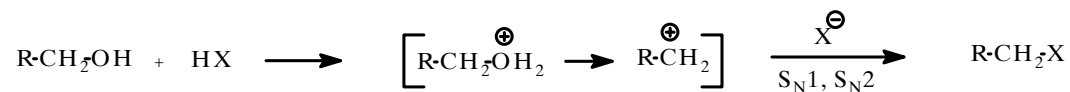


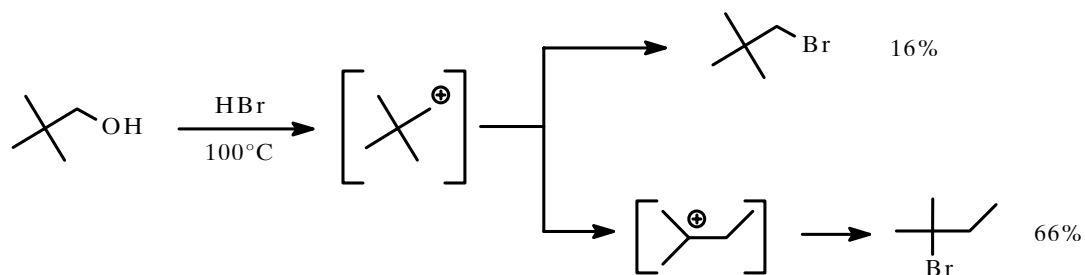
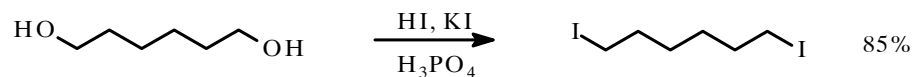
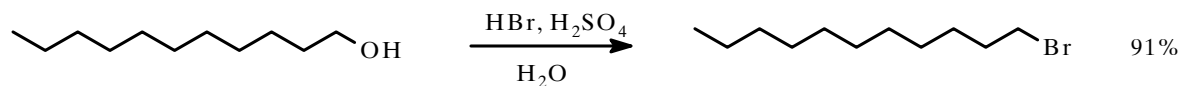
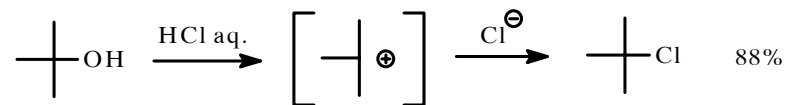
# HALOGENOVANJE

- 1) Nukleofilne supstitucije;
- 2) Adicije HX, X<sub>2</sub> i sl.;
- 3) Halogenovanje karbonilnih jedinjenja;
- 4) Alilno i benzilno halogenovanje.

