

Poglavlje 13: Alkini

trostruka veza ugljenik-ugljenik

Nomenklatura:

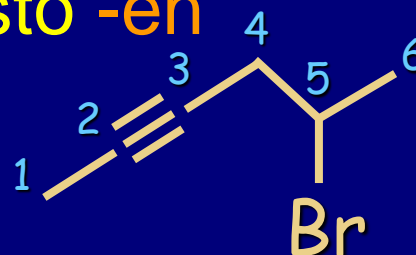
IUPAC-ova pravila za alkene važe za alkine, uz završetak **-in** umesto **-en**



etin

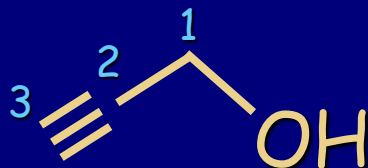


1-Pentin



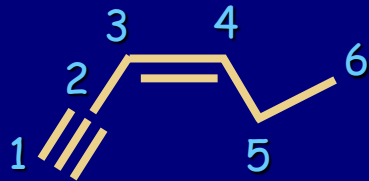
5-Brom-2-heksin

Prioritet:
-ol > -in

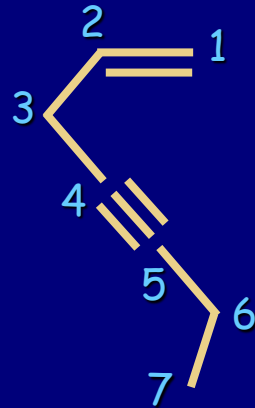


2-Propin-1-ol

Kada alkin sadrži dvostruku vezu, naziva se **enin**.
Niz se numerički polazeći sa kraja najbližem bilo
kojoj funkcionalnoj grupi:

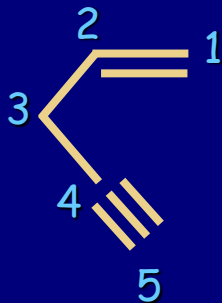


3-Heksen-1-in



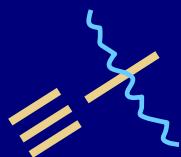
1-Hepten-4-in

Ukoliko su dvostruka i trostruka veza ekvivalentne u
pogledu svog položaja u molekulu, dvostruka veza
zadobija manji broj: **en prvo** (abecedni red)

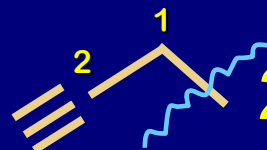


1-Penten-4-in

Supstituenti:

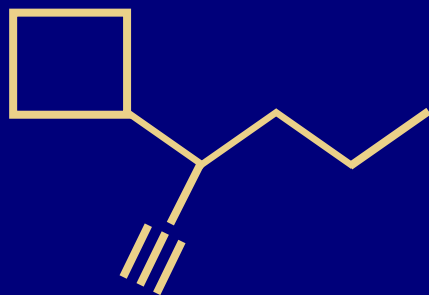


Etinil

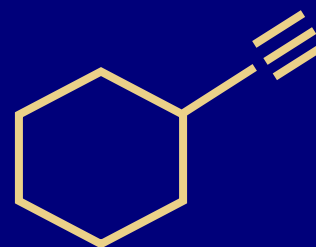


2-Propinil (ili propargil)

Ciklični sistemi: imenovanje kao i za ugljovodonike manji R je supstituent većem R

