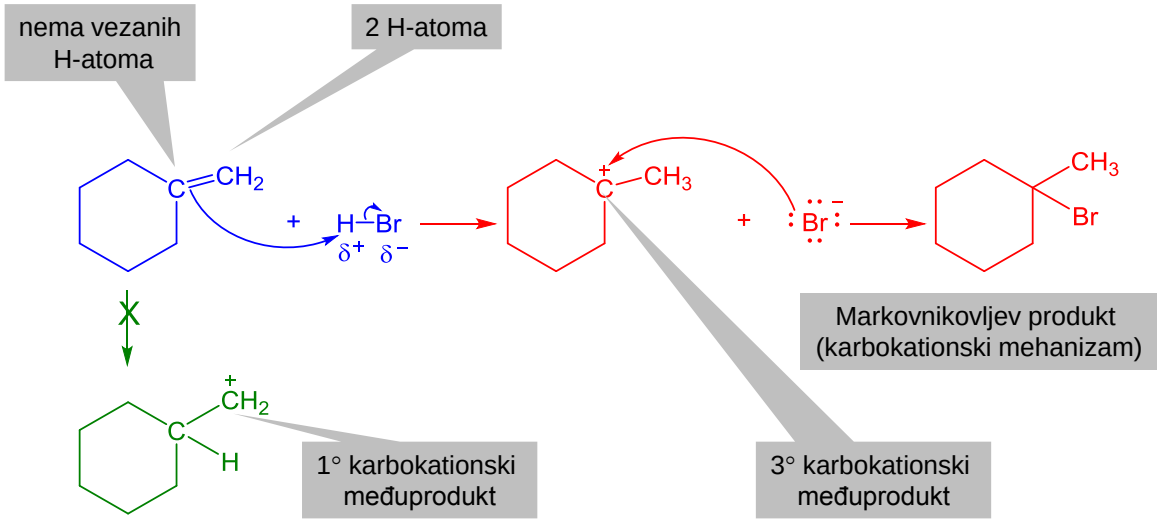
ili

3-metilbut-1-en

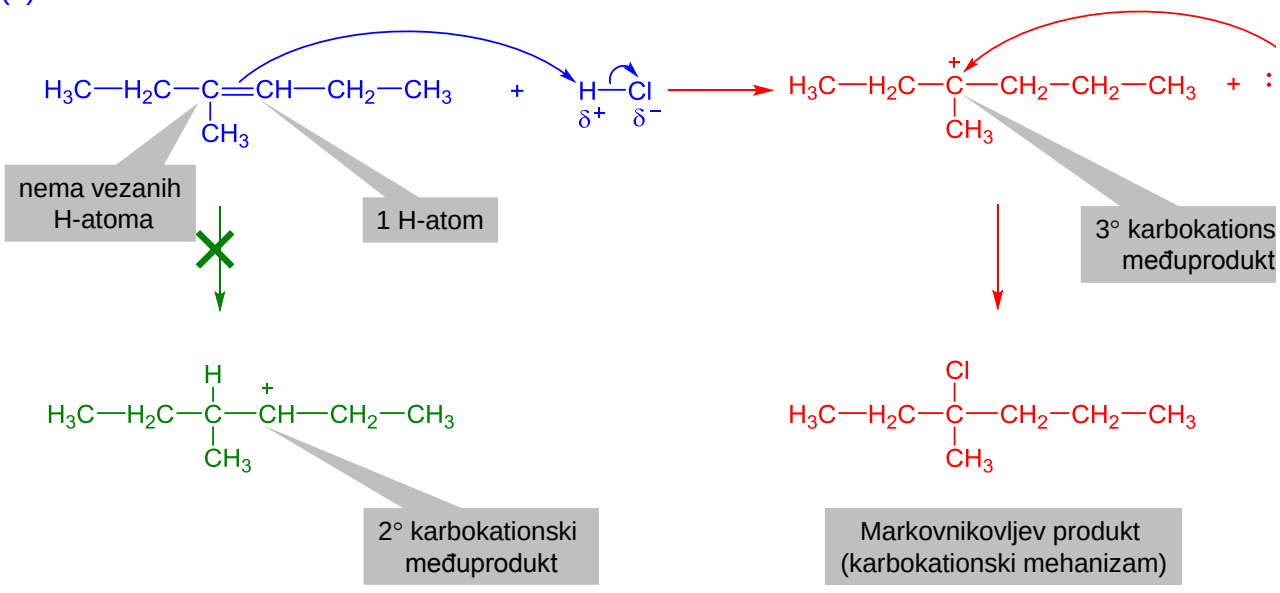
Rješenja

4.1.

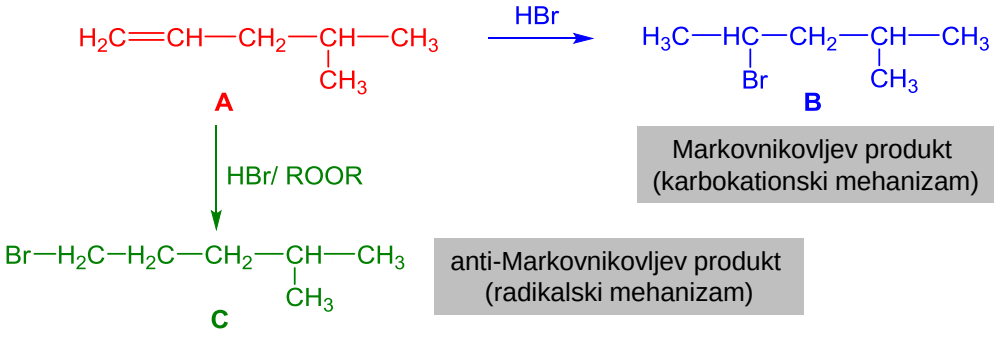
(a)



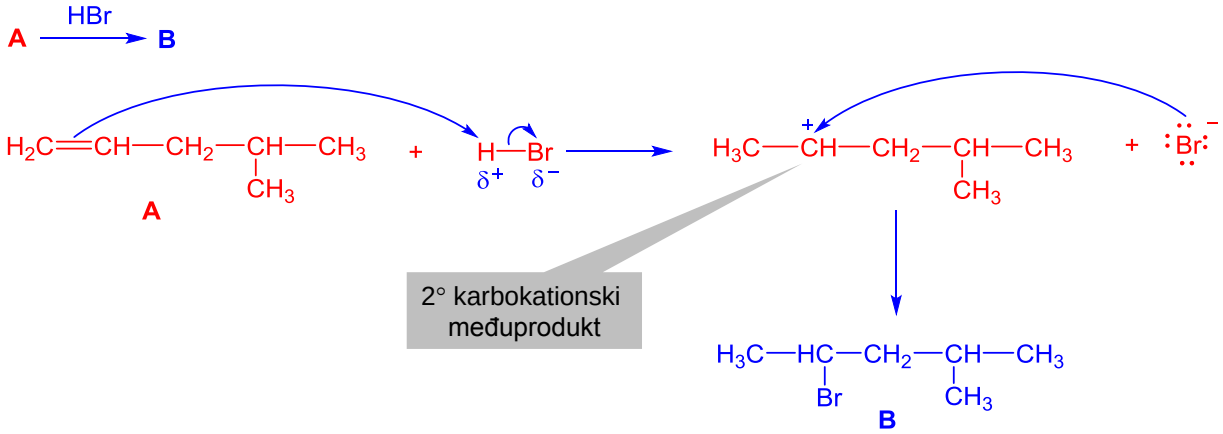
(b)



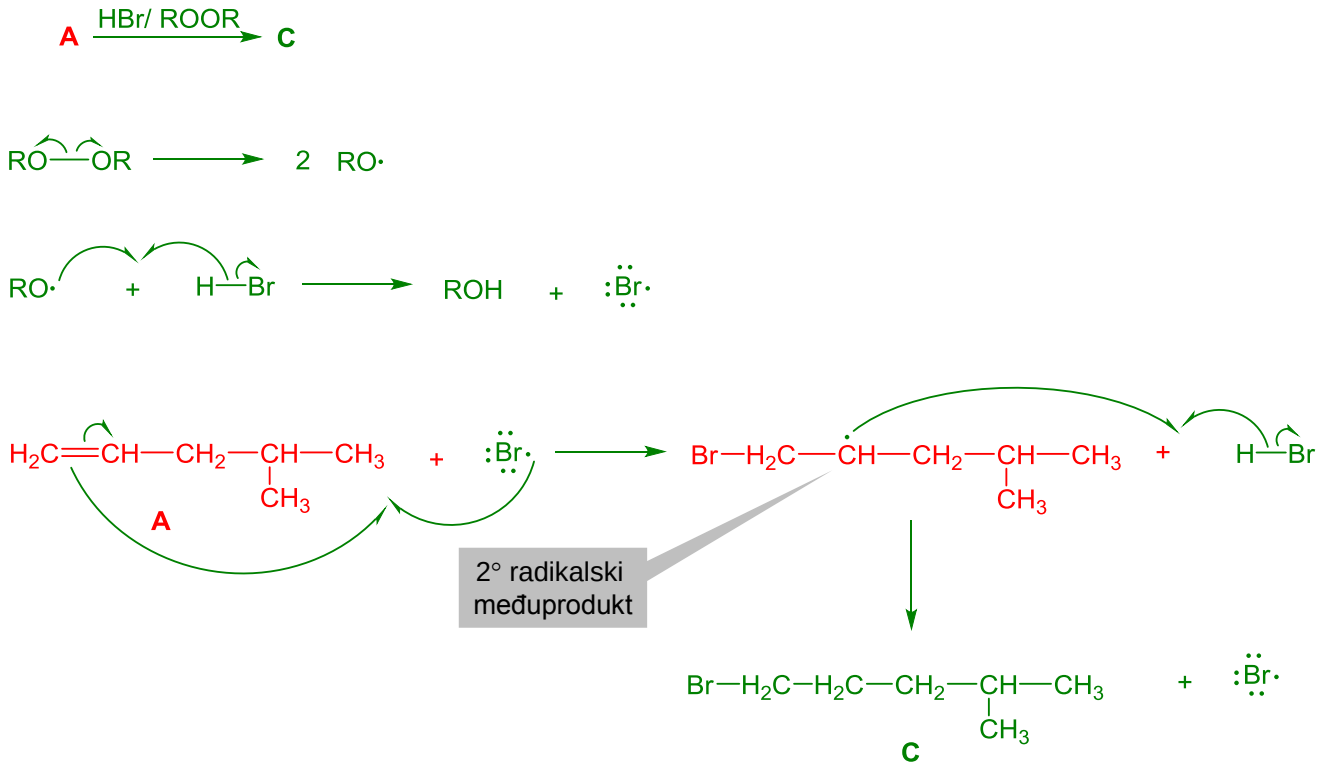
4.2.



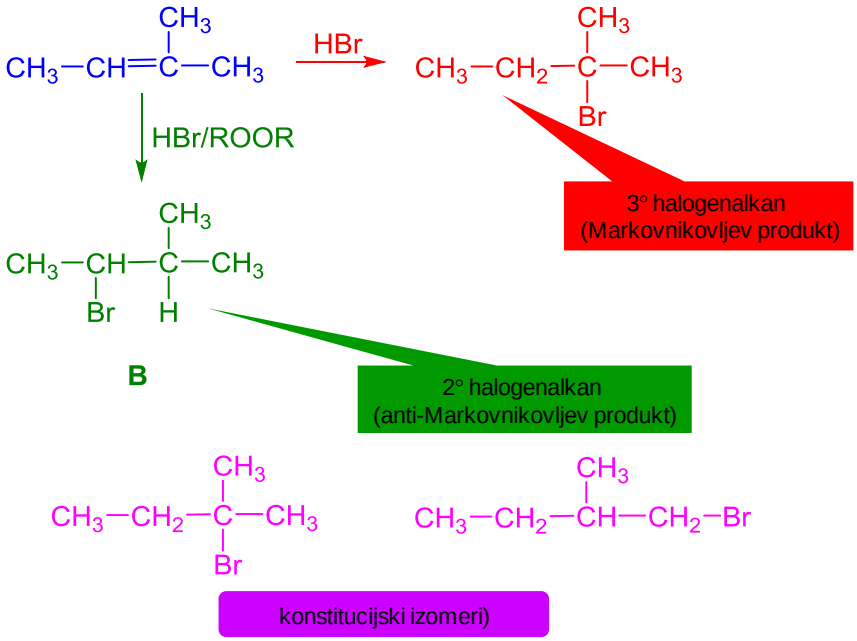
Mehanizam pretvorbe A→B



Mehanizam pretvorbe A→C

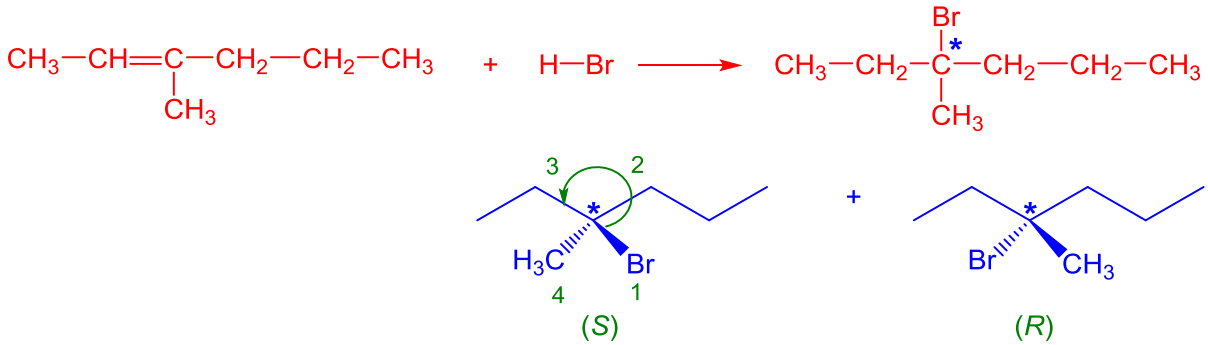


4.3.

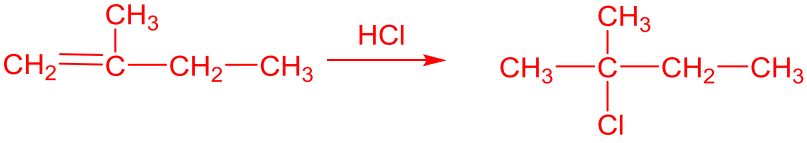


4.4.

(a)



(b)

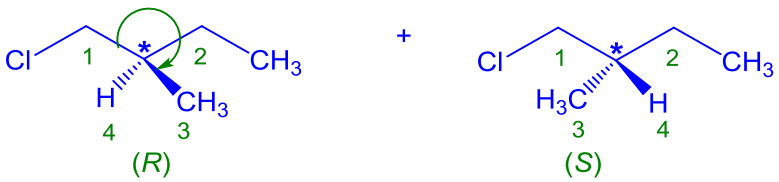


Akiralan spoj

Markovnikovljev produkt
(karbokationski mehanizam)

(c)

anti-Markovnikovljev produkt
(radikalski mehanizam)

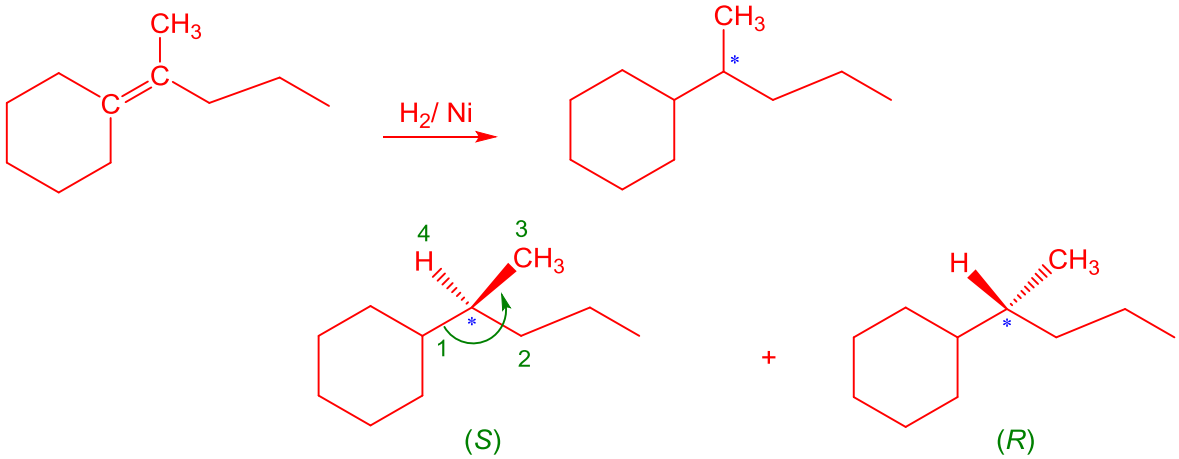


(d)


HCl
simetrični alken

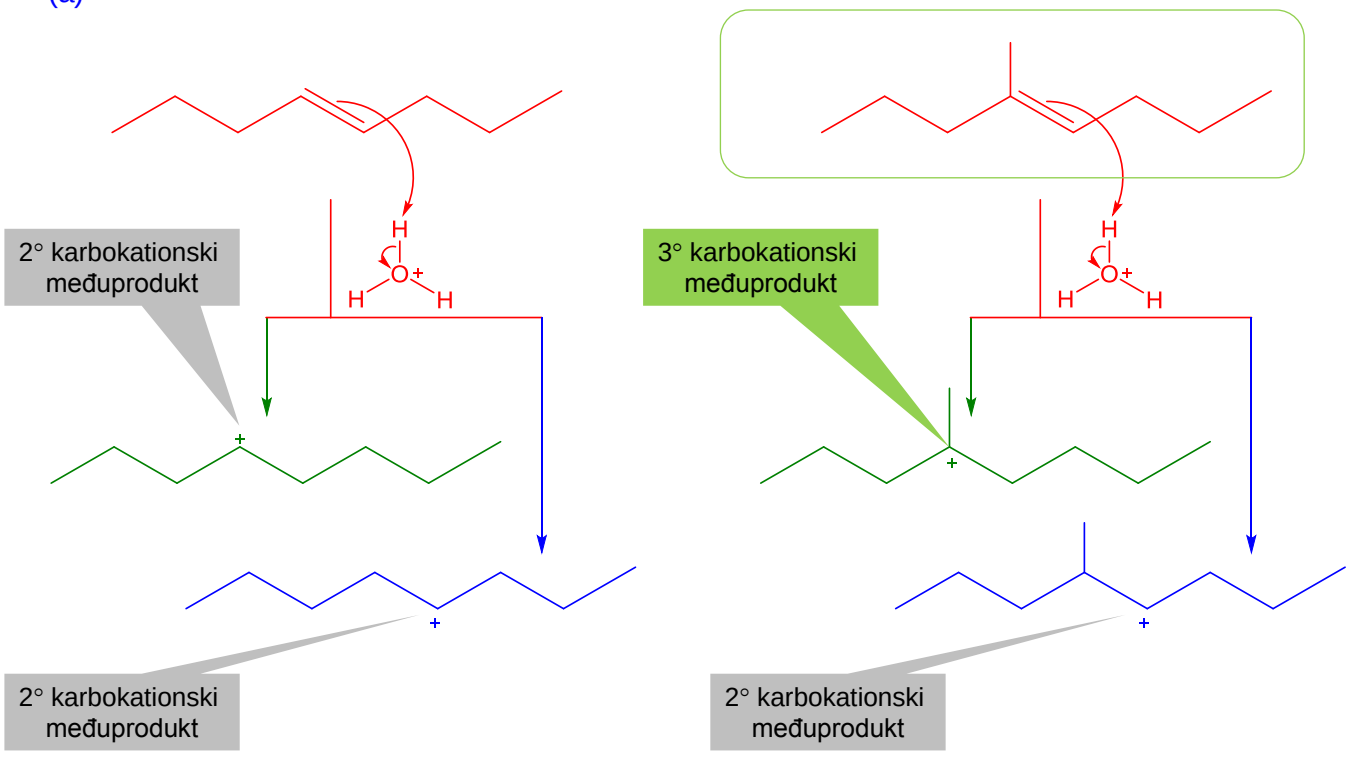

(R)
(S)

(e)

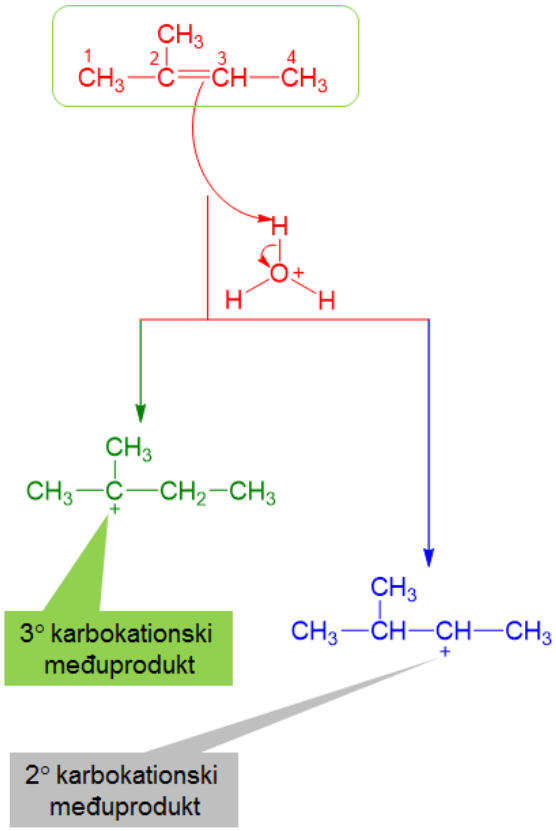

H2/ Ni
(S)
(R)

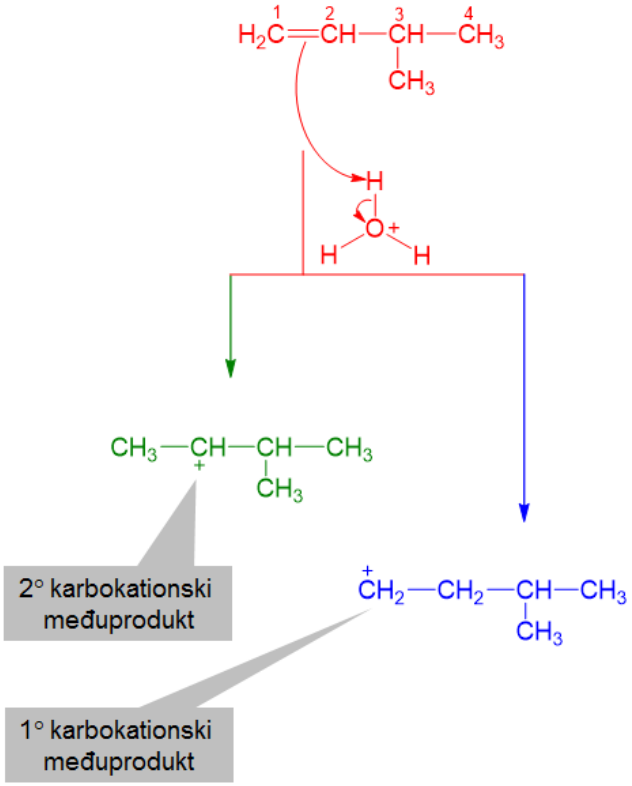
4.5.

(a)


2° karbokationski međuprodukt
3° karbokationski međuprodukt
2° karbokationski međuprodukt
2° karbokationski međuprodukt

(b)

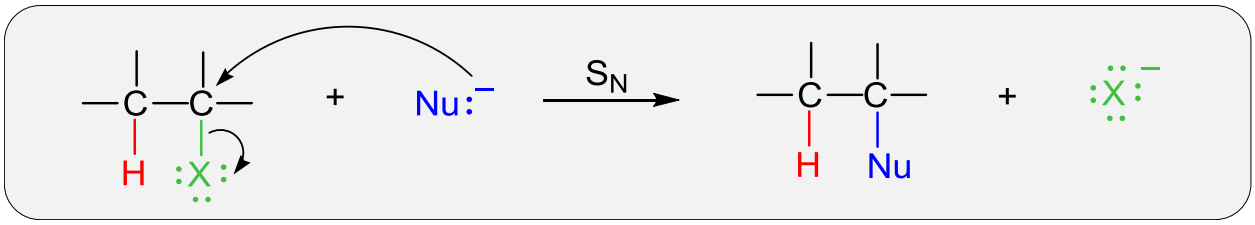

3° karbokationski međuprodukt
2° karbokationski međuprodukt


2° karbokationski međuprodukt
1° karbokationski međuprodukt

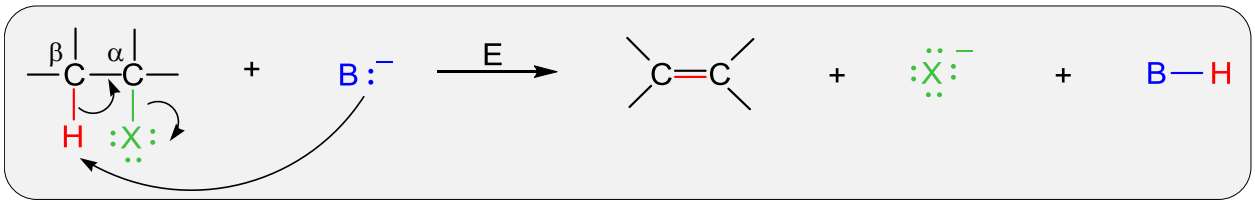
5. Halogenalkani. Nukleofilna supstitucija. Eliminacija.