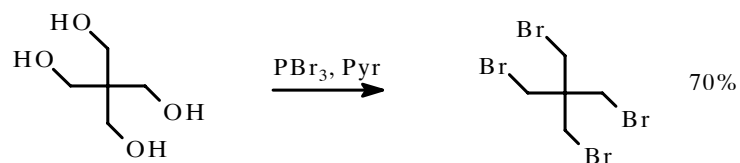
## 1) Nukleofilne supstitucije



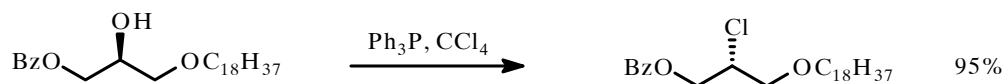
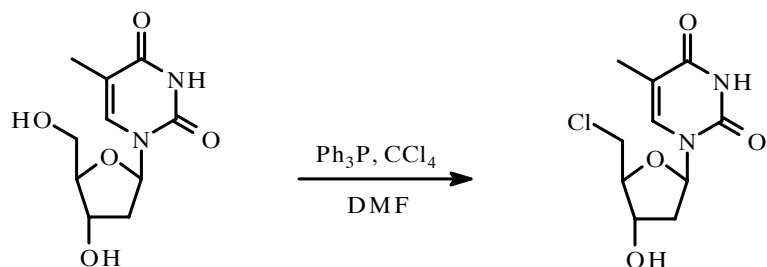
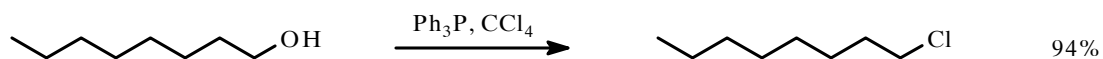
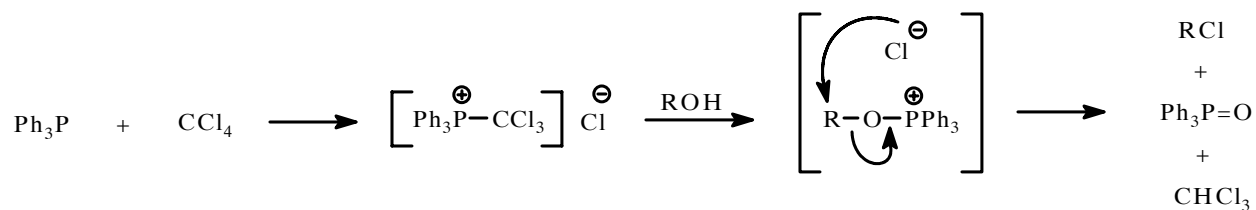
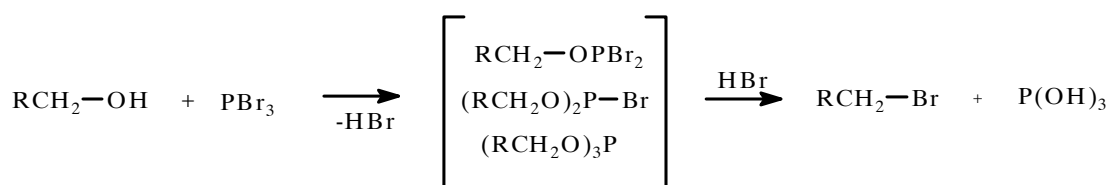
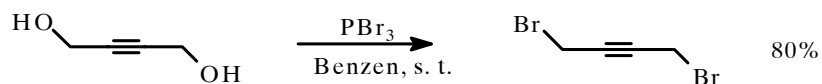
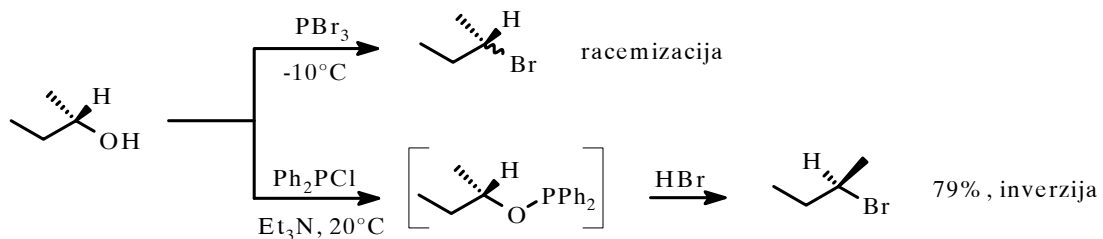
Pomoću mineralnih kiselina - HX

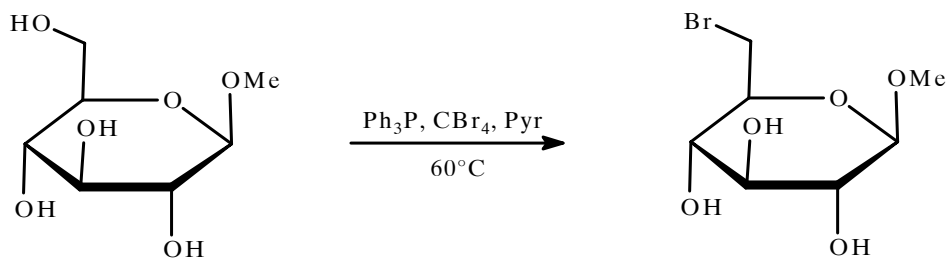
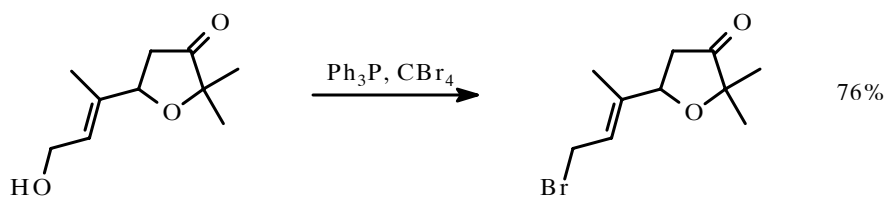


