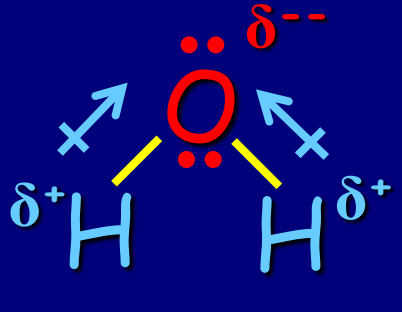
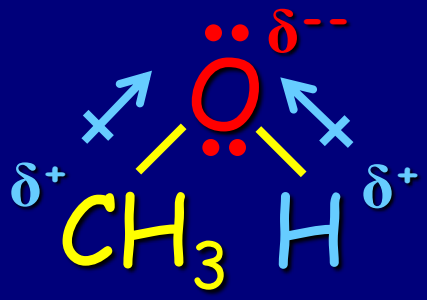
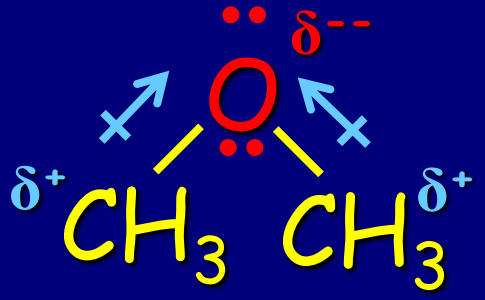
Poglavlje 8: Alkoholi R–OH



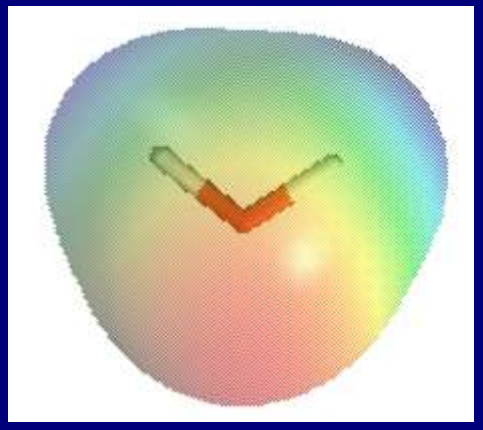
voda

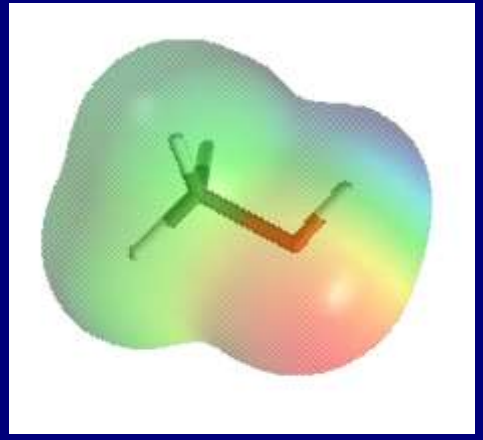


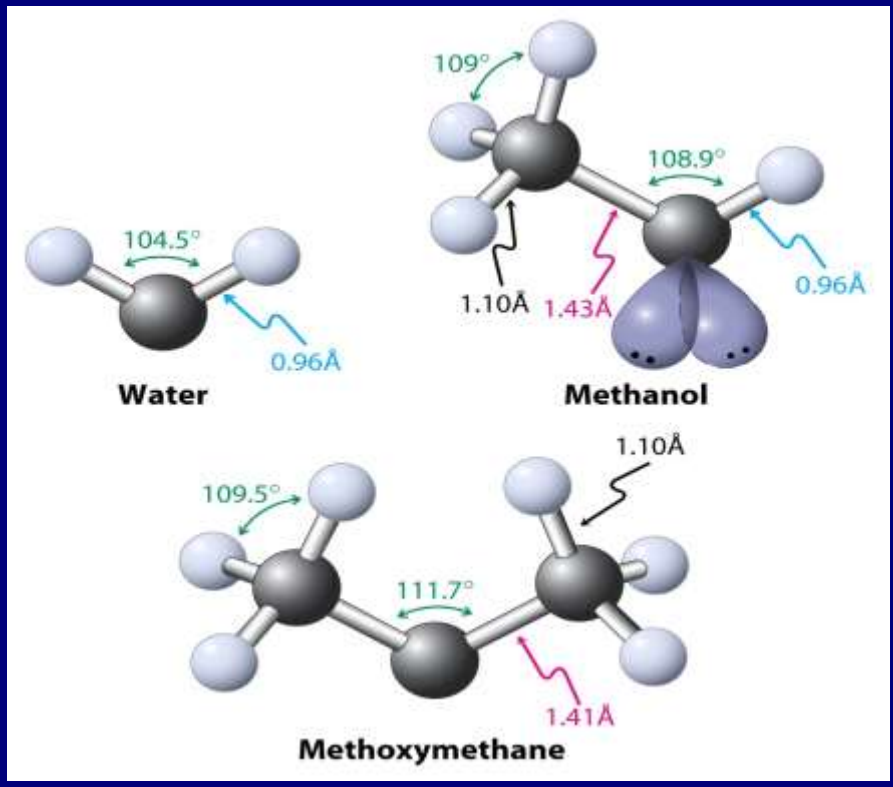
alkohol



etar







https://www.youtube.com/watch?v=9YSZZbw31Lc

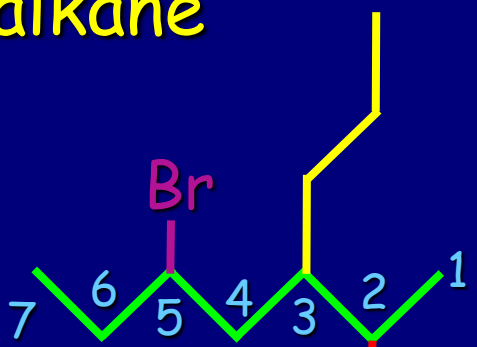
Nomenklatura

1. Pronaći najduži lanac koji sadrži –OH grupu: alkan → alkanol. Važno: Ovo ne mora biti i najduži lanac u molekulu!

2. Numerisanje tako da ugljenik na kome se nalazi OH grupa (HO-C) bude označen najmanjim brojem

3. Ostala pravila su ista kao i za alkane

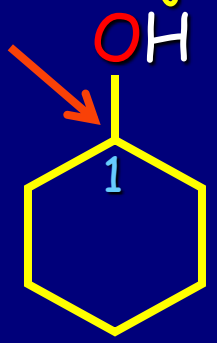
4,4-Dimetil-1-nonanol



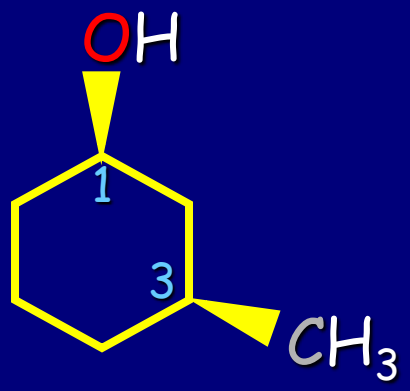
5-Brom-3-propil-2-heptanol
(najduži niz je C8)

Ciklični alkoholi su cikloalkanoli:

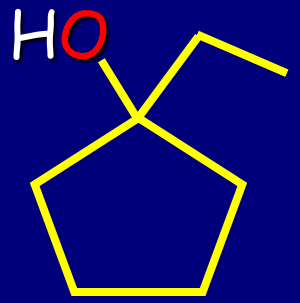
Definiše se kao C1,
nema numeracije u nazivu!!!



Cikloheksanol



Cis-3-metil-cikloheksanol



1-Etilciklo-pentanol

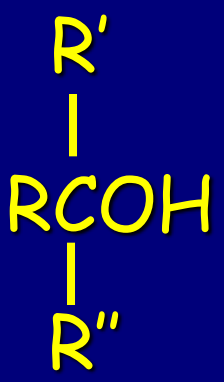
-OH kao supstituent je hidroksi

-OR je alkoksi: Etri R-O-R', alkoksialkani

RCH_2OH

Primarni

Sekundarni



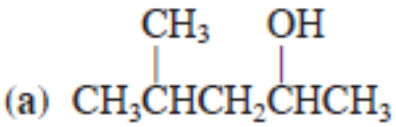
Tercijarni alkoholi

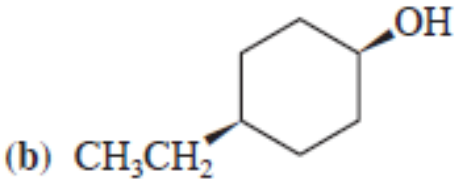
Vežba 8-1

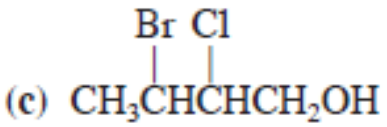
Nacrtajte strukture datih alkohola. (a) (*S*)-3-Metil-3-heksanol; (b) *trans*-2-bromciklopentanol; (c) 2,2-dimetil-1-propanol (neopentil-alkohol).

Vežba 8-2

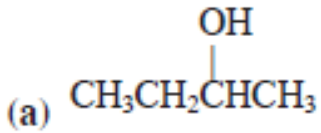
Imenujte sledeća jedinjenja.

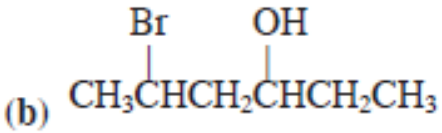




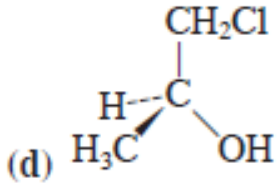


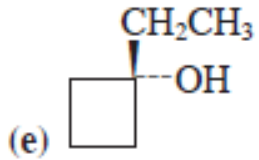
21. Imenujte navedene molekule prema IUPAC-ovom sistemu nomenklature. Naznačite u svakom posebnom slučaju stereohemiju (ukoliko postoji), i da li je molekul primarni, sekundarni ili tercijarni alkohol.

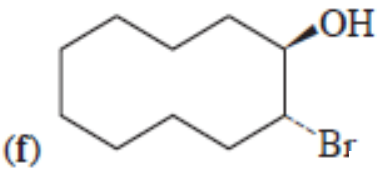




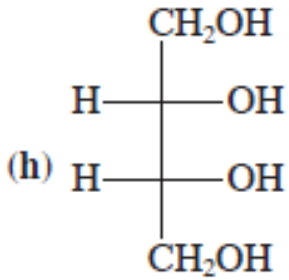
(c) $HOCH_2CH(CH_2CH_2CH_3)_2$

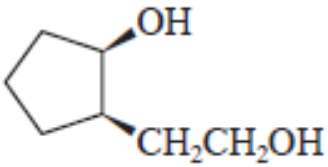


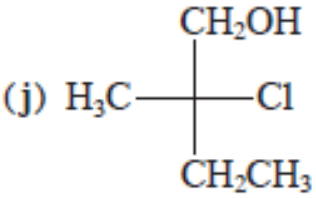




(g) $C(CH_2OH)_4$

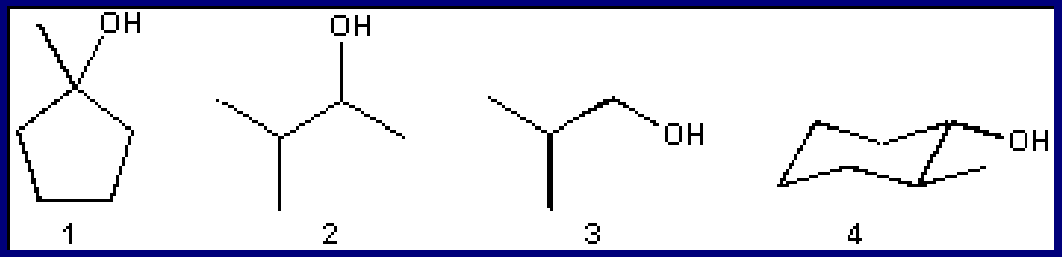






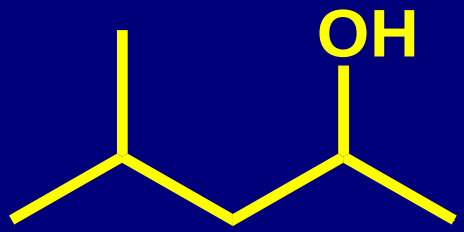
22. Nacrtajte strukturne formule datih alkohola. (**a**) 2-(Trimetilsilil)etanol; (**b**) 1-metilciklopropanol; (**c**) 3-(1-metiletil)-2-heksanol; (**d**) (*R*)-2-pentanol; (**e**) 3,3-dibromcikloheksanol.

Koje od sledećih jedinjenja je sekundarni alkohol?



Koji je naziv ispravan za sledeće jedinjenje:

A. 2-metil-4-pentanol
B. 1,3-dimetil-1-butanol
C. 4-hidroksi-2-metilpentan
D. 4-metil-2-pentanol
E. 2-hidroksi-4-metilpentan



Struktura

O se može zamisliti kao sp^3-hibridizovan, "tetraedarski", to jest molekul alkohola je savijen - nije linearan

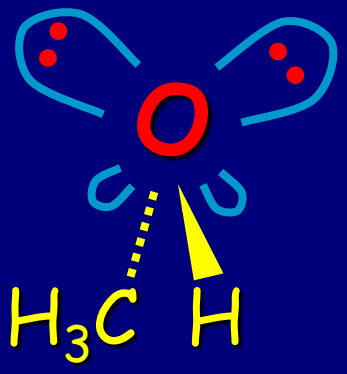
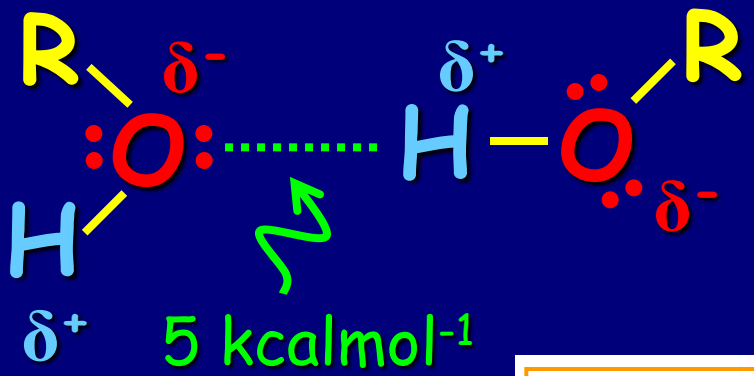


TABELA 8-1 Fizičke osobine alkohola i odabranih halogenalkana i alkana

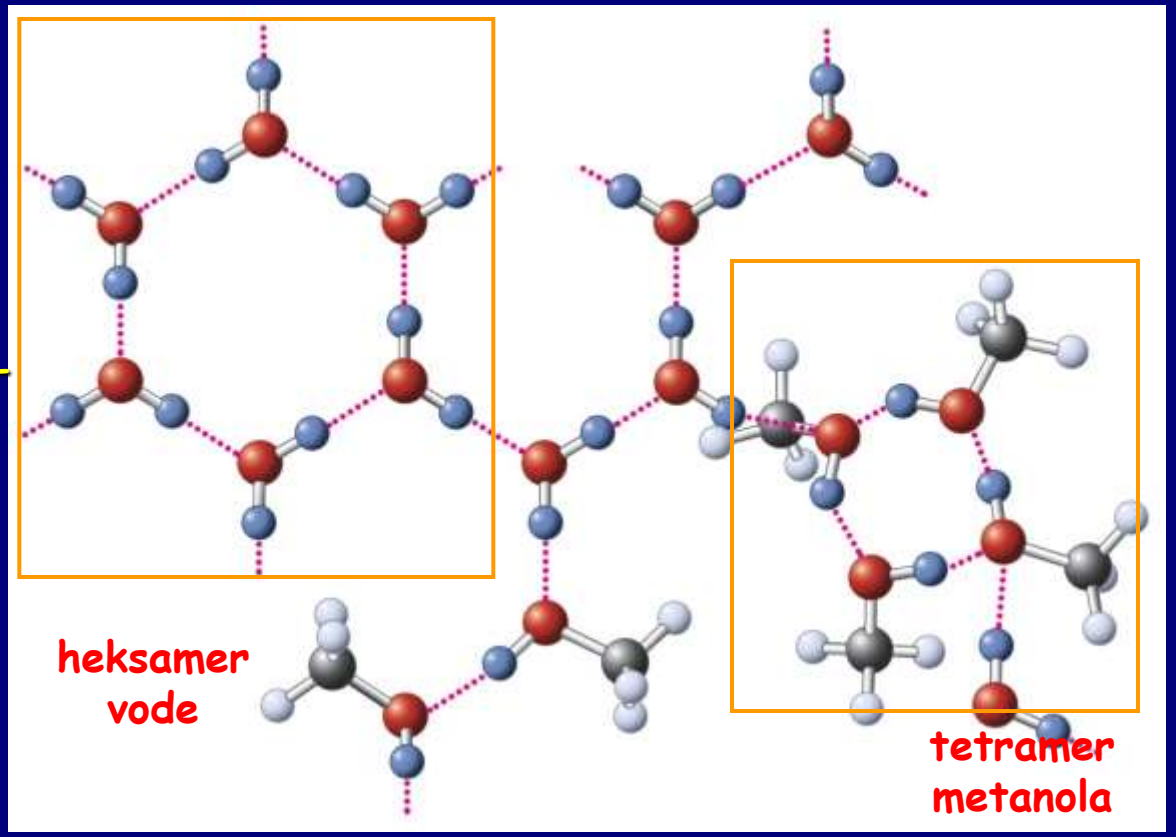
Jedinjenje	Ime prema IUPAC-u	Uobičajeno ime	Tačka topljenja (°C)	Tačka ključanja (°C)	Rastvorljivost u H_2O na 23°C
CH_3OH	metanol	metil-alkohol	−97,8	65,0	neograničeno
CH_3Cl	hlormetan	metil-hlorid	−97,7	−24,2	0,74-g/100-mL
CH_4	metan		−182,5	−161,7	3,5-mL (gas)/100-mL
CH_3CH_2OH	etanol	etil-alkohol	−114,7	78,5	neograničeno
CH_3CH_2Cl	hloretan	etil-hlorid	−136,4	12,3	0,447-g/100-mL
CH_3CH_3	etan		−183,3	−88,6	4,7-mL (gas)/100-mL
$CH_3CH_2CH_2OH$	1-propanol	propil-alkohol	−126,5	97,4	neograničeno
$CH_3CH_2CH_3$	propan		−187,7	−42,1	6,5-mL (gas)/100-mL
$CH_3CH_2CH_2CH_2OH$	1-butanol	butil-alkohol	−89,5	117,3	8,0-g/100-mL
$CH_3(CH_2)_4OH$	1-pentanol	pentil-alkohol	−79	138	2,2-g/100-mL

Najupečatljivije: Relativno visoke tačke topljenja i tačke ključanja; veoma dobra rastvorljivost u vodi. Zašto?