Halogenalkani su organski spojevi u kojima je na sp^3-hibridizirani ugljikov atom vezan elektronegativni atom halogena, a podliježu reakcijama supstitucije (S_N) i/ili eliminacije (E).

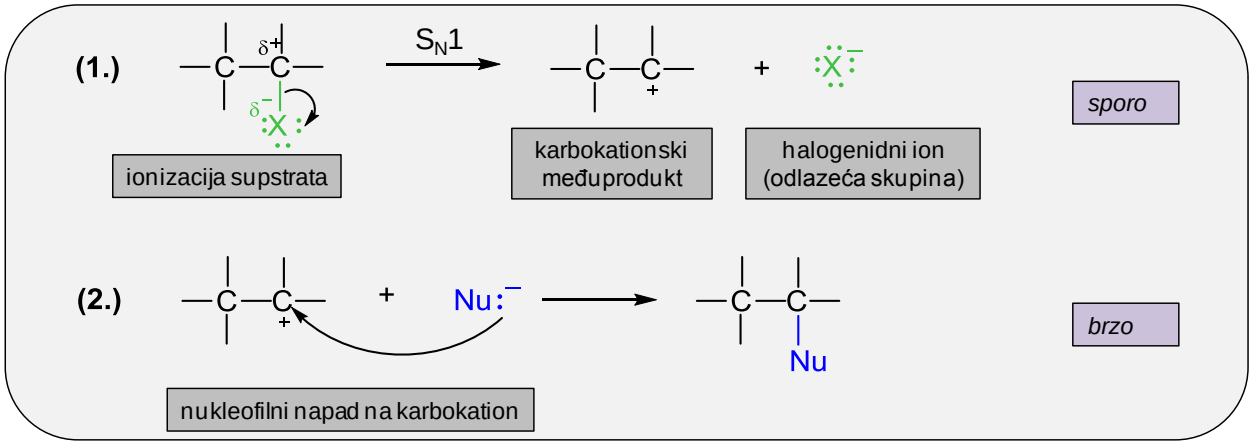
U supstitucijskim reakcijama halogenalkana, elektronegativni atom halogena X (F, Cl, Br, I) zamjenjuje se (supstituira) drugim atomom ili skupinom (nukleofilom). Nukleofil koristi svoj nevezni elektronski par za tvorbu nove veze s C-atomom.



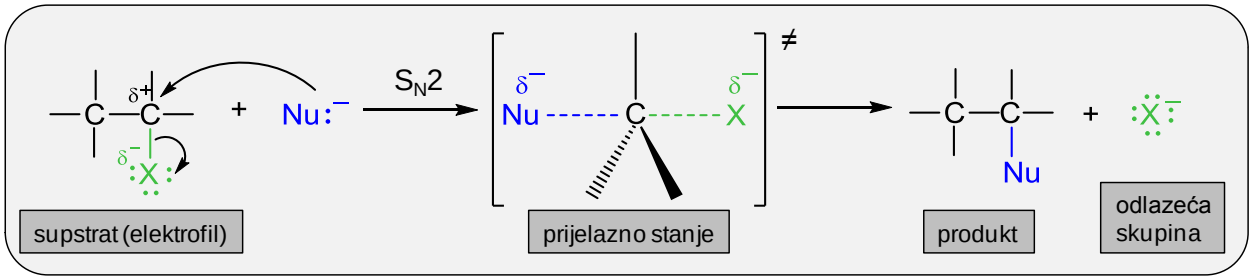
U reakcijama eliminacije, molekulu halogenalkana osim halogenog atoma X napušta i vodikov atom sa susjednog C_β-atoma uslijed akceptorskog utjecaja baze (dehidrohalogeniranje). Pri tom nastaje π-veza. Dakle, u reakcijama eliminacije reagens ima svojstvo baze (proton-akceptora).



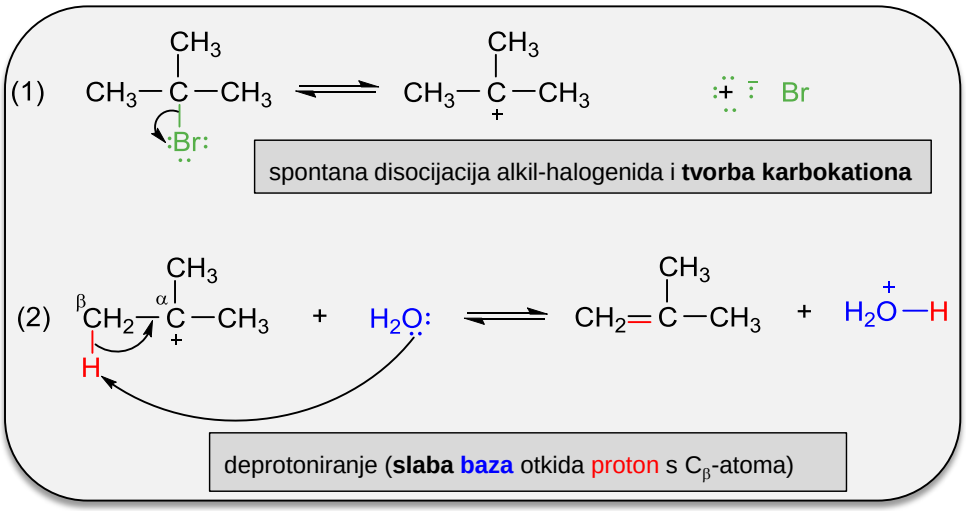
S_N1-reakcija (dvostupanjska, monomolekulska)



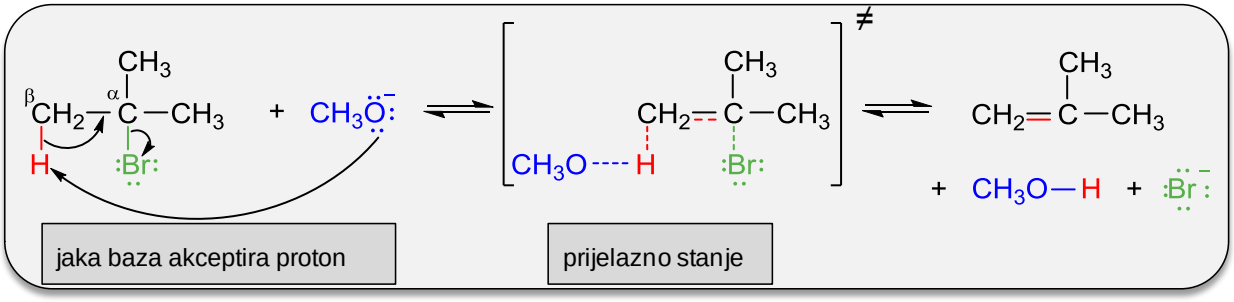
S_N2-reakcija (jednostupanjska, bimolekulska)



E1-reakcija (dvostupanjska, monomolekulska)

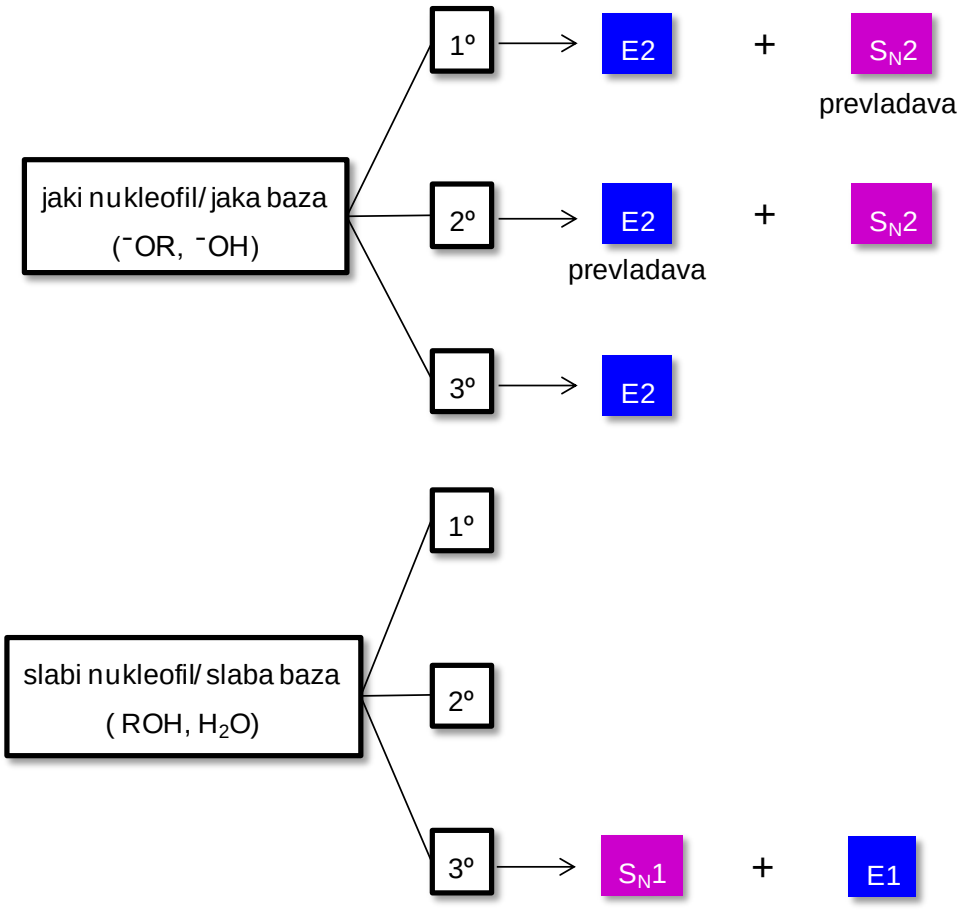


E2-reakcija (jednostupanjska, bimolekulska)



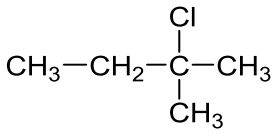
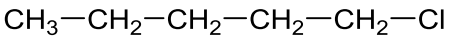
	Regiokemijski ishod	Stereokemijski ishod
S_N2	nukleofil napada C_α-atom na kojeg je vezana odlazeća skupina	nukleofil supstituira odlazeću skupinu uz inverziju konfiguracije
S_N1	nukleofil napada karbokation nastao nakon odcjepljenja odlazeće skupine	nukleofil supstituira odlazeću skupinu uz racemizaciju
E2	općenito prevladava Zajcevljev produkt (Hofmannov produkt je favoriziran u prisutnosti voluminozne baze)	stereoselektivna i stereospecifična reakcija; favoriziran je *trans*-disupstituirani alken.
E1	uvijek prevladava Zajcevljev produkt	stereoselektivna reakcija; favoriziran je *trans*-disupstituirani alken

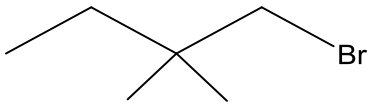
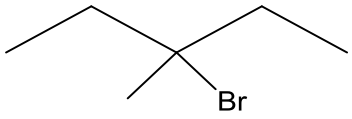
Procjena dolazi li do supstitucije ili eliminacije

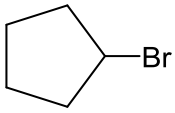
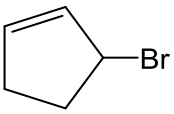


Zadaci

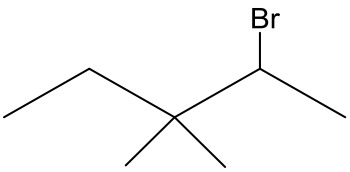
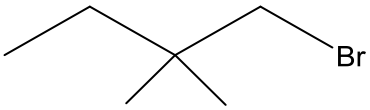
5.1. Koji će član u prikazanim parovima brže reagirati u S_N1 reakcijama?

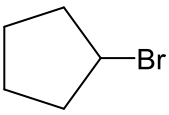
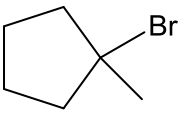
(a)  ili 

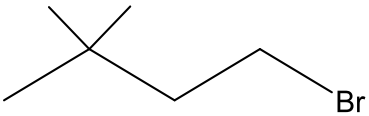
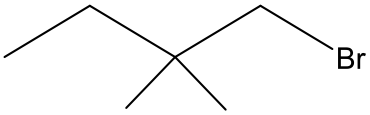
(b)  ili 

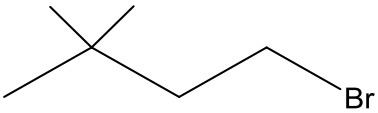
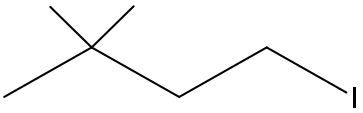
(c)  ili 

5.2. Koji će član u prikazanim parovima brže reagirati u S_N2 reakcijama?

(a)  ili 

(b)  ili 

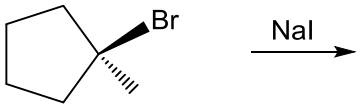
(c)  ili 

(d)  ili 

5.3. Označite prikazana otapala kao protična ili aprotična.

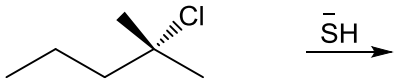
otapalo	**DMF**	**DMSO**	**voda**	**etanol**	**amonijak**
protično					
aprotično					

5.4. Predvidite reakcijski mehanizam i prikažite stereokemijski ishod sljedeće reakcije:

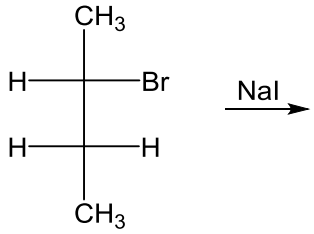


5.5. Prikažite produkte sljedećih supstitucijskih reakcija:

(a)

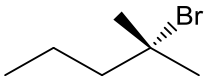


(b)

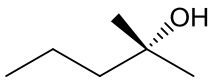


5.6. Objasnite je li potrebno prethodno protoniranje za provođenje S_N1 reakcija na prikazanim supstratima.

(a)



(b)

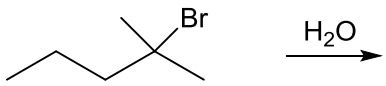


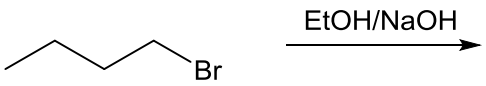
5.7. Favoriziraju li prikazani nukleofili S_N1 ili S_N2 reakciju?

(a) $CH_3—OH$ (b) $CH_3—CH_2—SH$ (c) $Na—CN$

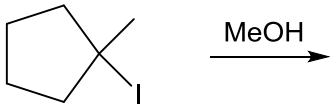
(d) $Na—OH$ (e) $CH_3—\bar{O}$

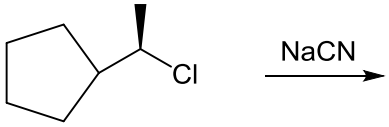
5.8. Predvidite mehanizme sljedećih supstitucijskih reakcija.

(a) 

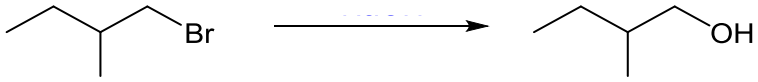
(b) 

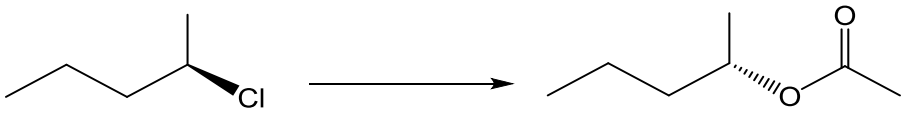
5.9. Objasnite odvijaju li se prikazane reakcije S_N1 ili S_N2 mehanizmom. Prikažite produkte tih reakcija.

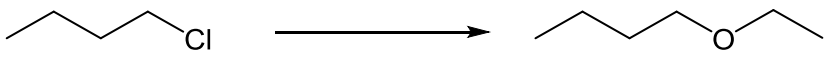
(a) 

(b) 

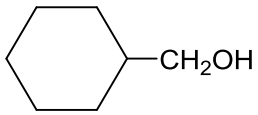
5.10. Napišite reagense potrebne za provođenje sljedećih reakcija:

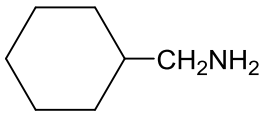
(a) 

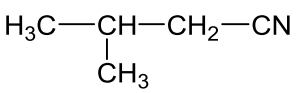
(b) 

(c) 

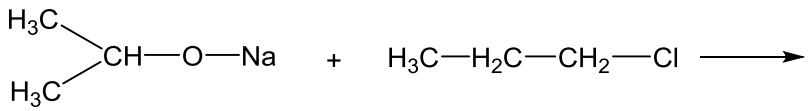
5.11. Predložite sintezu prikazanih spojeva S_N2-reakcijom iz odgovarajućih halogenalkana.

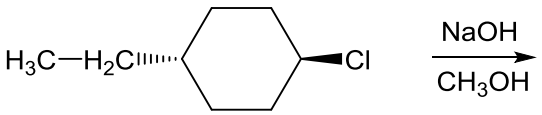
(a) 

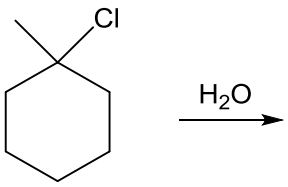
(b) 

(c) 

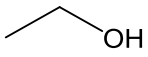
5.12. Napišite produkte prikazanih supstitucijskih reakcija. Pretpostavite o kojim se mehanizmima radi (S_N1 ili S_N2).

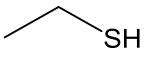
(a) 

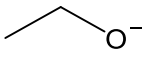
(b) 

(c) 

5.13. Za svaki od prikazanih spojeva navedite radi li se o jakom ili slabom nukleofilu, odnosno jakoj ili slaboj bazi.

(a) 

(b) 

(c) 

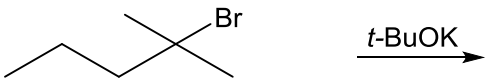
(d) Na−OEt

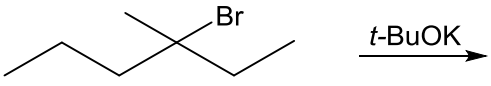
(e) Na—OH

(f) Br^-

5.14. Prikažite sve produkte koji bi mogli nastati u sljedećim E2-reakcijama:

(a) 

(b) 

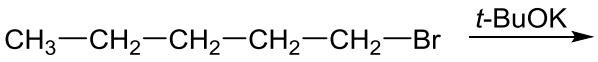
(c) 

5.15. Pretpostavite kojim će se mehanizmom odvijati reakcije 1-brompentana sa sljedećim nukleofilima: (a) NaOH, (b) NaSH, (c) *t*-BuOK.

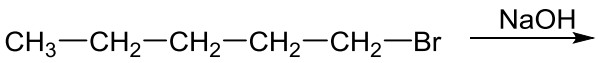
5.16. Pretpostavite kojim će se mehanizmom odvijati reakcije 3-brom-3-metilheksana sa sljedećim nukleofilima: (a) NaI, (b) NaOH, (c) *t*-BuOK, (d) NaOEt, (e) EtOH.

5.17. Navedite sve moguće produkte prikazanih reakcija i naznačite njihov udio u nastaloj smjesi (manje ili više):

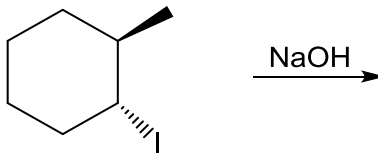
(a)



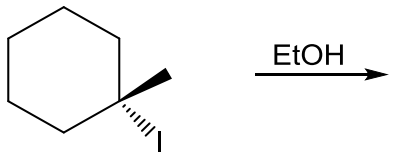
(b)



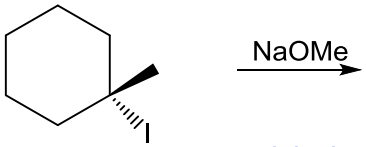
(c)



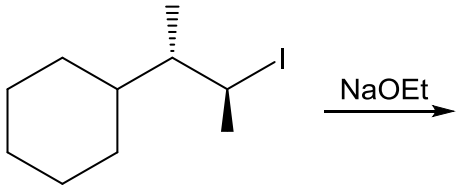
(d)



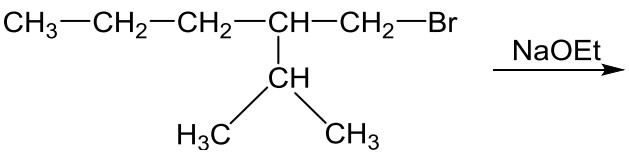
(e)



(f)

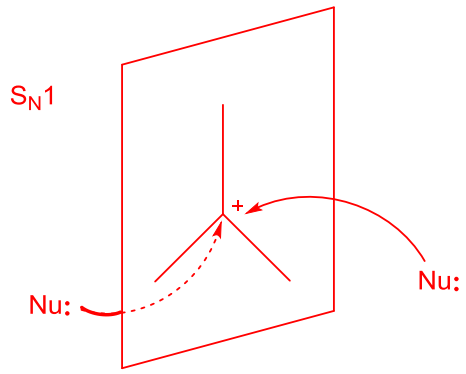


(g)

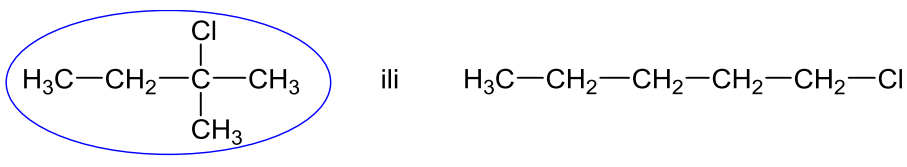


Rješenja

5.1.



(a)



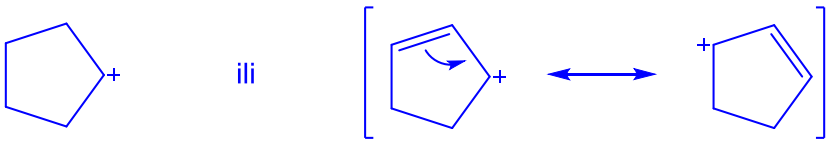
3° 1°

(b)

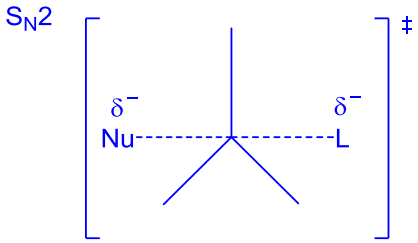
1° **3°**

(c)

2° 2°



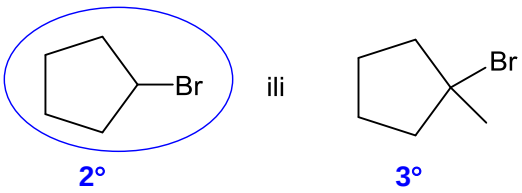
5.2.



(a)

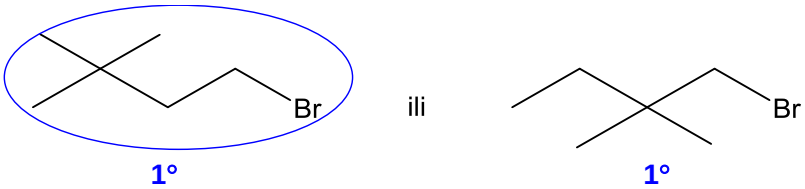
2° **1°**

(b)



2° **3°**

(c)



1° **1°**

manje razgranat u blizini reaktivnog središta

(d)

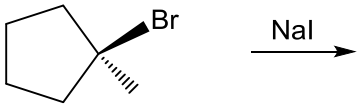
1° 1°

I^- je slabija baza (bolja odlazeća skupina) od Br^-

5.3.

otapalo	**DMF**	**DMSO**	**voda**	**etanol**	**amonijak**
protično			**+**	**+**	**+**
aprotično	**+**	**+**			

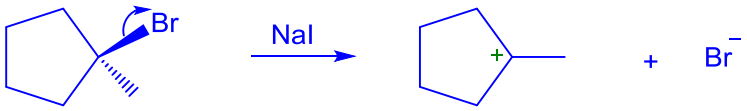
5.4.