Pomoću PBr<sub>3</sub>



Stereohemijski ishod reakcije sa  $\text{PBr}_3$



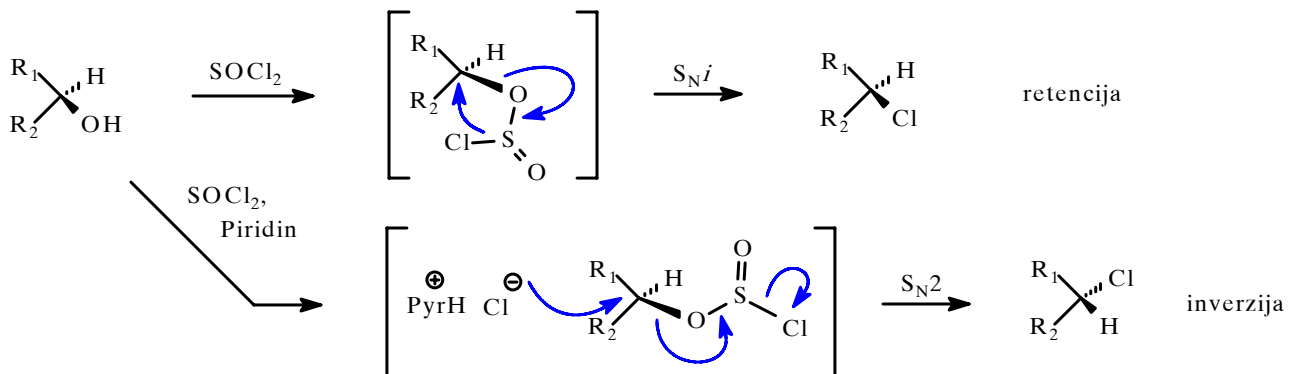


Selektivno prevodi primarne alkohole u bromide, u prisustvu sekundarnih (u piridinu)

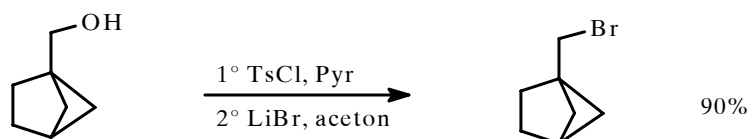
Ostali fosforni reagensi:  $\text{Ph}_3\text{P}/\text{Br}_2$ ;  $(\text{PhO})_3\text{P}/\text{MeI}$

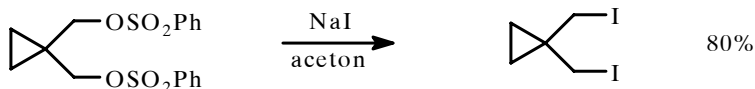


$\text{SOCl}_2$ : reagens koji omogućava supstituciju uz retenciju konfiguracije



$\text{TsCl} / \text{NaI}$



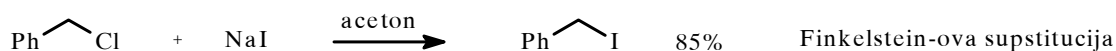


Rastvarači za supstitucije pojedinim halogenidima:

Cl: LiCl u EtOH, DMF

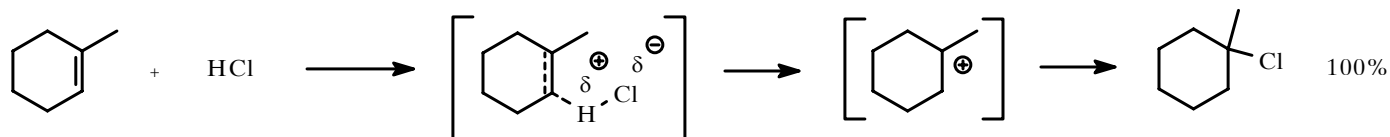
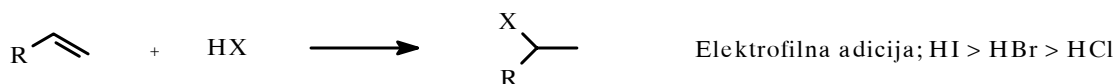
Br: NaBr u DMF, DMSO, HO-CH<sub>2</sub>-CH<sub>2</sub>-OH

I: NaI u ketonskim rastvaračima

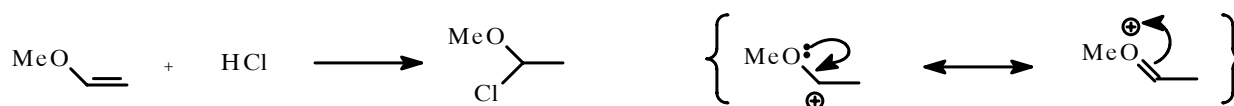


## 2) Adicije HX i X<sub>2</sub>

HX

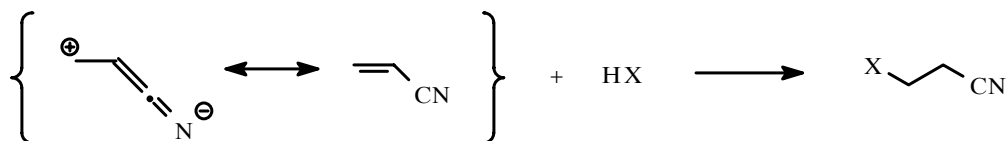


Uticaj supstituenata: Markovnikovljevo pravilo

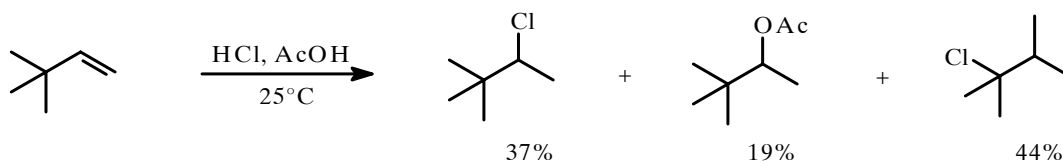


Izuzeci od Markovnikov-ljevog pravila:

1. Supstituenti sa -I i -R efektom
2. Radikalni mehanizam

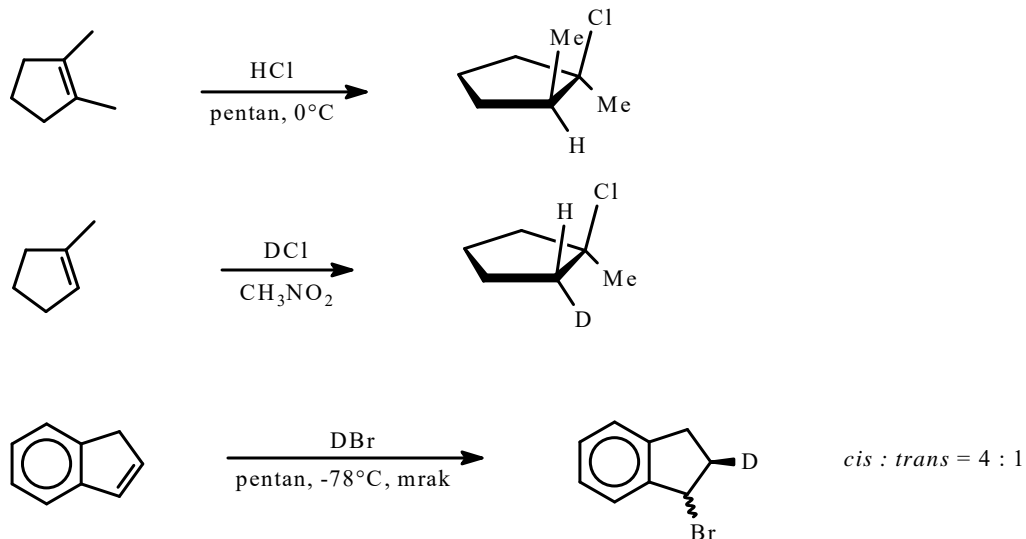


Slično se ponašaju:  $\text{CH}_2=\text{CH-CF}_3$   $\text{CH}_2=\text{CH-NO}_2$



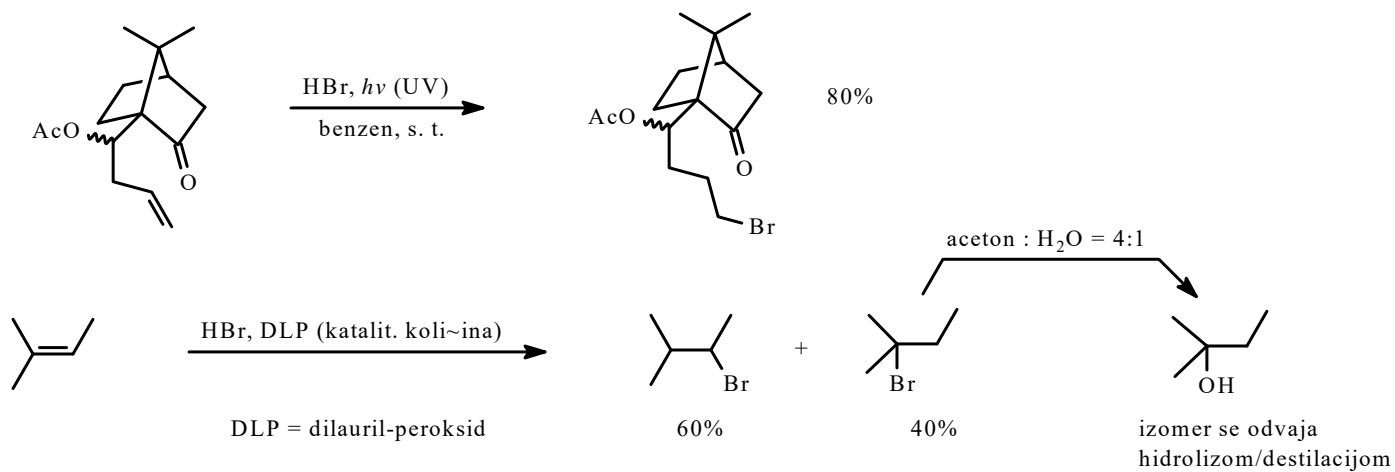
Stereohemija adicije: uglavnom *trans*

Kada se vrši preko stabilnog karbokatjona: smesa izomera u kojoj može da dominira *cis*

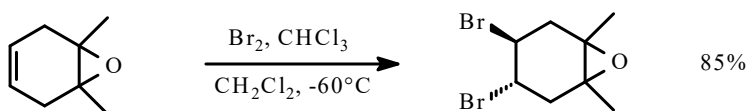
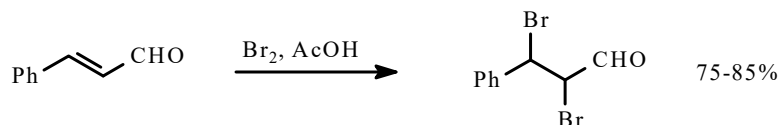
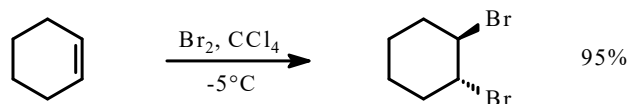