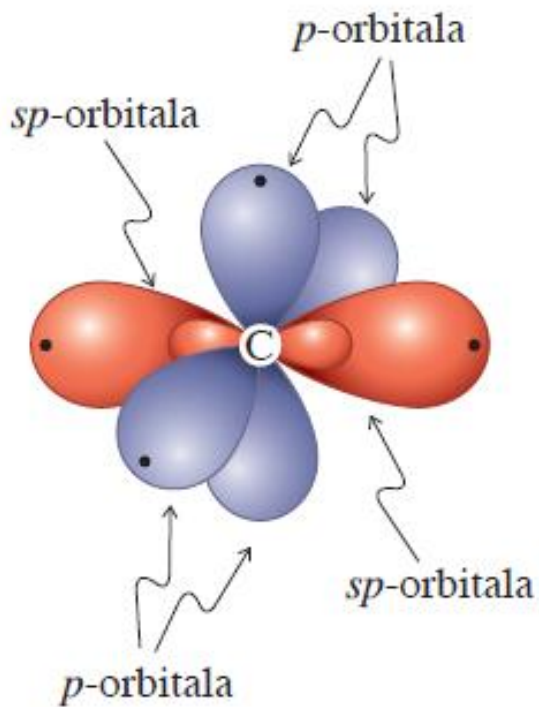


3-ciklobutil-1-heksin

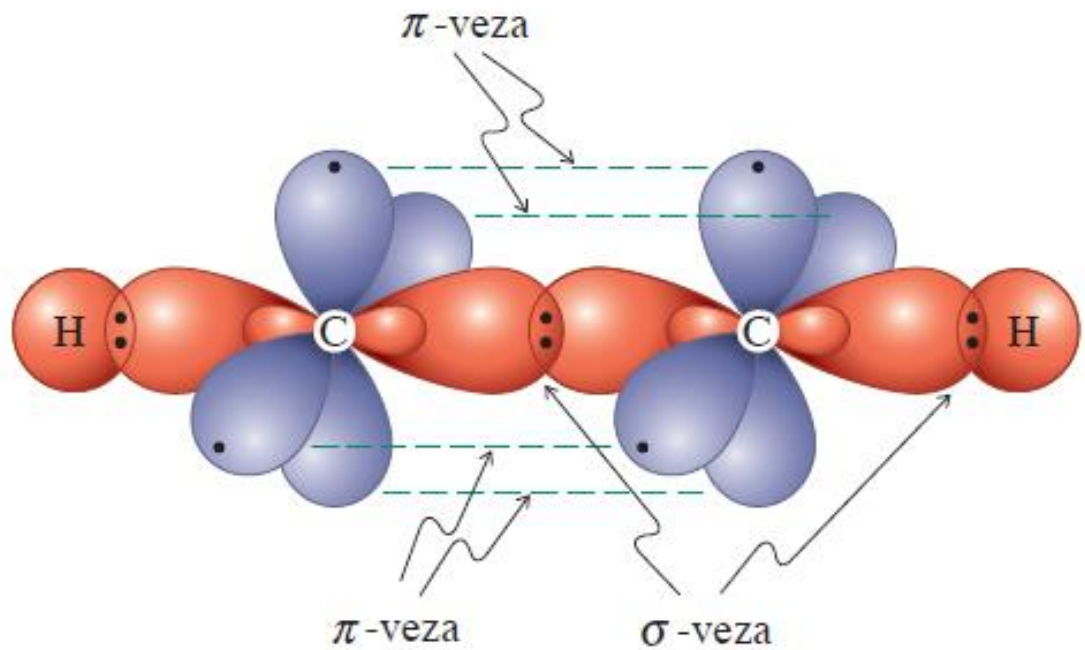


etinilcikloheksan

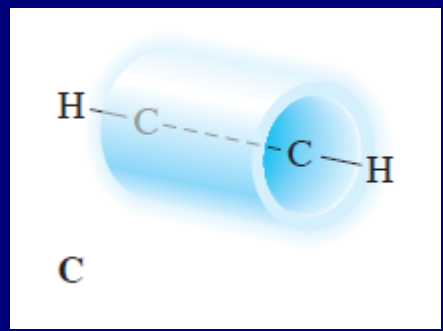
Dve normalne π veze; sp hibridizacija



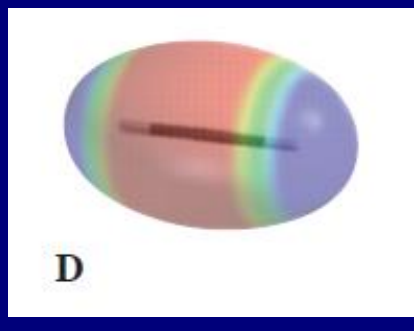
A



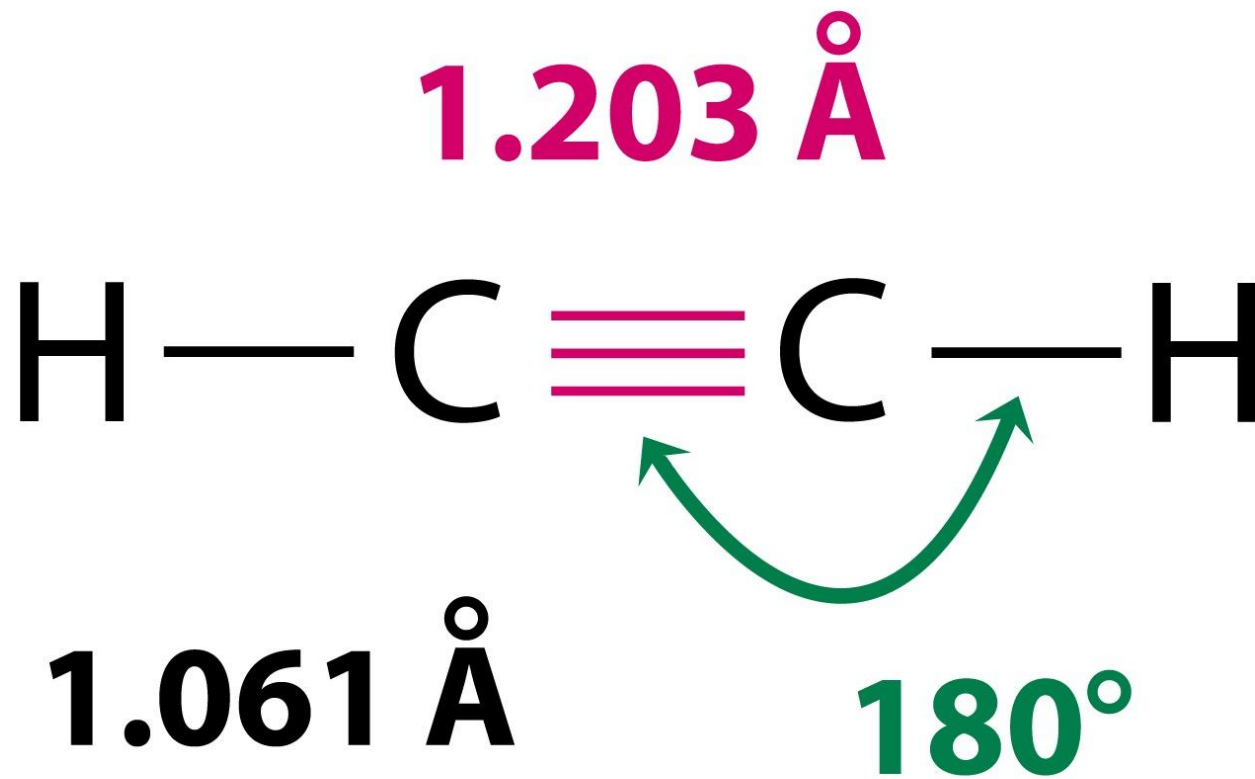
B



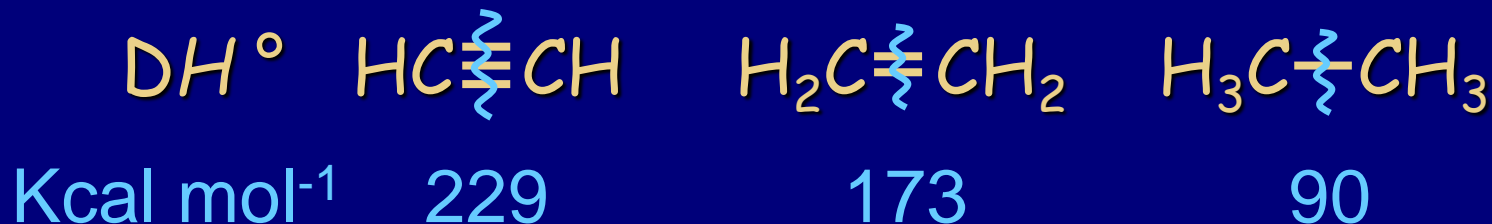
C



D



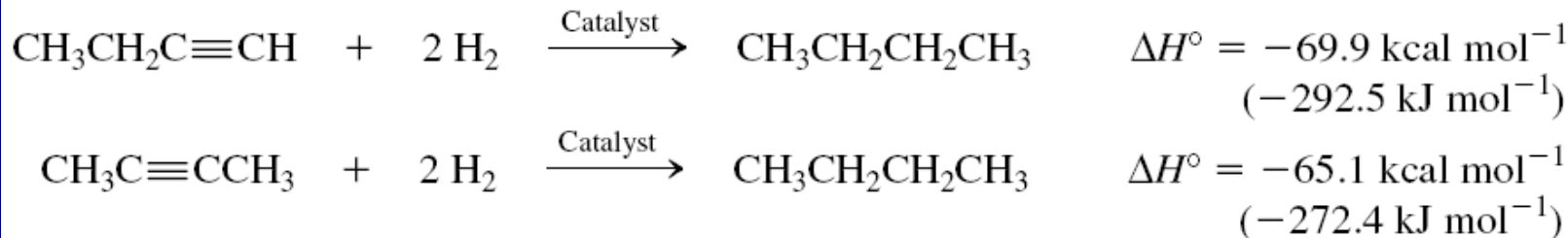
Trostruka veza je bogata energijom



Combustion of Ethyne

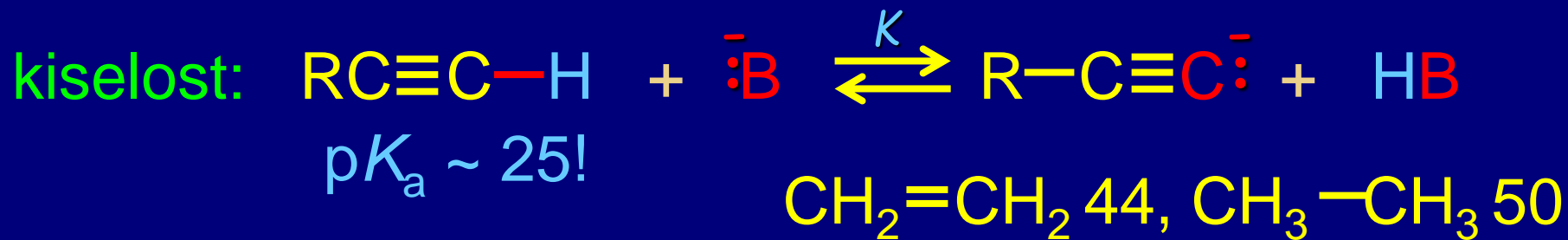


Toplota hidrogenizacije: više od dve alkenske π veze (koje su oko $\sim -60 \text{ kcal mol}^{-1}$)

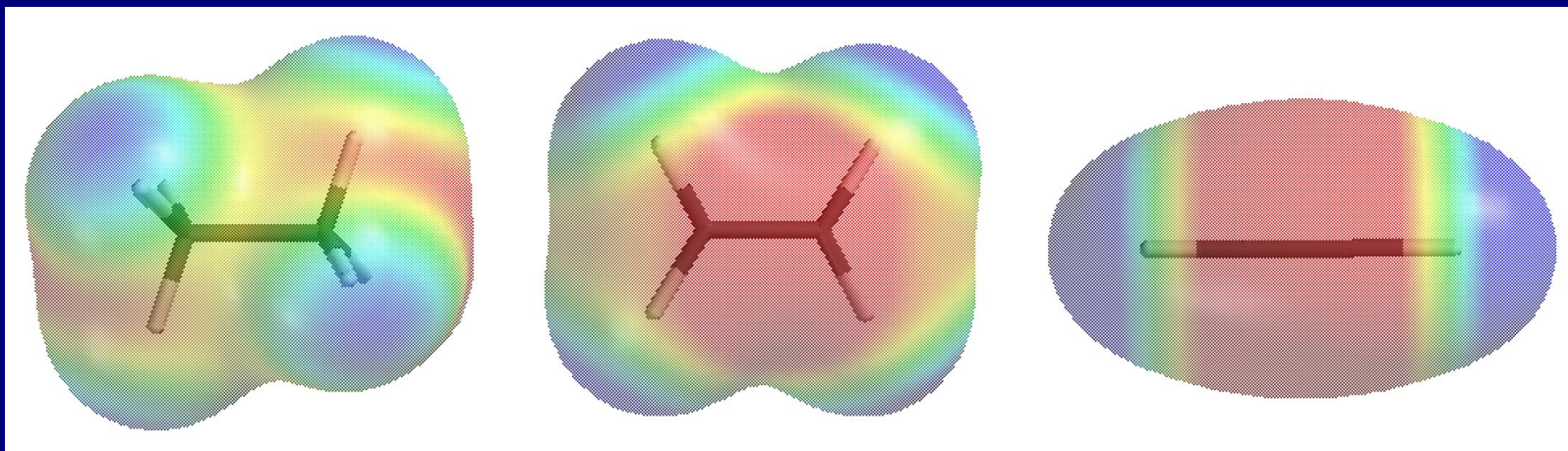


Zavarivanje pomoću acetilena



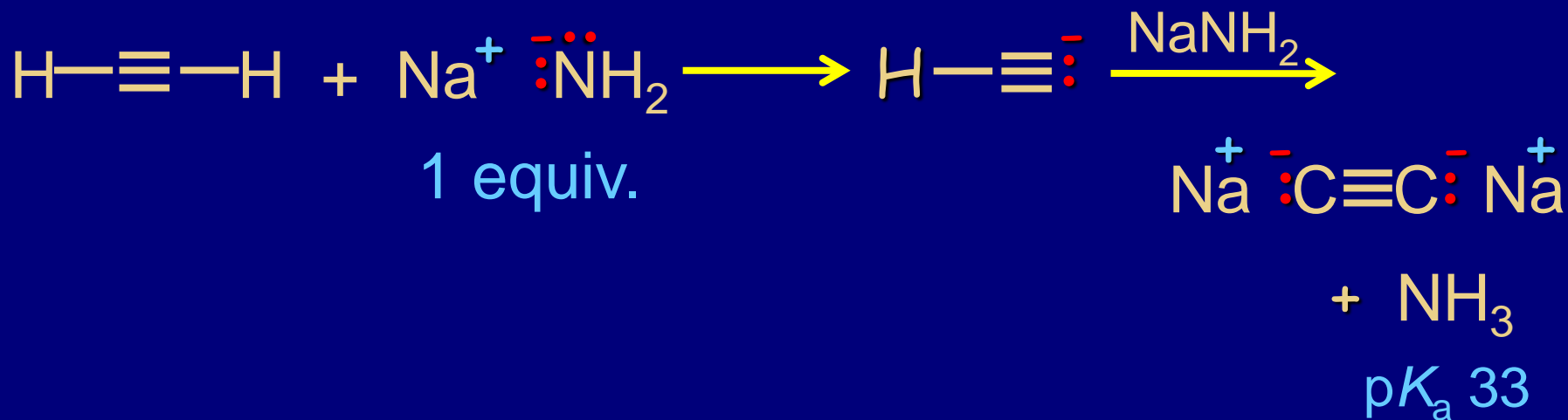
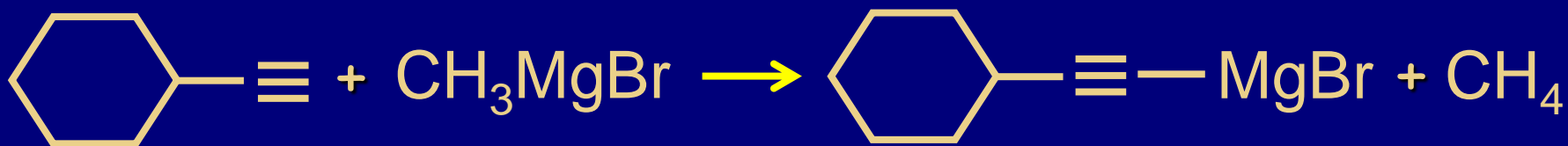
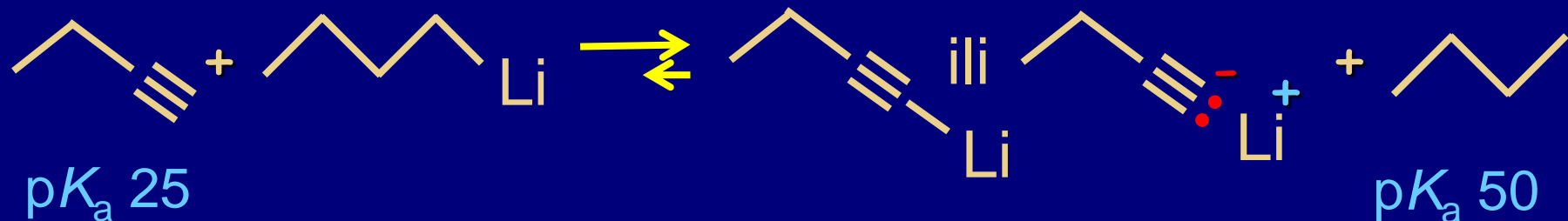


zašto? 50% s-karakter

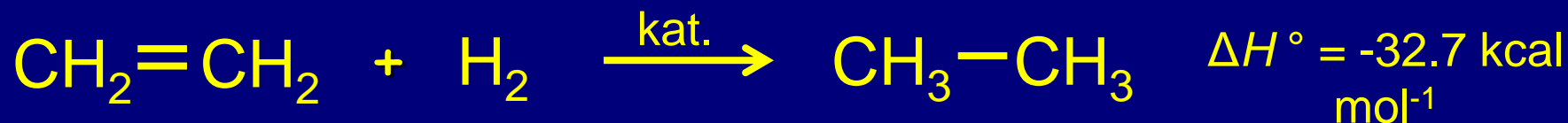
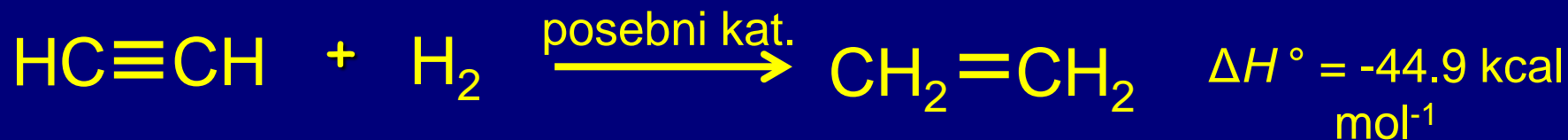