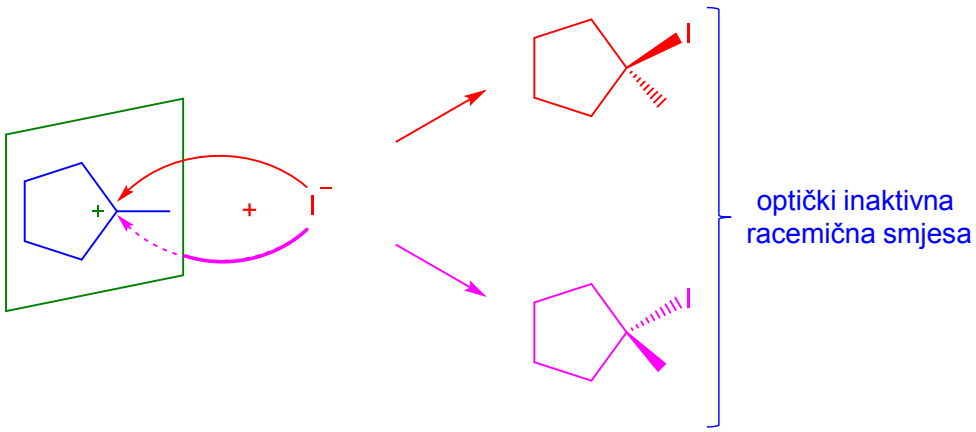
3° supstrat
(usmjerava prema S_N1)

jaki nukleofil
(jakost nukleofila nevažna za S_N1)

1.

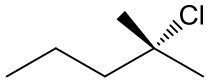


2.



5.5.

(a)

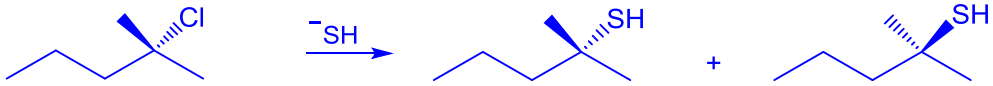


3° supstrat
(usmjerava prema S_N1)

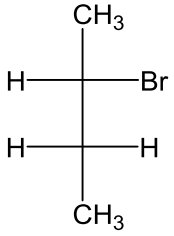
^-SH

jaki nukleofil
(jakost nukleofila nevažna za S_N1)

racemizacija



(b)

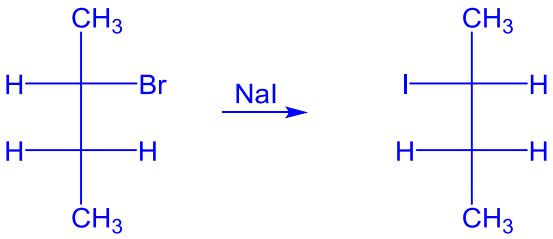


NaI

jaki nukleofil usmjerava prema S_N2

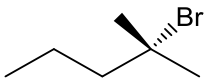
inverzija

2° supstrat
(moguć S_N1 i S_N2)



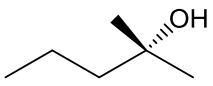
5.6.

(a)

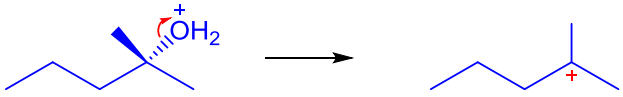


Ne. Br^- je dobra izlazna skupina (konjugirana baza jake kiseline, slaba baza).

(b)



H^+



Da. ^-OH je loša izlazna skupina (konjugirana baza slabe kiseline, jaka baza).

5.7.

(a) $CH_3—OH$ Slabi nukleofil (nenabijen) $\Rightarrow S_N1$

(b) $CH_3—CH_2—SH$ Jaki nukleofil (polarizabilan zbog veličine S-atoma) $\Rightarrow S_N2$

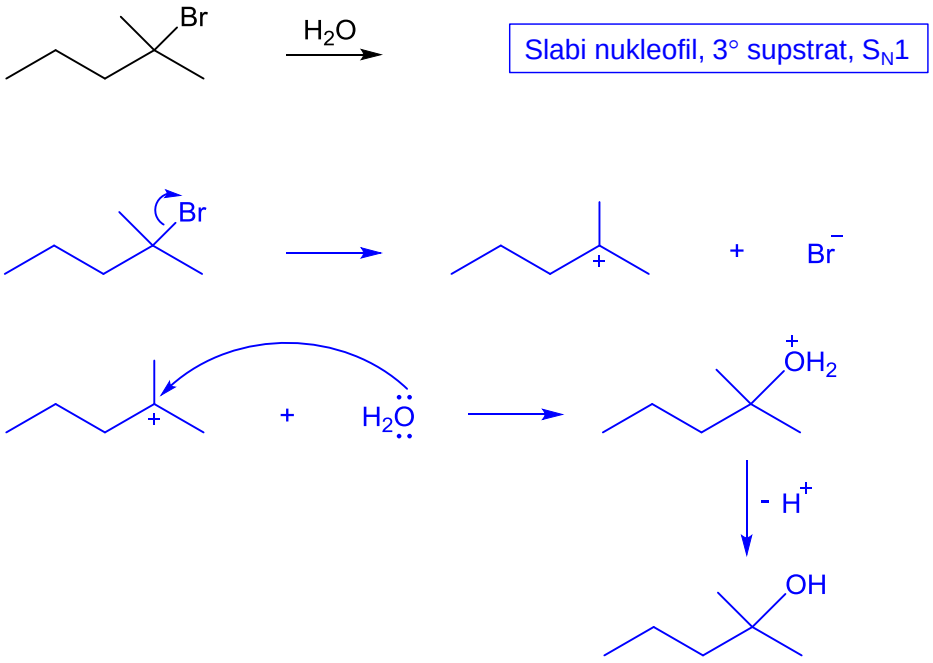
(c) $Na—CN$ Jaki nukleofil (^-CN) $\Rightarrow S_N2$

(d) $Na—OH$ Jaki nukleofil (^-OH) $\Rightarrow S_N2$

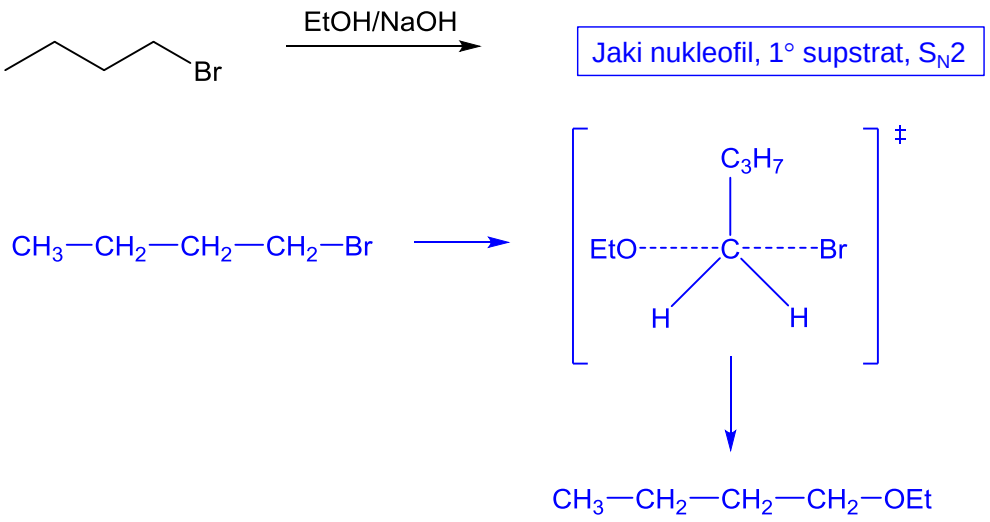
(e) $CH_3—\bar{O}$ Jaki nukleofil (nabijen) $\Rightarrow S_N2$

5.8.

(a)

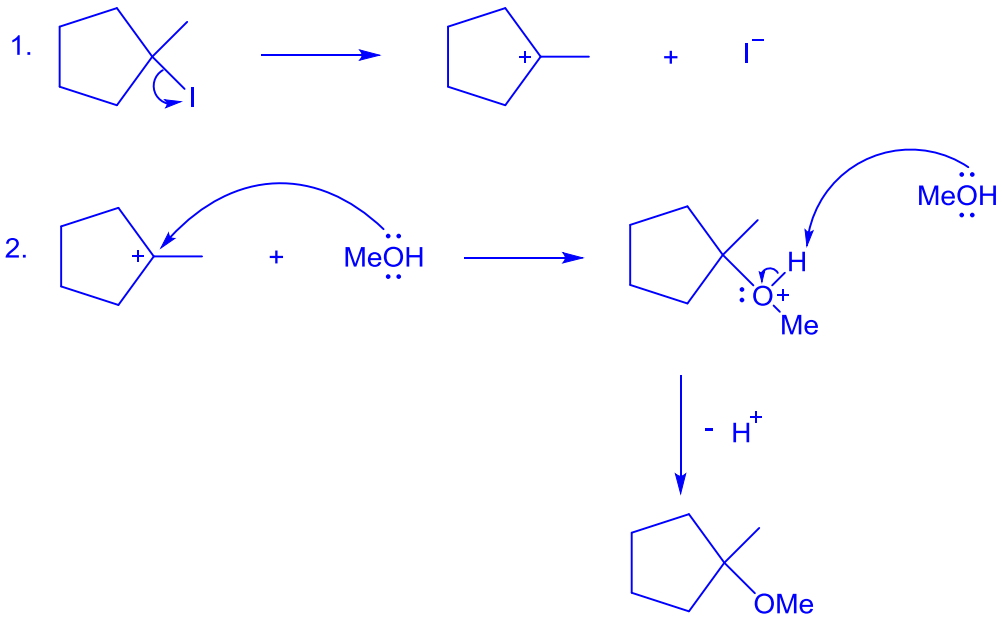


(b)

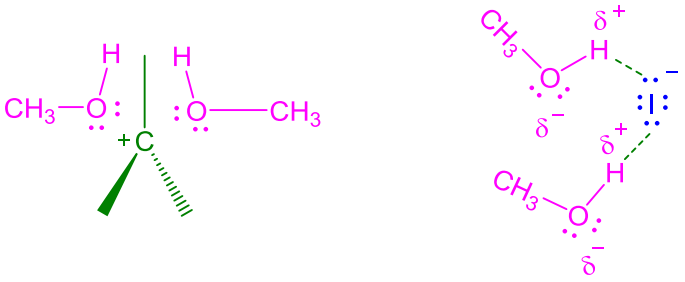


5.9.

(a)

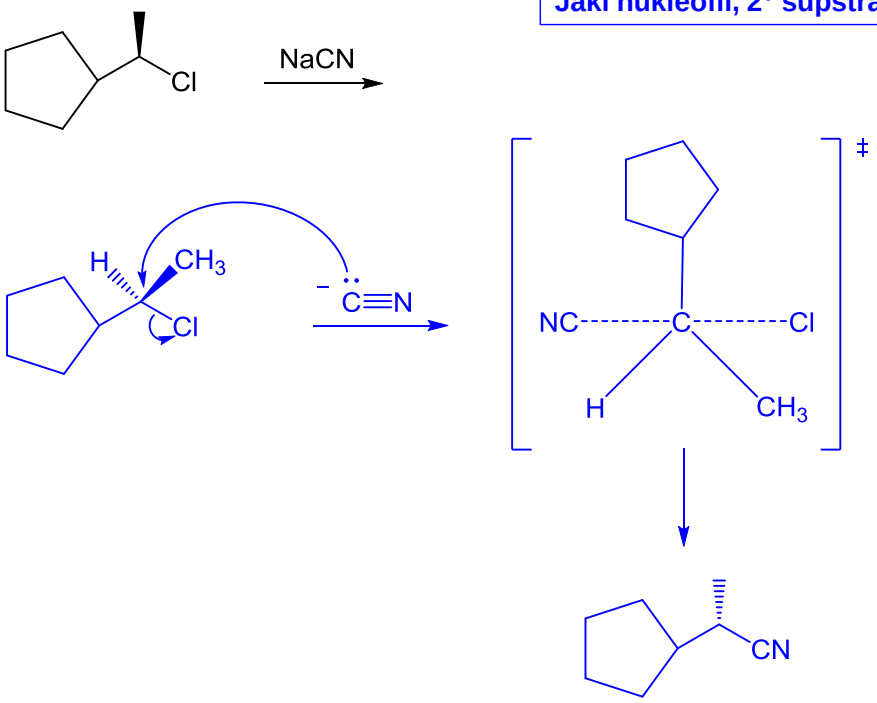


Polarno protično otapalo stabilizira i karbokationski međuprodukt i izlaznu skupinu.



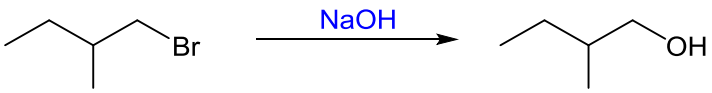
(b)

Jaki nukleofil, 2° supstrat, S_N2



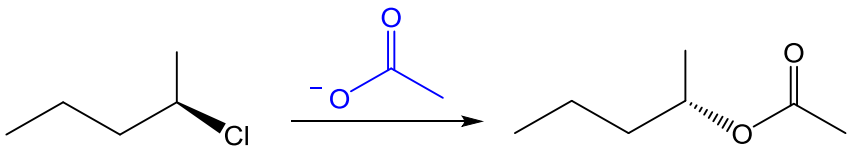
5.10.

(a)



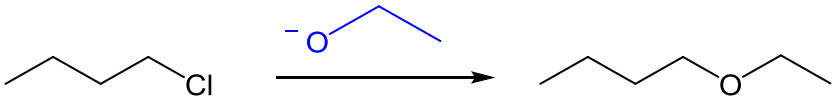
1° supstrat ⇒ S_N2 ⇒ jaki nukleofil

(b)



2° supstrat, inverzija konfiguracije ⇒ S_N2 ⇒ jaki nukleofil

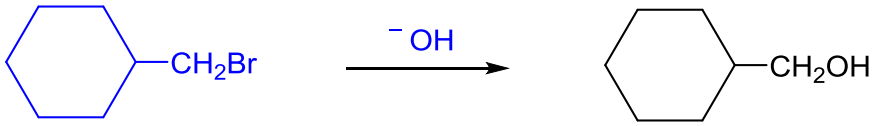
(c)



1° supstrat ⇒ S_N2 ⇒ jaki nukleofil

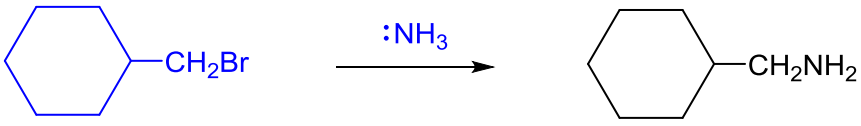
5.11.

(a)



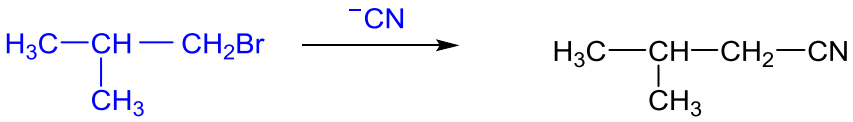
1° supstrat ⇒ S_N2 ⇒ jaki nukleofil

(b)



1° supstrat ⇒ S_N2 ⇒ jaki nukleofil (N je manje elektronegativan od O te je stoga NH_3 jači nukleofil od npr. H_2O).

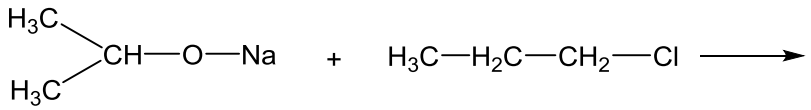
(c)



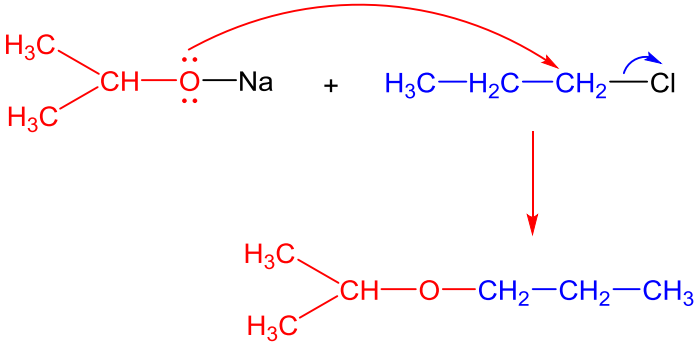
1° supstrat ⇒ S_N2 ⇒ jaki nukleofil

5.12.

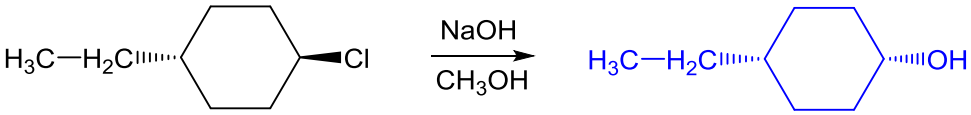
(a)



1° supstrat, jaki nukleofil ⇒ S_N2

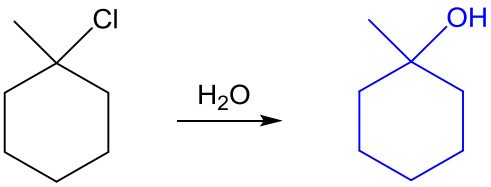


(b)



2° supstrat, jaki nukleofil ⇒ S_N2 ⇒ inverzija konfiguracije

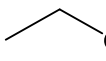
(c)



3° supstrat, slabi nukleofil ⇒ S_N1

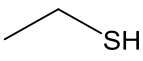
5.13.

(a)



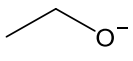
slabi nukleofil, slaba baza

(b)



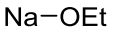
jaki nukleofil (polarizabilnost), slaba baza

(c)



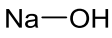
jaki nukleofil, jaka baza

(d)



jaki nukleofil, jaka baza

(e)



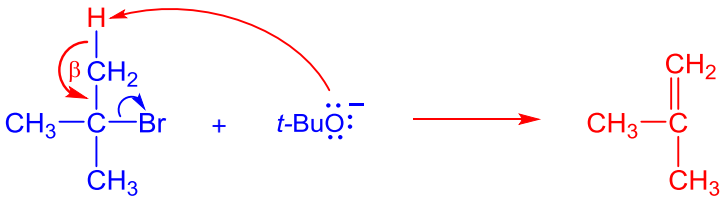
jaki nukleofil, jaka baza

(f)

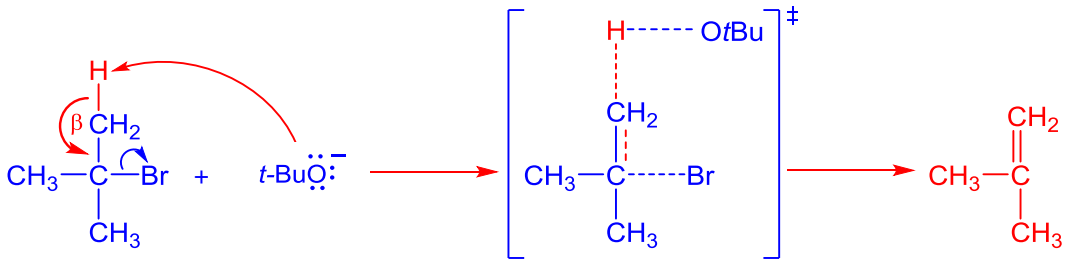
jaki nukleofil, slaba baza

5.14.

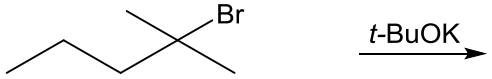
(a)

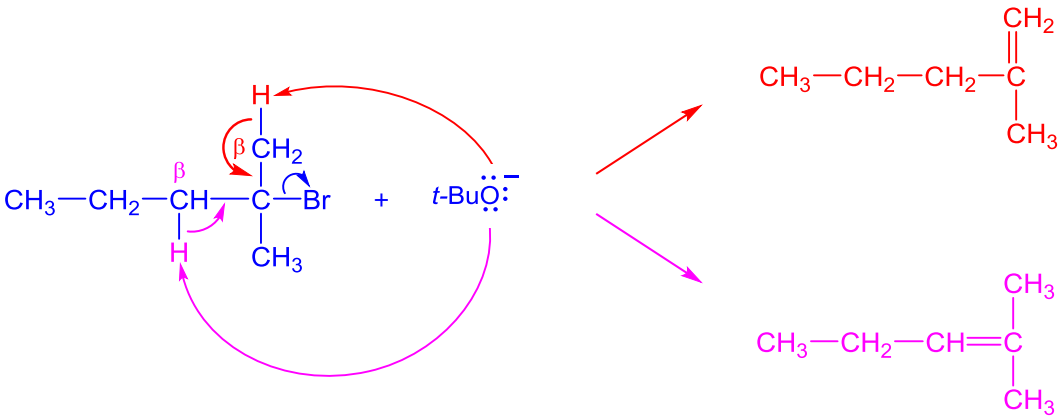


E2-mehanizam

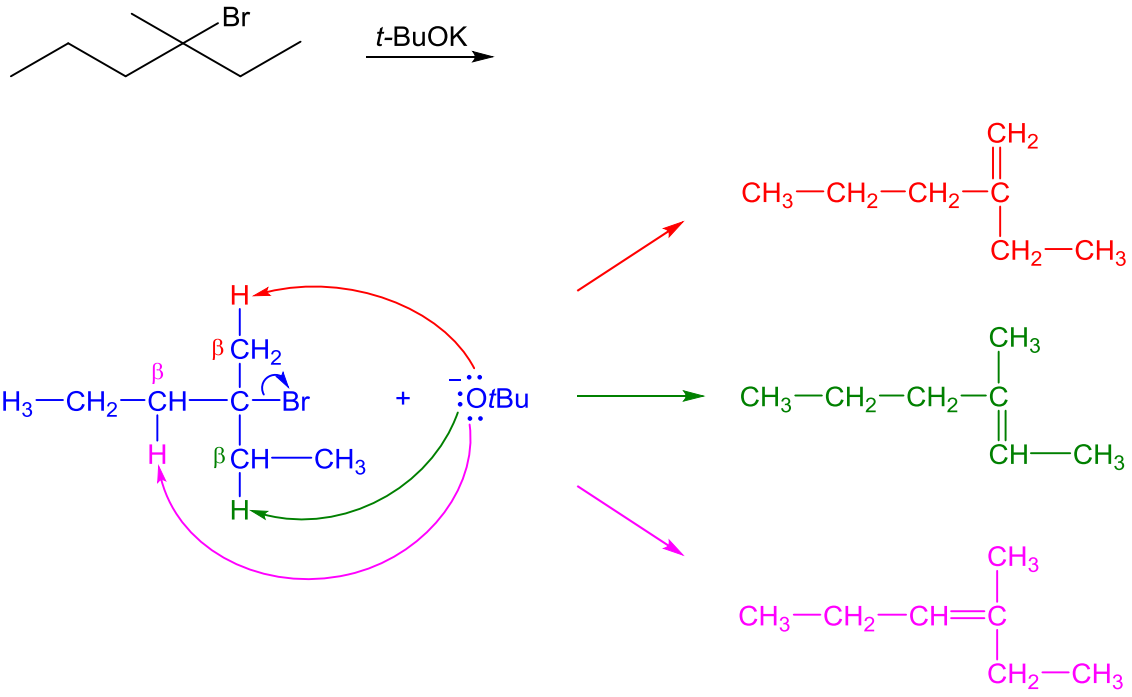


(b)





(c)



5.15.

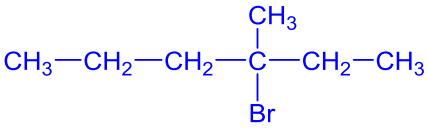
$CH_3—CH_2—CH_2—CH_2—CH_2—Br$ 1° halogenalkan

NaOH Jaka baza, jaki nukleofil ⇒ S_N2 ili E2. Prevladava S_N2 produkt.

NaSH Slaba baza, jaki nukleofil ⇒ S_N2. Prevladava S_N2 produkt.

t-BuOK Jaka baza, slabi nukleofil ⇒ E2. Prevladava E2 produkt.