Vodonične veze

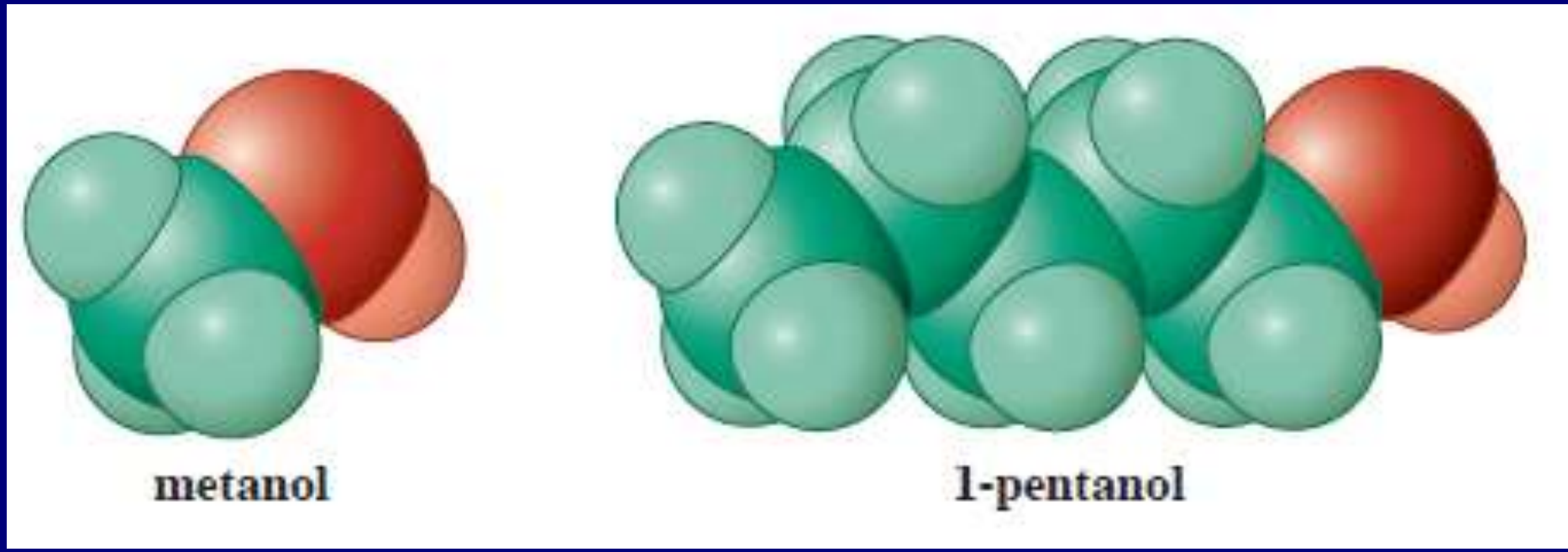


Sposobnost vodoničnog vezivanja vode i alkohola- alkoholi se dobro rastvaraju u vodi.



Hidrofobno-Hidrofilno

R——OH



Rastvorljivost u vodi:
sa povećanjem hidrofobnog alkil-dela opada rastvorljivost alkohola u vodi.

Kiselost

$ROH + H_2O \overset{K}{\rightleftharpoons} RO^- + H_3O^+$ pK_a

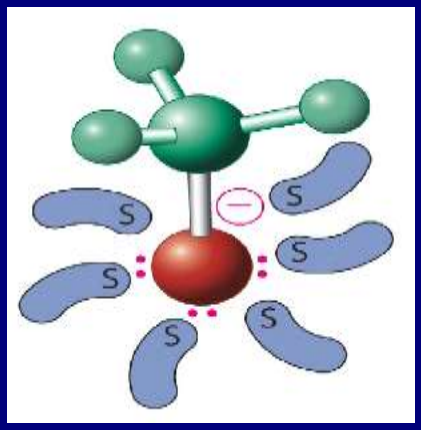
H_2O	15.7
CH_3OH	15.5
CH_3CH_2OH	15.9
$(CH_3)_2CHOH$	17.1
$(CH_3)_3COH$	18
$ClCH_2CH_2OH$	14.3
CF_3CH_2OH	12.4
$CF_3CH_2CH_2OH$	15.4

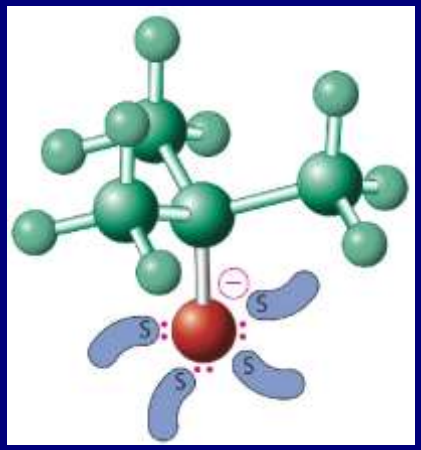
sterna zaklonjenost

Induktivni efekat

opada sa rastojanjem.

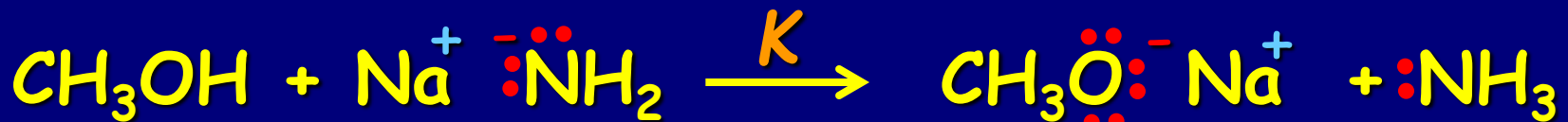
Manji metoksidni jon je bolje solvatisan nego veći tercijarni butoksidni jon

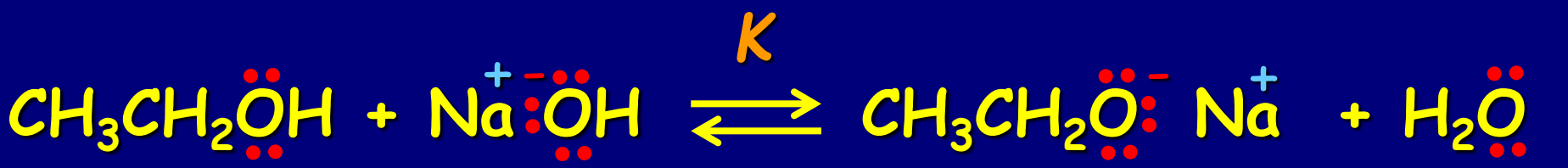




Alkoksidi RO^-

Dobijanje:

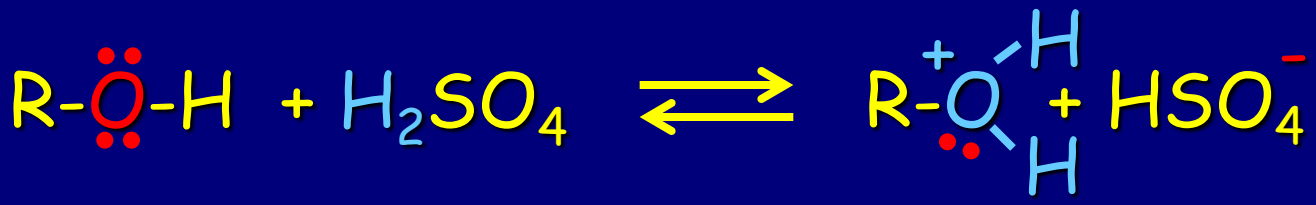




Kada je CH_3CH_2OH rastvarač, ravnoteža je pomerena udesno

Alkoholi su i baze:

Slobodan e-par se može protonovati. Molekuli koji su i kiseli i bazni, zovu se amfoterni



Oksonijum jon pK_a ~ -3

poređenje 

Amonijum jon pK_a ~10

TABELA 8-3

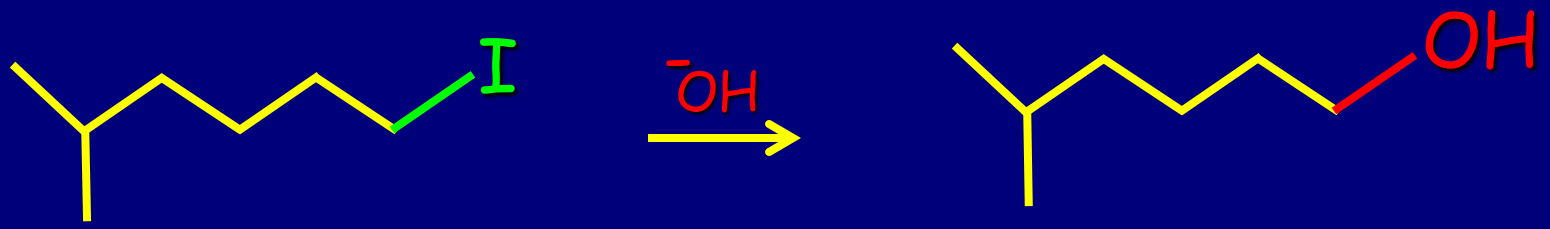
pK_a vrednosti četiri protonovana alkohola

Jedinjenje	pK_a
$CH_3\overset{+}{O}H_2$	−2,2
$CH_3CH_2\overset{+}{O}H_2$	−2,4
$(CH_3)_2CH\overset{+}{O}H_2$	−3,2
$(CH_3)_3C\overset{+}{O}H_2$	−3,8

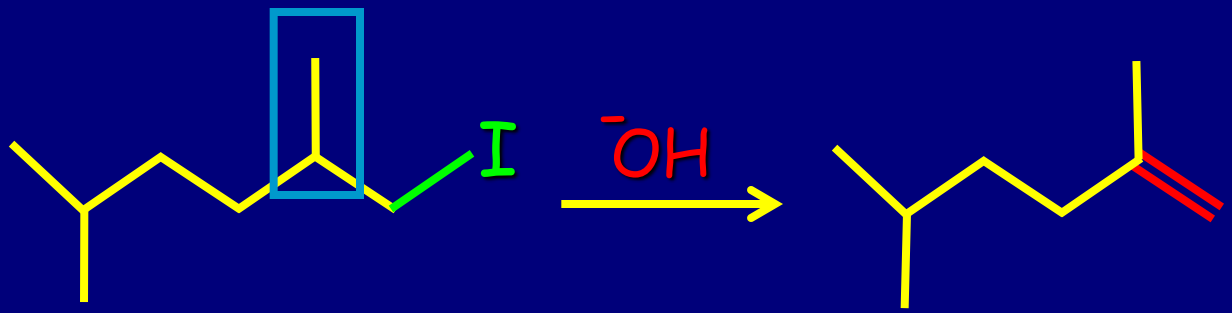
Sinteze alkohola R-OH

1. R-X ⋯⋯→ R-OH Nukleofilnom supstitucijom

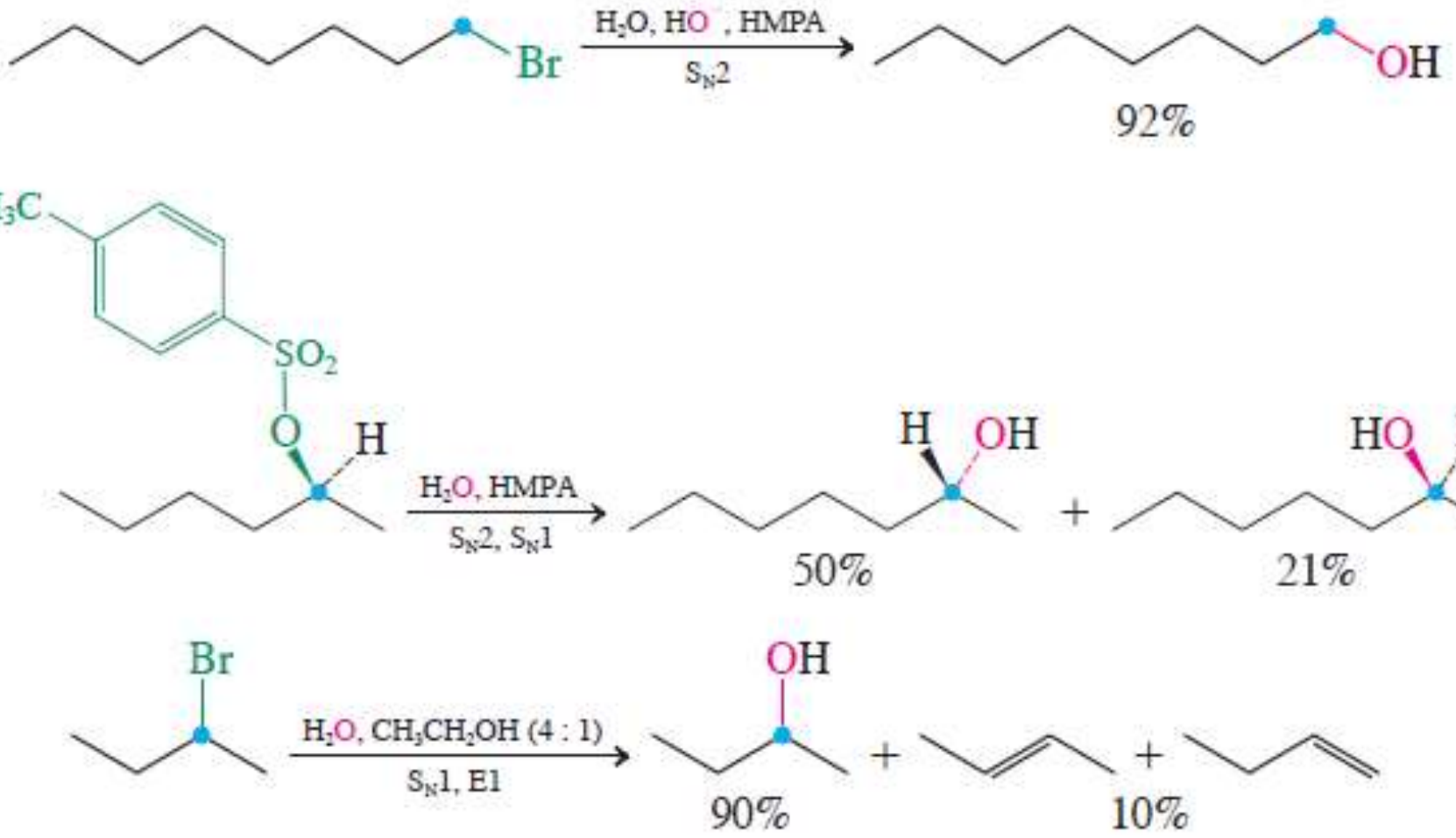
S_N2: R_{prim}-X



Problem: β-račvanje → E2 (⁻OH = baza)