Relativna kislost: alkani < alkeni < alkini

Značaj kiselosti u sintezi

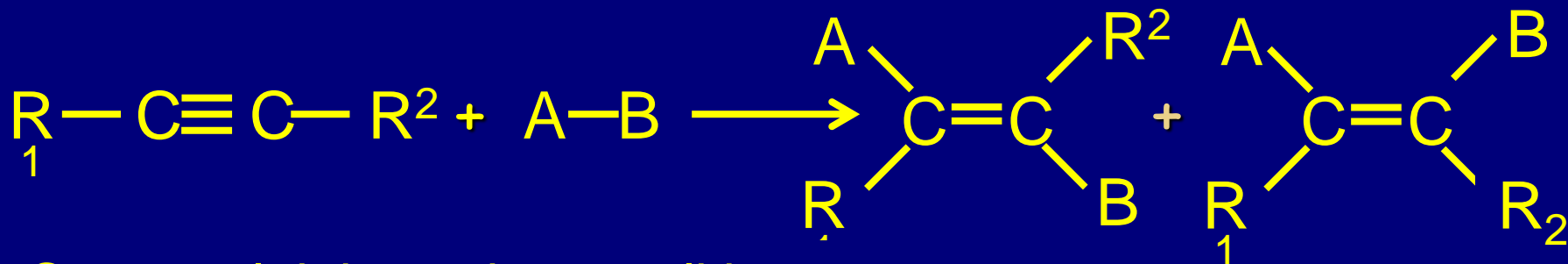


Stabilnost alkina: toplota hidrogenizacije



Prva π veza je energetski bogatija i reaktivnija.

Zato su moguće selektivne adicije:



Stereoselektivna sinteza alkina

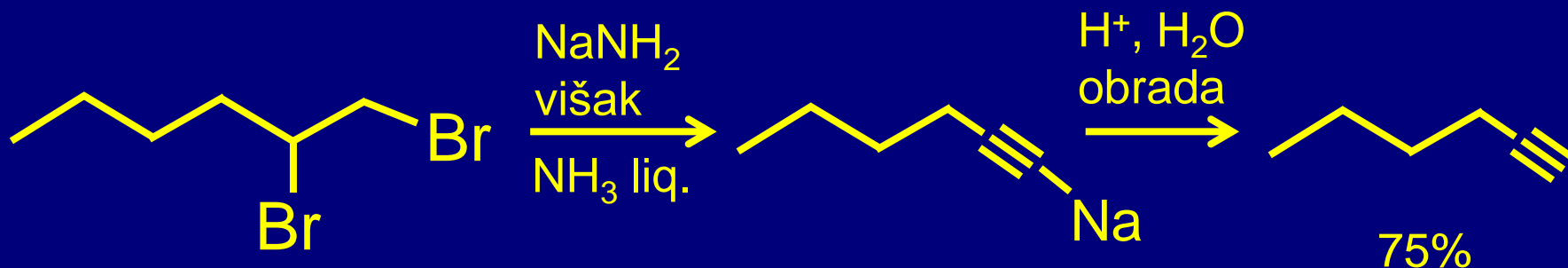
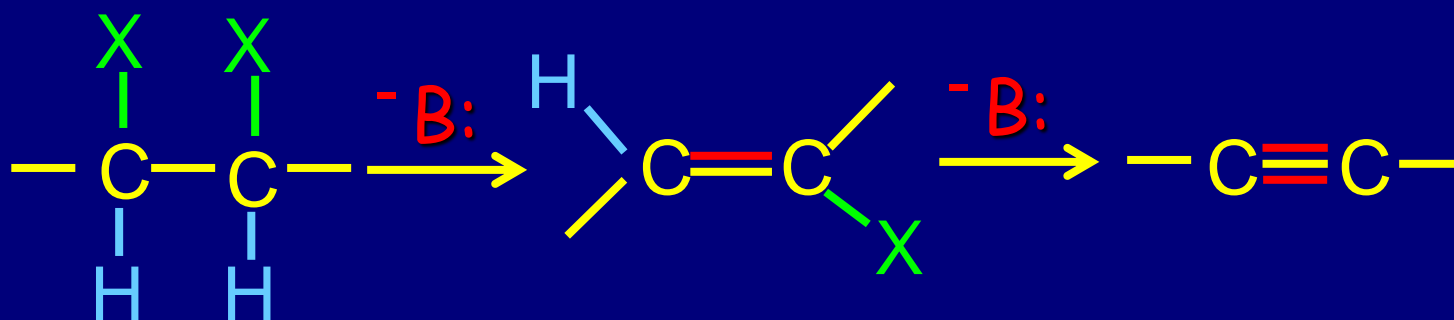
Unutrašnji alkini su stabilniji od terminalnih



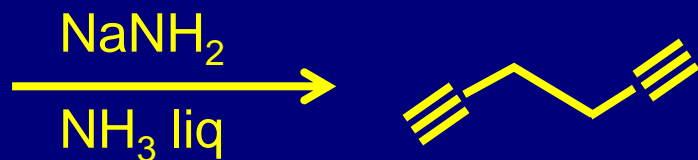
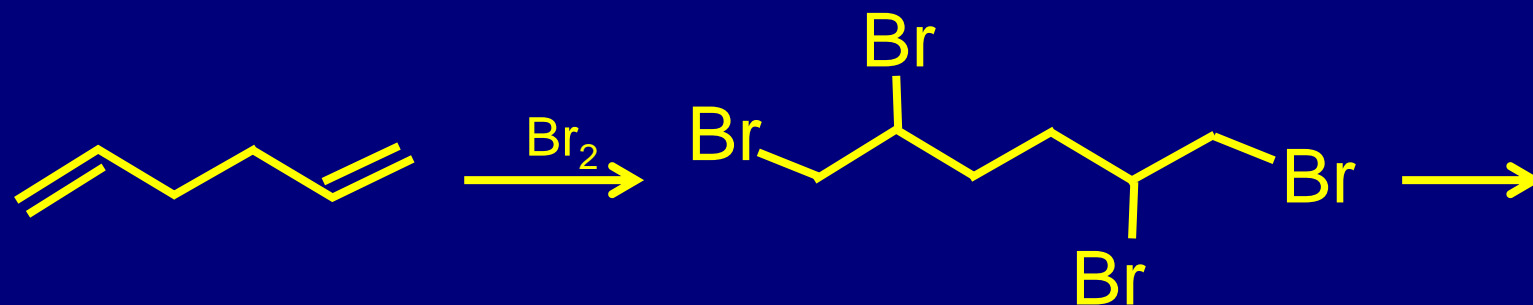
Isti razlozi kao i kod alkena: hiperkonjugacija

Dobijanje

Dvostruka eliminacija dihalogenalkana



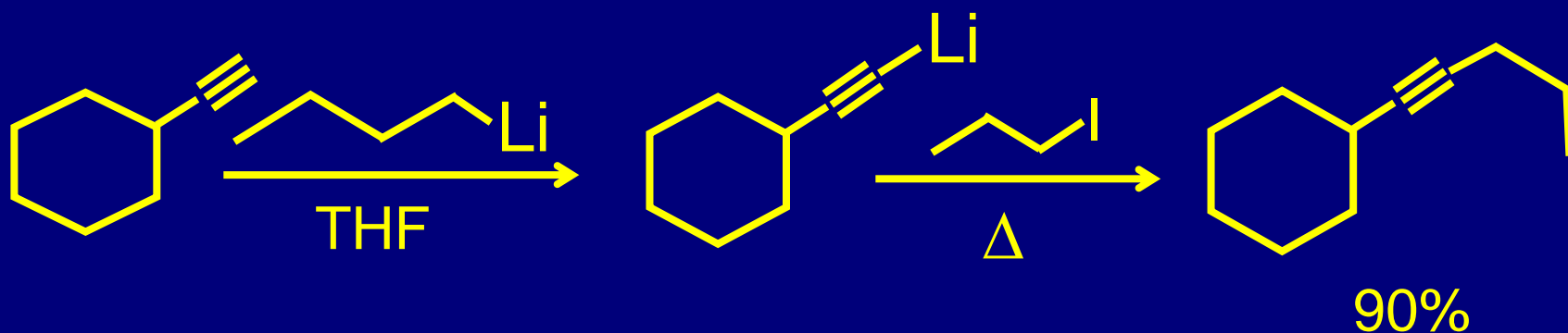
Primena u sintezi:



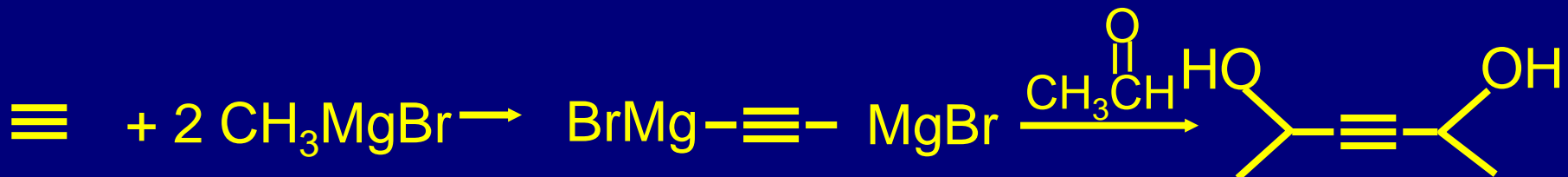
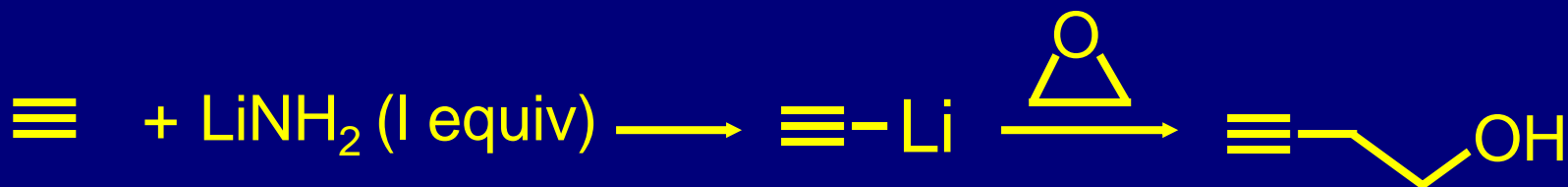
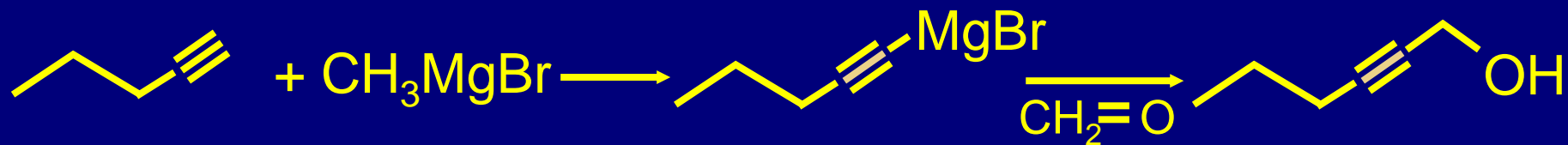
1,5-Heksadiin

Alkilovanje alkinil-anjona

S_N2 reakcija



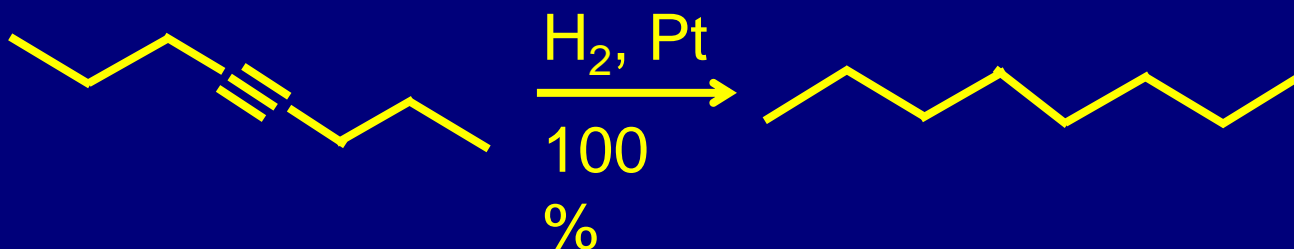
Reakcije alkinil-anjona



Reakcije

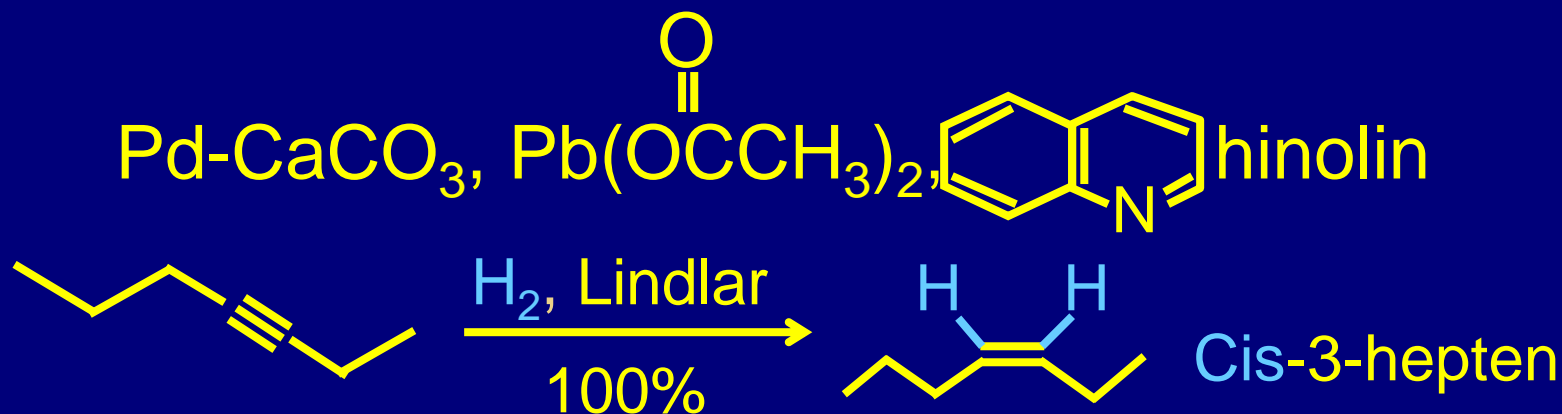
Redukcije

Potpuna hidrogenizacija



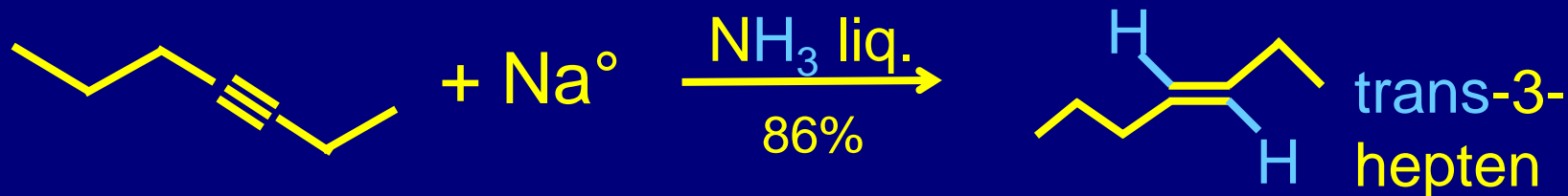
Delimična hidrogenizacija:

“zatrovani” Lindlar’ov katalizator- cis alkeni!



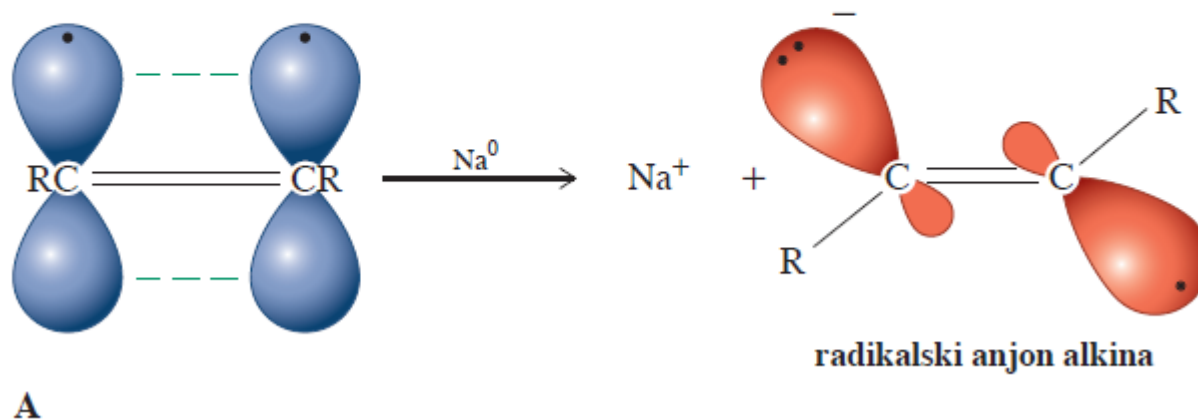
Redukcija sa natrijumom.