5.16.



3° halogenalkan

NaI Slaba baza, jaki nukleofil ⇒ S_N1 ili S_N2. Prevladava S_N1 produkt.

NaOH Jaka baza, jaki nukleofil ⇒ S_N2 ili E2. Prevladava E2 produkt.

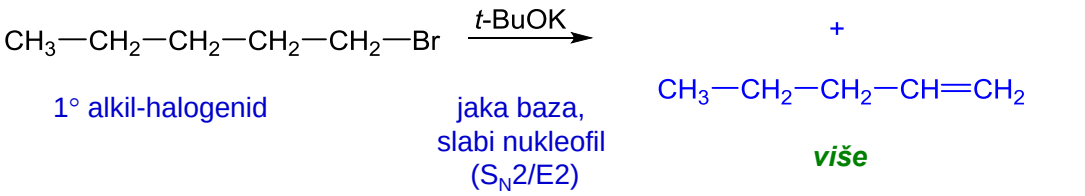
t-BuOK Jaka baza, slabi nukleofil ⇒ E2. Prevladava E2 produkt.

NaOEt Jaka baza, jaki nukleofil ⇒ S_N2 ili E2. Prevladava E2 produkt.

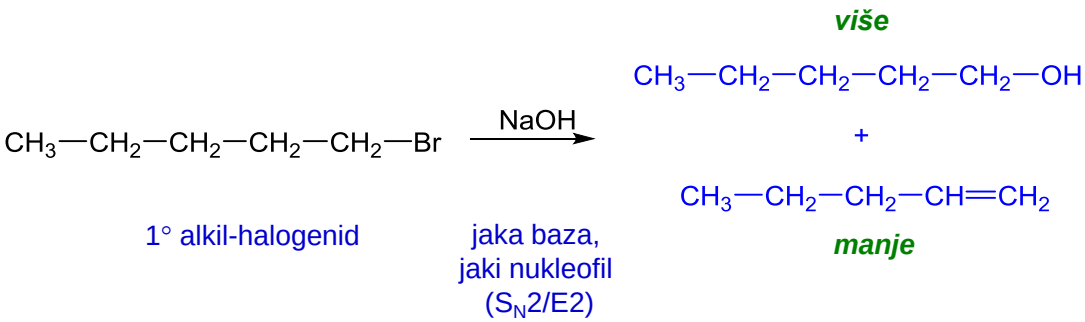
EtOH Slaba baza, slabi nukleofil ⇒ S_N1 ili E1. Prevladava S_N1 produkt, dok će pri višim temperaturama prevladavati E1 produkt..

5.17.

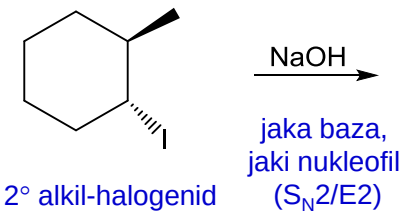
(a)

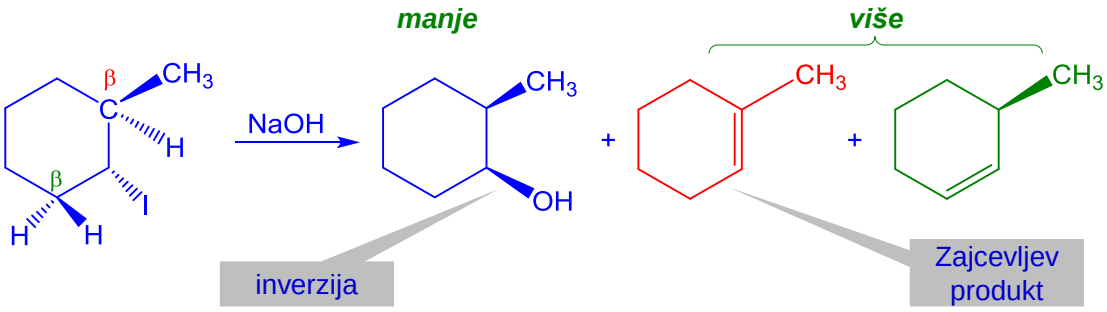

manje
CH3—CH2—CH2—CH2—CH2—OtBu
+
CH3—CH2—CH2—CH=CH2
više
CH3—CH2—CH2—CH2—CH2—Br
t-BuOK
1° alkil-halogenid
jaka baza,
slabi nukleofil
(SN2/E2)

(b)

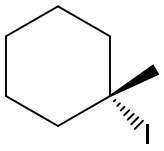

više
CH3—CH2—CH2—CH2—CH2—OH
+
CH3—CH2—CH2—CH=CH2
manje
CH3—CH2—CH2—CH2—CH2—Br
NaOH
1° alkil-halogenid
jaka baza,
jaki nukleofil
(SN2/E2)

(c)


NaOH
jaka baza,
jaki nukleofil
(SN2/E2)
2° alkil-halogenid


manje
više
β
CH3
C
H
β
I
H
H
NaOH
CH3
OH
+
CH3
+
CH3
inverzija
Zajcevljev
produkt

(d)

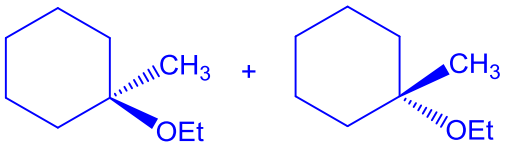


3° alkil-halogenid

EtOH

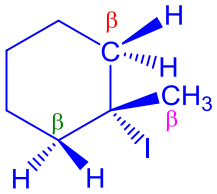
slaba baza,
slabi nukleofil
(S_N1/E1)

više

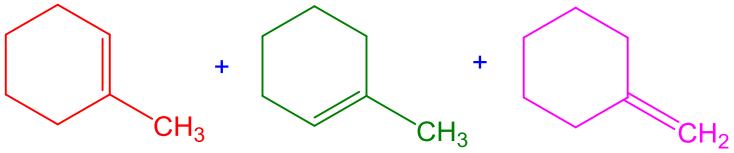


racemizacija

+

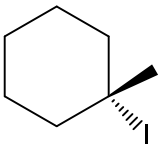


EtOH



manje

(e)

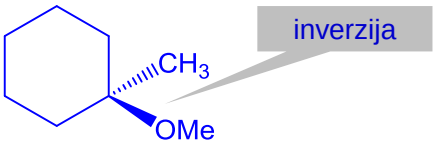


3° alkil-halogenid

NaOMe

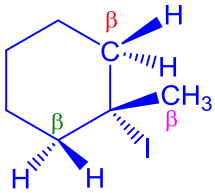
jaka baza,
jaki nukleofil
(S_N2/E2)

manje

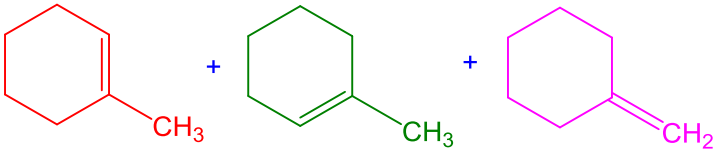


inverzija

+

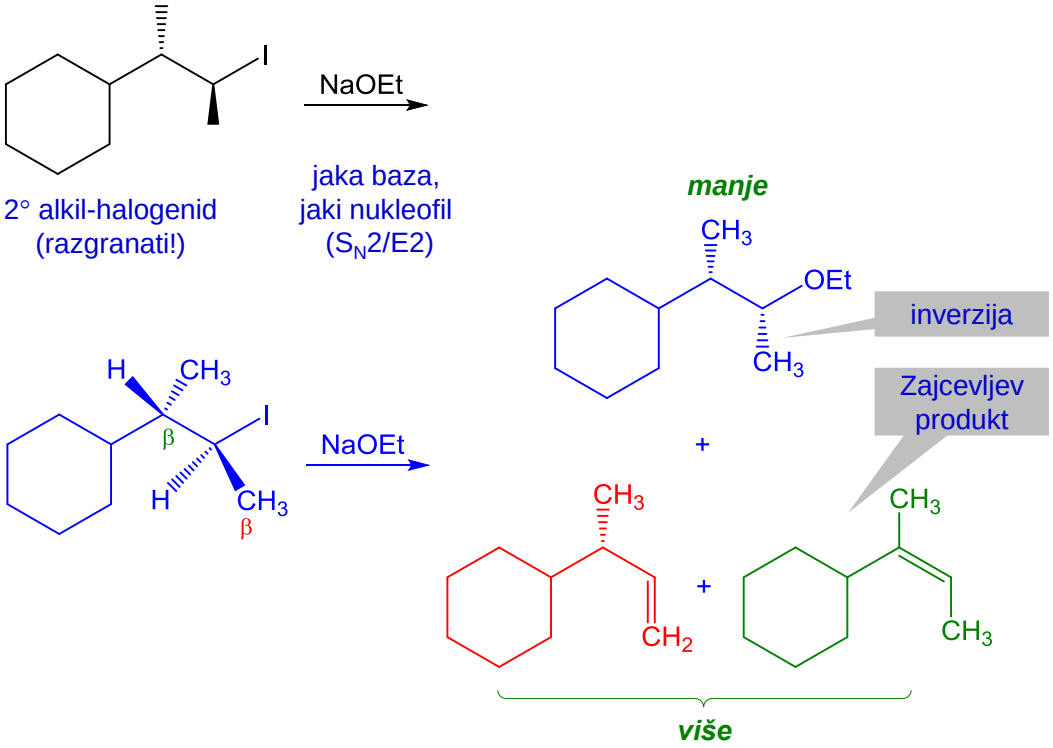


NaOMe

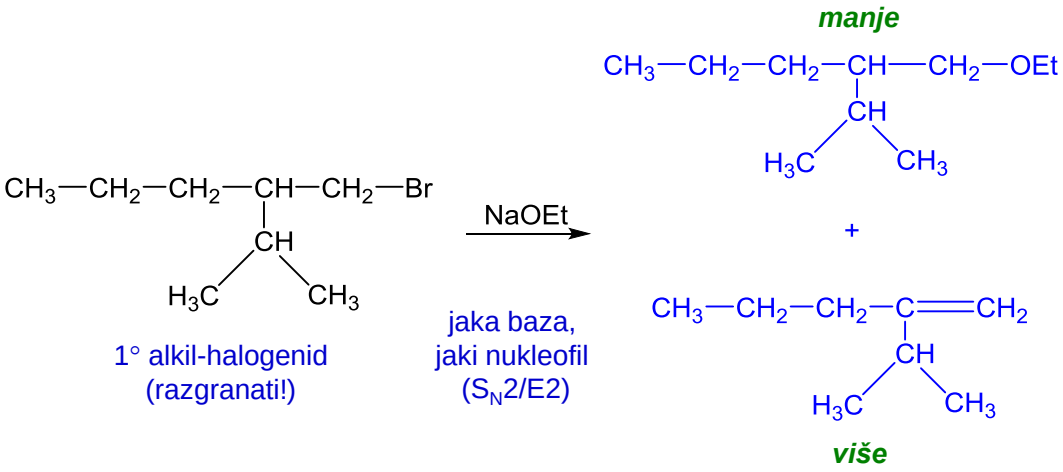


više

(f)

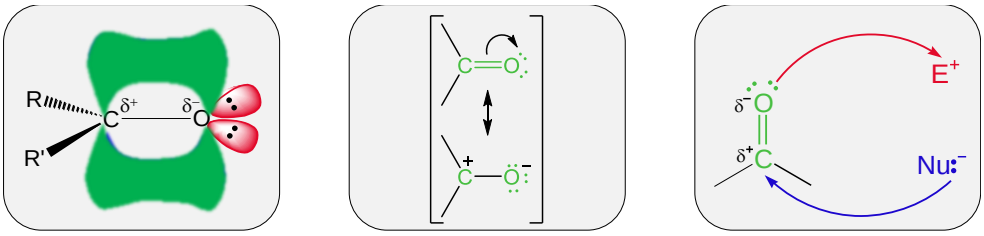

NaOEt
2° alkil-halogenid
(razgranati!)
jaka baza,
jaki nukleofil
(SN2/E2)
manje
OEt
inverzija
Zajcevljev
produkt
+
+
više

(g)

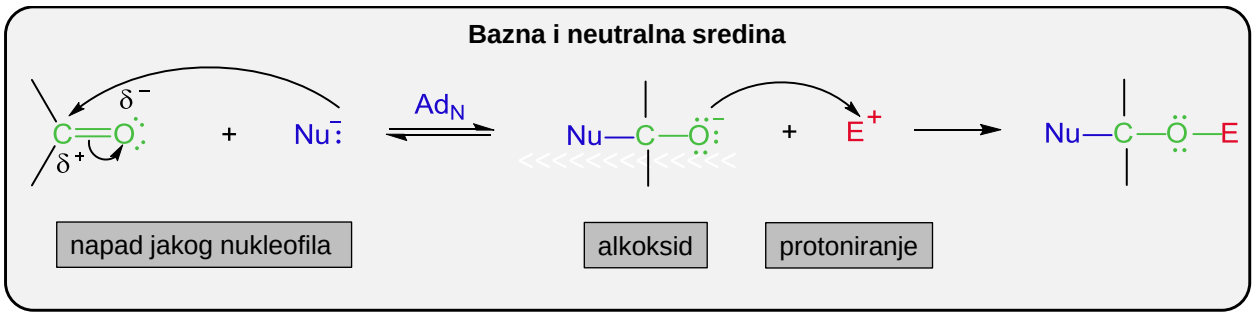

NaOEt
1° alkil-halogenid
(razgranati!)
jaka baza,
jaki nukleofil
(SN2/E2)
manje
+
više

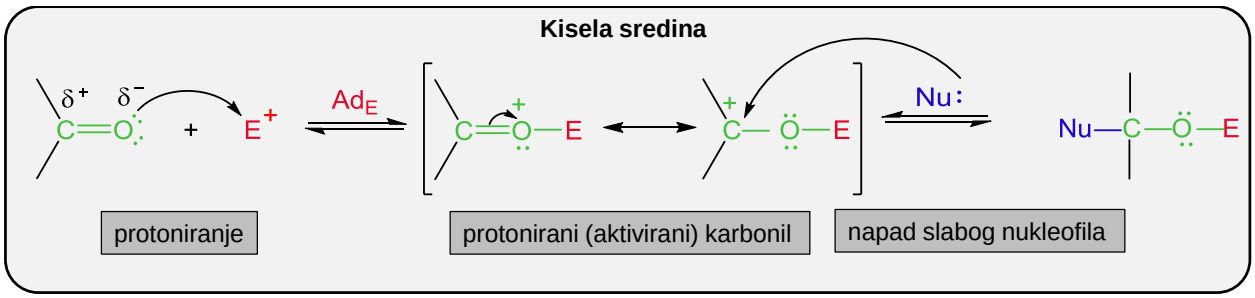
6. Aldehidi i ketoni. Nukleofilna adicija

sp^2-Hibridizirani karbonilni ugljikov atom tvori tri koplanarne σ-veze, dok se njegova nehibridizirana *p*-orbitala preklapa s nehibridiziranom *p*-orbitalom sp^2-hibridiziranog kisikova atoma tvoreći π-vezu.



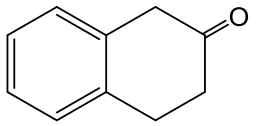
Uslijed veće elektronegativnosti kisikova atoma u odnosu na ugljik, njihovi vezni elektroni nisu simetrično raspoređeni između ta dva atoma. Slabije vezani π-elektroni privučeni su od strane kisikova atoma, uslijed čega se aldehidi i ketoni odlikuju velikim dipolnim momentom. Takva **polarizacija karbonilne skupine određuje njezinu reaktivnost**. **Pozitivno polarizirani ugljikov atom ponaša se kao elektrofil (Lewisova kiselina), dok negativno polarizirani kisikov atom djeluje kao nukleofil (Lewisova baza).**

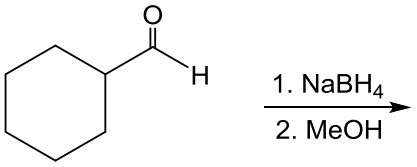


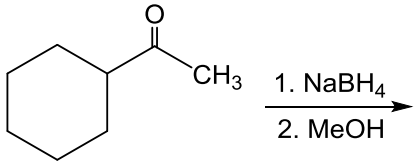


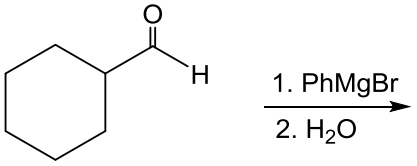
Zadaci

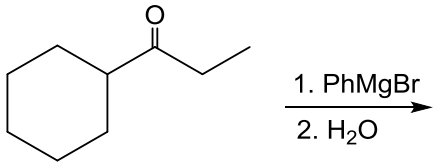
6.1. Predvidite glavne produkte prikazanih reakcija:

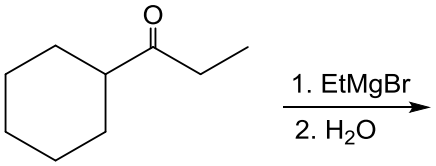
(a) 

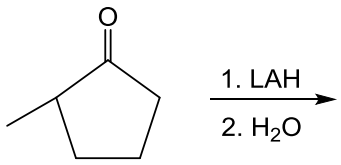
(b) 

(c) 

(d) 

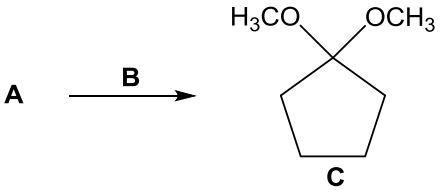
(e) 

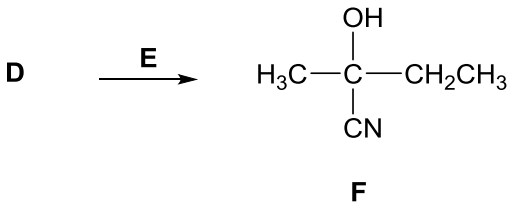
(f) 

(g) 

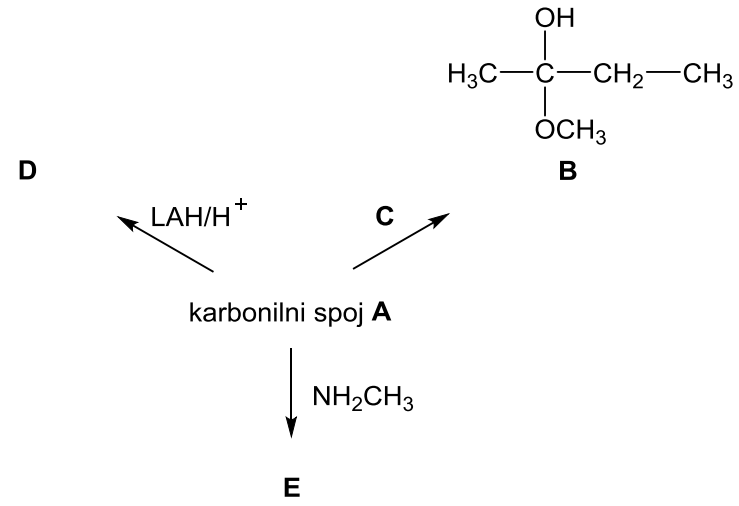
6.2. Prikažite structure Grignardovih reagensa i ketona potrebnih za pripravu (a) 3-metilpentan-3-ola i (b) 4-fenilnonan-4-ola.

6.3. Predložite sintezu spojeva C i F iz odgovarajućih karbonilnih prekursora i napišite mehanizme tih reakcija.

(a) 

(b) 

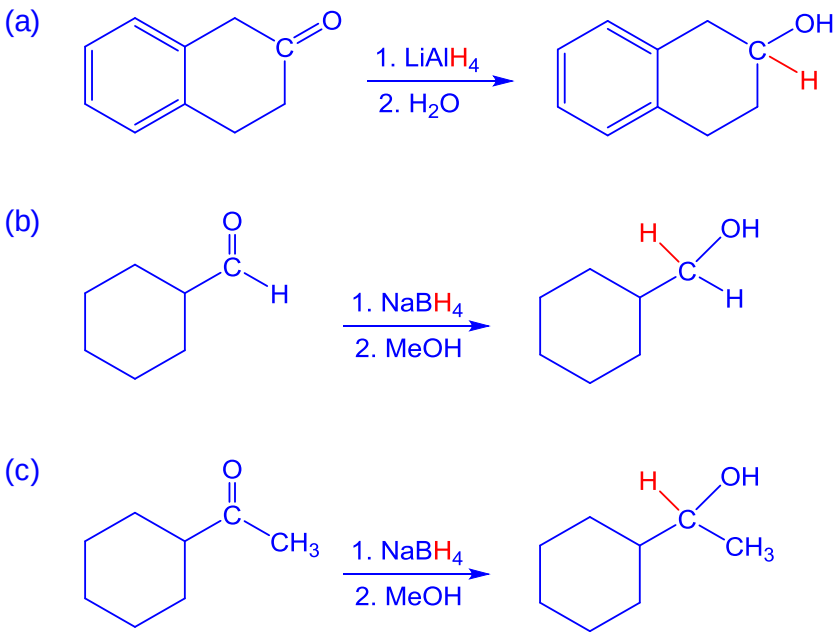
6.4. (a) Nacrtajte strukturne formule molekula **A**, **C**, **D** i **E**. (b) Predložite reakcijski mehanizam pretvorbe **A**→**E**.



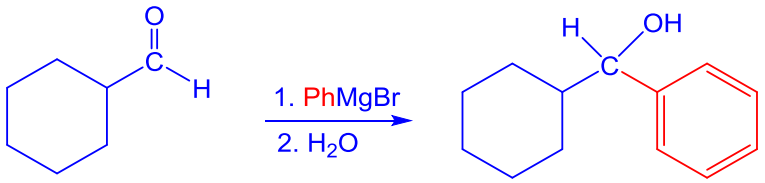
6.5. Predložite Grignardove sinteze ravnolančanog *sec*-alkohola s 5 C-atoma iz odgovarajućih karbonilnih spojeva, te predložite reakcijski mehanizam jedne od prikazanih reakcija.

Rješenja

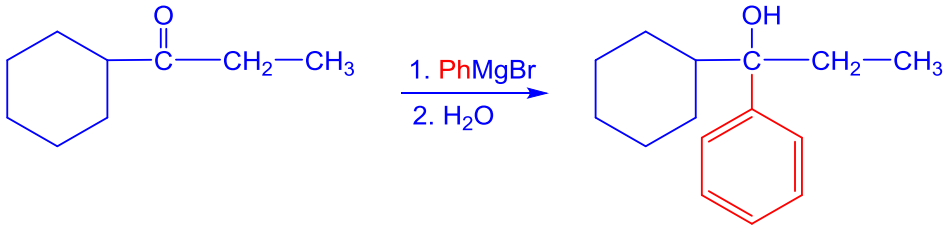
6.1.