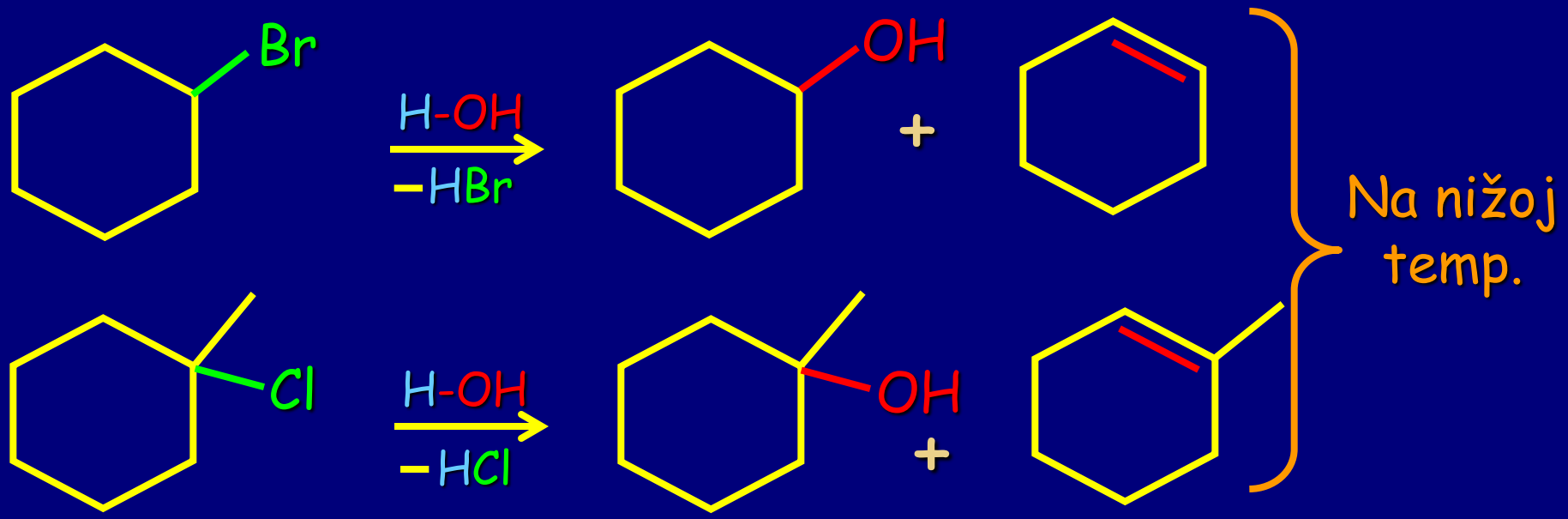


Dobijanje alkohola nukleofilnom supstitucijom

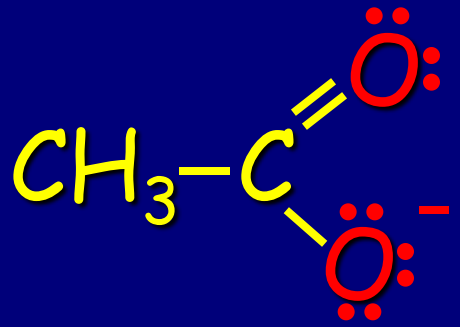


S_N1: $R_{sec}-X$, $R_{tert}-X$

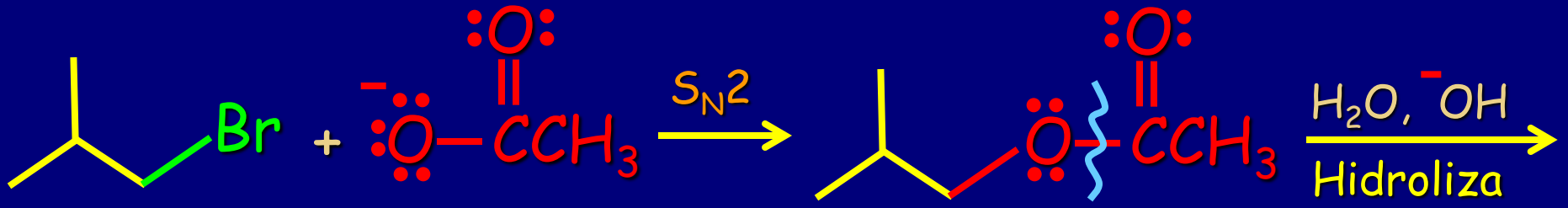
Problem: E1

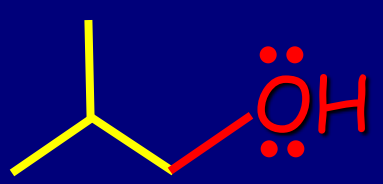


Rešenje za problem sa E2: Upotreba kiseoničnih nukleofila koji su manje bazni od vode, "maskirani" OH-ekvivalent



Acetat (za račvaste R_{prim}, ili R_{sec})

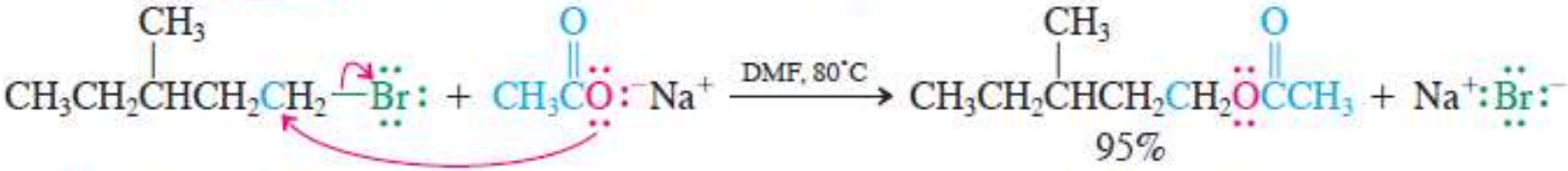




+ CH_3CO^-, uklanjaje obradom reakcione smeše

Alkoholi iz halogenalkana supstitucijom acetatom i hidrolizom

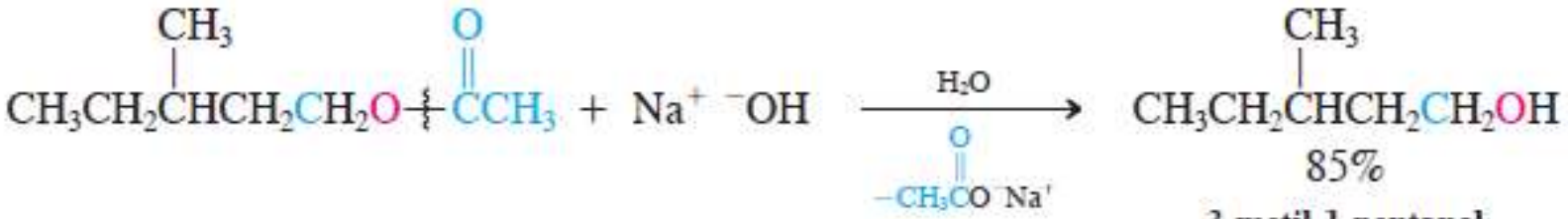
FAZA 1. Dobijanje acetata (S_N2-reakcija)



1-brom-3-metilpentan

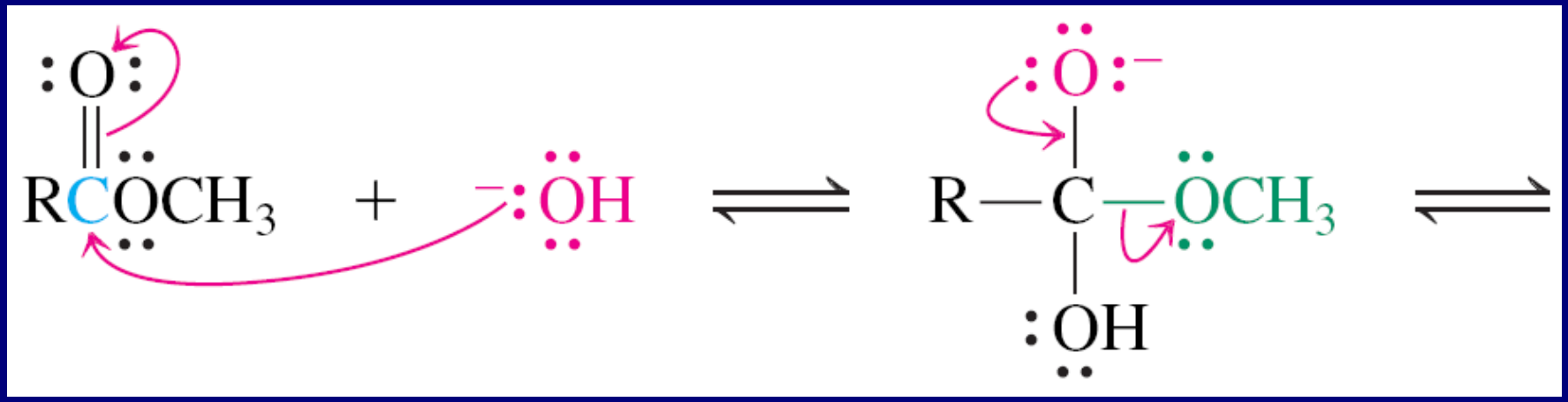
3-metilpentil-acetat
(estar)

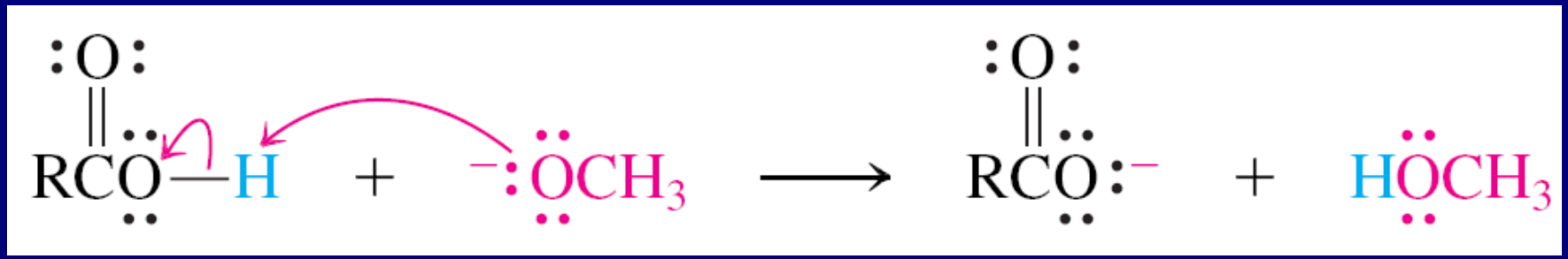
FAZA 2. Prevođenje u alkohol (hidroliza estra)



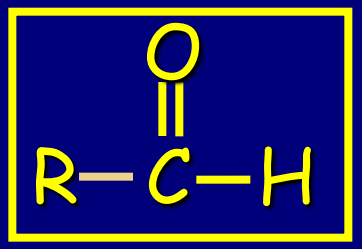
3-metil-1-pentanol

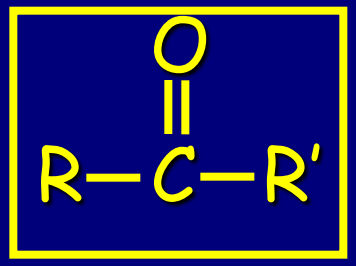
Hidroliza estara



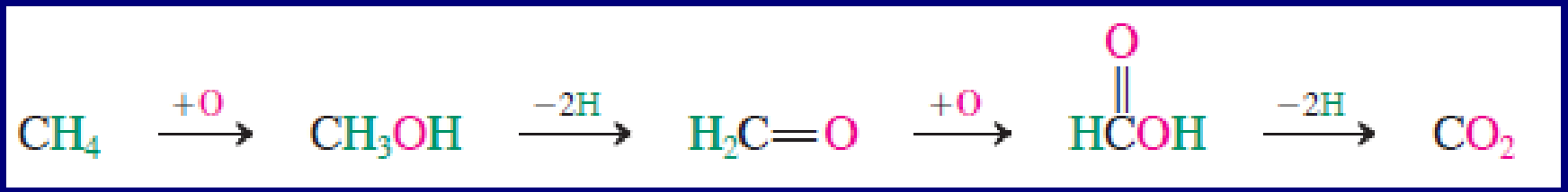


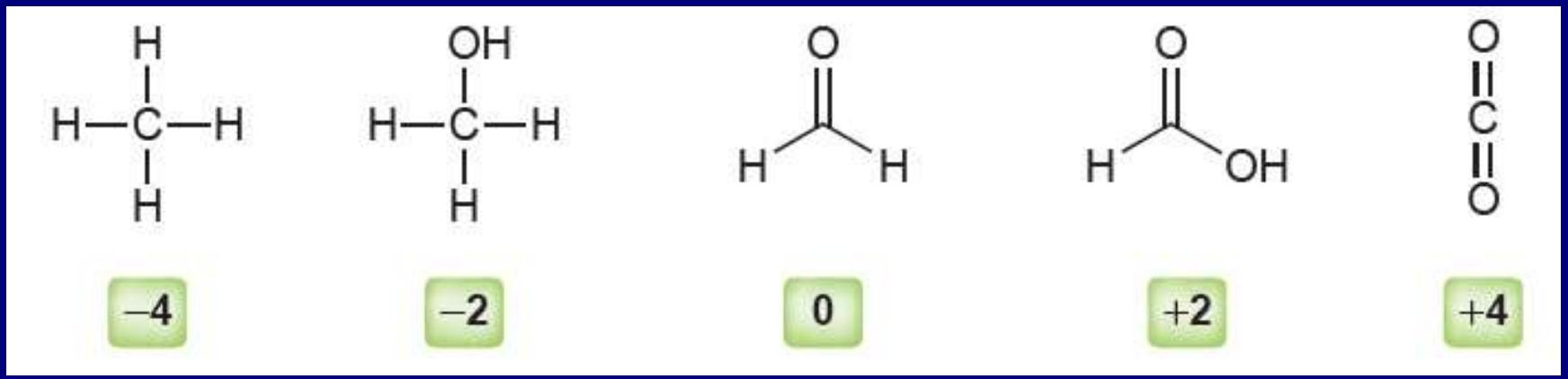
2. Redukcija aldehida i ketona





Redoks odnosi:



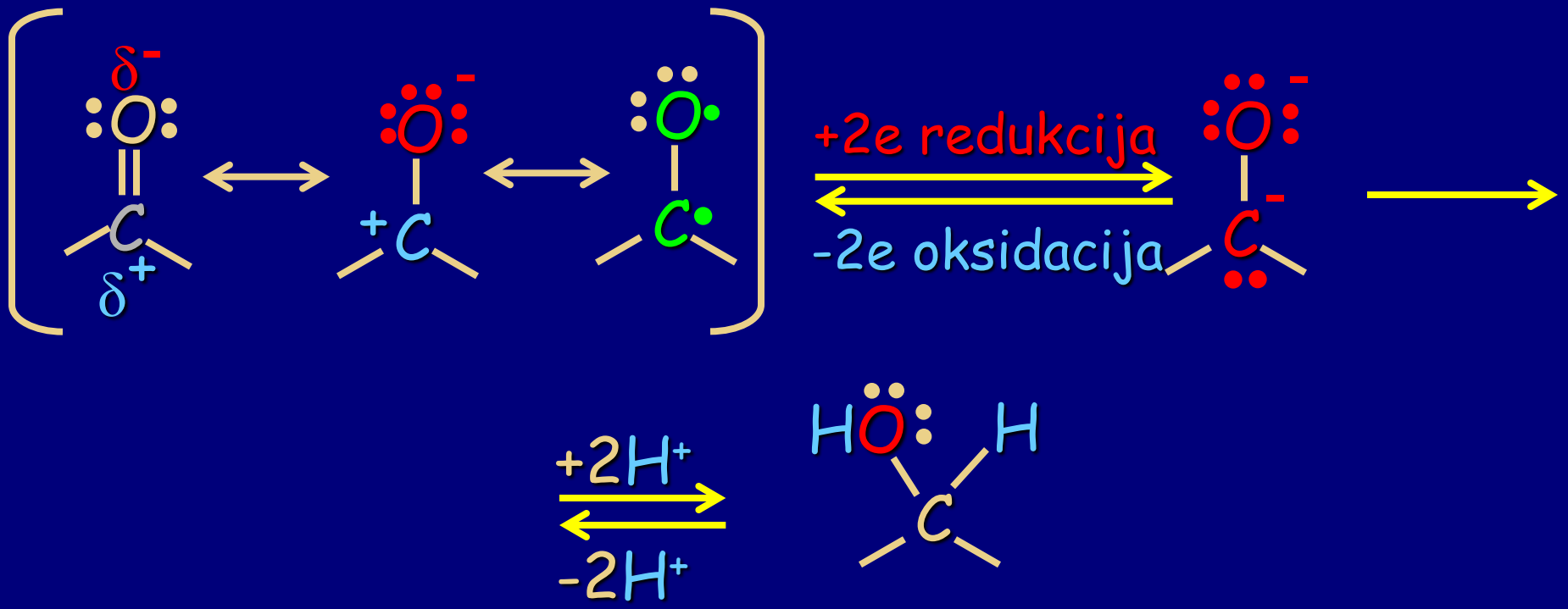


Oksidacija:

- otpuštanje elektrona
- proces kojim se molekulu dodaju elektronegativni atomi, kao što su halogeni ili kiseonik, ili iz koga se uklanja vodonik

Redukcija:

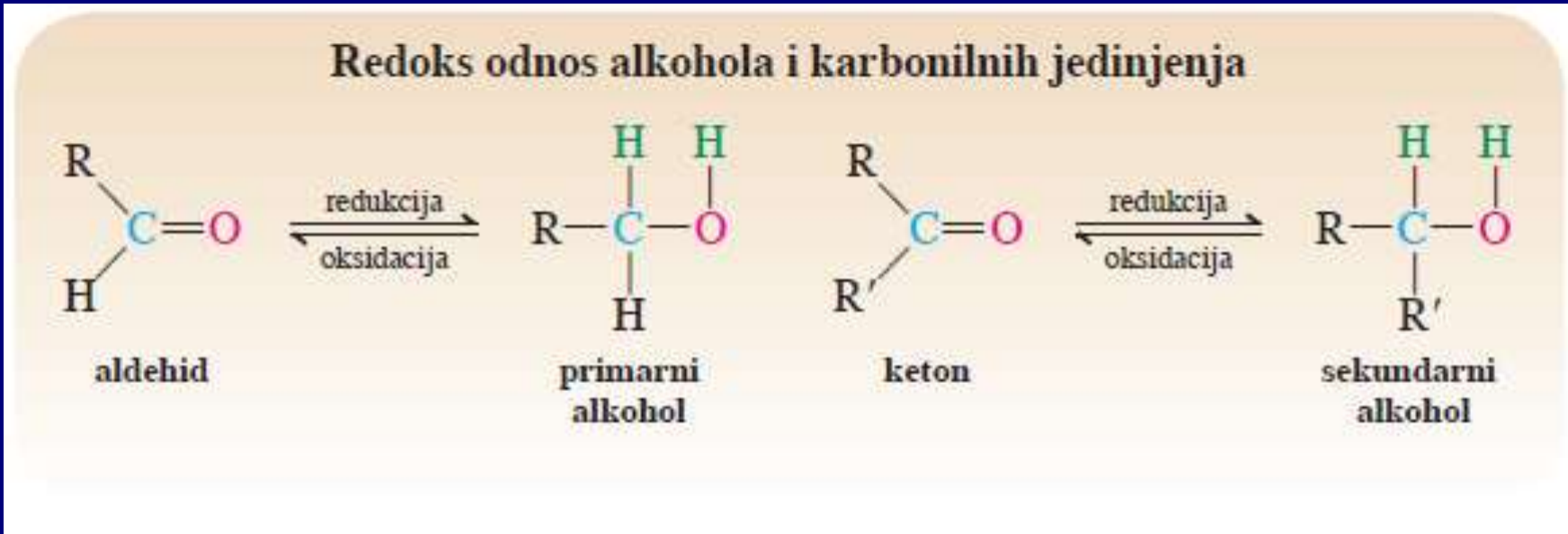
- primanje elektrona
- uklanjanje kiseonika ili dodavavanje vodonika



Ketoni $\underset{ox}{\overset{red}{\rightleftharpoons}}$ R_{sec}-OH

Aldehidi $\underset{ox}{\overset{red}{\rightleftharpoons}}$ R_{prim}-OH

} Reagensi?



Ketoni $\underset{ox}{\overset{red}{\rightleftharpoons}}$ R_{sec}-OH

Aldehidi $\underset{ox}{\overset{red}{\rightleftharpoons}}$ R_{prim}-OH

} Reagensi?

Redukcija

- Hidrogenizacija: H_2 (obično pod pritiskom) i katalizatori (Pd, Pt)
- Primena hidridnih reagenasa $H:^-$ kompleksi: natrijum-borhidrid i litijum-aluminijumhidrid. U odnosu na LiH i NaH kompleksni hidridi su manje bazni i rastvorljivi u organskima rastvaračima

$$Na^+H:^- + \underset{sp^2}{BH_3} \longrightarrow Na^+\underset{sp^3}{BH_4}^-$$

$$Li^+H^- + AlH_3 \longrightarrow Li^+AlH_4^- \text{ (LAH)}$$

Hidridni kompleksi su bazni i podležu hidrolizi. Velika razlika u reaktivnosti

$NaBH_4$ je manje reaktivan ali je selektivniji reagens:

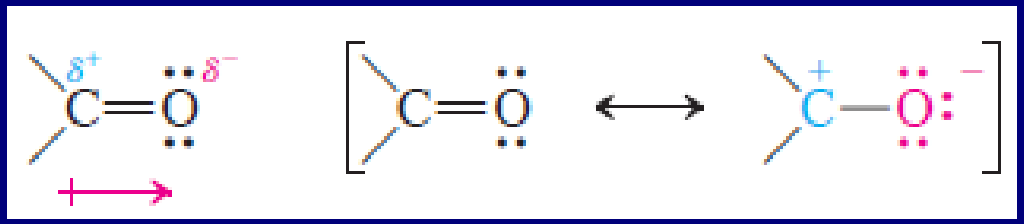
sporo, kao rastvarač se može koristiti CH_3OH

Ali:

Reaguje burno sa protičnim rastvaračim, za redukcije sa ovim reagensom koriste se aprotični rastvarači (etri)

$LiAlH_4$ (ali ne i $NaBH_4$) može redukovati i halogenide:

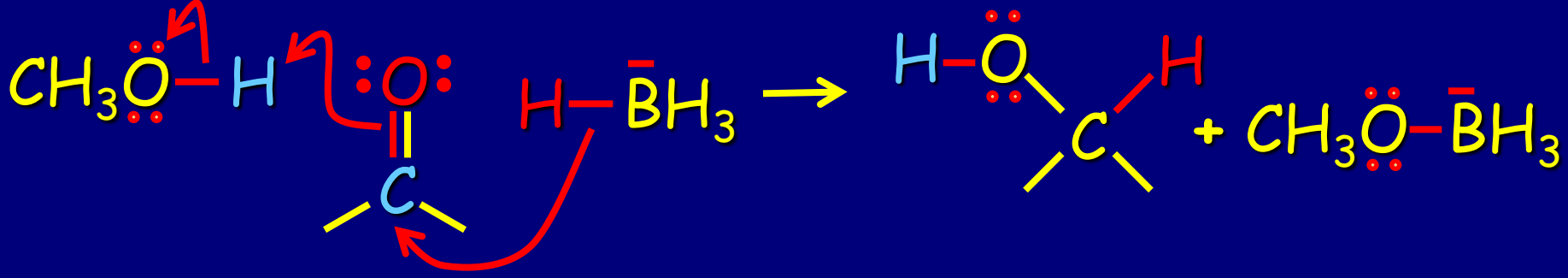
Mehanizam

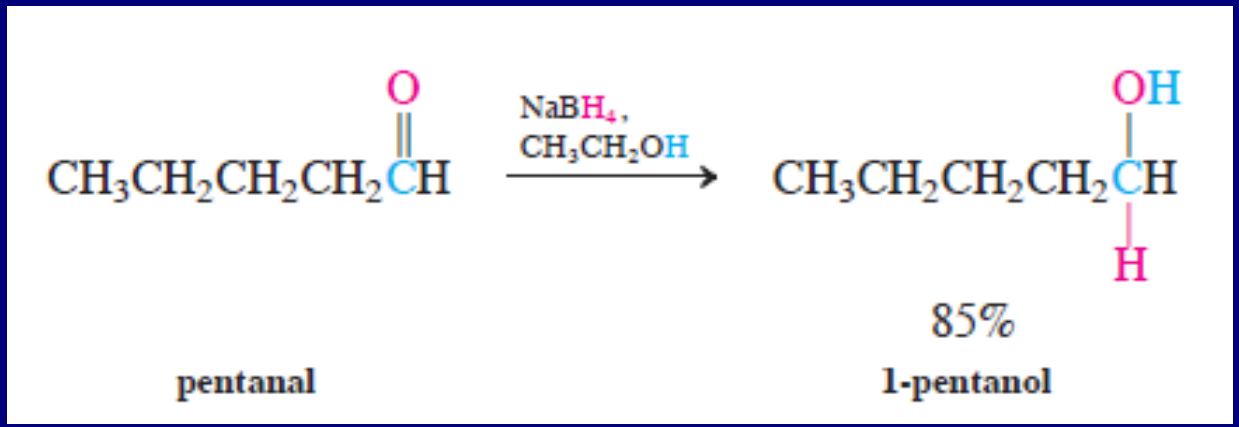


$NaBH_4$: Trimolekulski, usklađeni

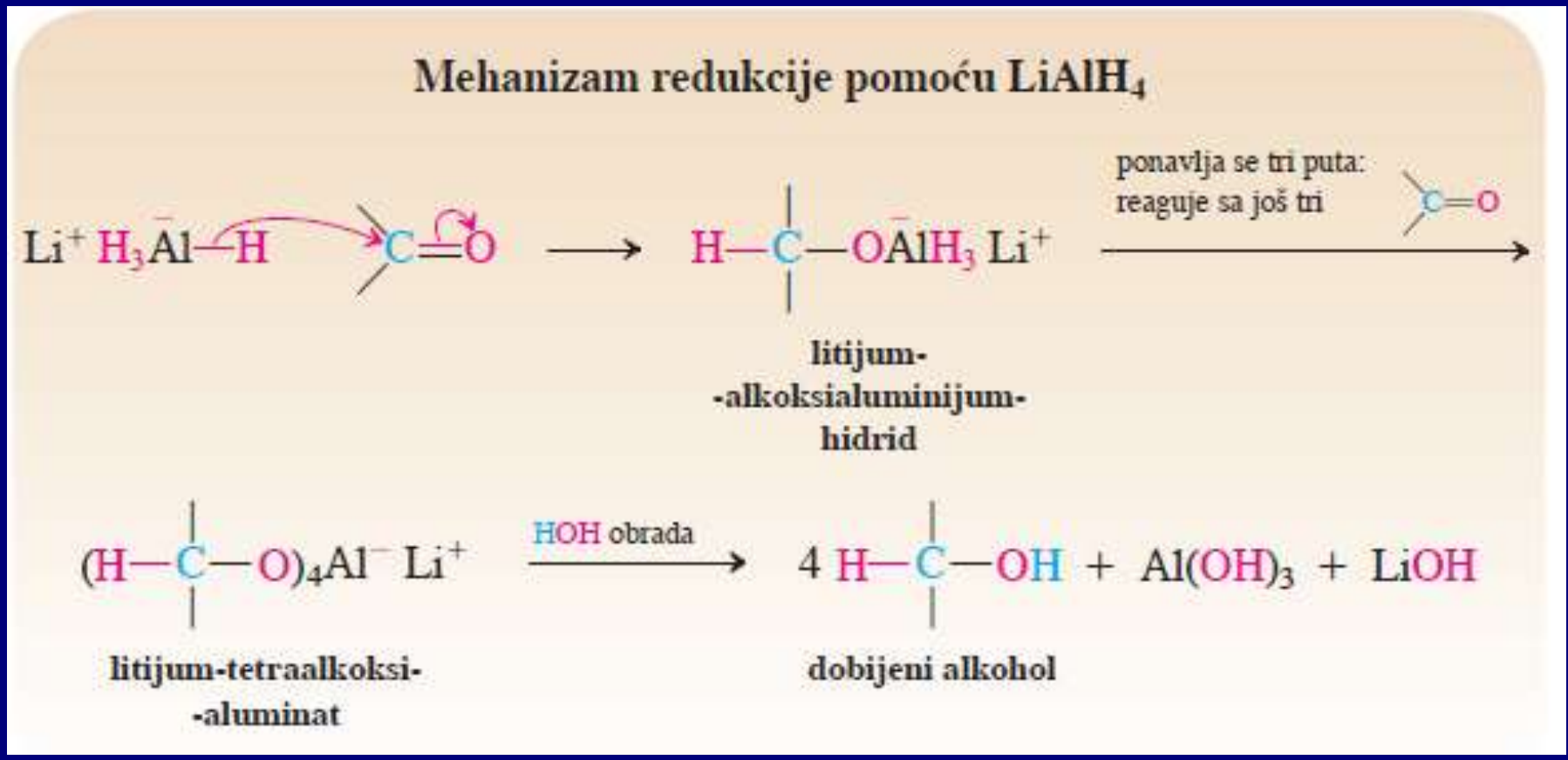
Istovremena adicija H^- i H^+

Jedan ekvivalent borhidrida može redukovati četiri ekvivalenta aldehida ili ketona u alkohol





$LiAlH_4$: postepeno vezivanje, prvo, $H:^-$, potom, H^+ (obradom reakcione smese)



Reakcija litijum-aluminijumhidrida sa protičnim rastvaračima

$$LiAlH_4 + 4\,CH_3OH \xrightarrow{\text{brzo}} LiAl(OCH_3)_4 + 4\,H{-}H\uparrow$$

Vežba 8-7

Formulišite očekivane proizvode redukcije datih jedinjenja pomoću $NaBH_4$. (Pomoć: setite se moguće stereoizomerije.)

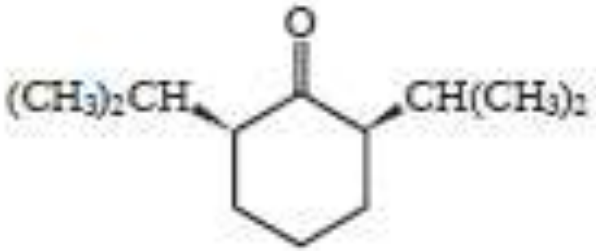
(a) $CH_3CCH_2CH_2CH_3$ (O)

(b) $CH_3CH_2CCH_2CH_3$ (O)

(c) $CH_3CH_2CC(=O)(CH_3)(CH_2CH_3)H$

Vežba 8-8

Hidridne redukcije često su stereoselektivne, sa transferom hidrida sa manje zaštićene strane molekula supstrata. Predvidite stereohemijski ishod dejstva $NaBH_4$ na jedinjenje A.



A

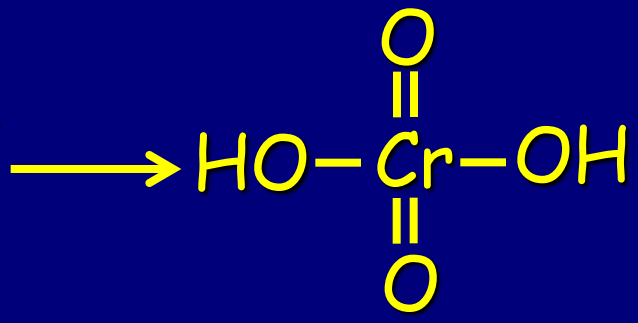
Vežba 8-9

Formulišite redukcije kojima se dobijaju navedeni alkoholi. (a) 1-Dekanol; (b) 4-metil-2-pentanol; (c) ciklopentilmetanol; (d) 1,4-cikloheksandiol.

Oksidacija

Cr^{VI} reagens $\xrightarrow{+3e}$ Cr^{III}

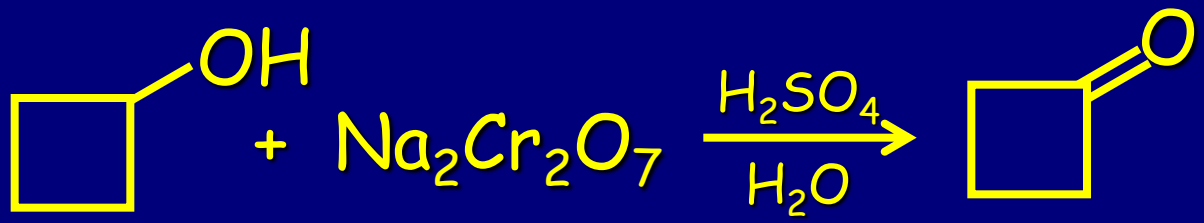
Obično se koriste $Na_2Cr_2O_7$ ili CrO_3 u H_2O, H_2SO_4



Hromna kiselina

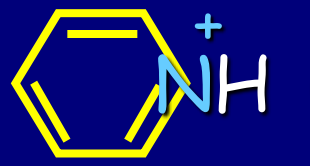
Dobar za R_{sec}-OH

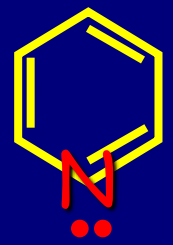
Primer:



Najbolje za oksidaciju sekundarnih alkohola do ketona. Pod ovim uslovima primarni alkoholi se oksiduju do kiselina

R_{prim}-OH:

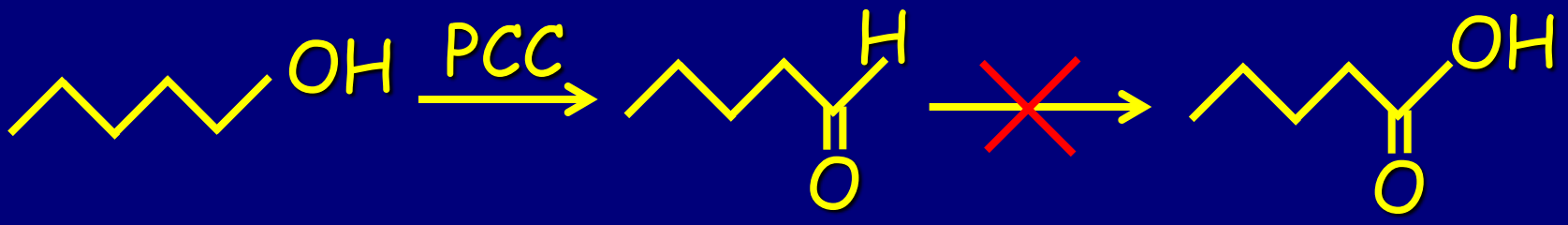




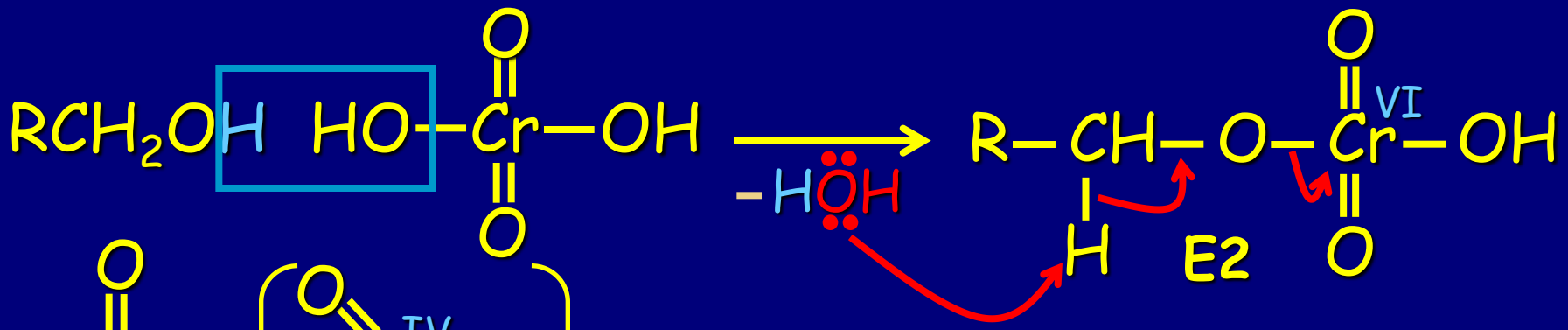
Piridin

Piridinijum hlorhromat: "PCC"

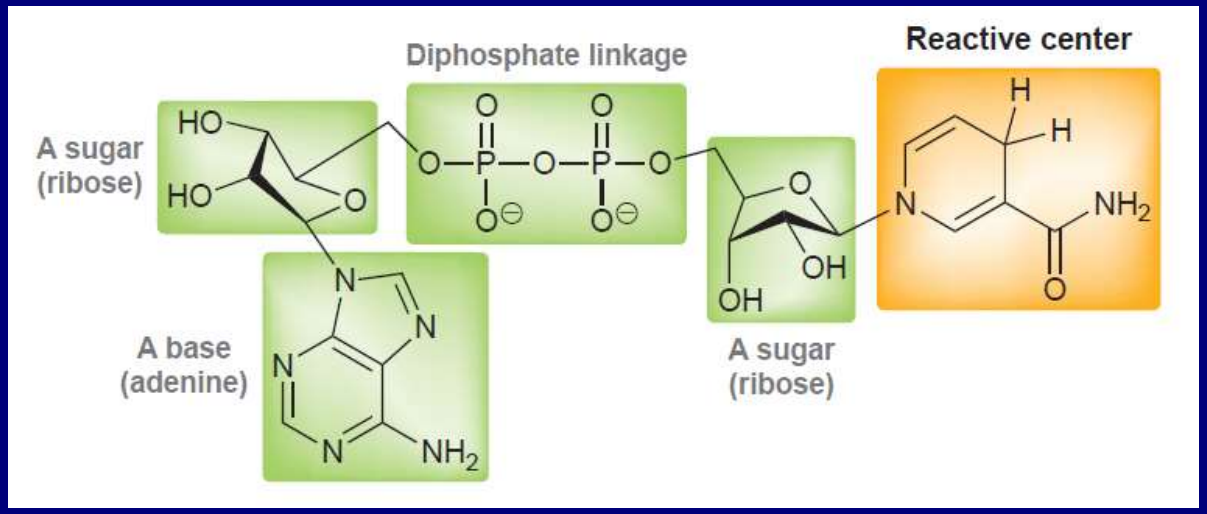
Selektivna oksidacija primarnih alkohola do RCHO

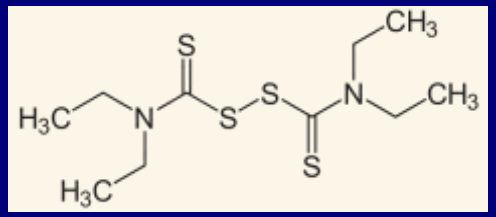


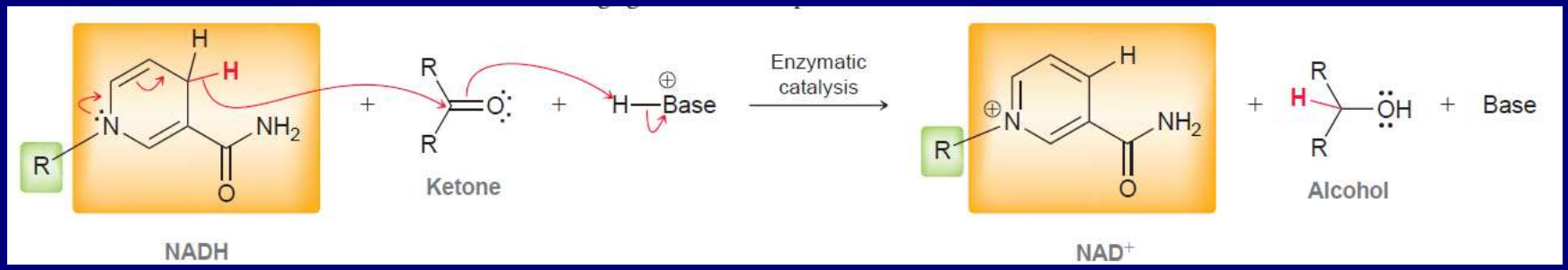
Mehanizam: preko hromatnog estra

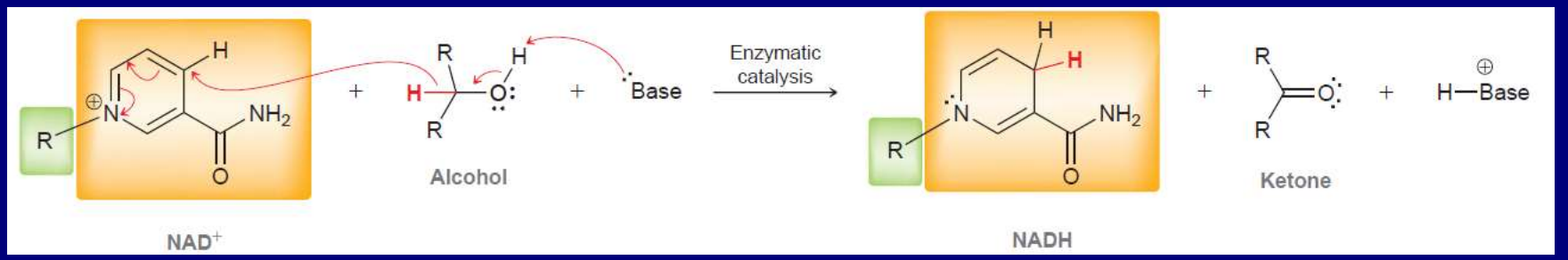


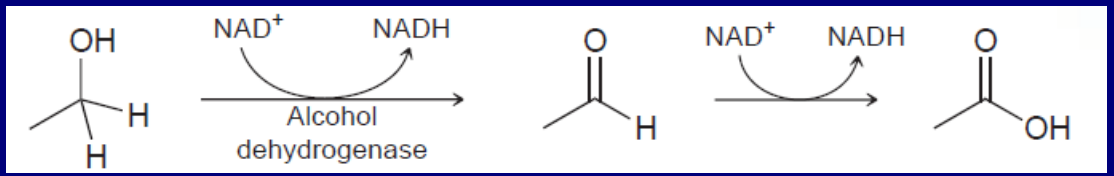
Redoks procesi u biološkim sistemima

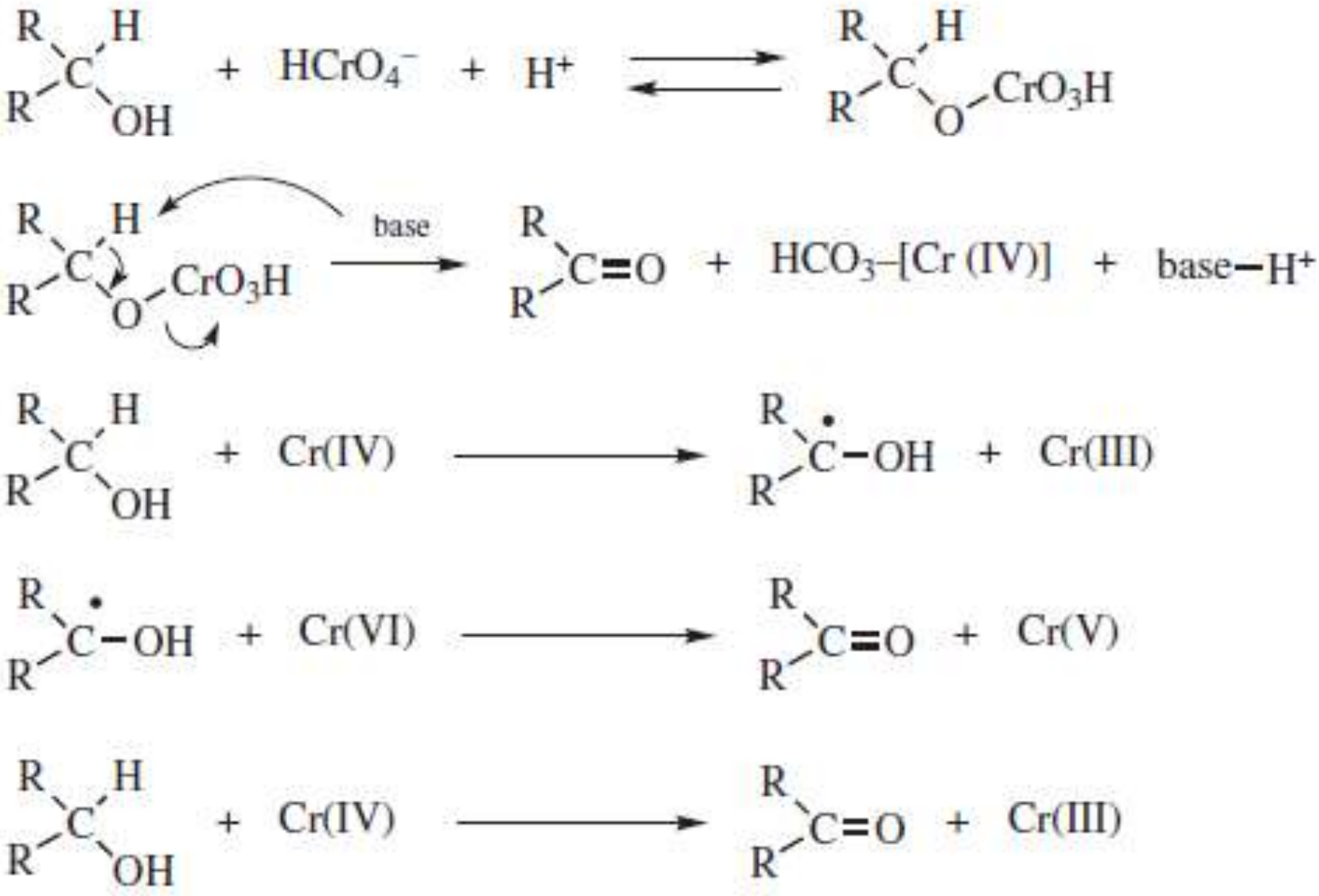






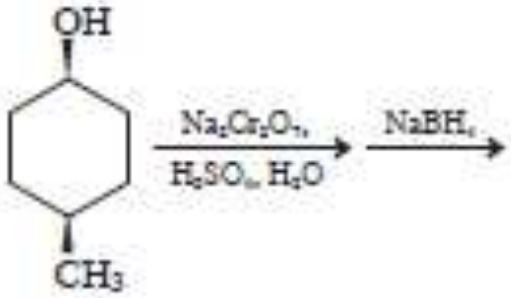





R
H
C
R
OH
+ HCrO4− + H+
R
H
C
R
O
CrO3H
base
R
C=O
+ HCO3–[Cr (IV)] + base–H+
+ Cr(IV)
R
C–OH
+ Cr(III)
+ Cr(VI)
+ Cr(V)

Vežba 8-10

Napišite proizvode svakog od navedenih koraka. Šta možete reći o stereohemiji?

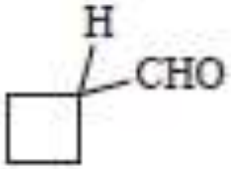


***cis*-4-metilcikloheksanol**

Vežba 8-11

Formulišite sintezu svakog od navedenih karbonilnih jedinjenja iz odgovarajućeg alkohola.

(a) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH(CH_3)_2$

(b) 

(c) 

3. Dobijanje alkohola reakcijom organometalnih reagenasa: $R:^-\ M^+$

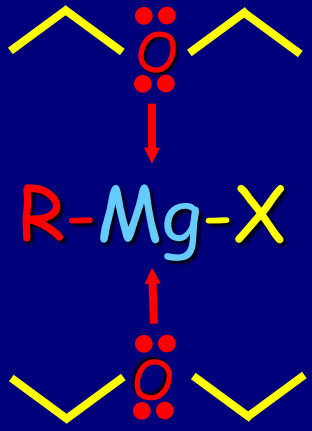
$$R\text{-}X + Li \xrightarrow[\text{ili etar}]{\text{heksan}} RLi + LiX$$

Alkillitijum

MeLi

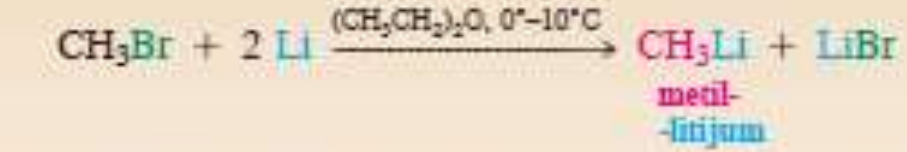
"Grinjarev reagens"
"RMgX"

$$R\text{-}X + Mg \xrightarrow[\text{etar}]{\text{neophodan}} R\text{-}Mg\text{-}X$$



MeMgBr

Sinteza alkillitijumovih jedinjenja



Sinteza alkilmagnezijumovih (Grignard-ovih) jedinjenja

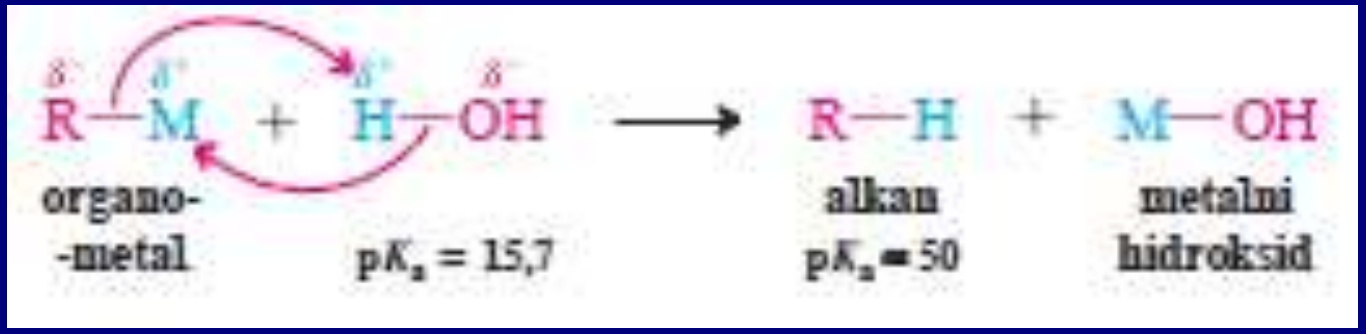
Veza ugljenik-metal kod alkillitijumovih i alkilmagnezijumovih jedinjenja

Victor A. F. Grignard (1871–1935)
a student of P. Barbier, discovered in 1899 the "Grignard" reagents, normally written as RMgX [74]. This class of compounds developed a broad chemistry as nucleophilic organyl-transfer reagents ("Grignard reaction"). Grignard was a professor of chemistry in Nancy and Lyon. He received the Nobel prize (together with Paul Sabatier) in 1912.