Jedno-elektronske redukcije alkina

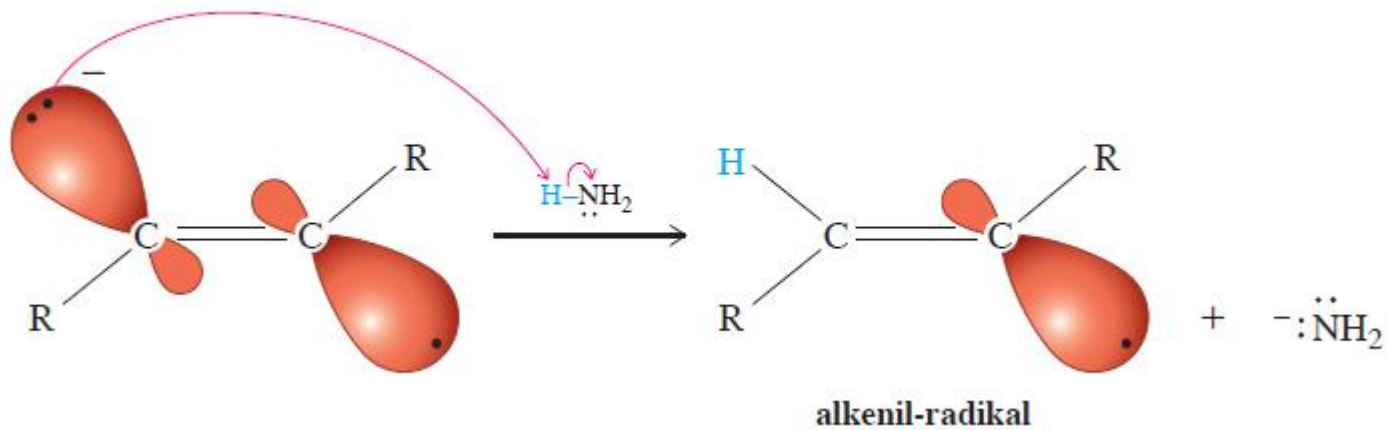


Mehanizam redukcije alkina natrijumom u tečnom amonijaku

FAZA 1. Prenos jednog elektrona

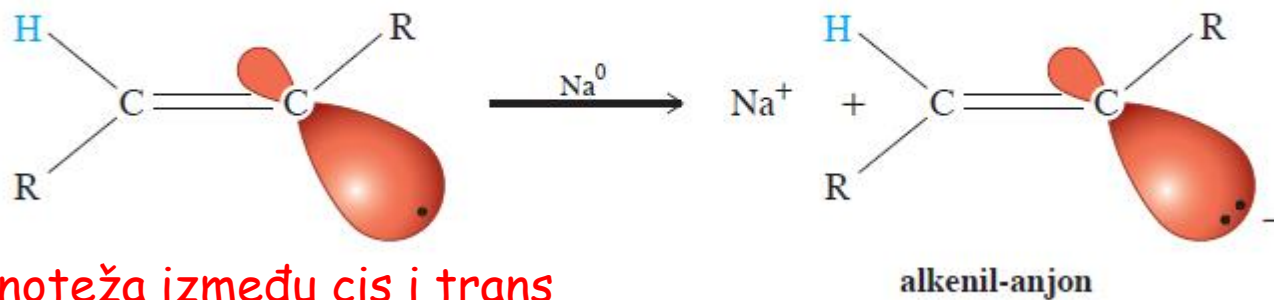


FAZA 2. Prvo protonovanje



B

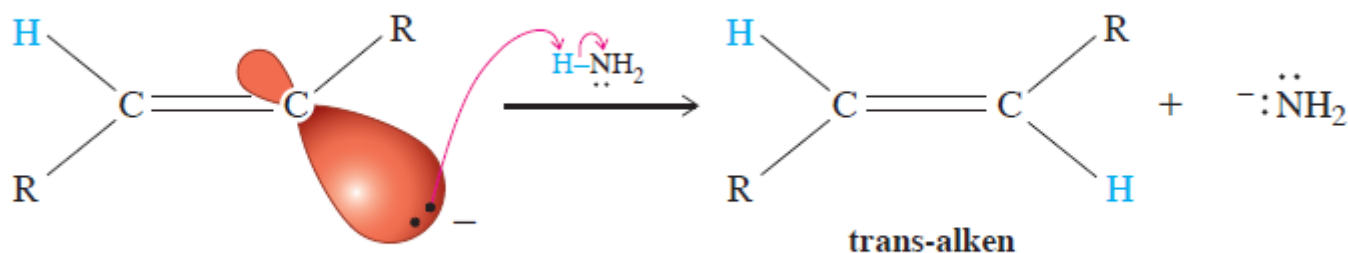
FAZA 3. Drugi prenos jednog elektrona



Ravnoteža između cis i trans

C

FAZA 4. Drugo protonovanje



D

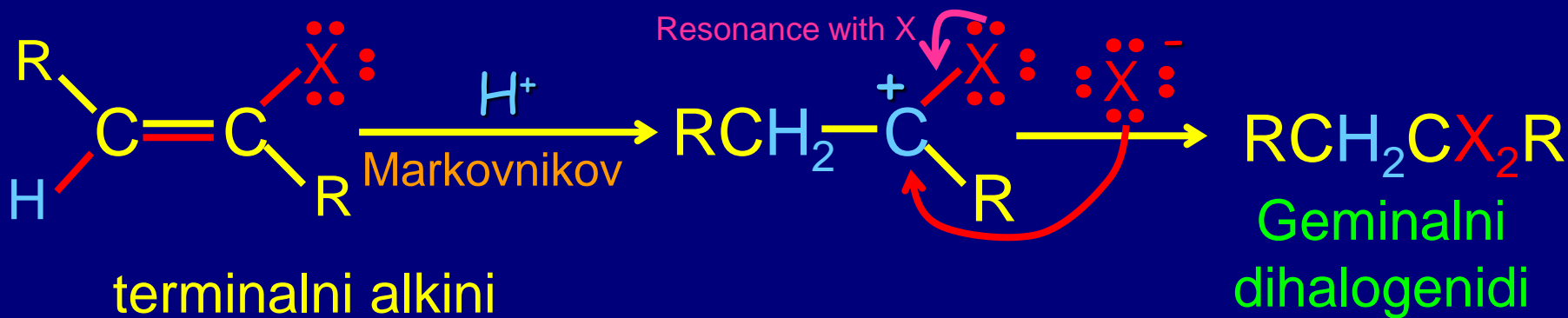
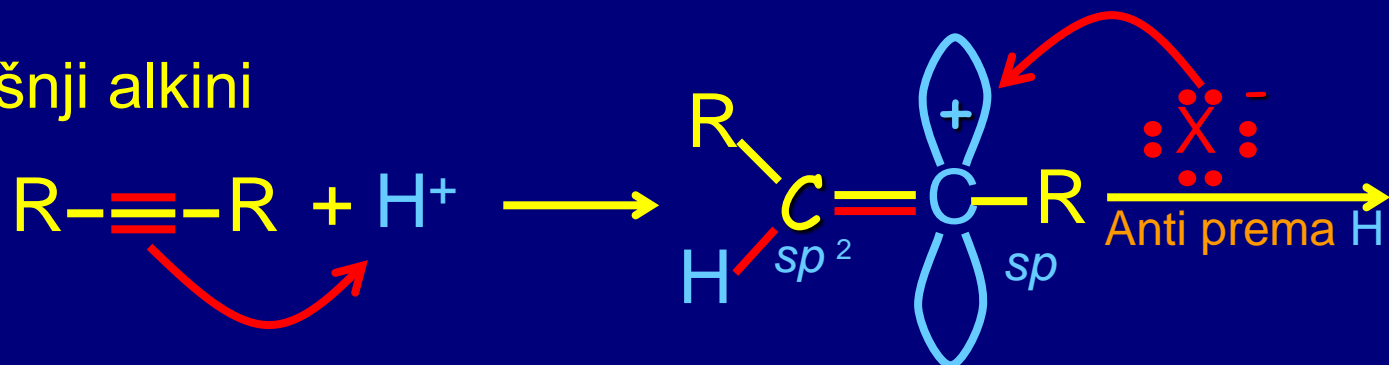
Vežba 13-11

Kada se na 1,7-undekadiin (11 ugljenikovih atoma) deluje smesom natrijuma i natrijum-amida u tečnom amonijaku, redukuje se samo unutrašnja veza, pri čemu se dobija *trans*-7-undecen-1-in. Objasnite. (**Pomoć:** koja reakcija se odvija između natrijum-amida i terminalnog alkina? Zabeležite da pK_a NH_3 iznosi 35.

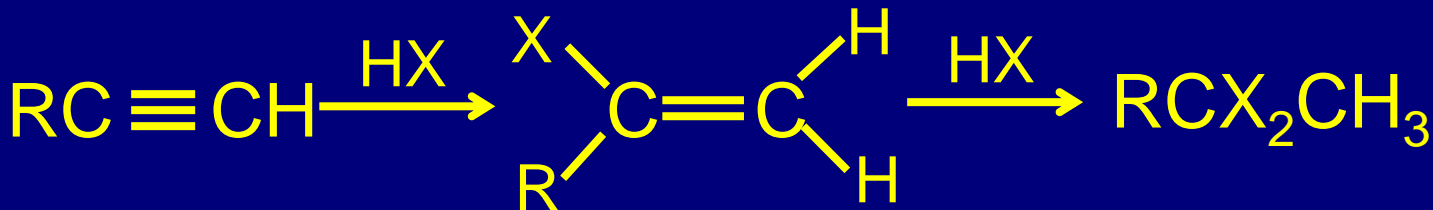
Elektrofilne adicije (slične alkenima)

HX:

Unutrašnji alkini

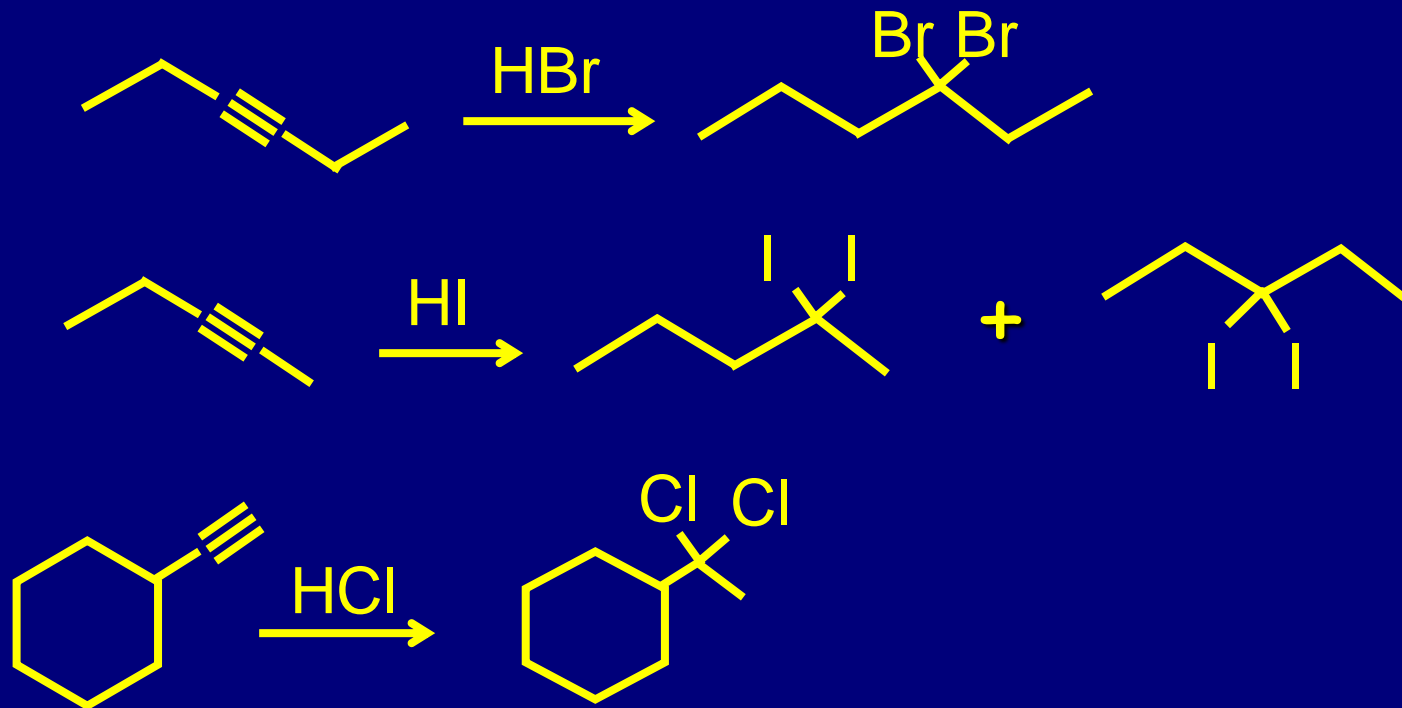


terminalni alkini

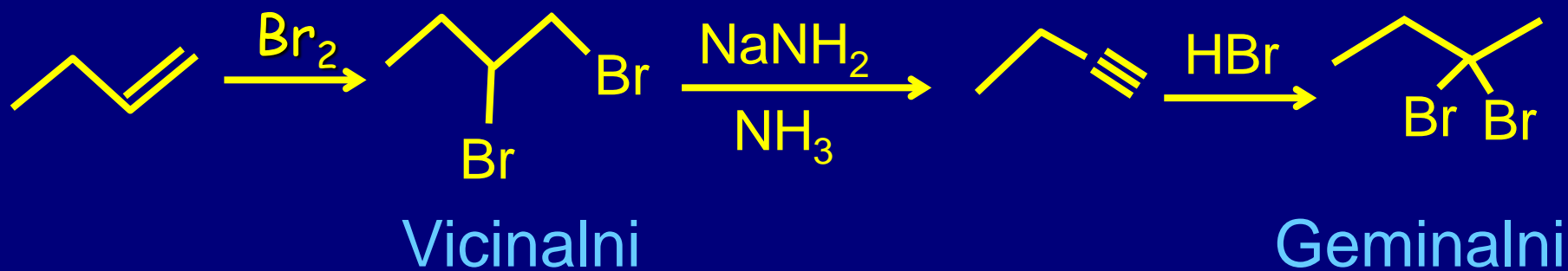


Dvostruka Markovnikov-ljeva adicija

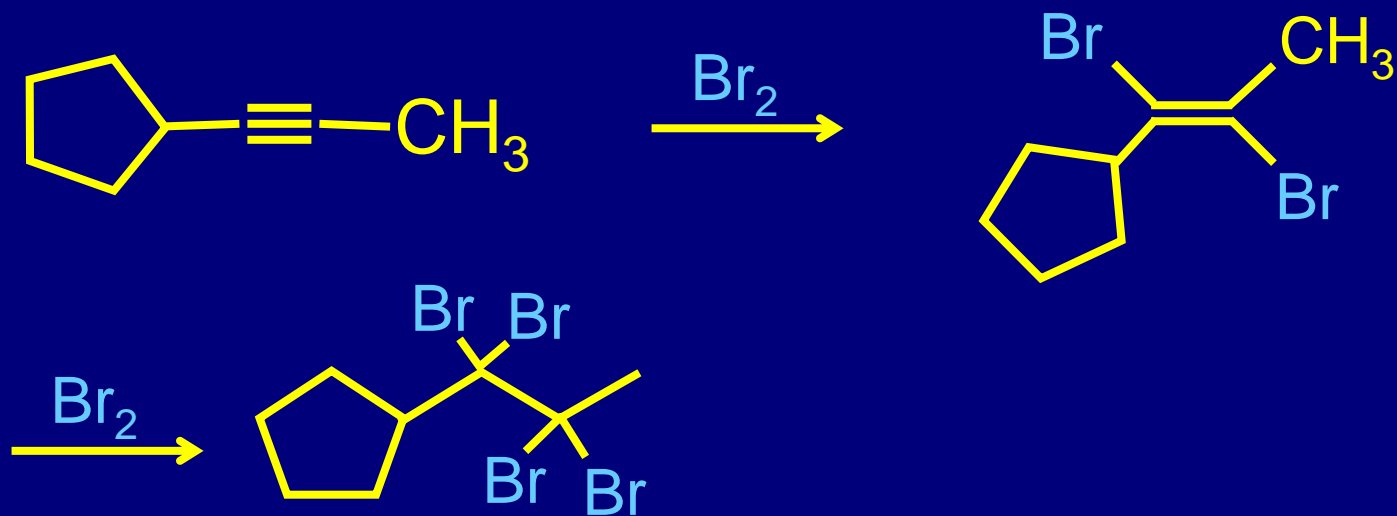
Primeri:



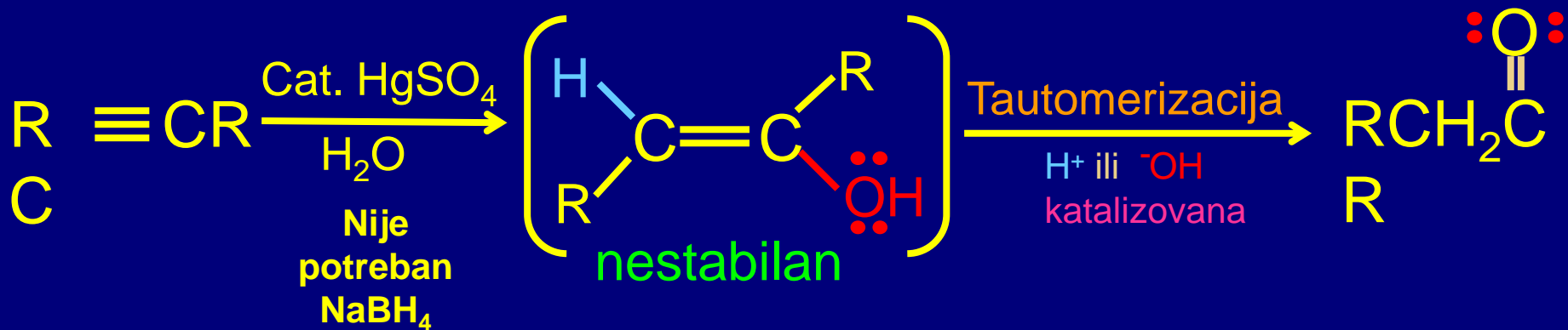
Važno:



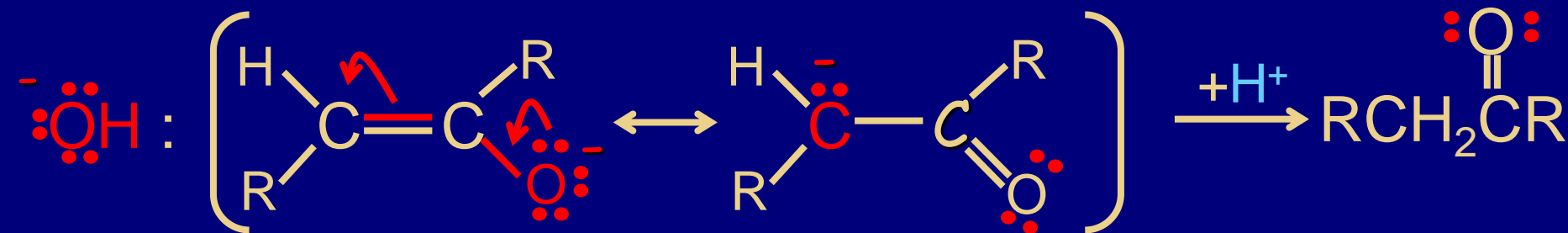
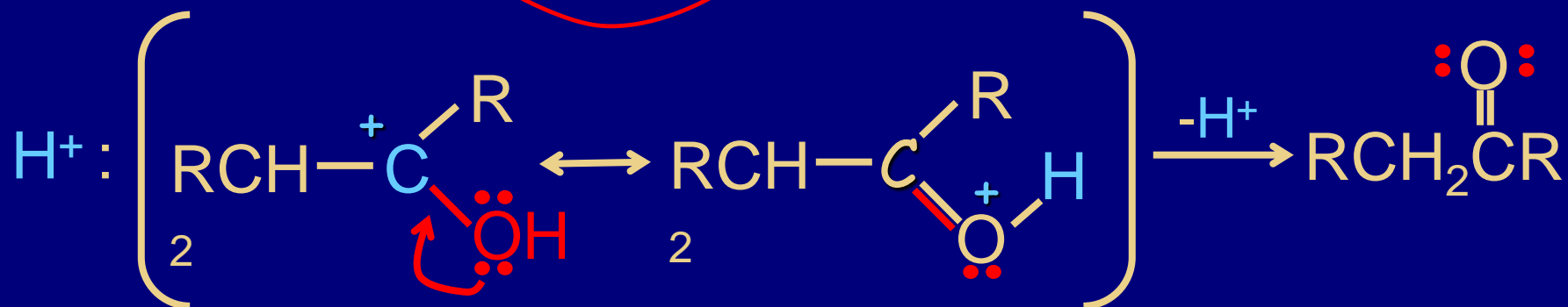
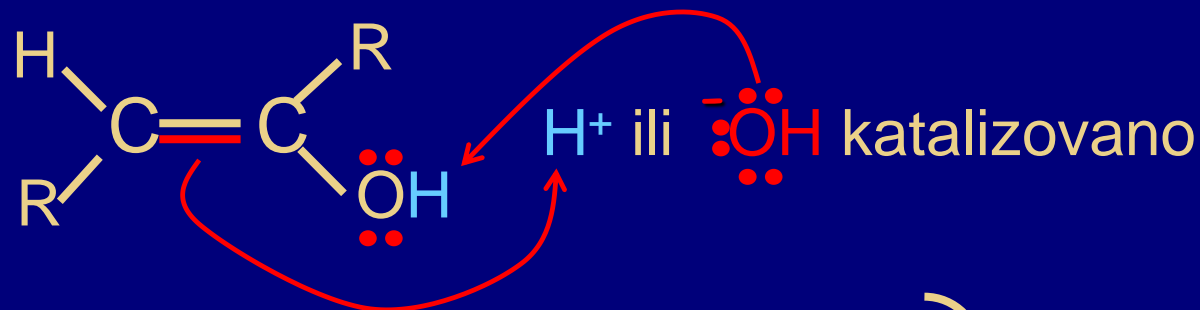
X_2 : Anti adicija, kao kod alkena