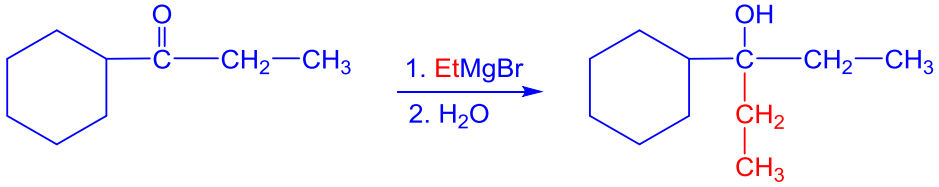
(d)


O
C
H
1. PhMgBr
2. H2O
H
OH
C

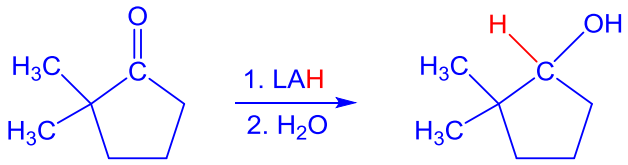
(e)


O
C
CH2—CH3
1. PhMgBr
2. H2O
OH
C
CH2—CH3

(f)

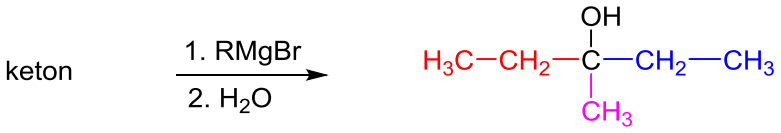

O
C
CH2—CH3
1. EtMgBr
2. H2O
OH
C
CH2—CH3
CH2
CH3

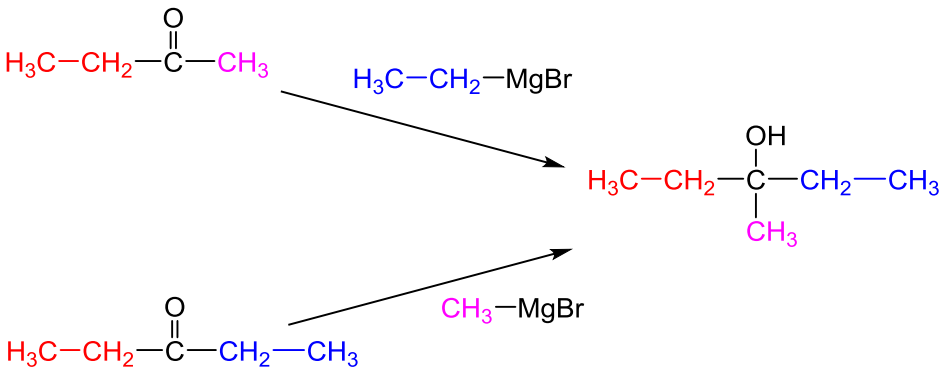
(g)


O
C
H3C
H3C
1. LAH
2. H2O
H
OH
C
H3C
H3C

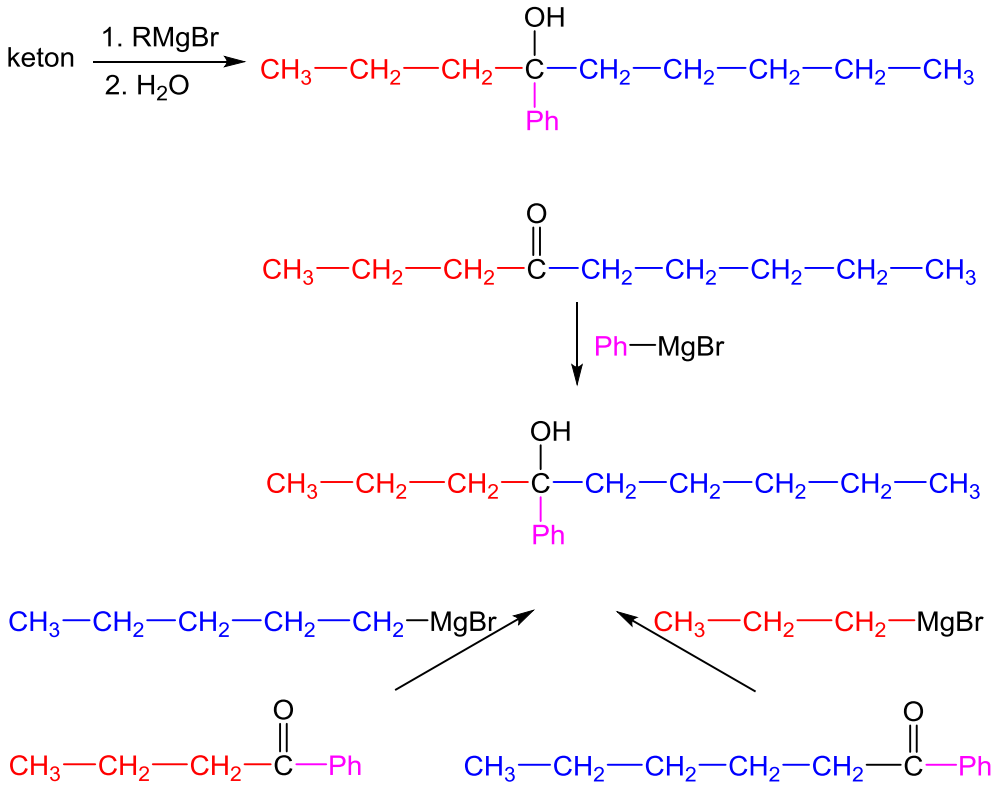
6.2.

(a)


keton
1. RMgBr
2. H2O
OH
H3C—CH2—C—CH2—CH3
CH3

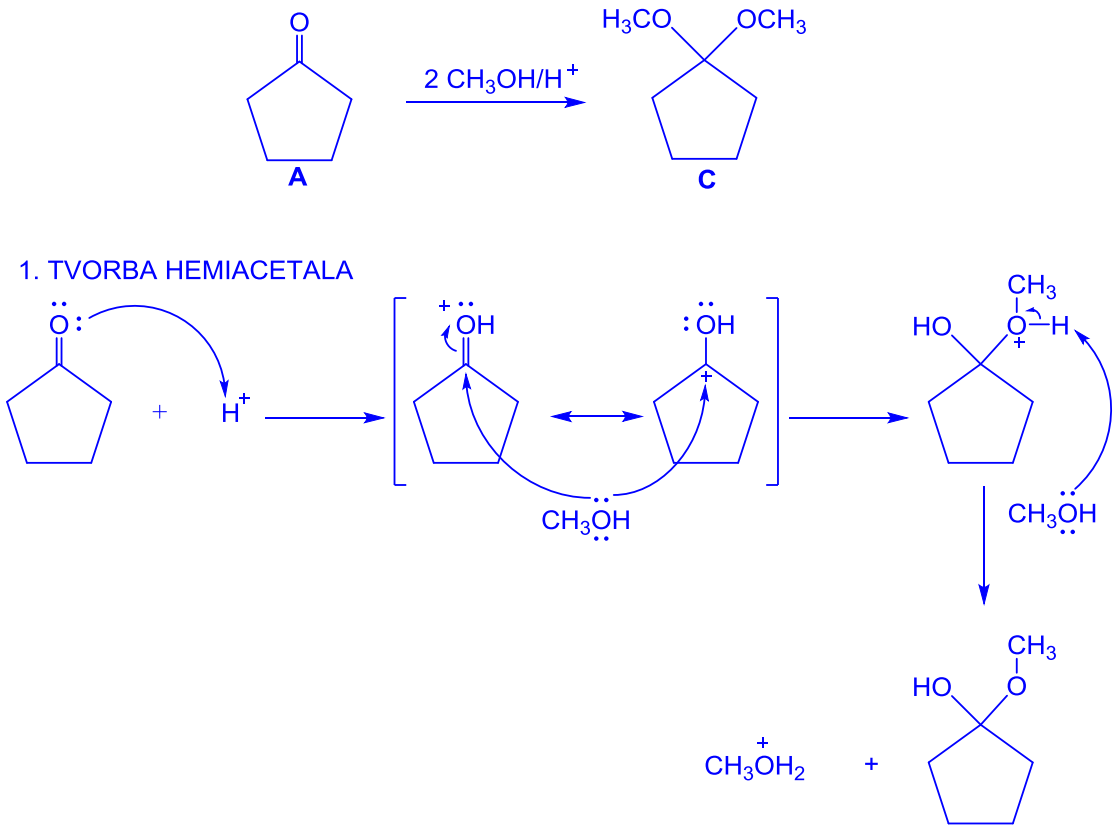

O
H3C—CH2—C—CH3
H3C—CH2—MgBr
OH
H3C—CH2—C—CH2—CH3
CH3
O
H3C—CH2—C—CH2—CH3
CH3—MgBr

(b)

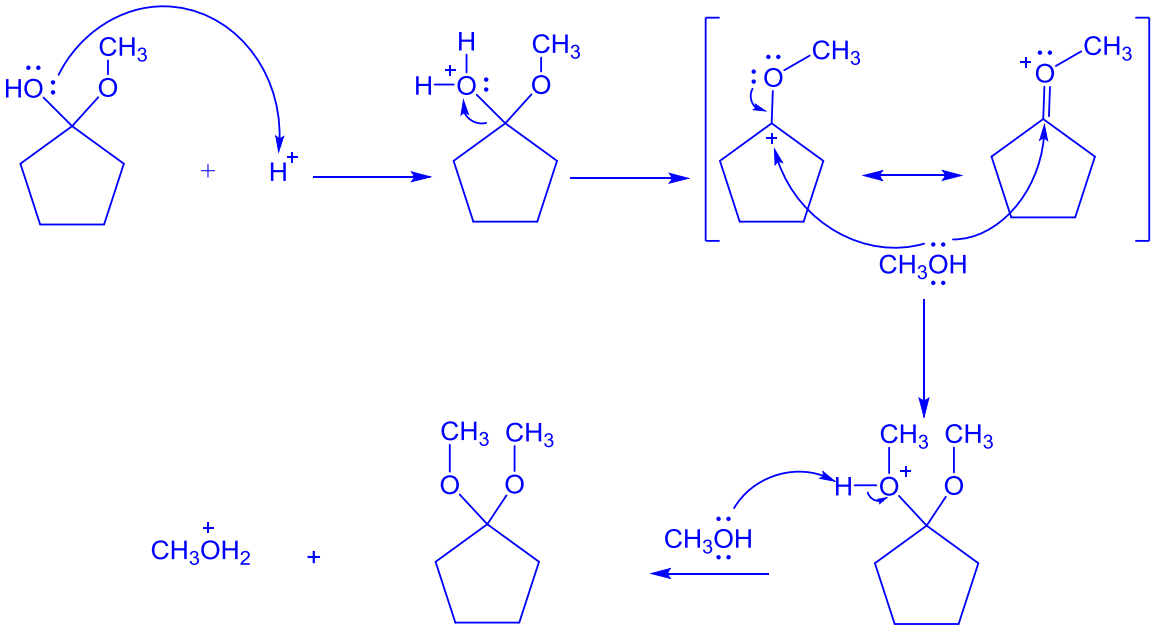

keton
1. RMgBr
2. H2O
OH
Ph
O
Ph—MgBr
CH3—CH2—CH2—MgBr
CH3—CH2—CH2—CH2—CH2—MgBr
A
C

6.3.

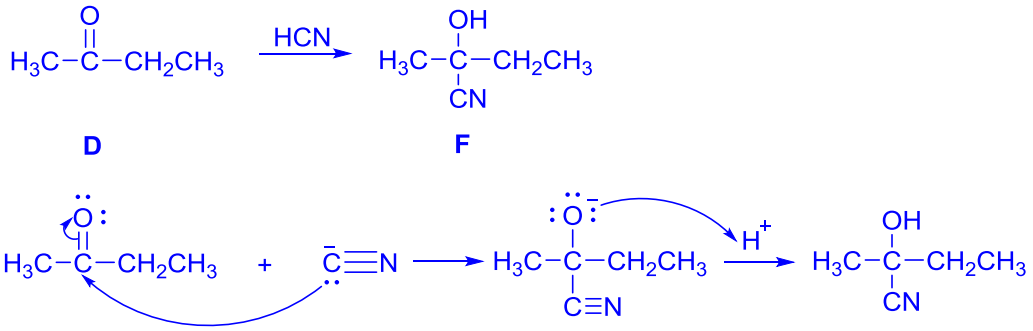
(a)


2 CH3OH/H+
A
C
1. TVORBA HEMIACETALA
CH3OH
CH3OH2

2. TVORBA ACETALA



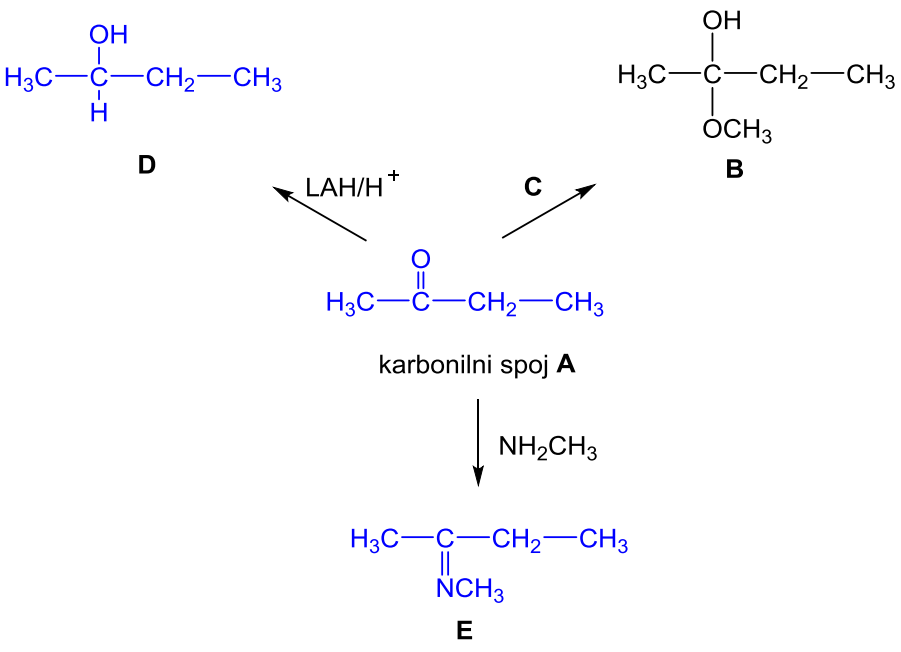
(b)



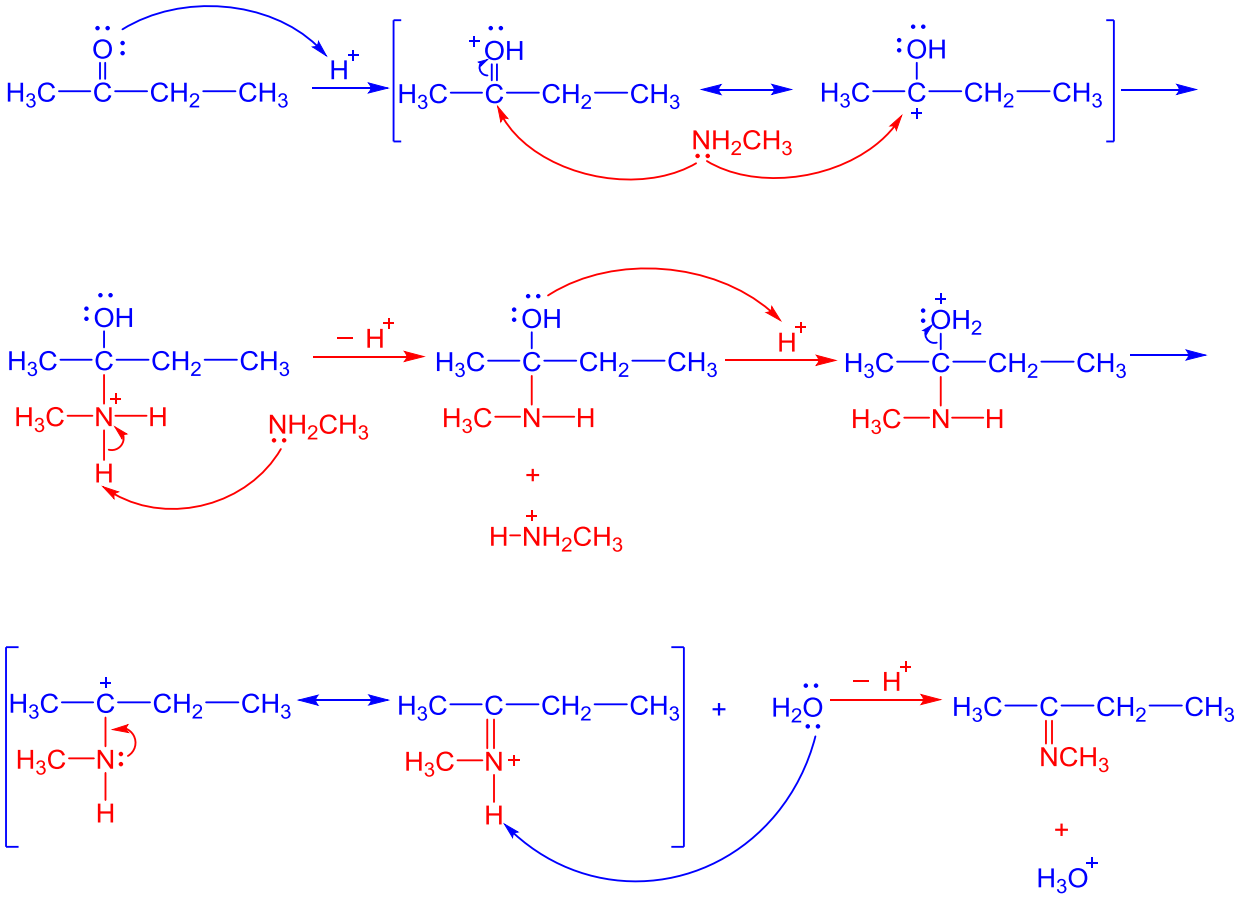
D **F**

6.4.

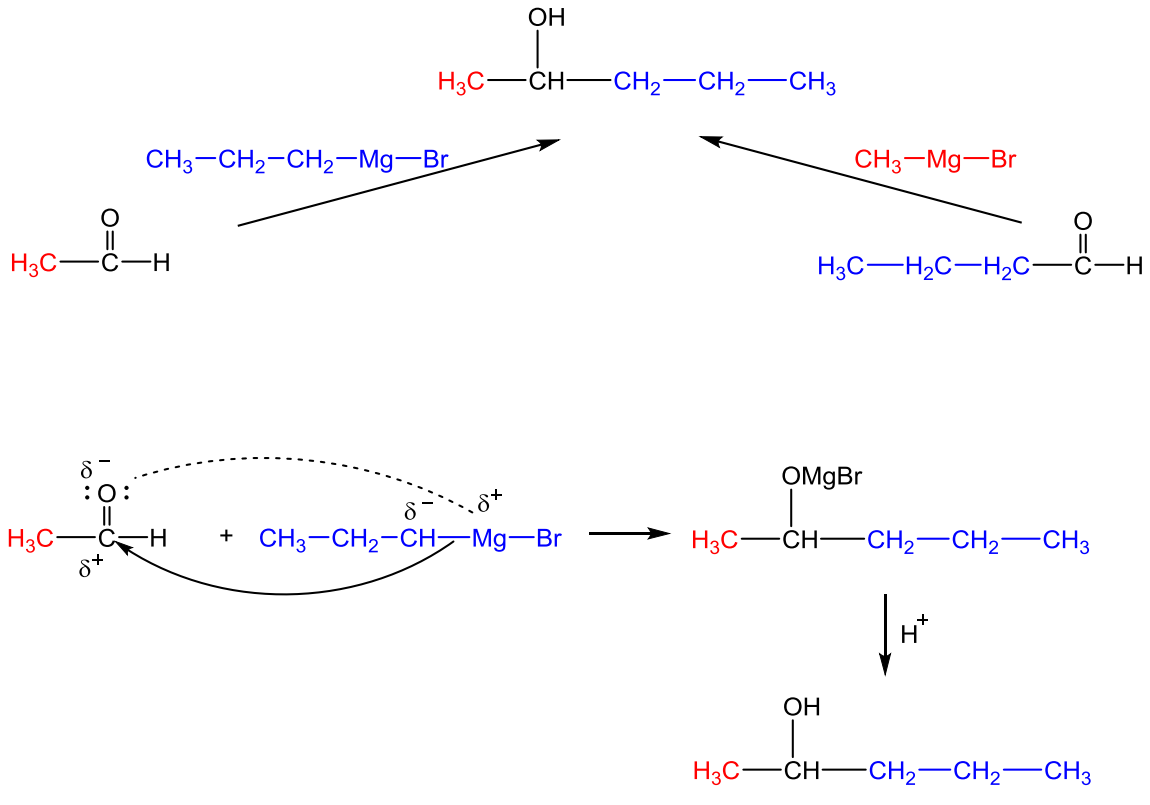
(a)



(b)

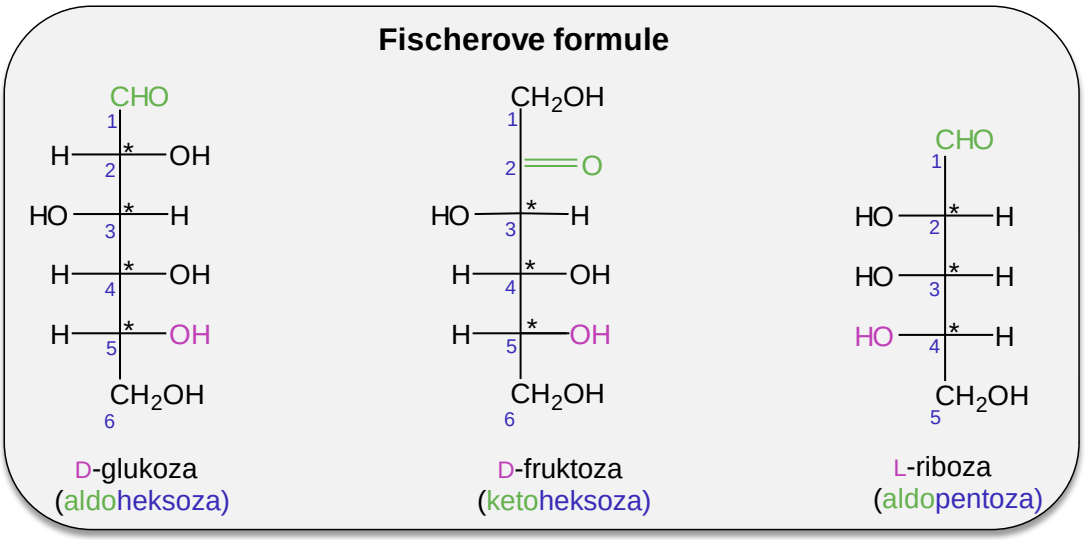


6.5.

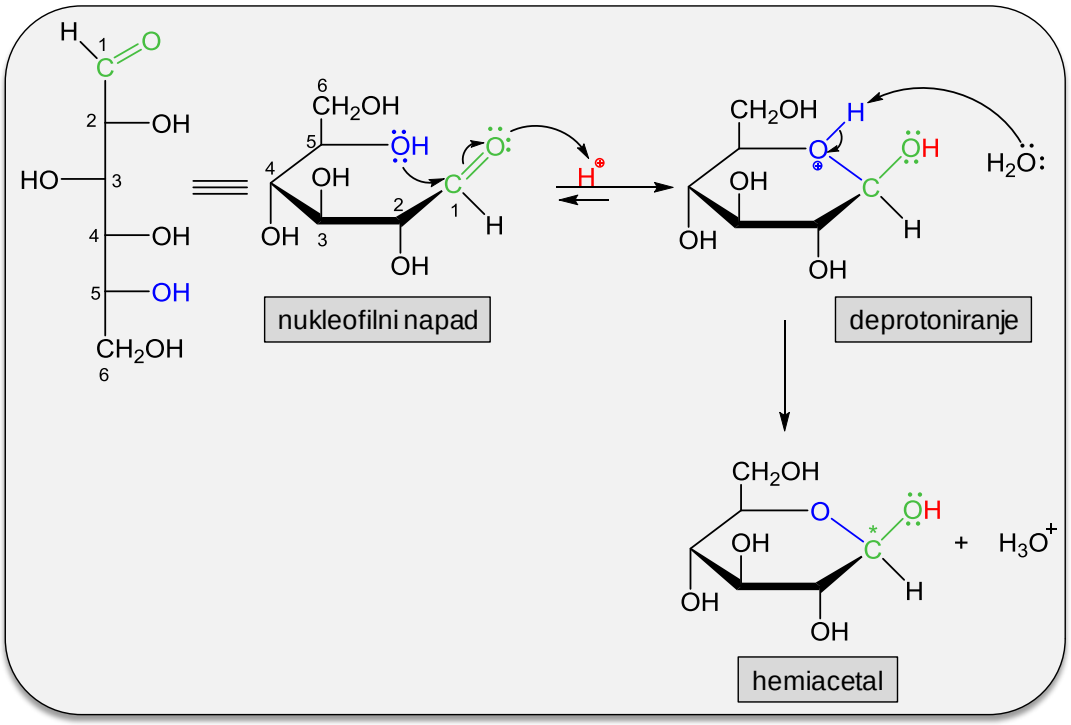


7. Ugljikohidrati

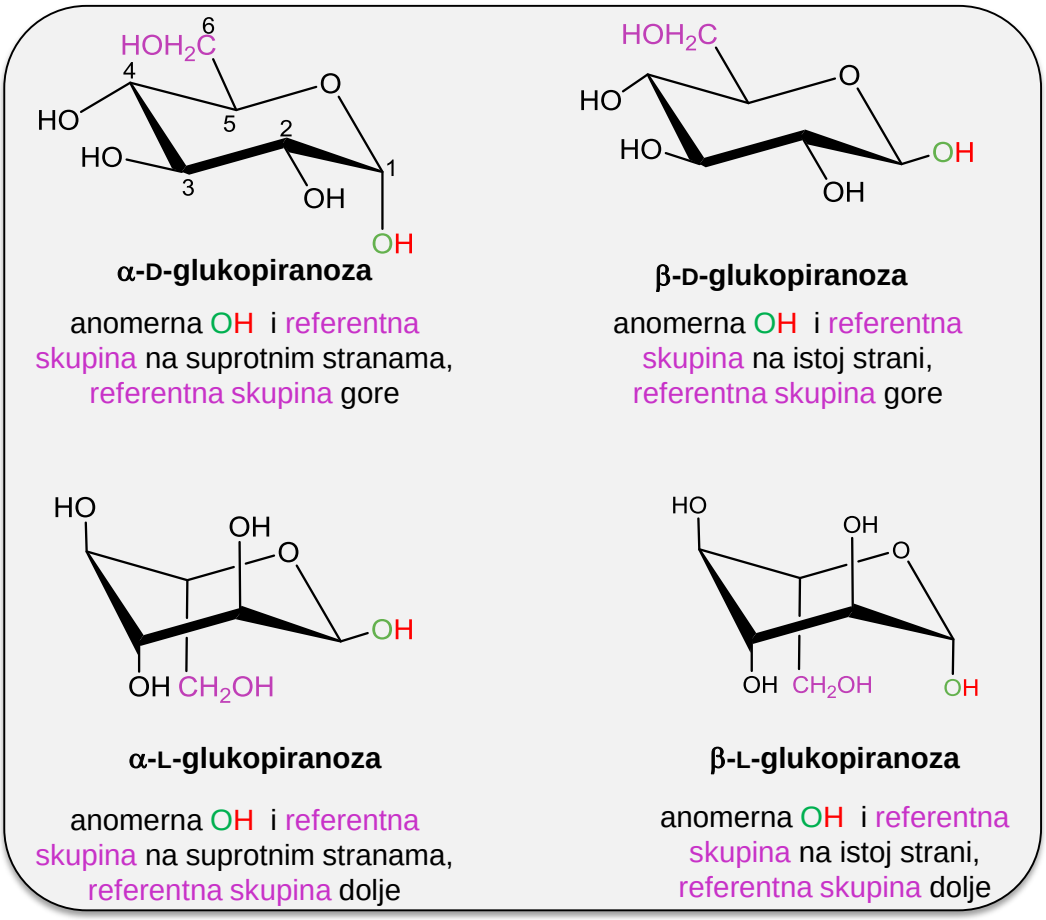
Šećeri D-niza (prirodni šećeri): OH-skupina asimetričnog C-atoma s najvišim rednim brojem (odnosno C-atoma koji je najniži u vertikalnoj Fischerovoj formuli) usmjerena je udesno.