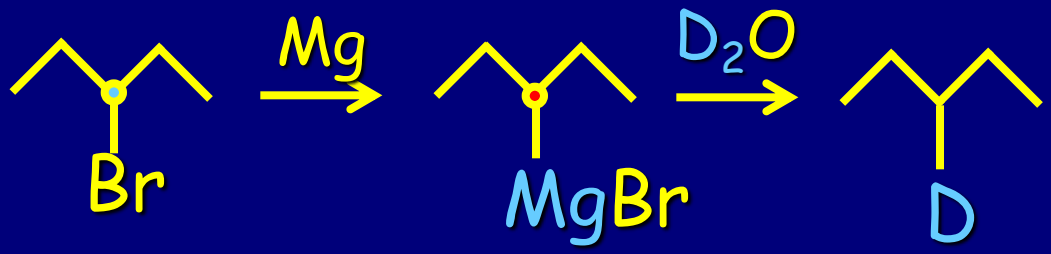
Obrnuta polarizacija RX ⟶ RM

RM je bazan i nukleofilan

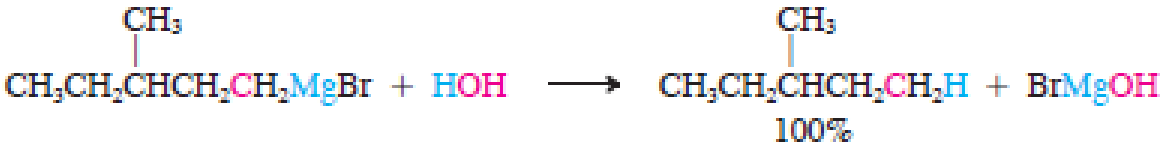
Baznost



Hidroliza:

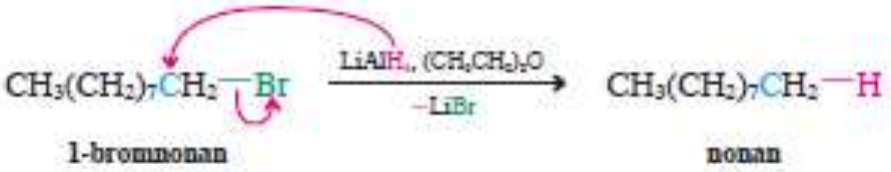


Hidroliza organometalnih reagenasa



3-metilpentilmagnezijum--bromid

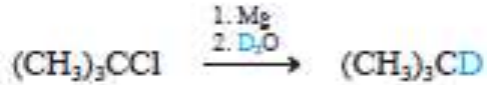
3-metilpentan

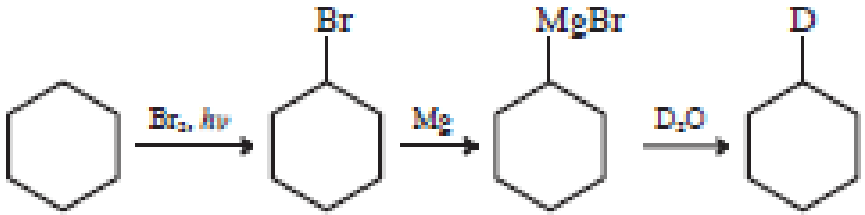


1-bromnonan

nonan

Uvođenje deuterijuma reakcijom organometalnog reagensa sa D_2O

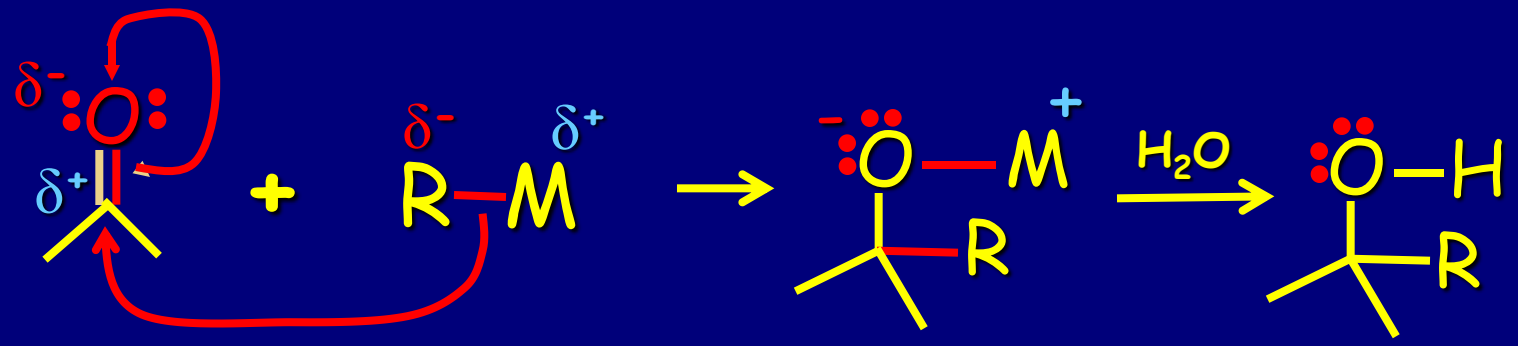




RM kao nukleofilli

Nije dovoljno dobar Nu za $R:^- M^+ + R'X \longrightarrow R\text{-}R'$

Ali sa karbonilnim jedinjenjuma:

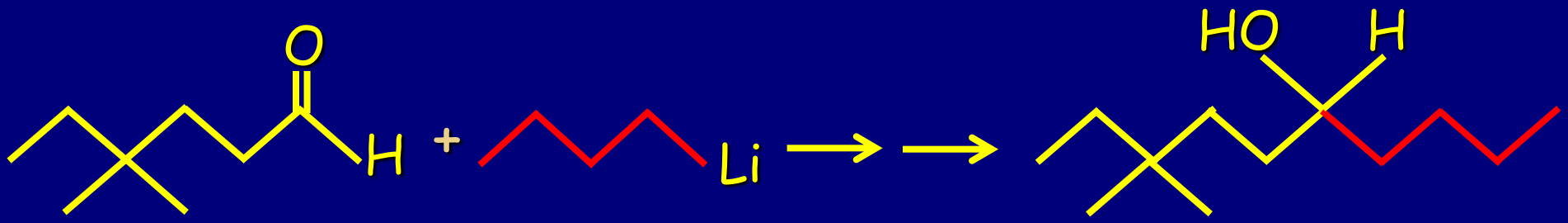


Reaguje sa aldehidima i ketonima

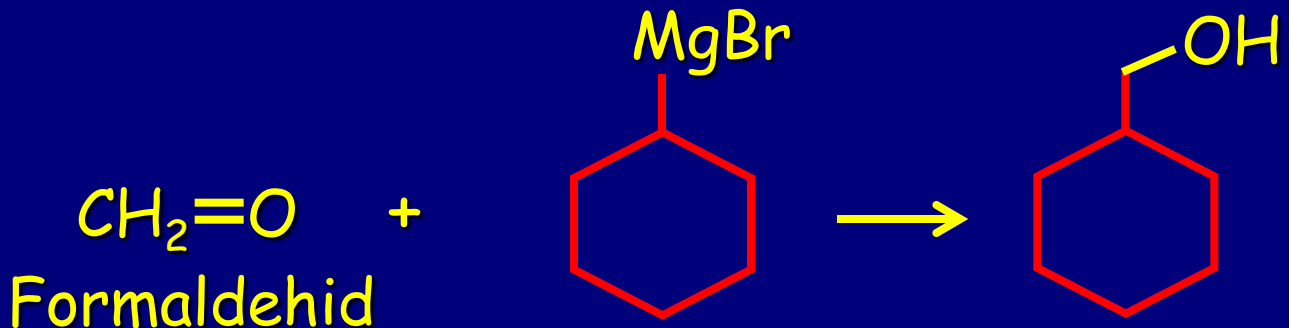
Ketoni:

tercijarni

Aldehidi:



sekundarni

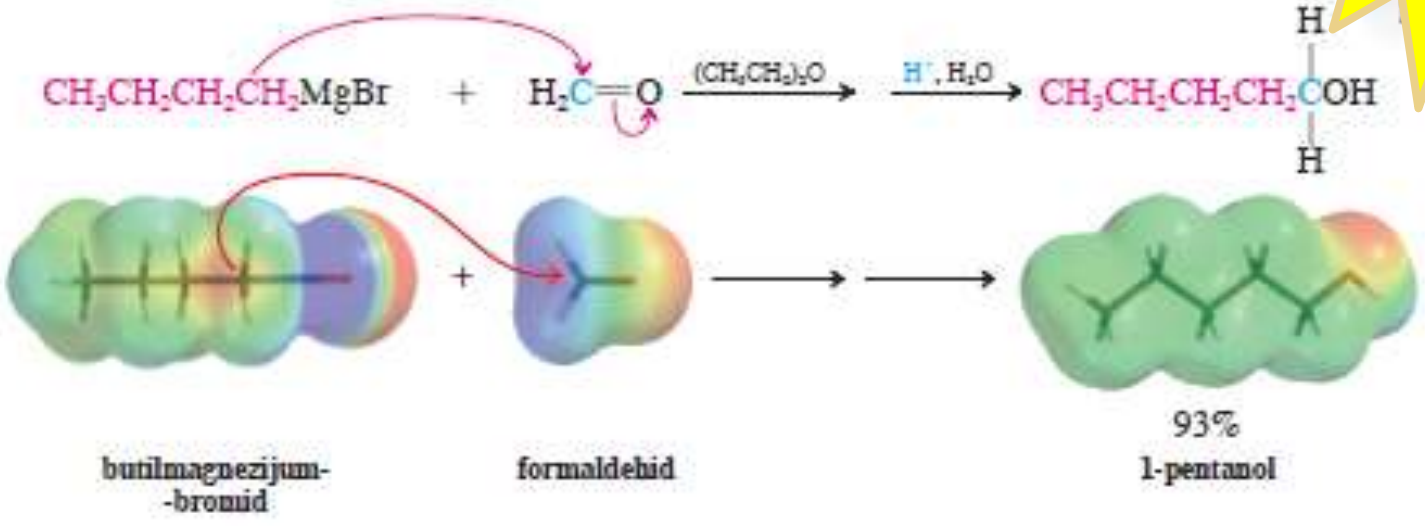


primarni

Grignard

Primarni alkoholi

Dobijanje primarnih alkohola iz Grignard-ovog reagensa i formaldehida



Vežba 8-13

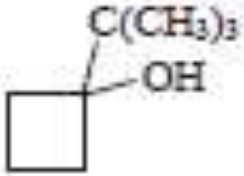
Napišite sintetičku shemu konverzije 2-brompropana, $(CH_3)_2CHBr$, u 2-metil-1-propanol, $(CH_3)_2CHCH_2OH$.

Vežba 8-14

Predložite efikasne sinteze navedenih proizvoda iz polaznih materijala koji ne sadrže više od četiri ugljenikova atoma.

(a) $CH_3(CH_2)_4OH$

(b) $CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2CH_3$

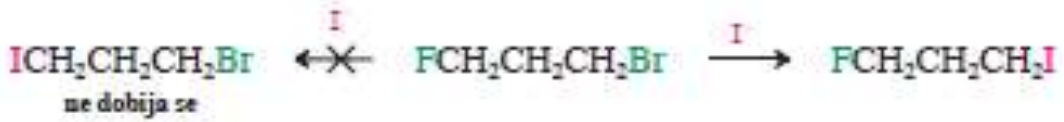
(c) 

(d) $CH_3CH_2CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}CH_2CH_3$

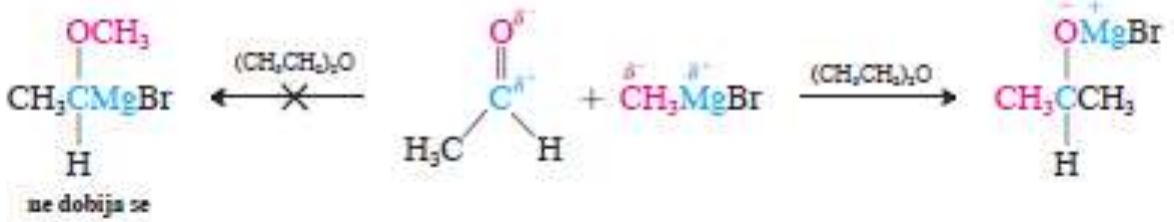
Retrosintetička analiza

Razrada sinteze unazad! Identifikovati sva moguća strategijska rastavljanja!

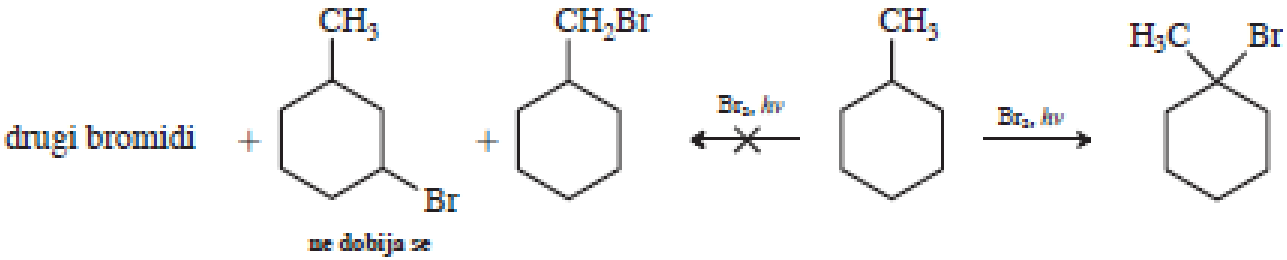
PRIMER 1. Šta se dešava pri dodavanju I^- u $FCH_2CH_2CH_2Br$?



PRIMER 2. Kako se Grignard-ov reagens adira na karbonilnu grupu?



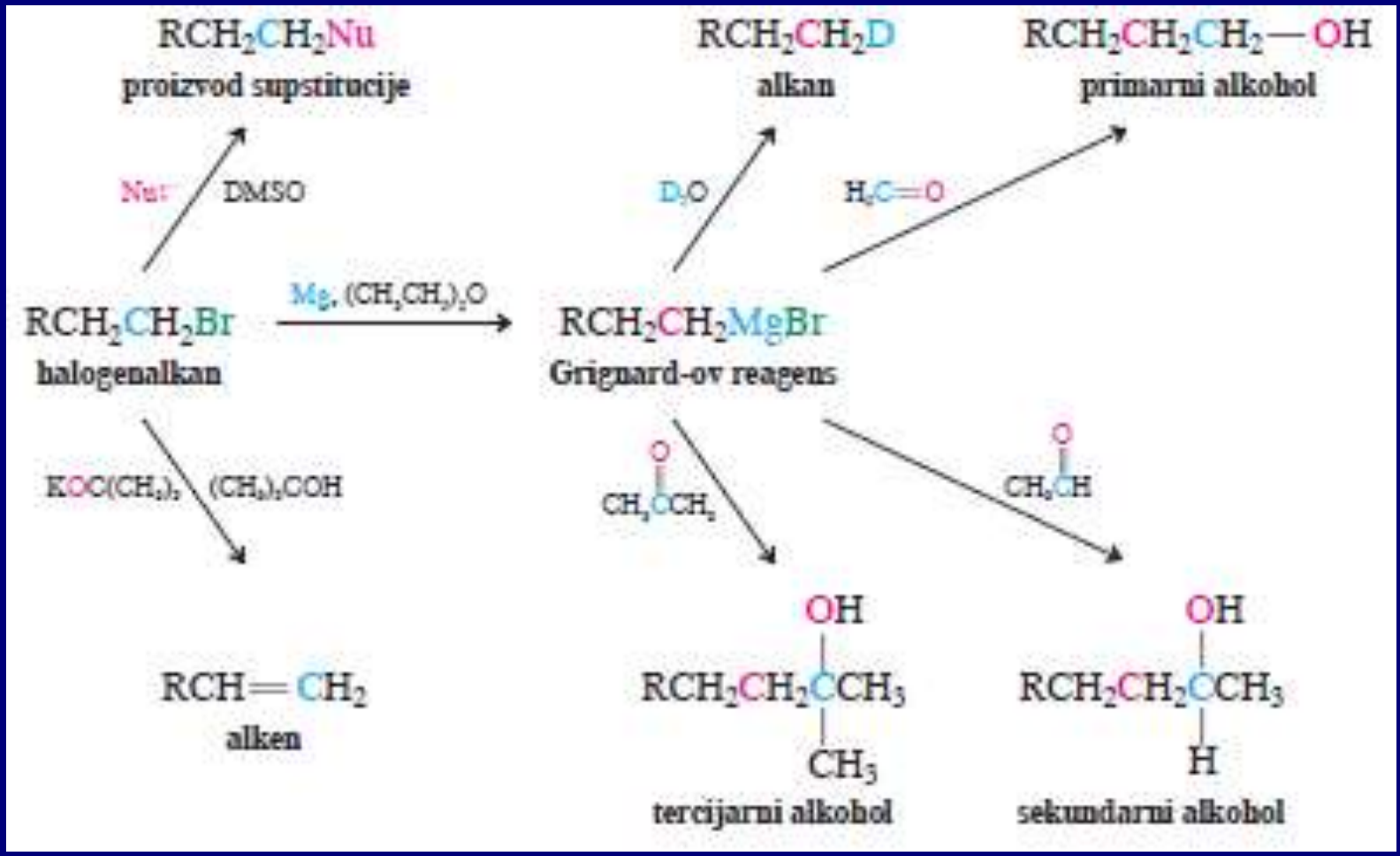
PRIMER 3. Koji proizvod nastaje radikalskim halogenovanjem metilcikloheksana?