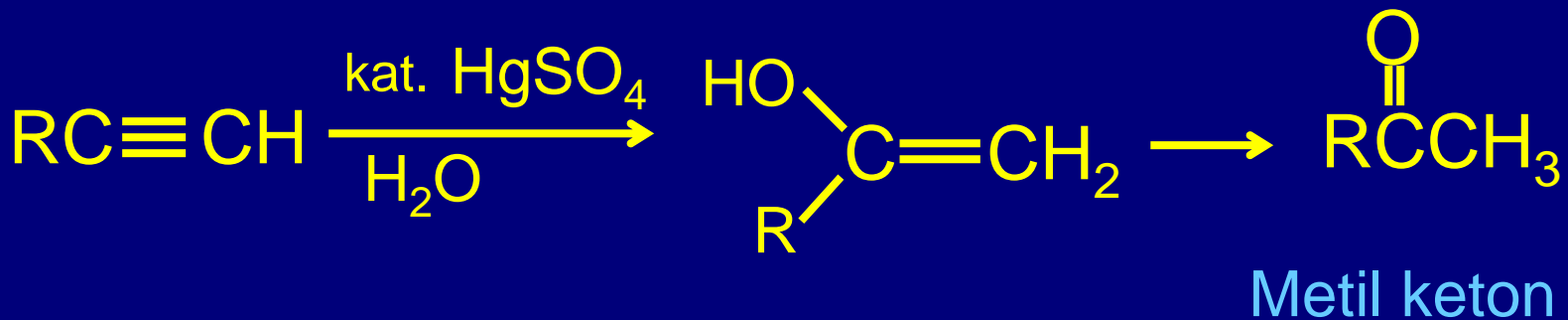


kat. $HgSO_4$, H_2O hidratacija, **Markovnikov**

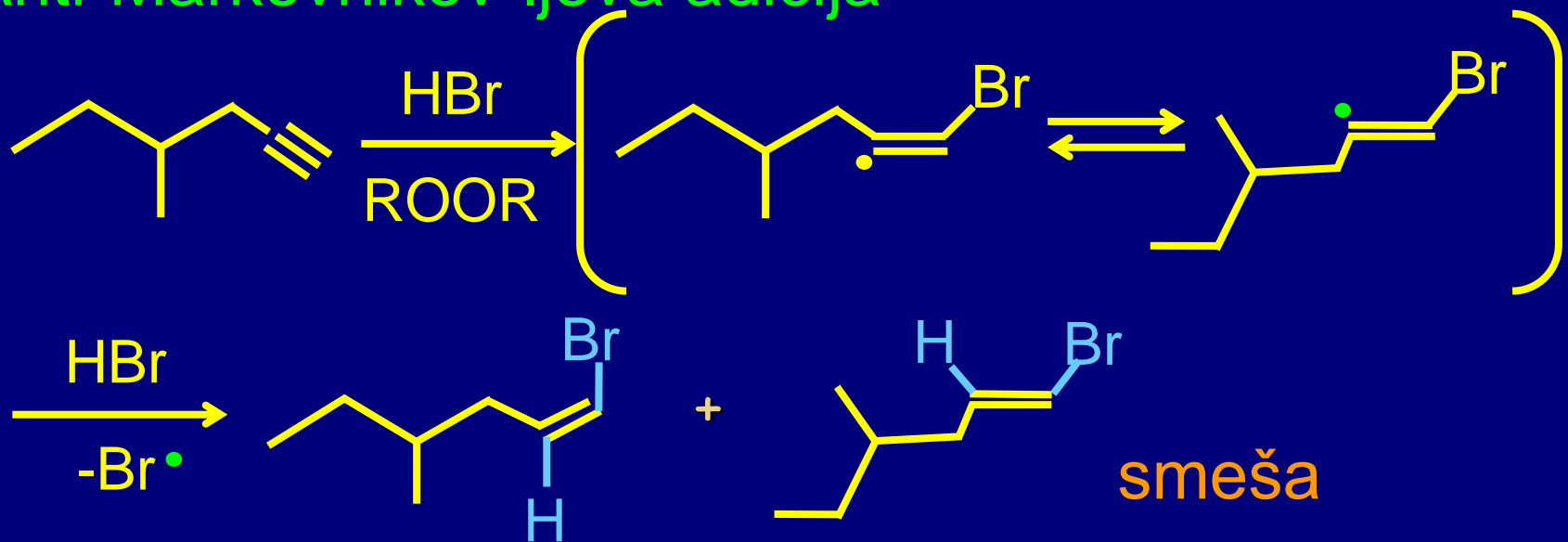


Mehanizam tautomerizacije



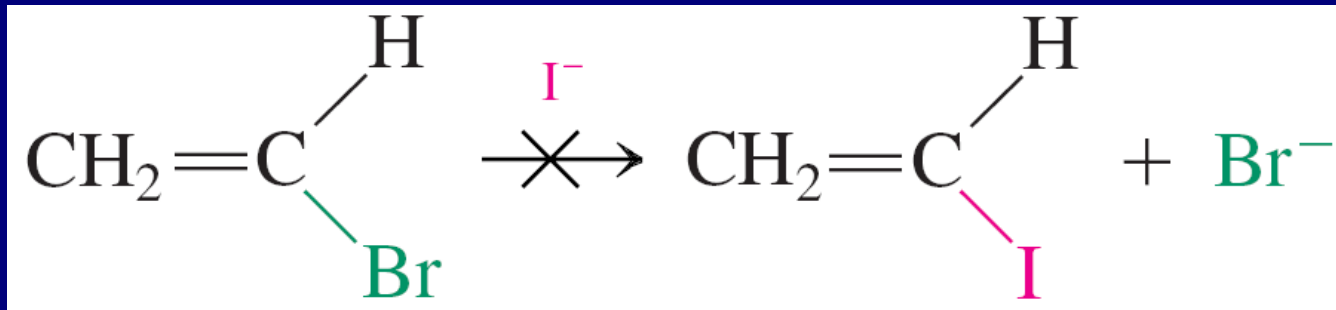


Radikalska adicija HBr: Anti-Markovnikov-ljeva adicija

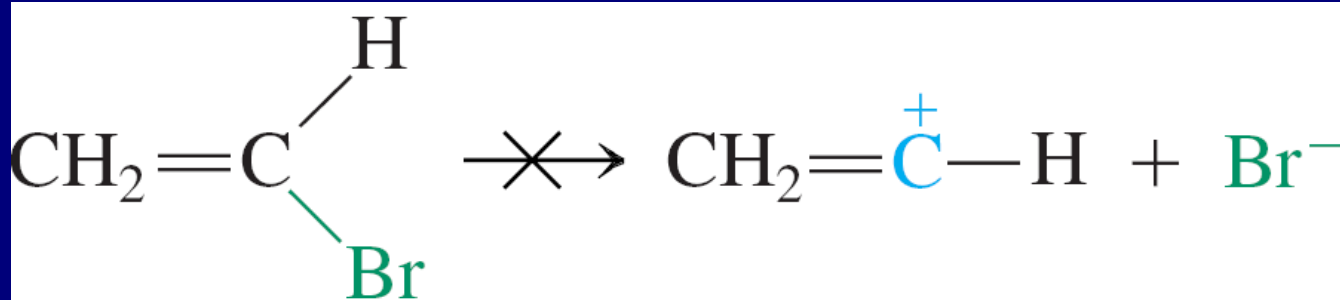


Hemija alkenil-halogenida

Nema S_N2 :

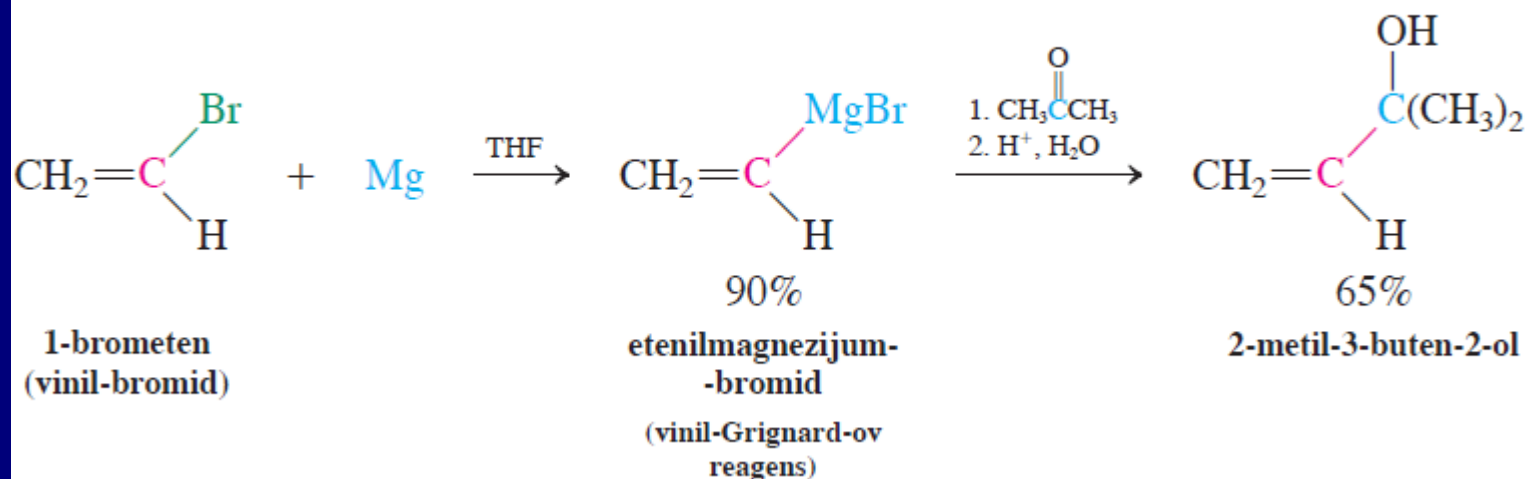


Nema S_N1 :