U čvrstom stanju aldoze se javljaju u obliku cikličkih hemiacetala. U otopini aldoze uspostavljaju ravnotežu između cikličkog i lančastog oblika, s tim da je ravnoteža pomaknuta prema cikličkom obliku.



Glukoza u obliku cikličkog hemiacetala najčešće se prikazuje konformacijama stolca.



Zadaci

7.1. Fischerovom formulom prikažite L-galaktozu i njezin C4-epimer. Imenujte prikazani epimer. U kakvom su stereokemijskom odnosu?

7.2. Haworthovim formulama prikažite anomere D-ksiloze.

7.3. Konformacijskim formulama prikažite i imenujte anomere D-manoze. Označite stabilniji anomer. Prikažite konformacijskom formulom enantiomer stabilnijeg anomera.

7.4. Nacrtajte produkte dobivene sljedećim reakcijama:

(a) D-ksiloza + H_2/Ni (b) L-manoza + H_2/Ni (c) D-fruktoza + $NaBH_4$

(d) D-galaktoza + Br_2 (e) L-manoza + Felinghova otopina

(f) D-fruktoza + Br_2 (g) D-ksiloza + Felinghova otopina

7.5. Konformacijskim formulama prikažite disaharide (a)-(c) i navedite radi li se o reducirajućim ili nereducirajućim šećerima.

(a) 4-O-α-D-glukopiranozil-β-L-manopiranozu

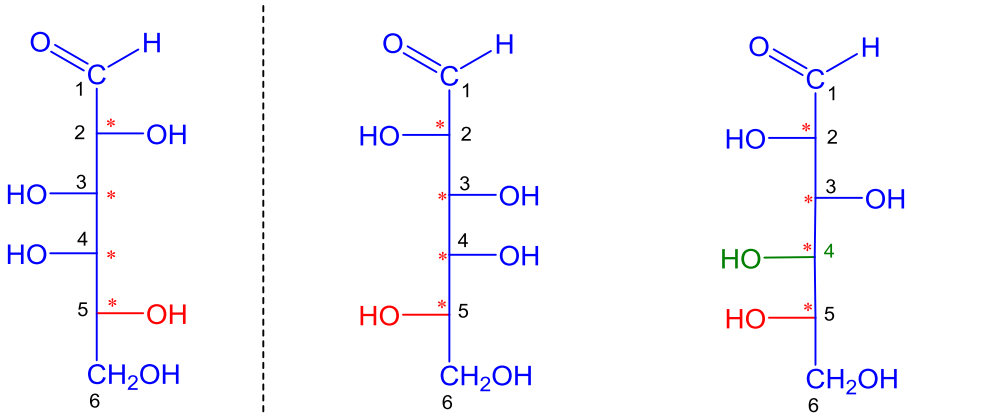
(b) α-D-ksilofuranozil-β-D manopiranozid

(c) 6-O-β-D-fruktofuranozil-α-L-galaktopiranozu

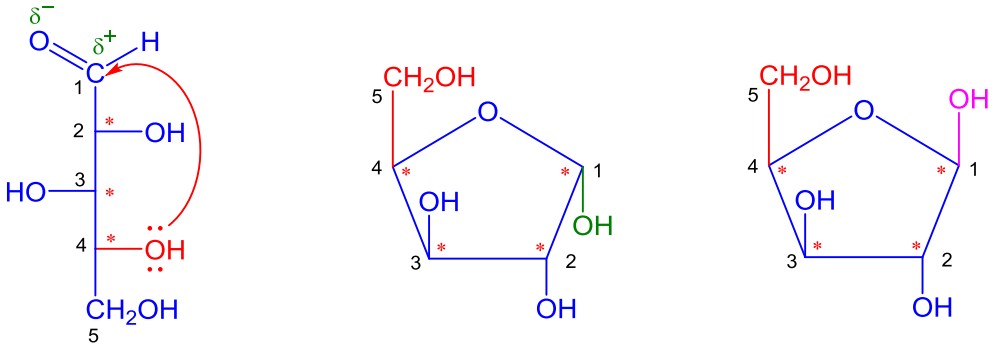
7.6. Konformacijskim formulama prikažite mehanizam nastajanja *tert*-butil-α-D-manopiranozida. Označite glikonski i aglikonski dio u prikazanoj strukturi.

Rješenja

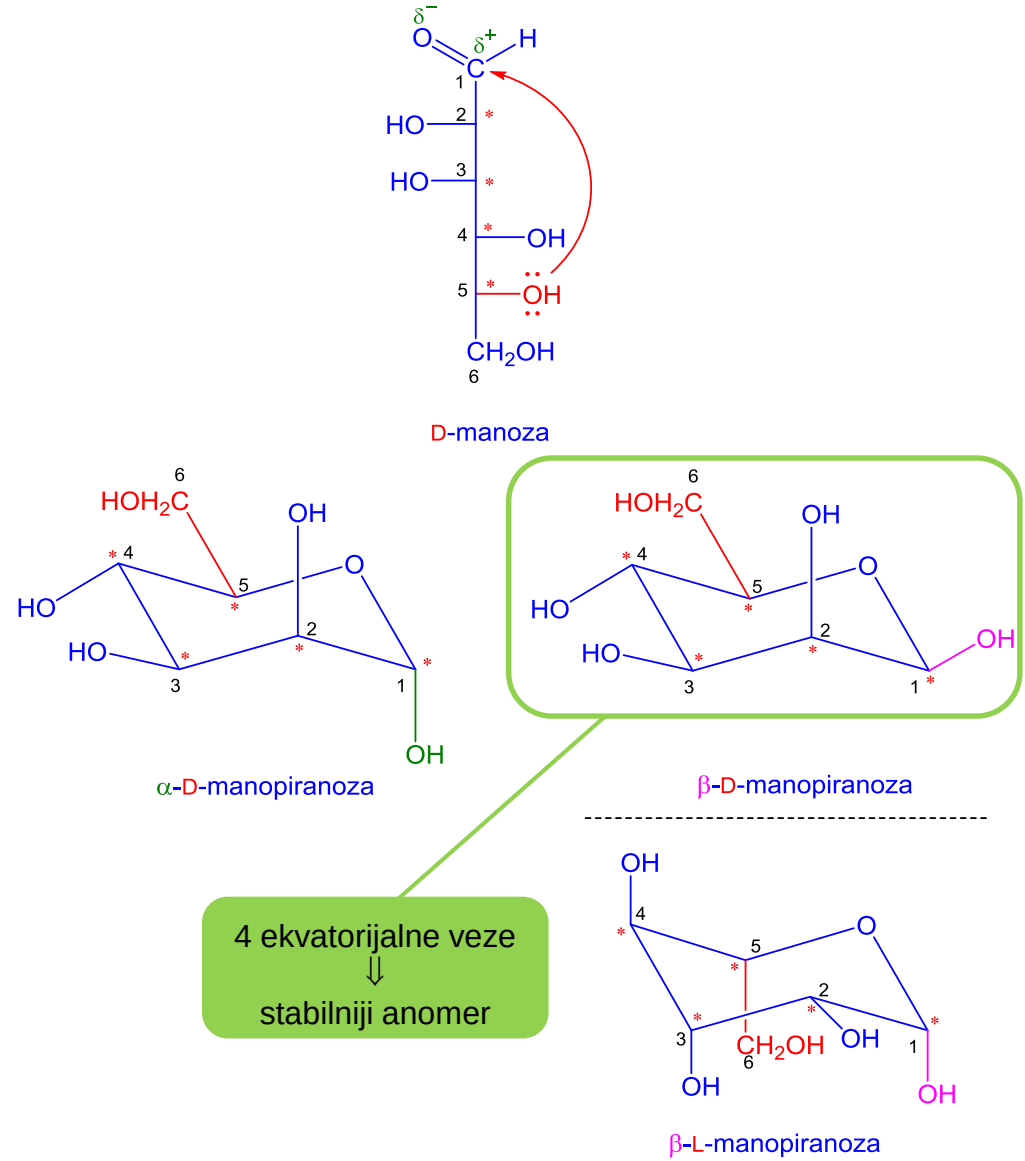
7.1.



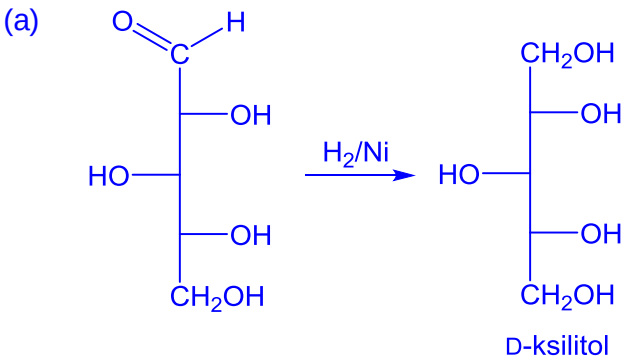
7.2.



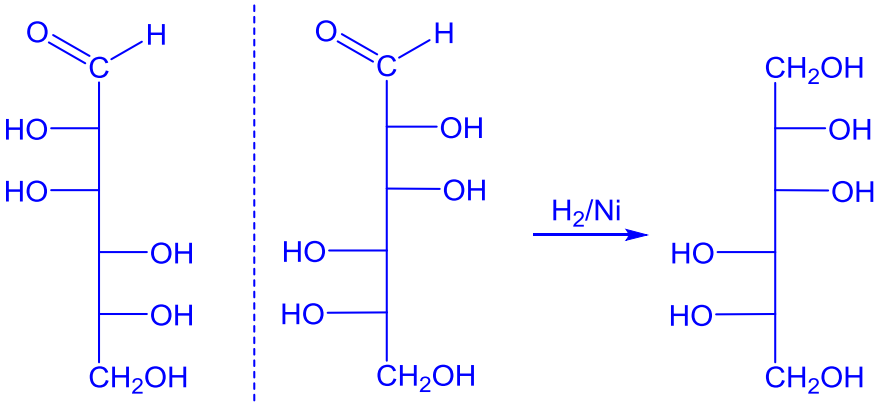
7.3.


D-manoza
α-D-manopiranoza
β-D-manopiranoza
4 ekvatorijalne veze
⇓
stabilniji anomer
β-L-manopiranoza

7.4.

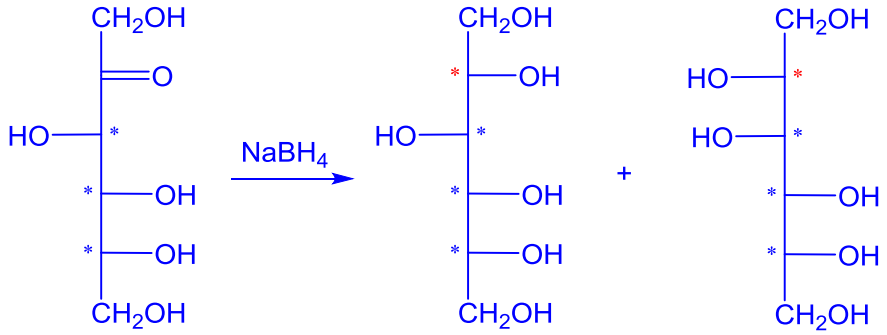

(a)
H2/Ni
D-ksilitol

(b)



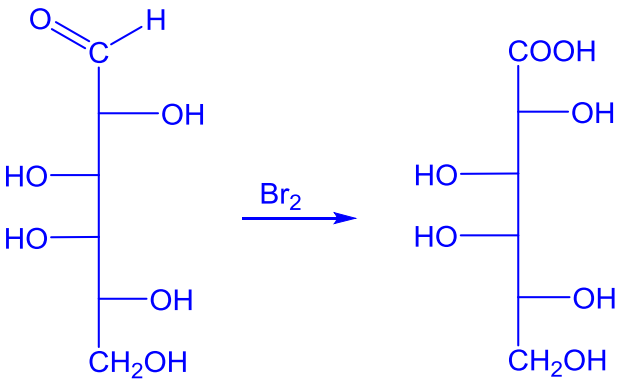
D-manoza L-manoza L-manitol

(c)



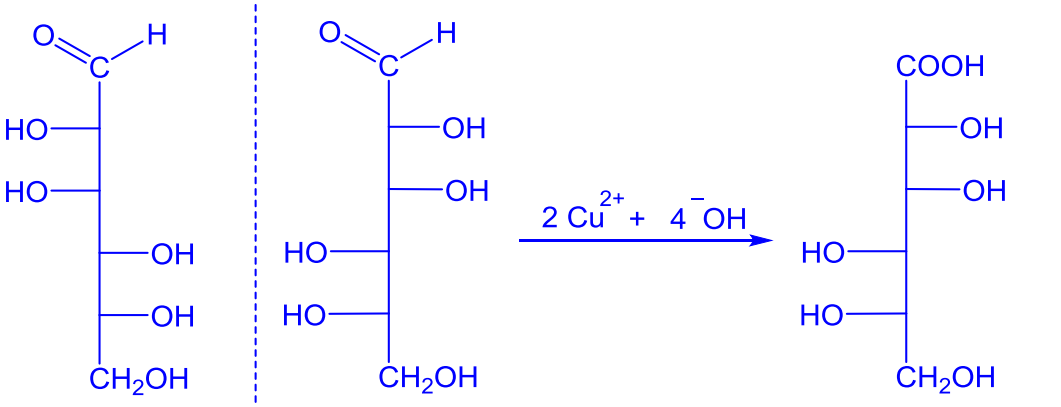
D-fruktoza D-glucitol D-manitol

(d)



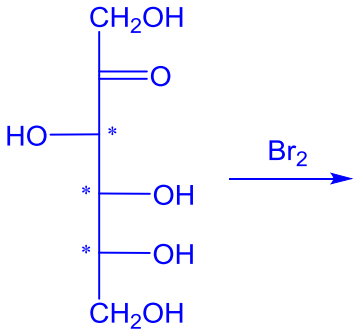
D-galaktoza D-galaktonska kiselina

(e)



D-manoza L-manoza D-manonska kiselina

(f)

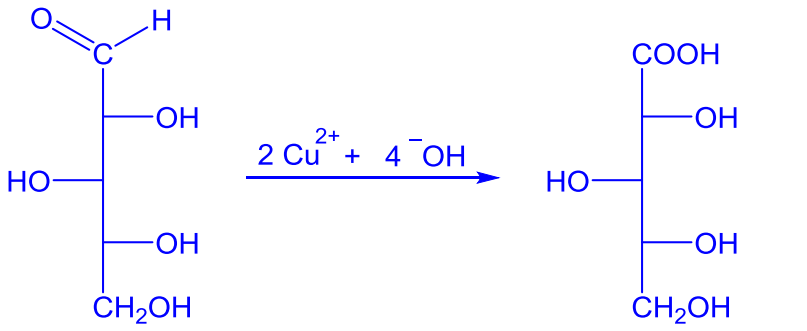


D-fruktoza

Br_2

Br_2 ne oksidira ketone!

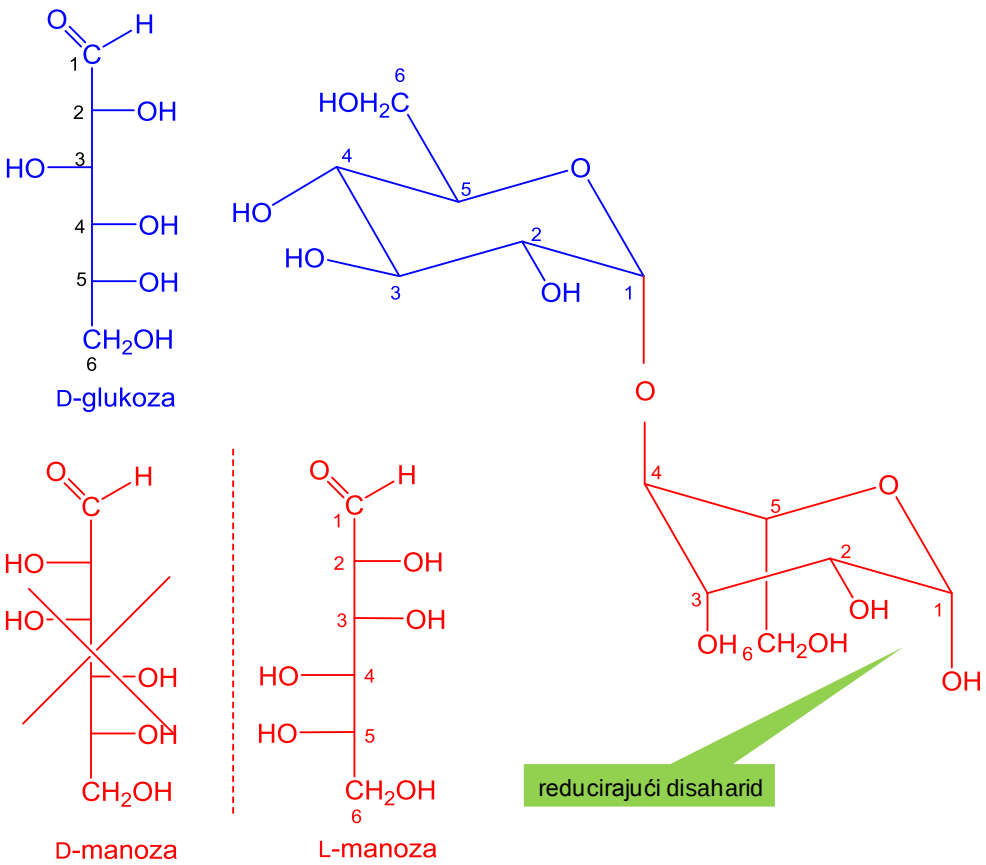
(g)



D-ksilonska kiselina

7.5.

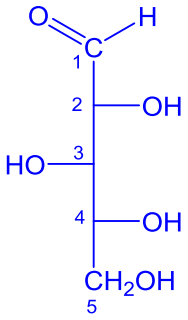
(a)



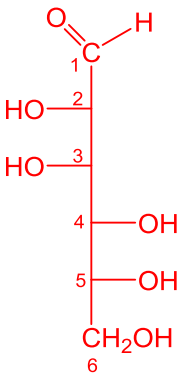
D-manoza

L-manoza

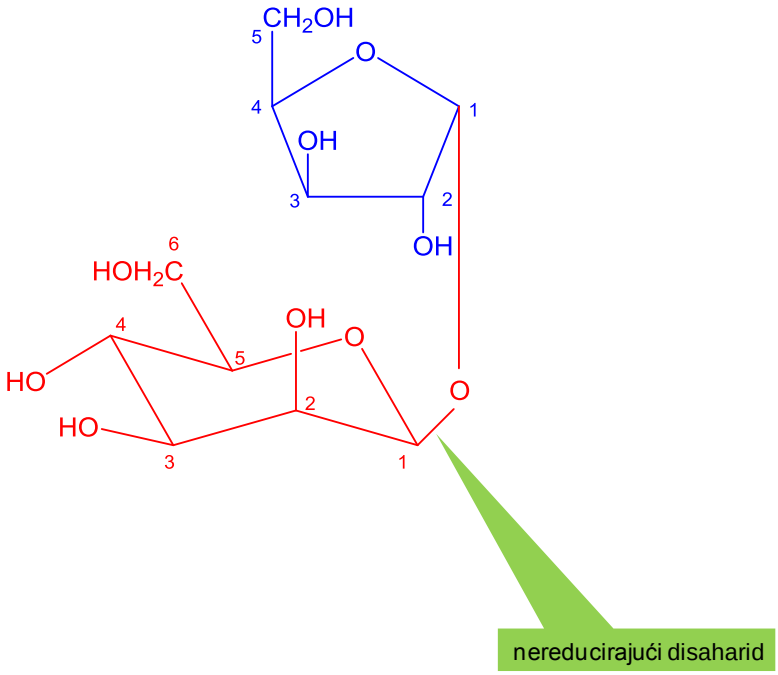
(b)



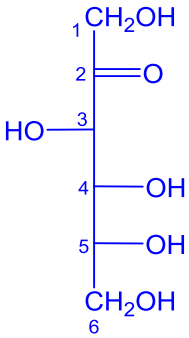
D-ksiloza

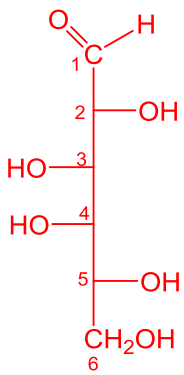


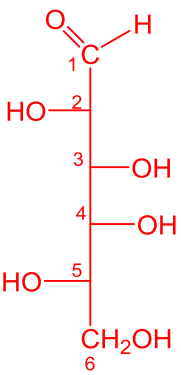
D-manoza

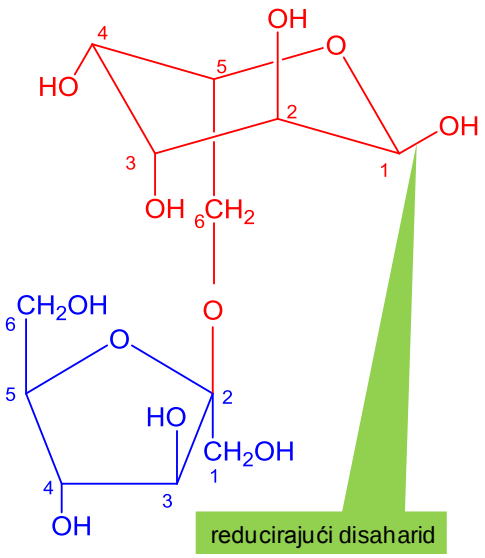


(c)