Sintetički plan:

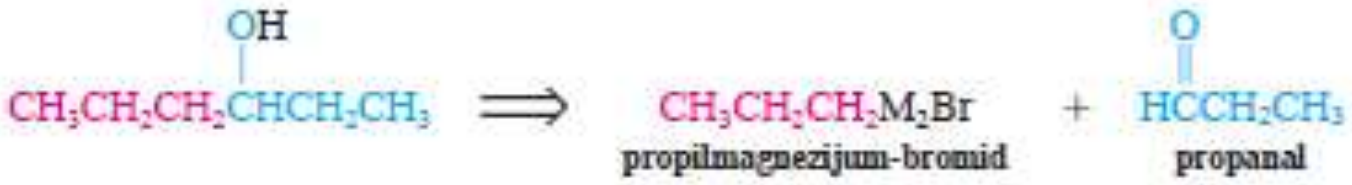
- poznavanje reakcija (rečnik)
- poznavanje mehanizma (gramatika)

Bromalkani su odličan polazni materijal za brojne transformacije

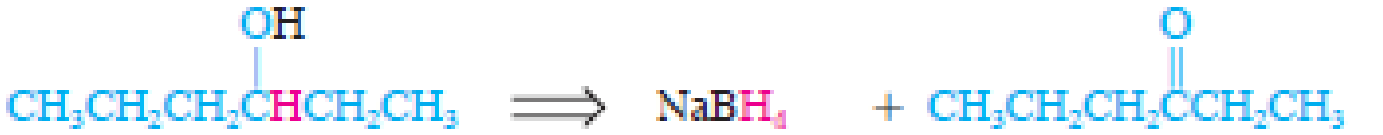


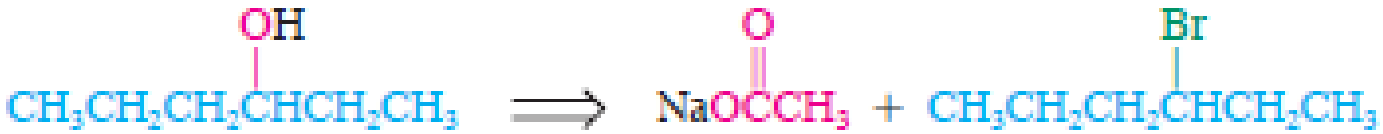
Sinteza 3-heksanola u kojoj je došlo do građenja C-C veze:

Retrosintetička analiza sinteze 3-heksanola
iz dva fragmenta od po tri ugljenikova atoma

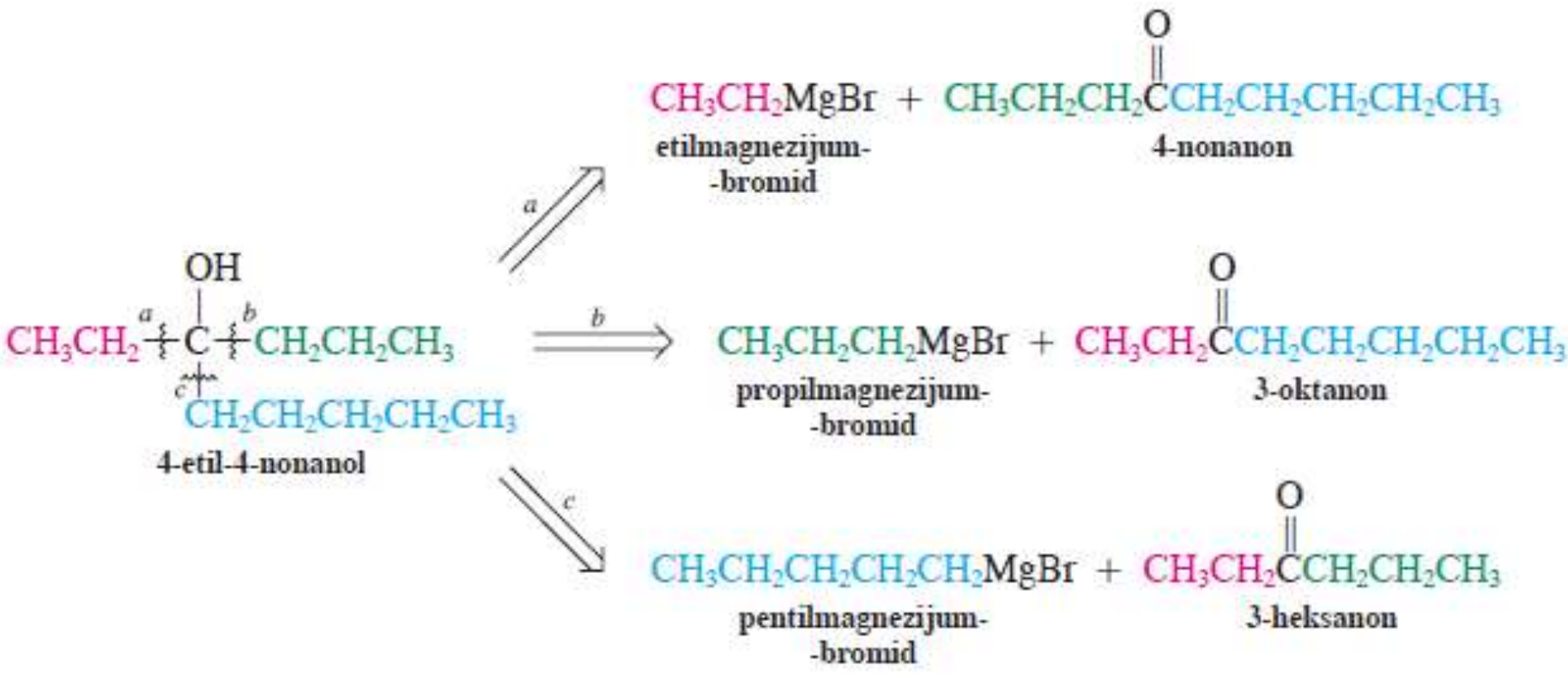


Sinteza 3-heksanola bez u kojoj nije stvorena C-C veza:



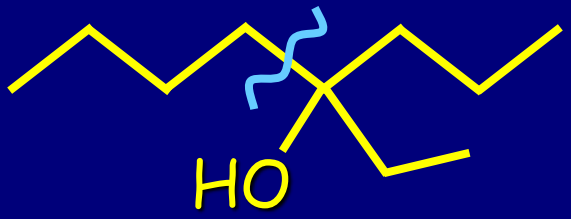


Parcijalna retrosintetička analiza sinteze 4-etil-4-nonanola

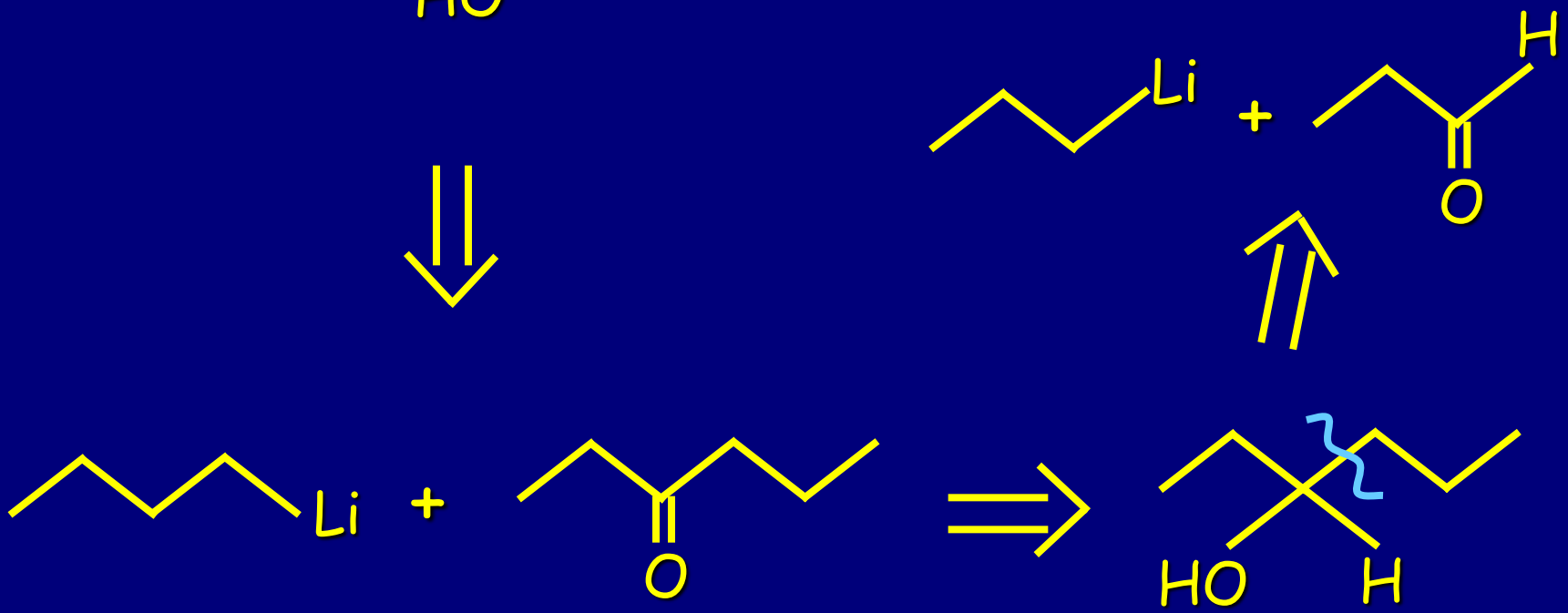


Primer:

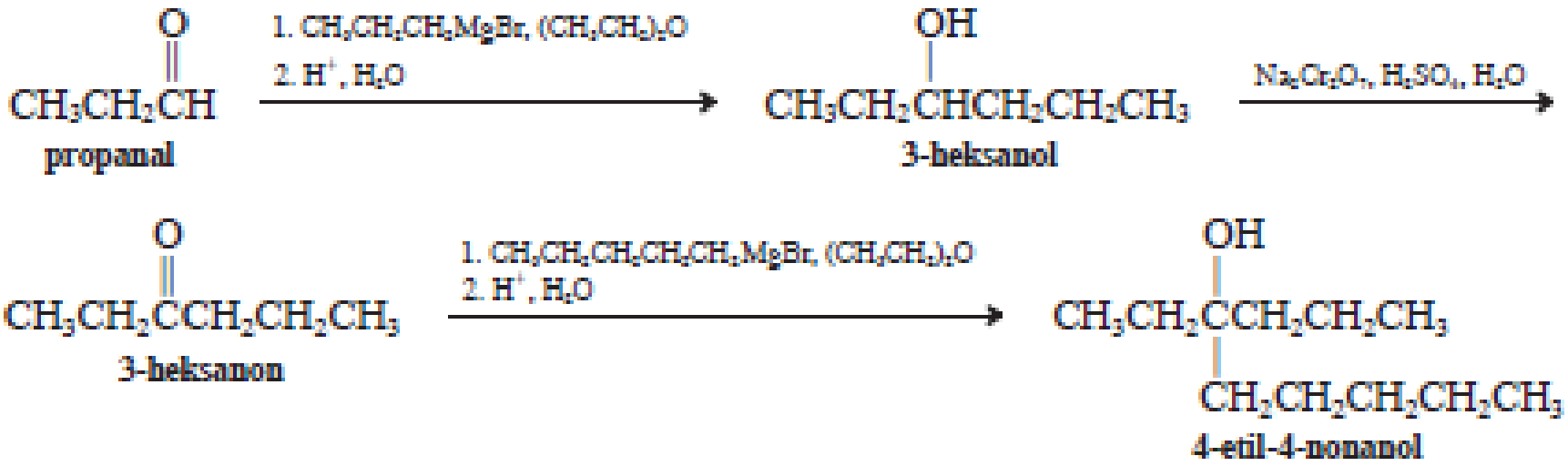
Ciljni molekul

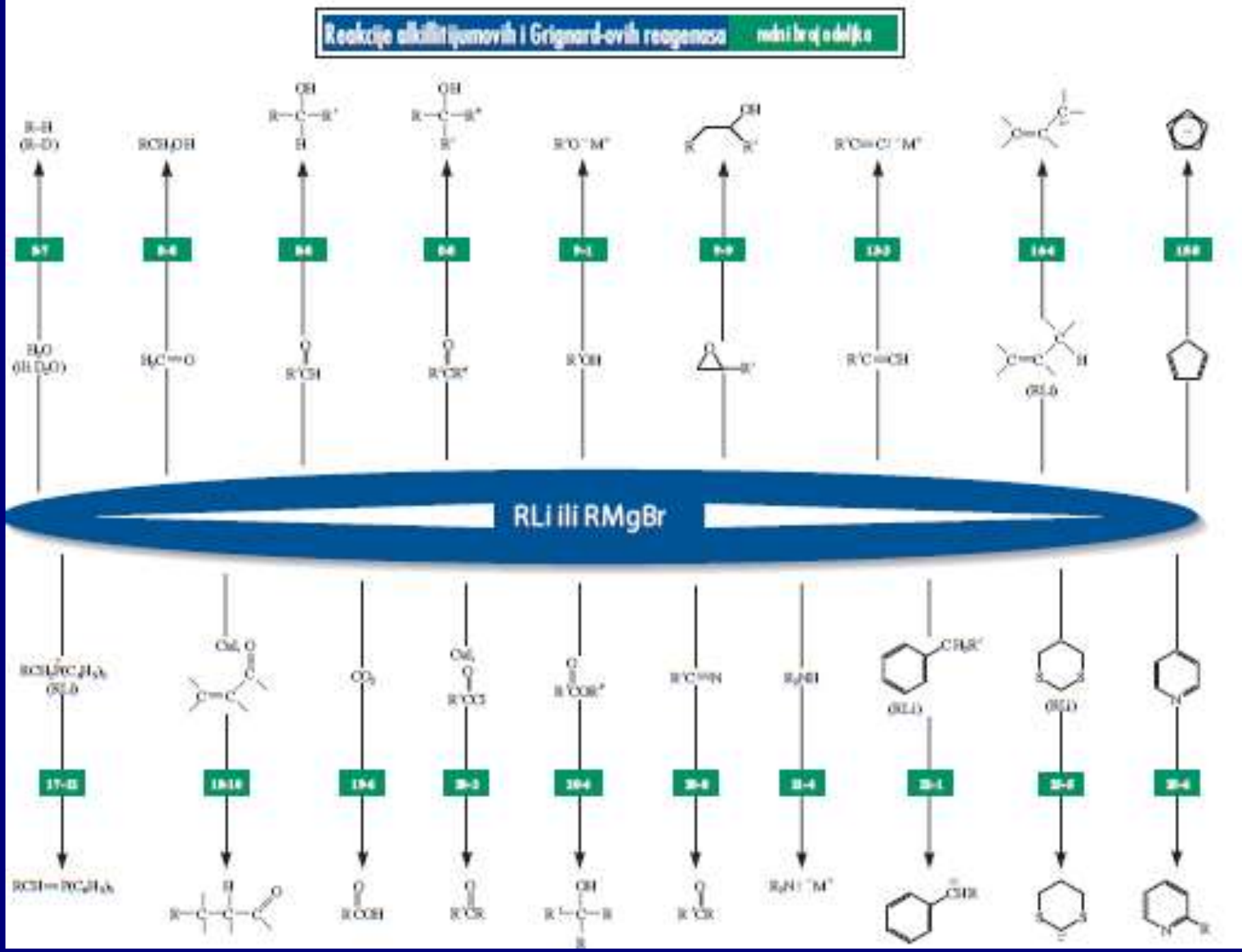


Polazni materijal sadrži 4 ugljenika ili manje!