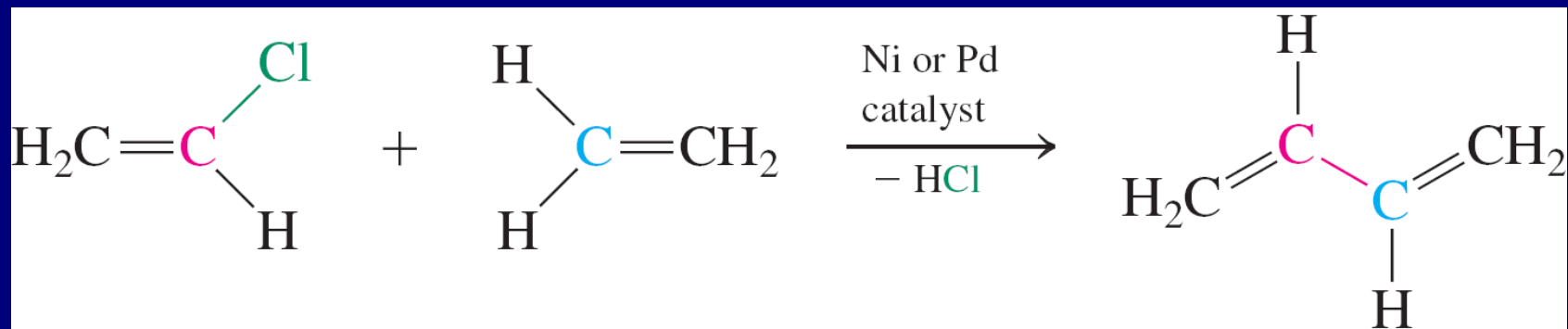


**Ethenyl (vinyl)
cation**

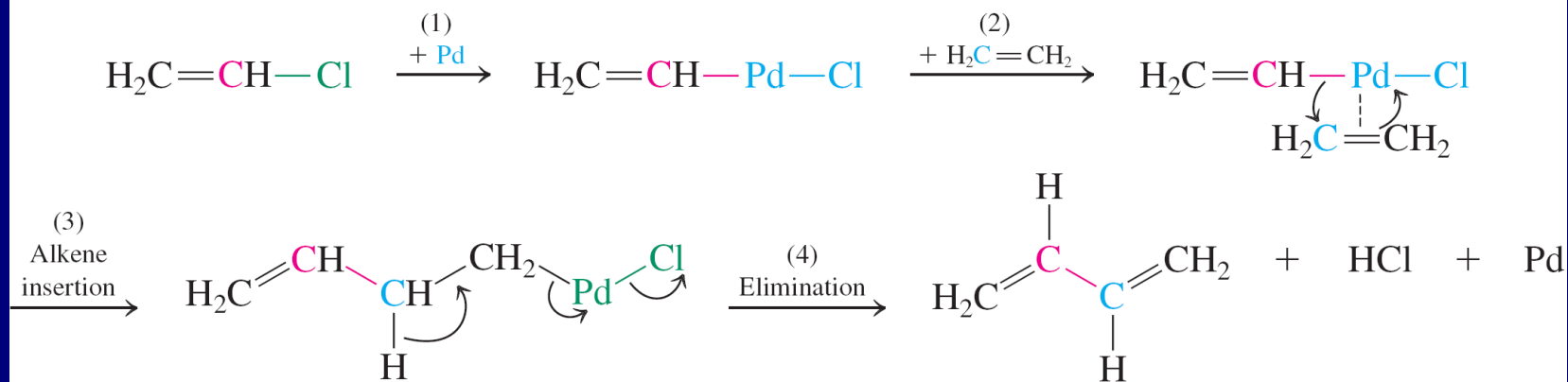
Alkenil-organometali u sintezi



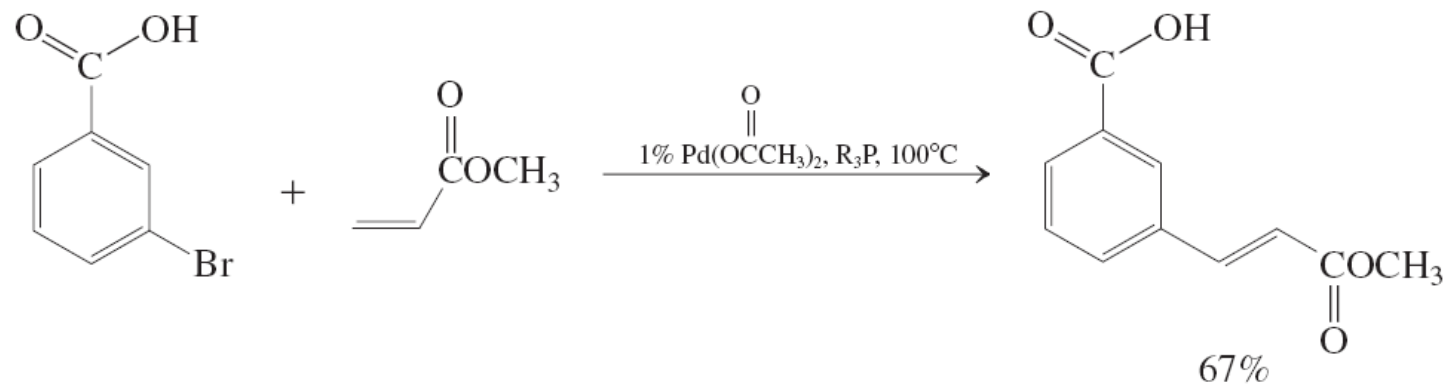
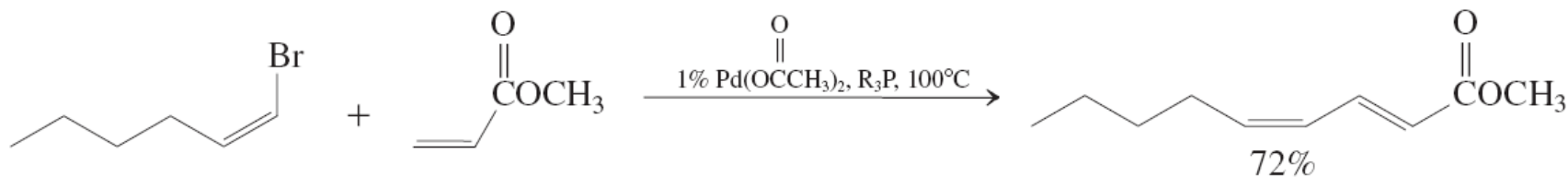
metalima katalizovano kuplovanje alkenil-halogenida i alkena poznato kao Heck-ova reakcija



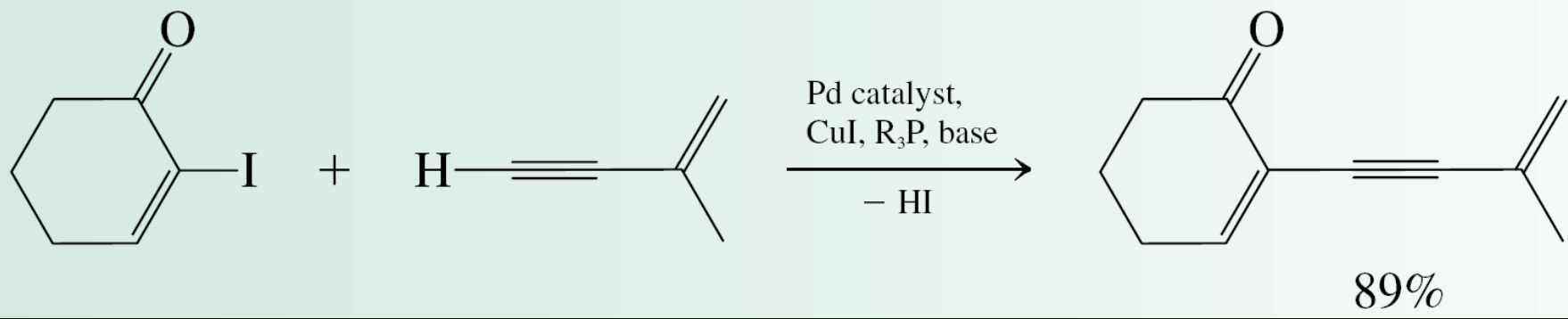
Mechanism of the Heck Reaction



Examples of Heck Reactions

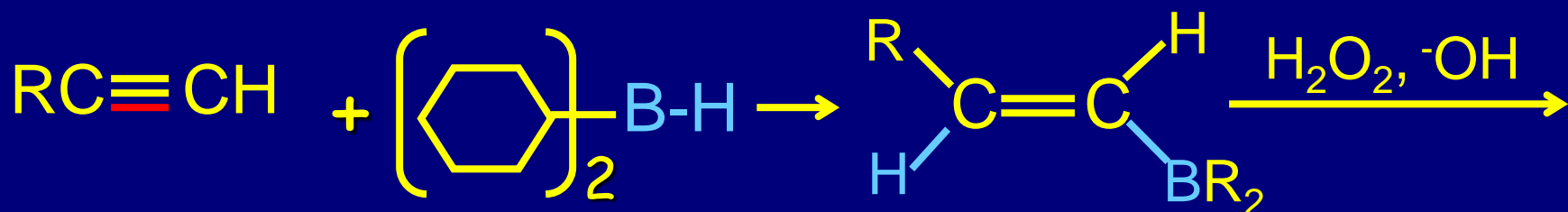


Sonogashira kuplovanje



Hidrobtorovanje-Oksidacija

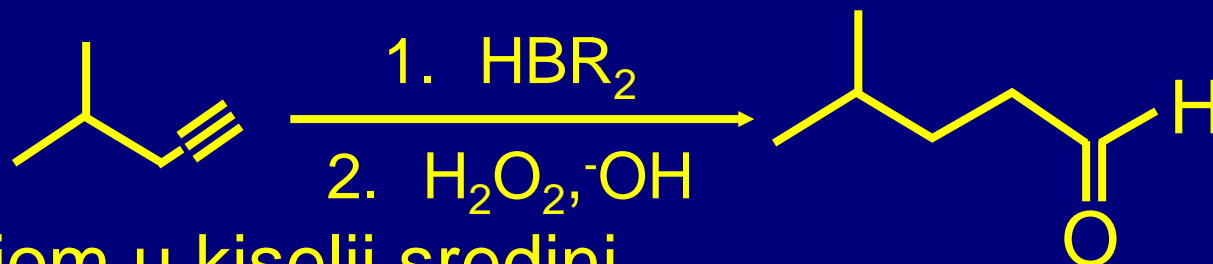
Reakcija R_2BH ($R = \text{voluminozna grupa}$) za zaštitu alkenilborana: $R = \text{cikloheksil}$



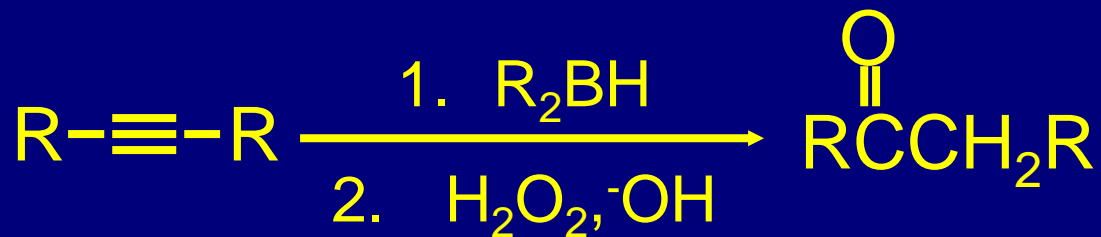
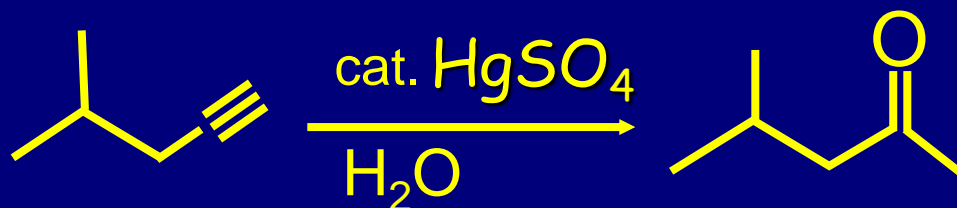
Sterna kontrola



Prema tome, hidroborovanje
oksidacija:



Dok hidratacijom u kiselij sredini



$\text{R} \neq \text{R}$: smeša proizvoda