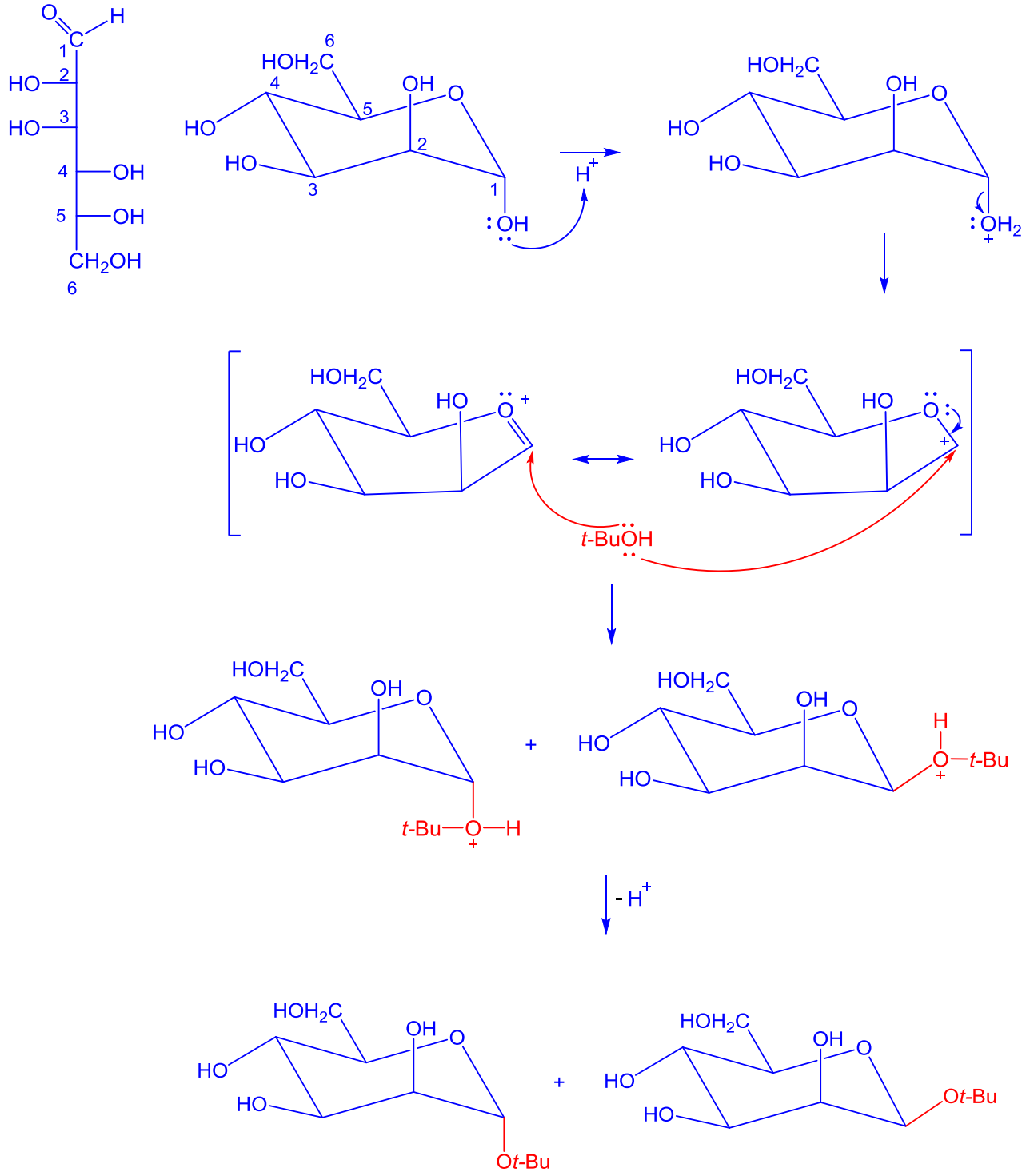






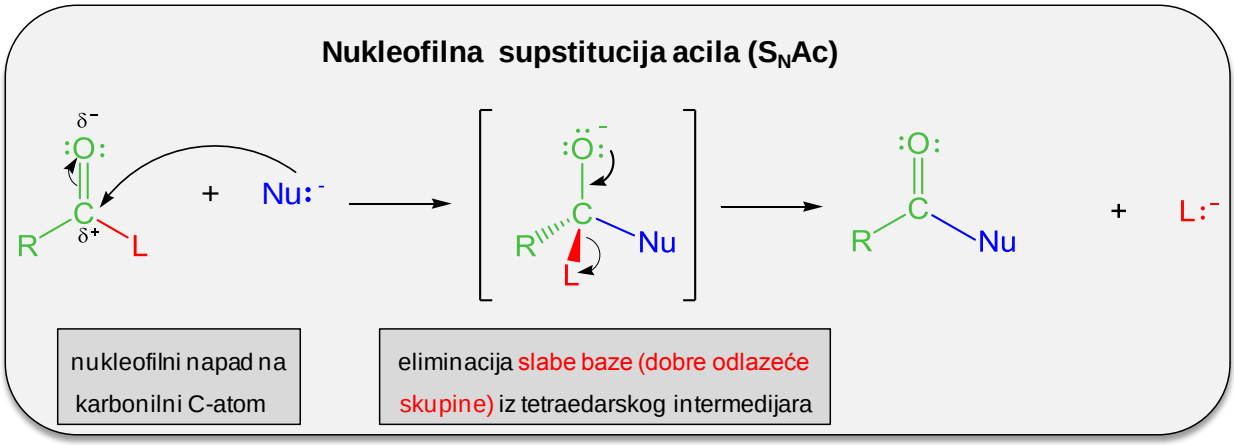


7.6.



8. Karboksilne kiseline i derivati. Nukleofilna supstitucija

Acilna skupina karboksilnih kiselina i njihovih derivata vezana je za atom ili skupinu koji se mogu supstituirati drugom skupinom [na njihovu acilnu skupinu (R–CO–) vezan je elektronegativni atom ili supstituent koji će molekulu napustiti kao stabilni anion - odlazeća skupina.



Zadaci

8.1. Napišite strukture produkata i reaktanata u prikazanim reakcijama.

(a) kiselina **(A)** + CH_3CH_2OH ⇌ $HCOOCH_2CH_3$

(b) acil-halogenid **(A)** + **B** → CH_3COOt-Bu

(c) CH_3COOt-Bu (**A**) $\xrightarrow{H^+}$ $\xrightarrow{OH^-}$

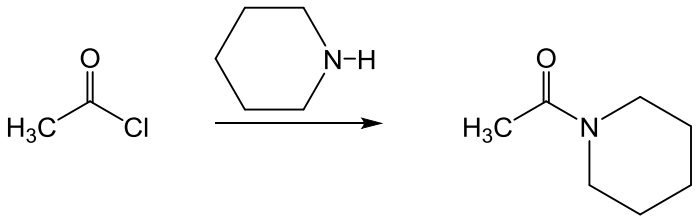
8.2. Predložite mehanizam reakcije kojom se pripravlja etil-metanoat.

8.3. Predložite mehanizam reverzibilne hidrolize *t*-butil-acetata.

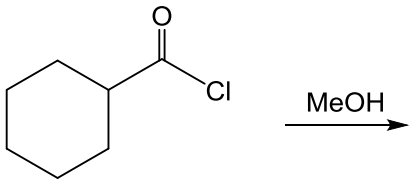
8.4. Predložite mehanizam ireverzibilne hidrolize *t*-butil-acetata.

8.5. Predložite reakcijske mehanizme sljedećih pretvorbi:

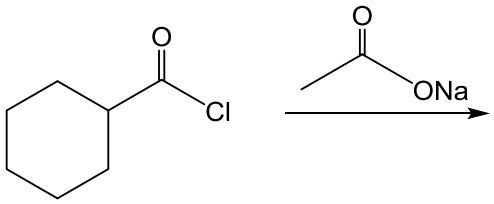
(a)



(b)



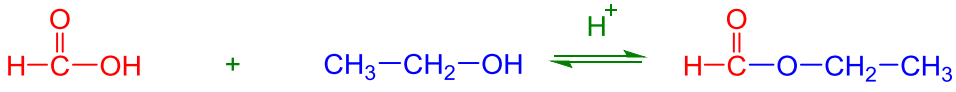
(c)



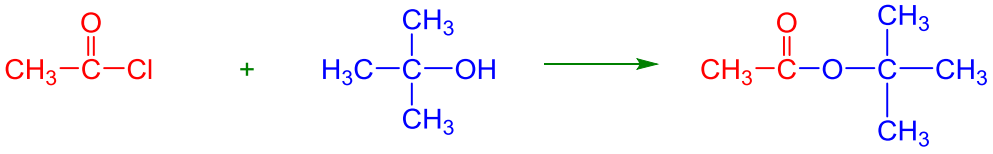
Rješenja

8.1.

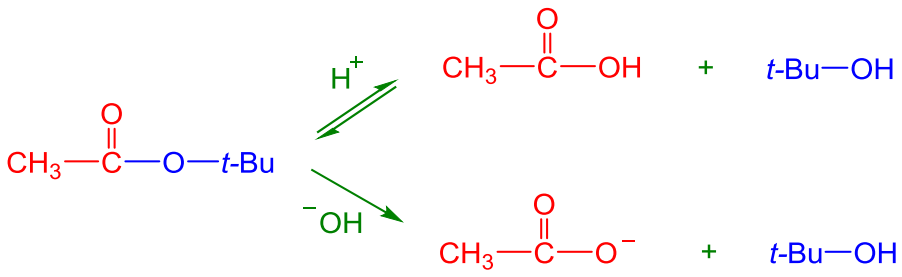
(a)



(b)

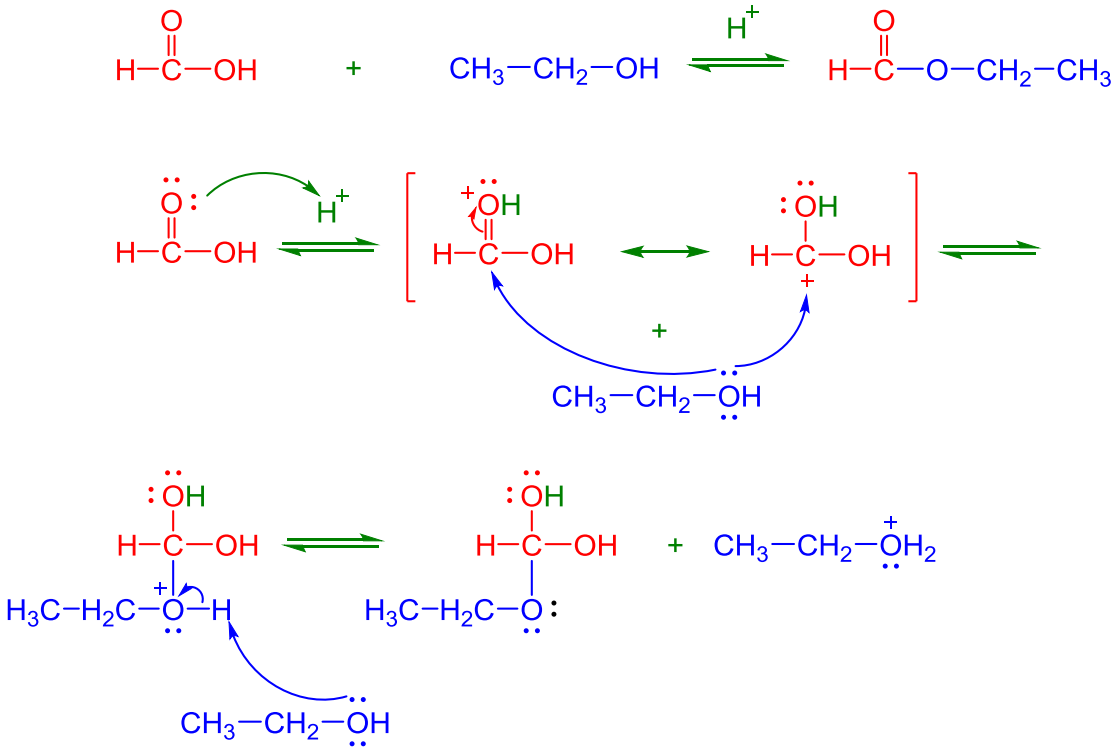


(c)

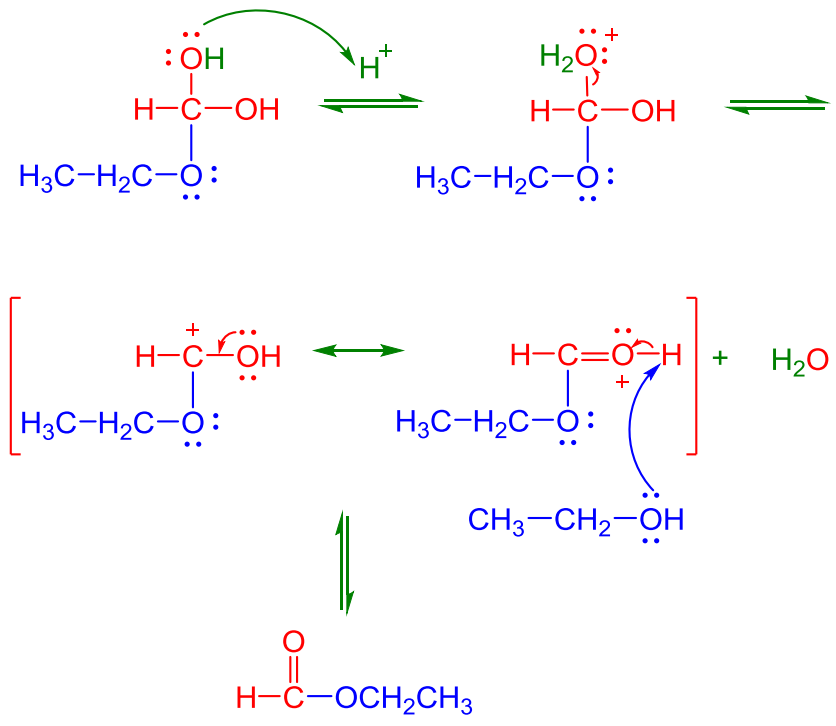


8.2.

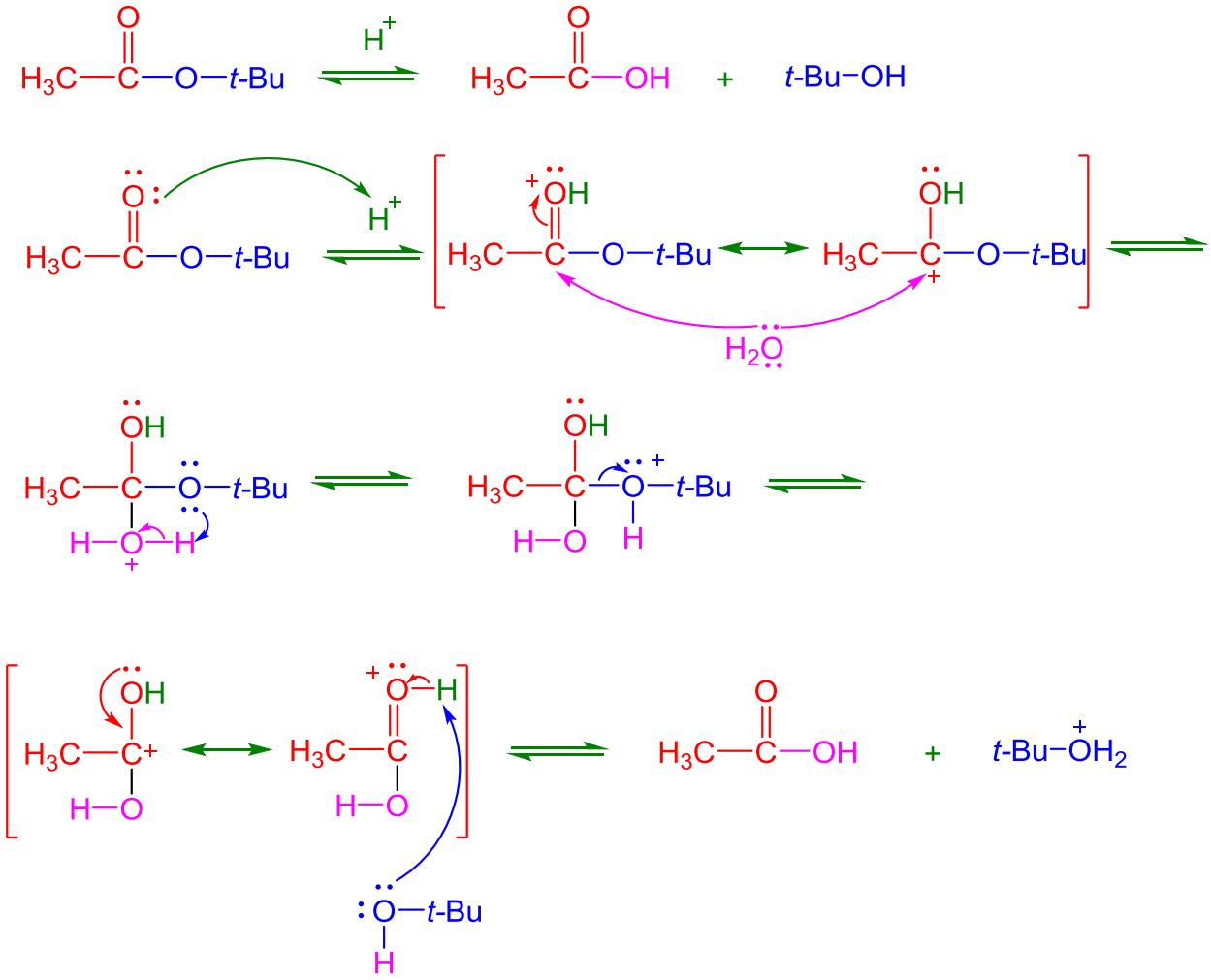
1. Kiselo-katalizirana adicija alkohola na karbonilnu skupinu



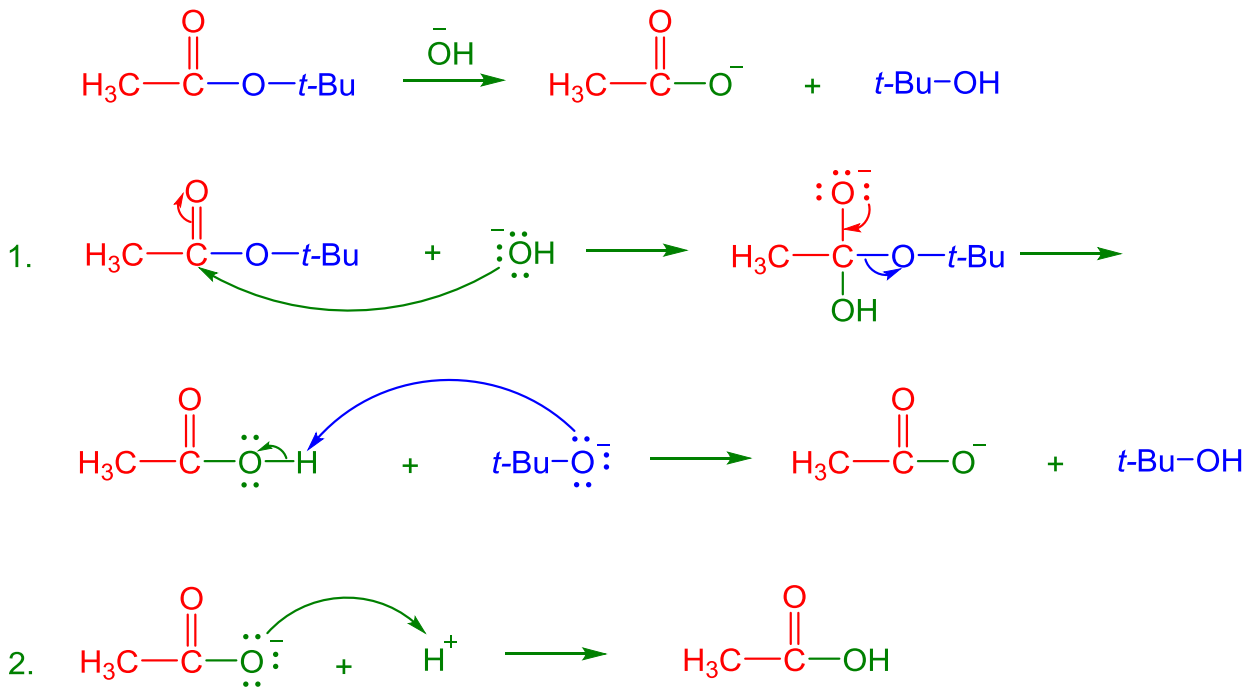
2. Kiselo-katalizirana dehidratacija



8.3.

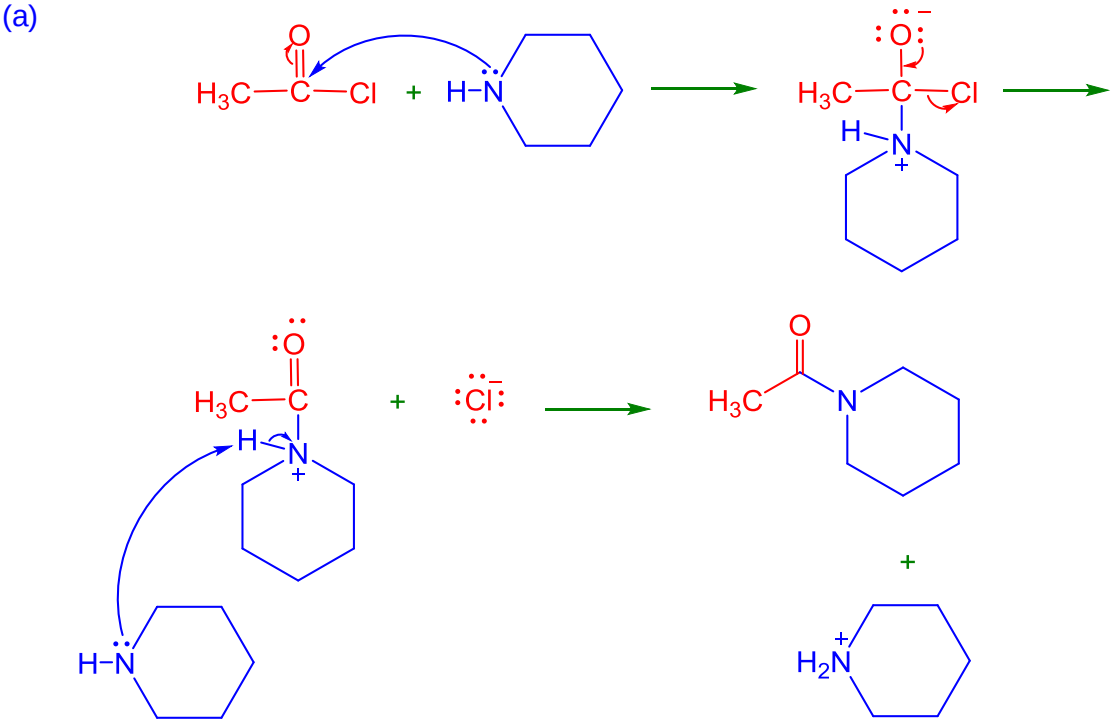


8.4.

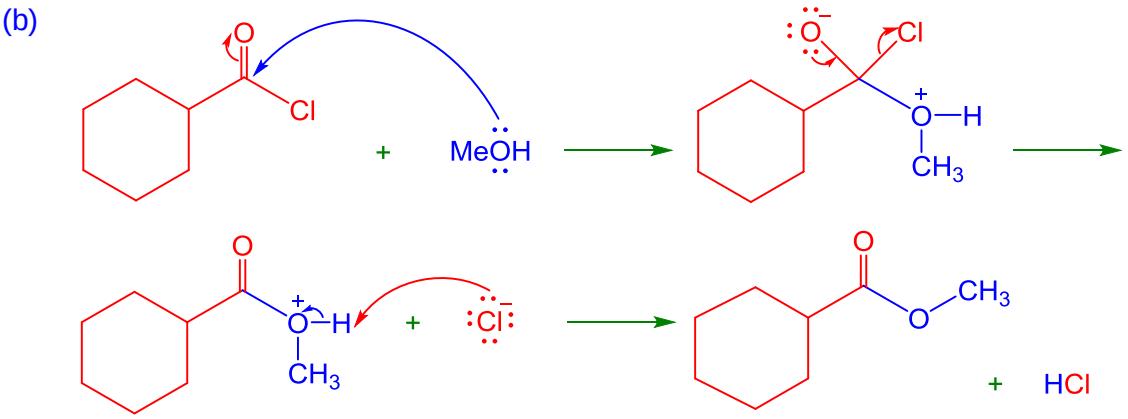


8.5.