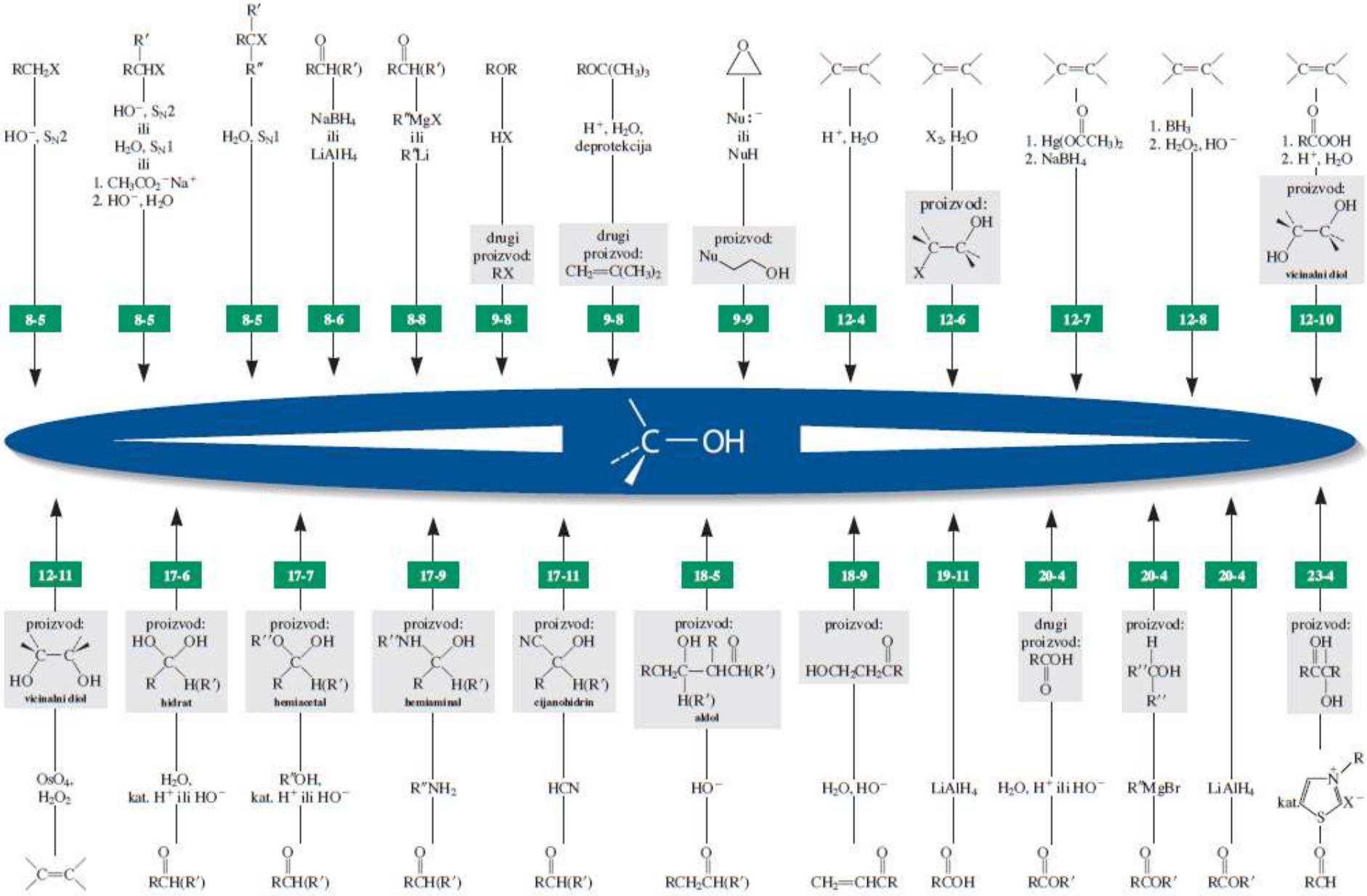


Sinteza 4-etil-4-nonanola

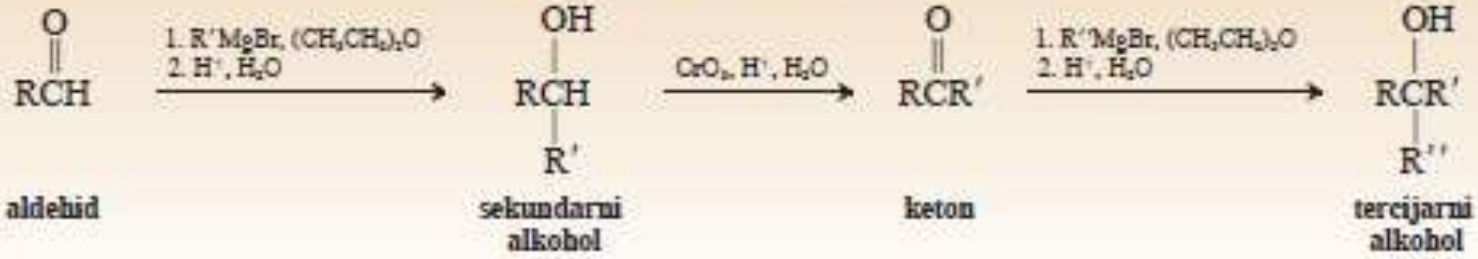



Reakcije alkalil litijumovih i Grignard-ovih reagenasa
RLi ili RMgBr

Sinteza alkohola — redni broj odeljka

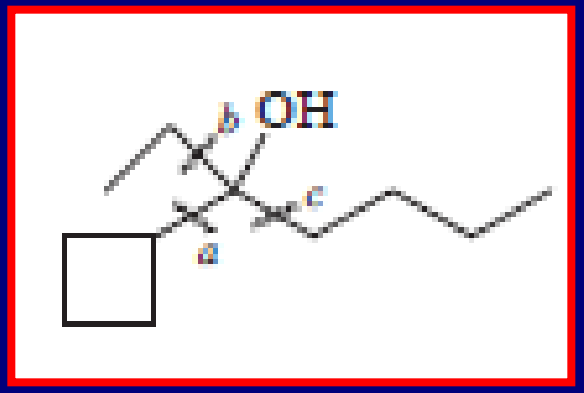


Korisna primena oksidacije alkohola u sintezi



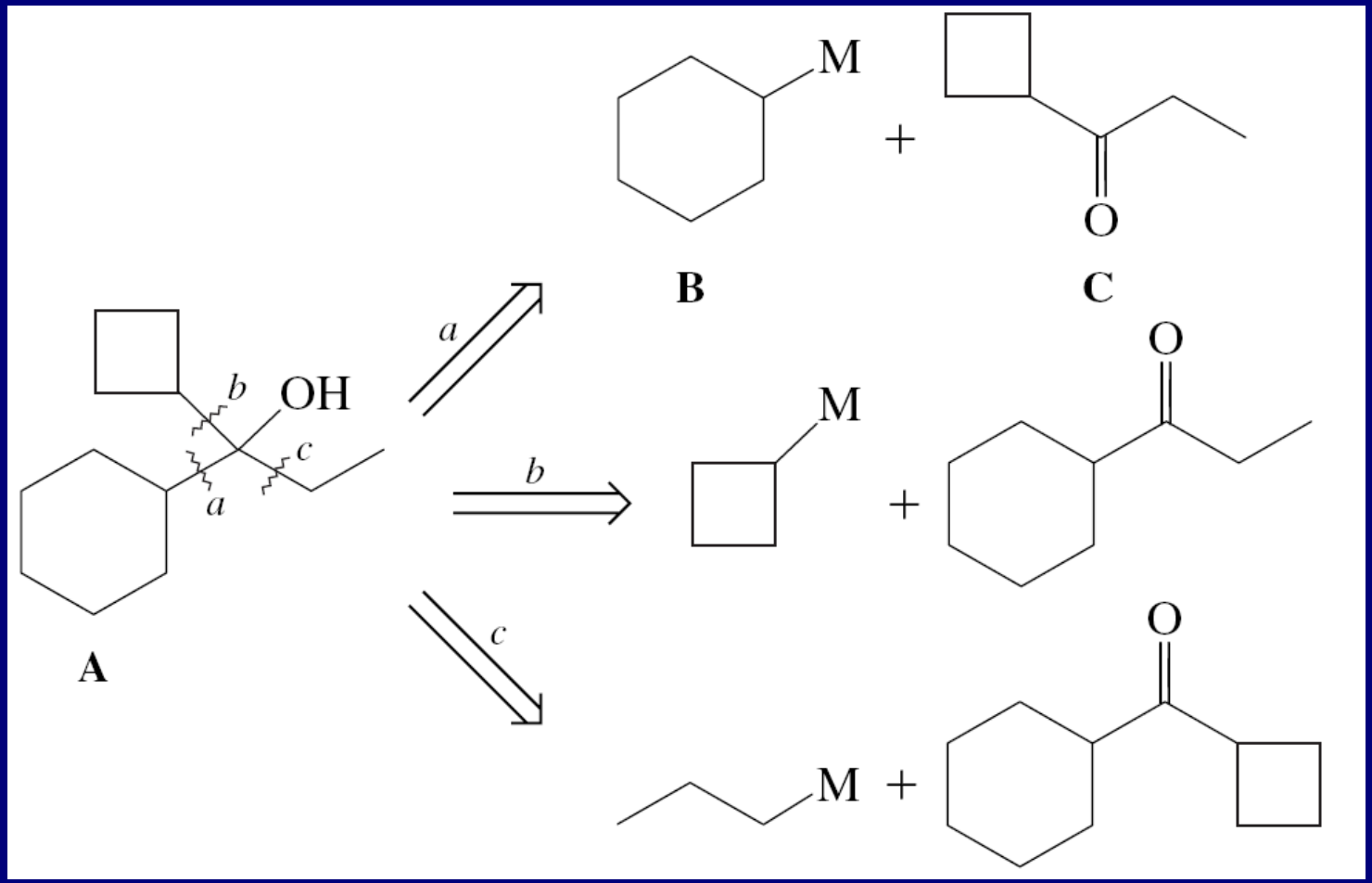
Vežba 8-17

Navedite retrosintetičku analizu sinteze 3-ciklobutil-3-heptanola, polazeći od jedinjenja koja sadrže četiri ili manje ugljenikovih atoma.



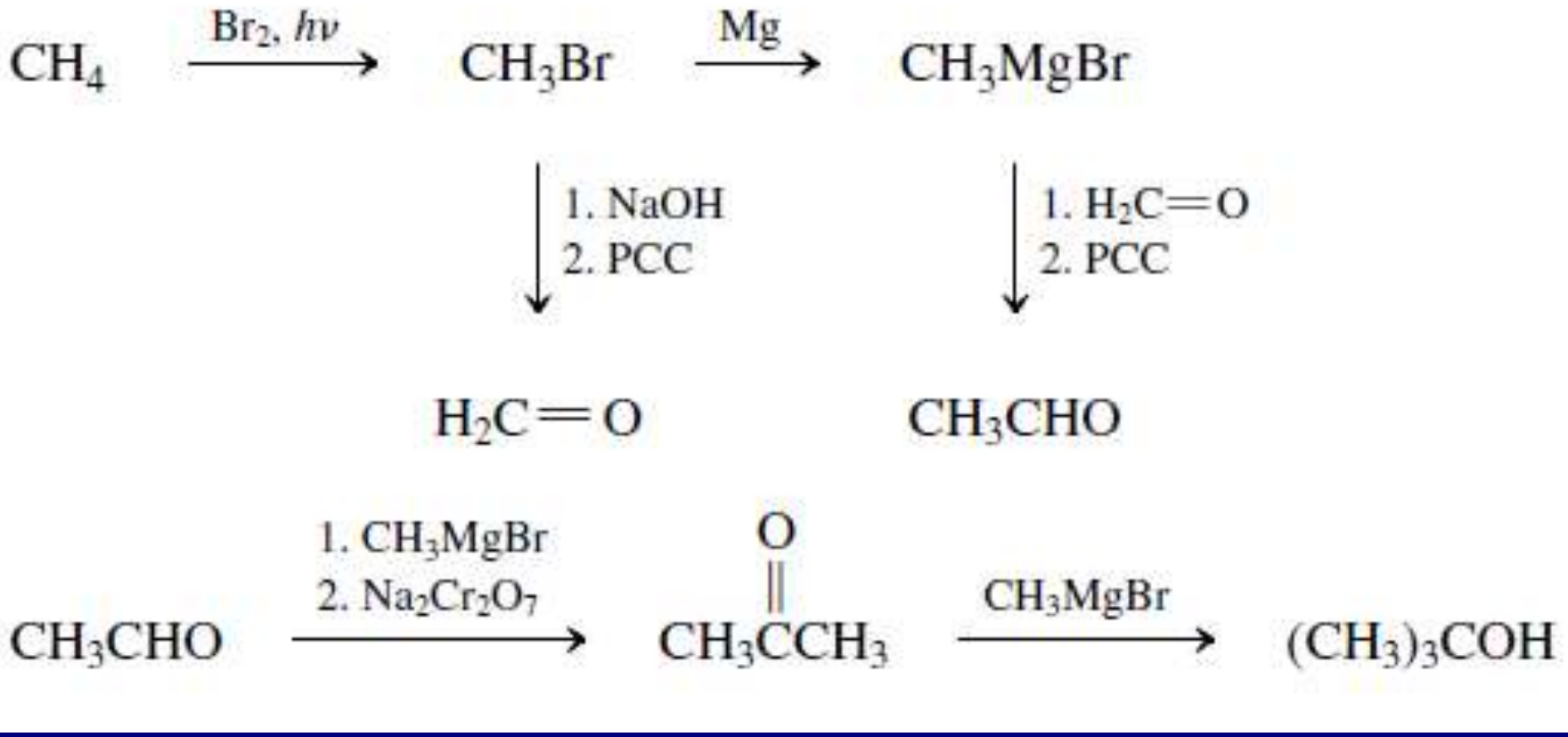
Problem:

8.19 Polazeći od cikloheksana i koristeći gradivne elementa koji sadrže četiri ili manje ugljenikovih atoma, uz sve druge neophodne reagense , formulišite sintezu tercijarnog alkohola *A*

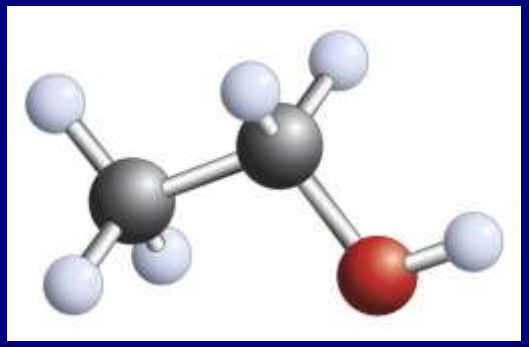


Vežba 8-17

Pokažite kako biste sintetisali 2-metil-2-propanol iz metana kao jedinog organskog polaznog materijala.



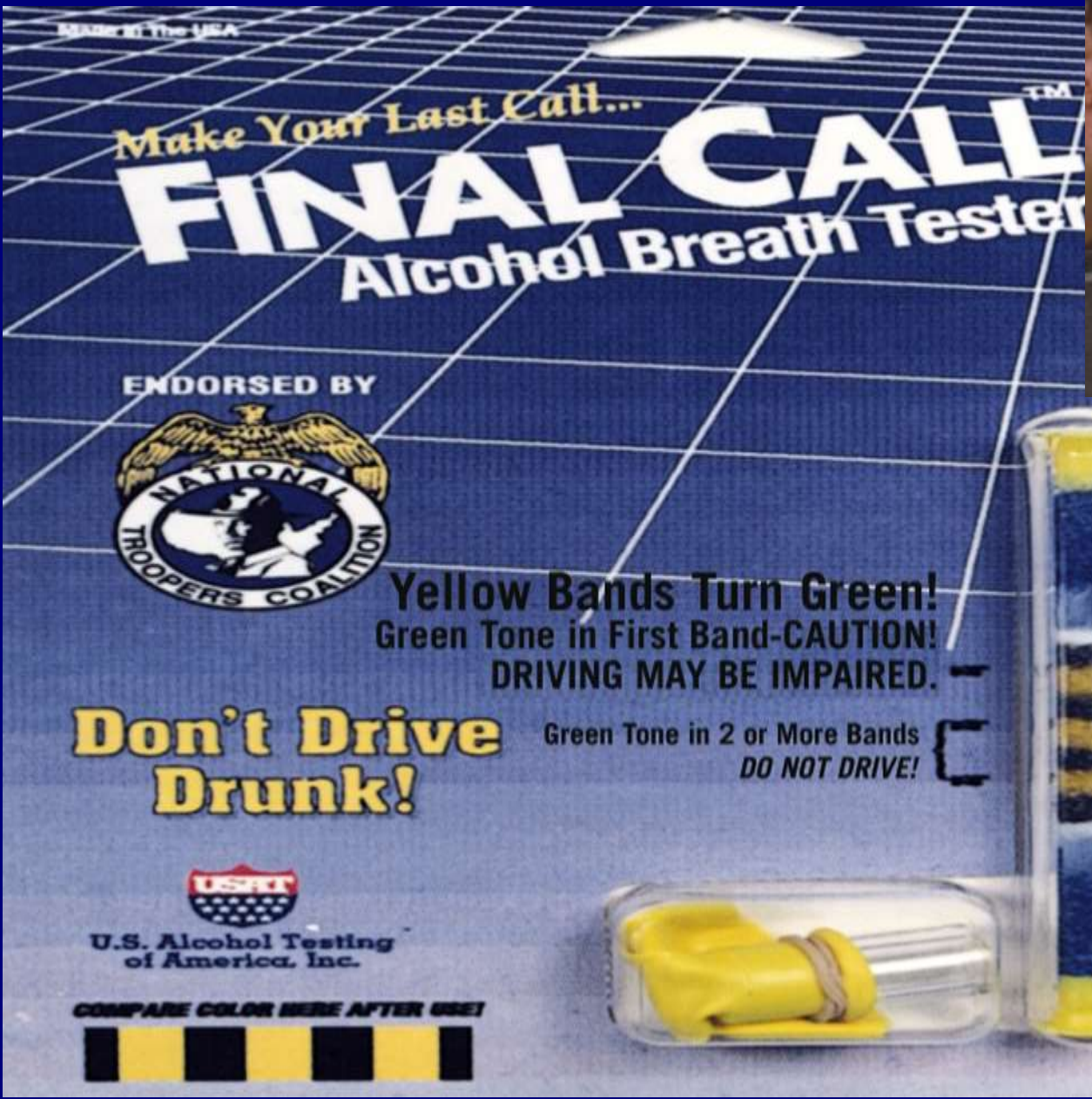
Etanol



Piće

hemikalija, gorivo

Zašto vozač pocrveni kada balon pozeleni!!!



ciroza