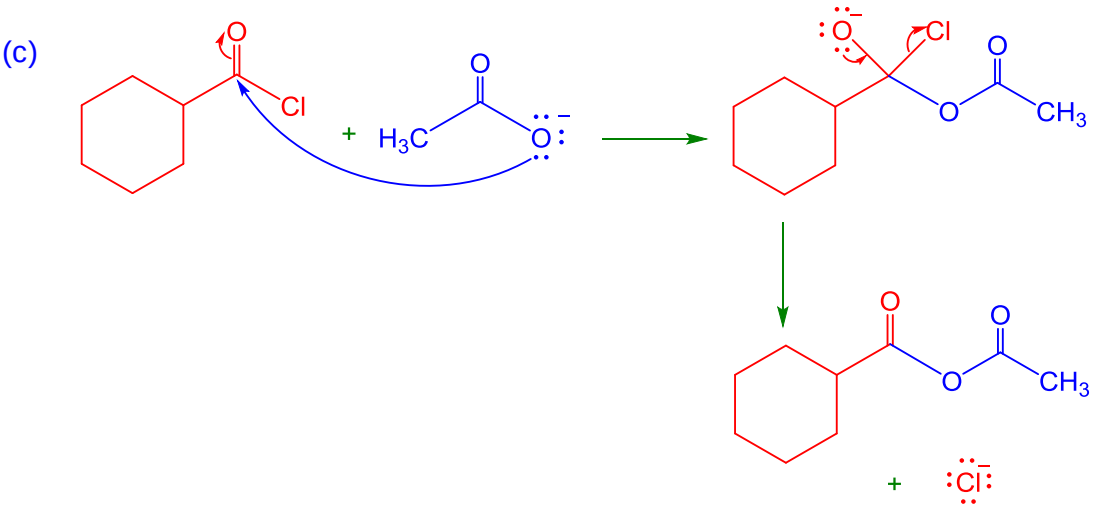
(a)



(b)



(c)



9. Aromatski spojevi. Elektrofilna aromatska supstitucija

Kriteriji koje moraju zadovoljavati aromatski spojevi:

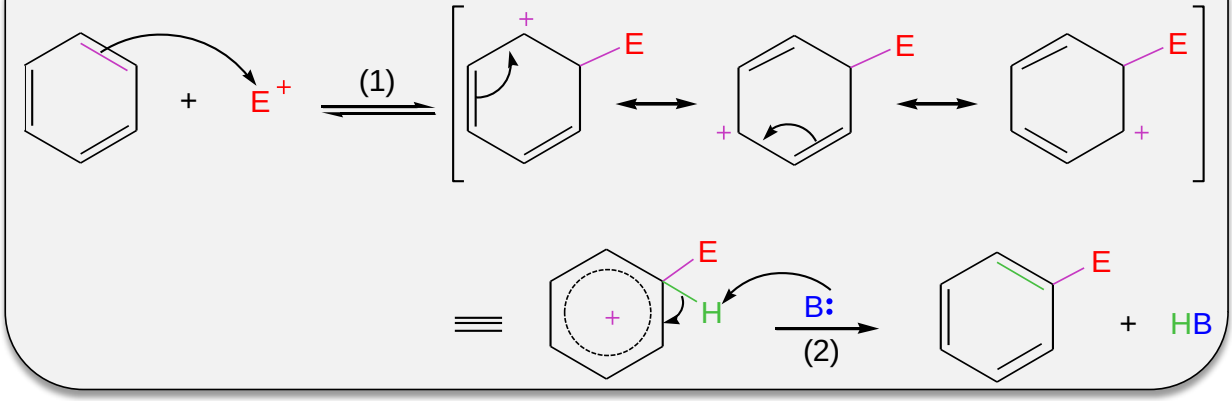
1) struktura mora biti *ciklička* i sadržavati *konjugirane π-veze*,
2) svaki atom u prstenu mora imati *nehibridiziranu* p-*orbitalu,*
3) nehibridizirane *p*-orbitale moraju se preklapati (*struktura mora biti planarna*),
4) delokalizacija π-elektrona mora dovesti do *smanjenja energije*.

Hückelovo pravilo za određivanje aromatičnosti:

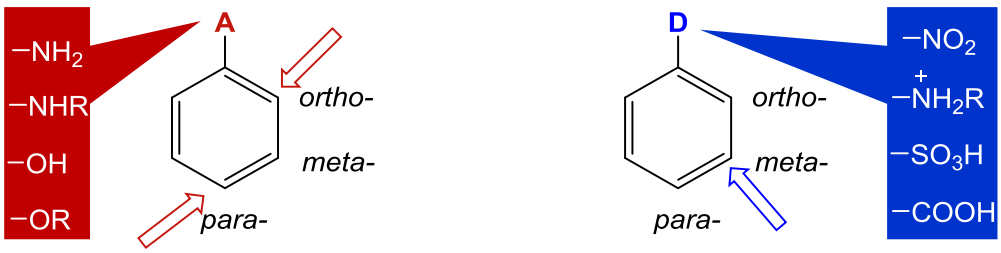
- (4n + 2) π-elektrona ⇒ aromatski spoj
- (4n) π-elektrona ⇒ antiaromatski spoj

} (n = 0, 1, 2, ...)

Opći mehanizam elektrofilne aromatske supstitucije



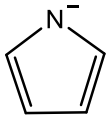
Priroda supstituenta vezanog na benzensku jezgru određuje mjesto daljnje supstitucije. Oni supstituenti koji imaju sposobnost doniranja elektrona karbokationskom međuproduktu stabilizirat će karbokation i ubrzati reakciju – **aktivirajući supstituenti A (usmjeravaju u *ortho* i *para*-položaj)**. Supstituenti koji imaju sposobnost odvlačenja elektrona iz benzenskog prstena destabilizirat će karbokation i smanjiti reaktivnost – **deaktivirajući supstituenti D (usmjeravaju u *meta*-položaj)**.

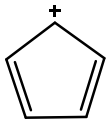


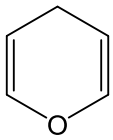
Zadaci

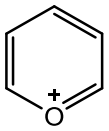
9.1. Označite prikazane molekule i ione kao aromatske, antiaromatske i nearomatske.

(a) 

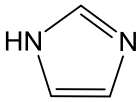
(b) 

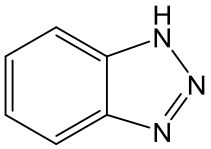
(c) 

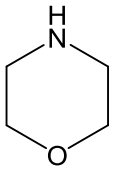
(d) 

(e) 

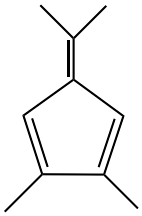
9.2. Označite dušikove atome kao jake odnosno slabe baze.

(a) 

(b) 

(c) 

9.3. Objasnite neuobičajenu kiselost prikazanog ugljikovodika.



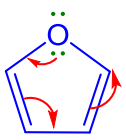
9.3. Predložite reakcijski mehanizam priprave toluena.

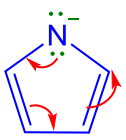
9.4. Prikažite sve moguće produkte koji nastaju kloriranjem toluena. Označite njihov udio (manje/više) i objasnite taj omjer.

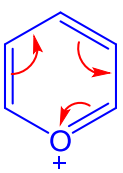
9.5. Prikažite sve moguće produkte koji nastaju kloriranjem nitrobenzena. Označite njihov udio (manje/više) i objasnite taj omjer.

Rješenja

9.1.

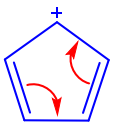
(a) 

(b) 

(e) 

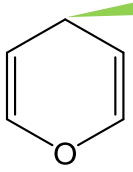
(4n + 2) π-elektrona = 6 π-elektrona ⇒ n = 1 ⇒ aromatski spojevi

(c)



(4n) π-elektrona = 4 π-elektrona ⇒ n = 1 ⇒ antiaromatski spoj

(d)



*sp*³-hibridizirani C-atom ⇒ antiaromatski spoj

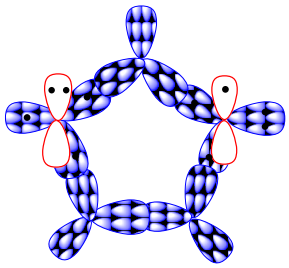
9.2.

(a)

p-orbitala (delokalizirani elektroni) ⇓ slaba baza

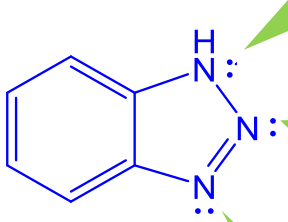
*sp*²-orbitala (lokalizirani elektroni) ⇓ jaka baza

(4n) π-elektrona = 6 π-elektrona ⇒ n = 1 ⇒ aromatski spoj



(b)

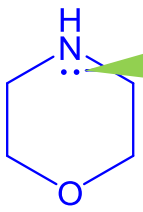
p-orbitala (delokalizirani elektroni) ⇓ slaba baza



*sp*²-orbitala (lokalizirani elektroni) ⇓ jaka baza

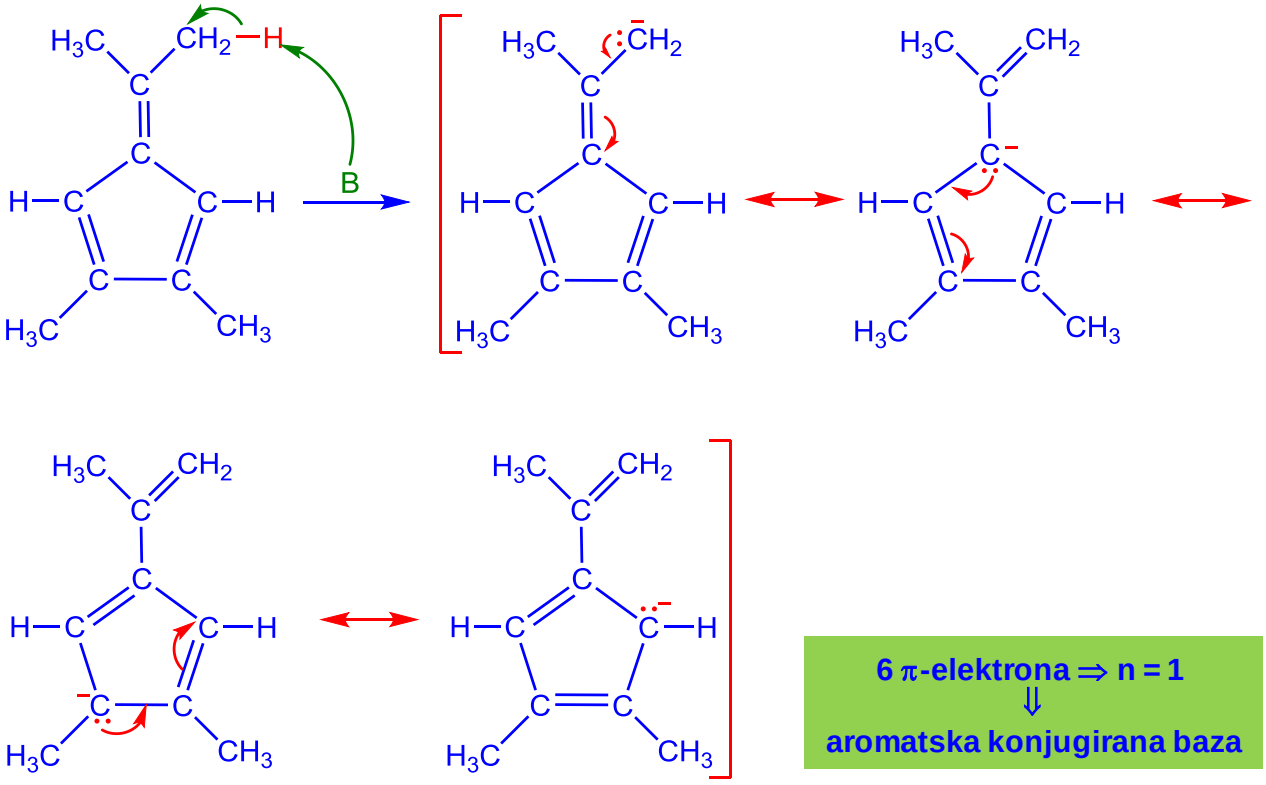
*sp*²-orbitala (lokalizirani elektroni) ⇓ jaka baza

(c)



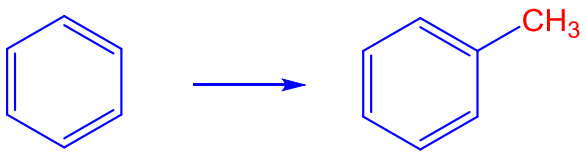
***sp*³-orbitala**
(lokalizirani elektroni)
⇓
jaka baza

9.3.



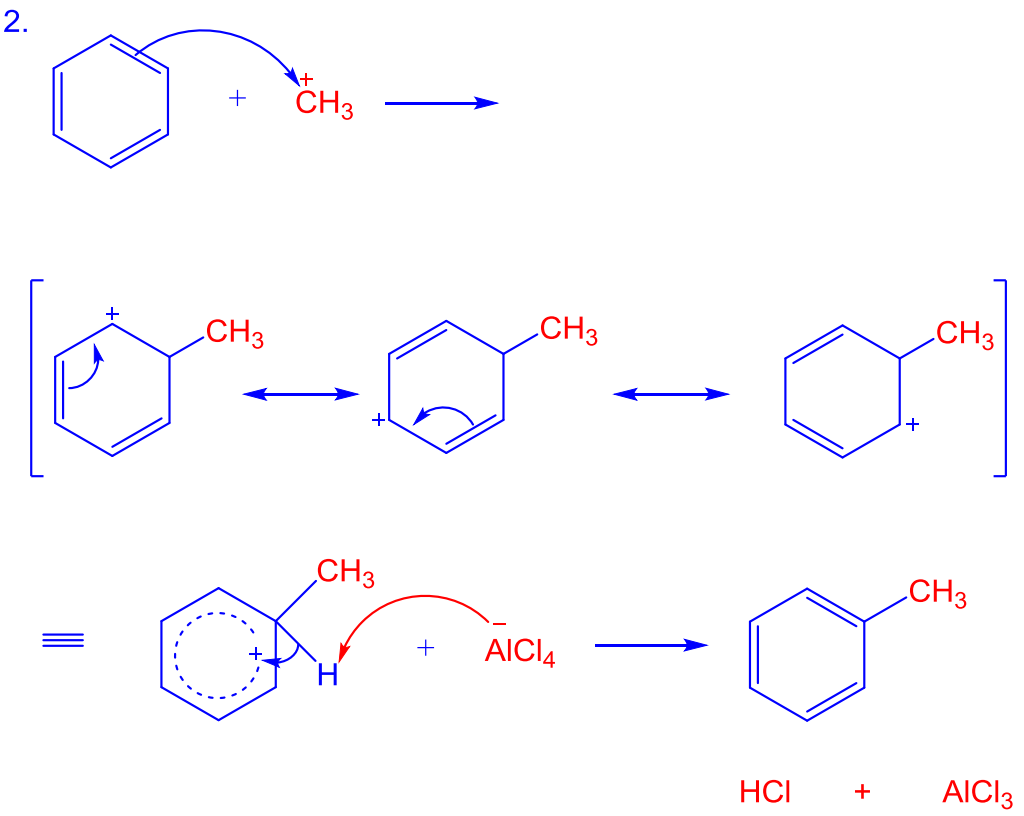
6 π-elektrona ⇒ n = 1
⇓
aromatska konjugirana baza

9.6.

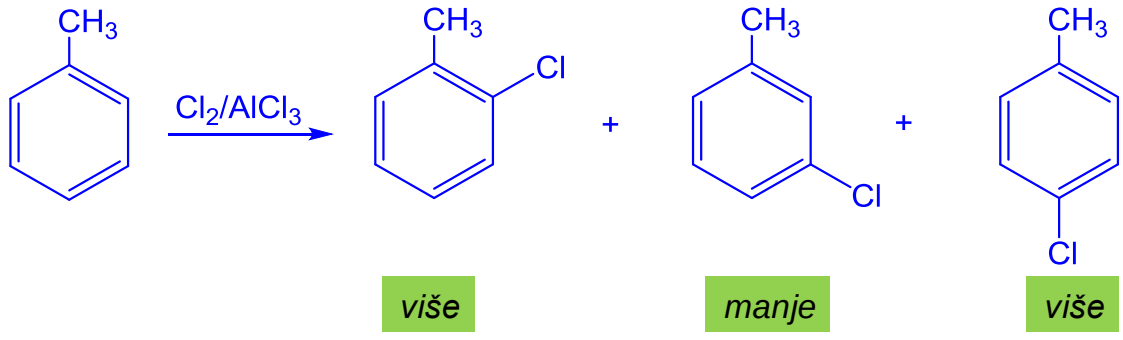


1. 

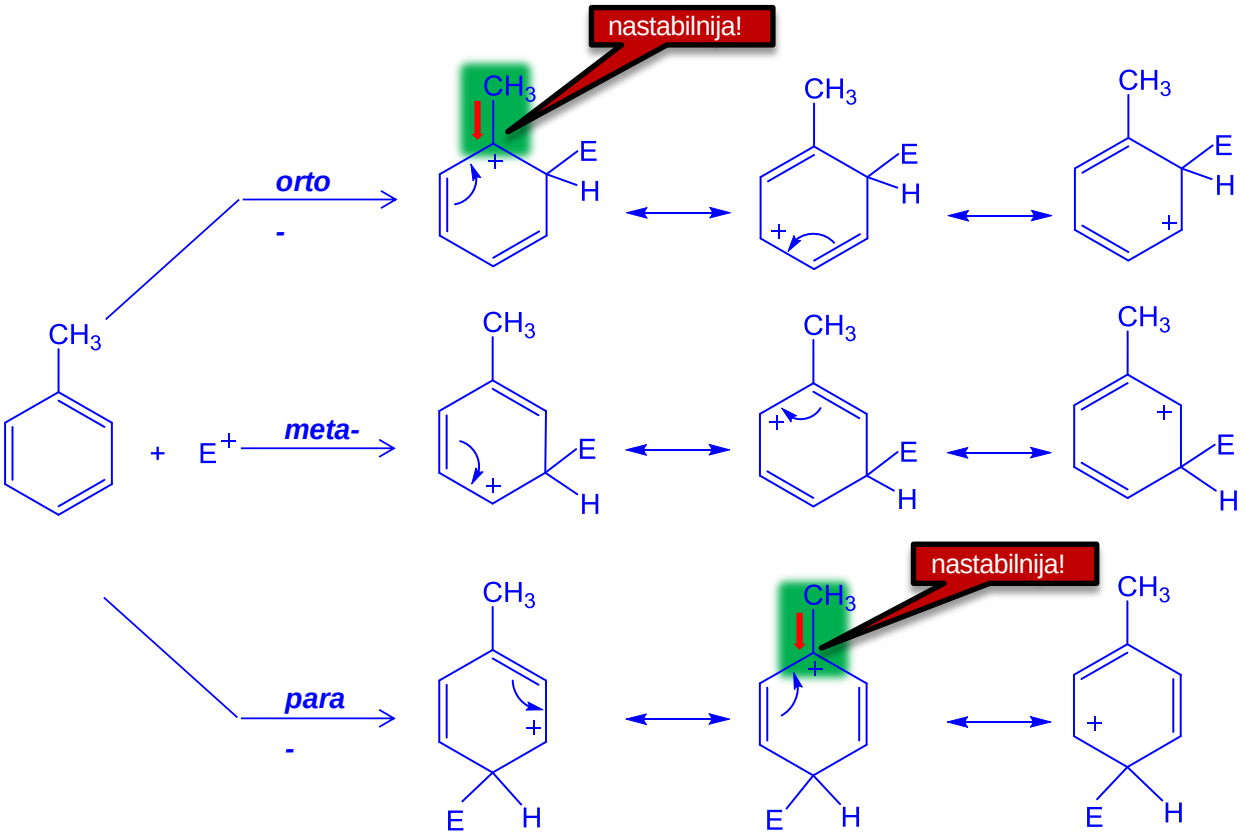
2.



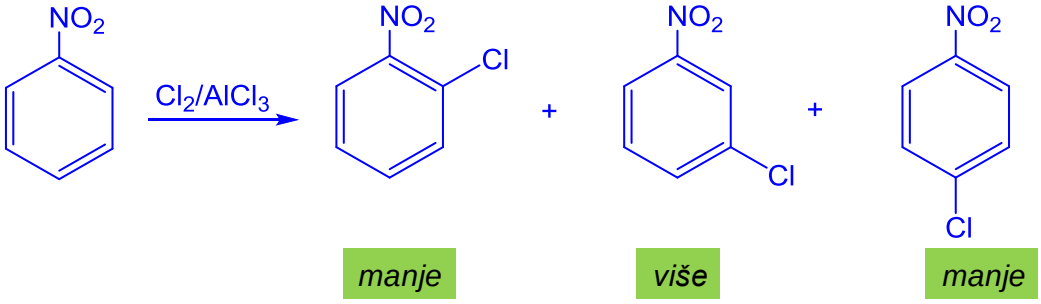
9.7.



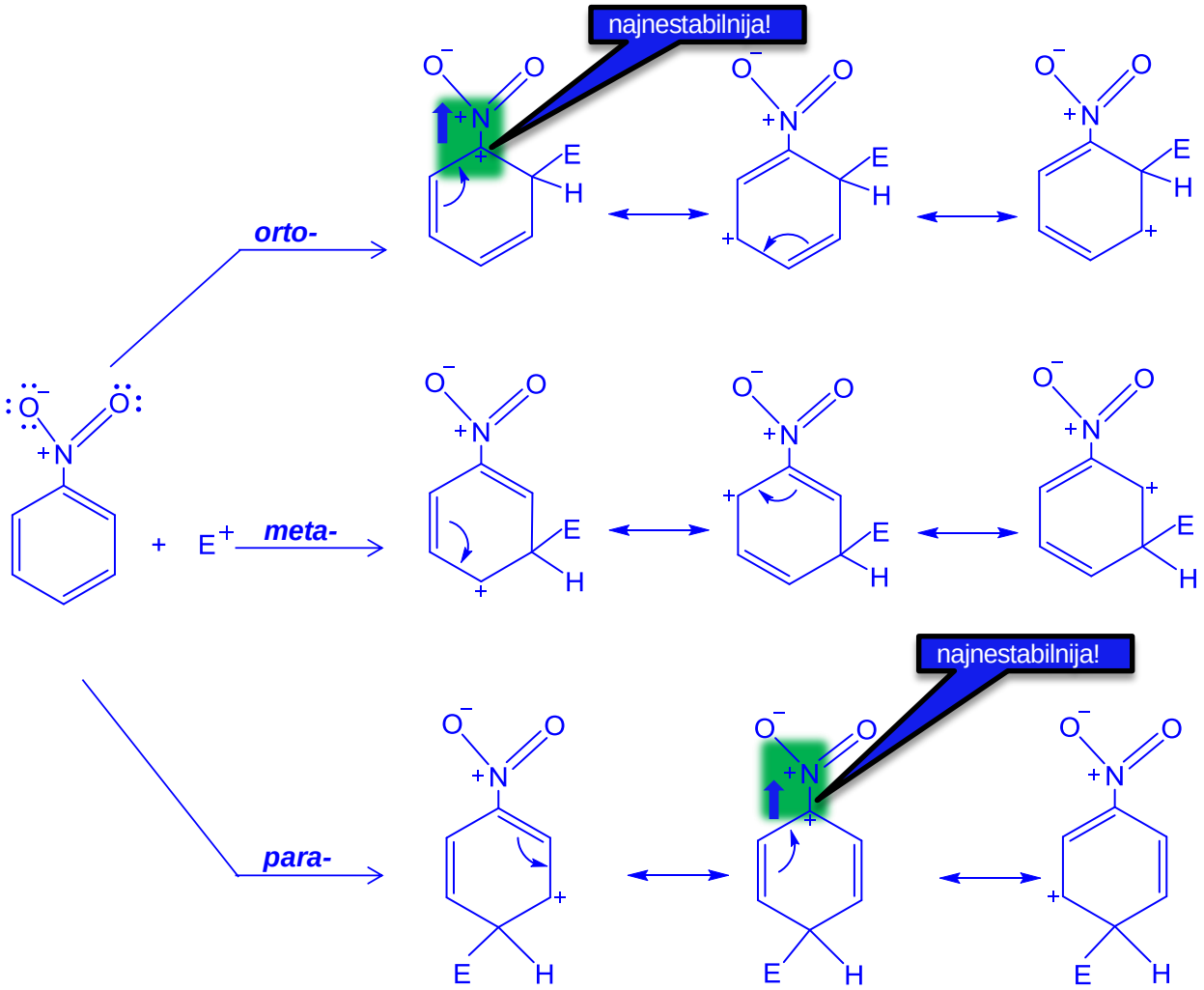
Alkilna skupina induktivnim utjecajem stabilizira karbokation nastao vezanjem elektrofila u *ortho*- odnosno *para*-položaj:



9.8.



Elektron-odvlačeća nitro-skupina induktivnim utjecajem destabilizira karbokation nastao vezanjem elektrofila u *ortho*- odnosno *para*-položaj. Jedino *meta*-supstitucijom ugljikov atom na koji je vezana nitro-skupina ne sudjeluje u podjeli pozitivnog naboja.


najnestabilnija!
orto-
meta-
najnestabilnija!
para-