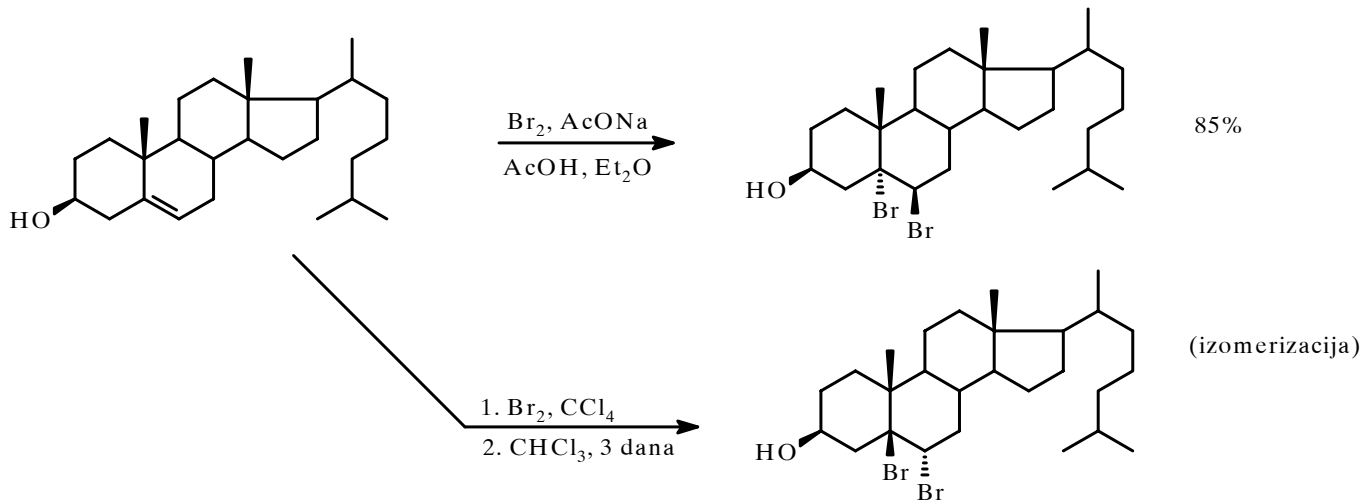
Kharash-eva adicija (anti-Markovnikov-ljevi proizvodi)

Radikalni mehanizam

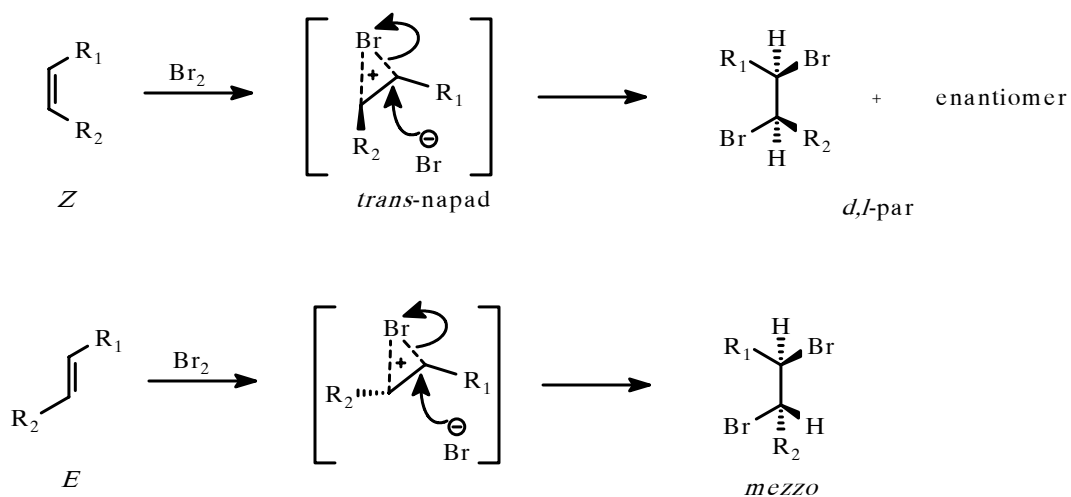


Adicija X<sub>2</sub> Br<sub>2</sub>, Cl<sub>2</sub> (rele), I<sub>2</sub> - povratna reakcija

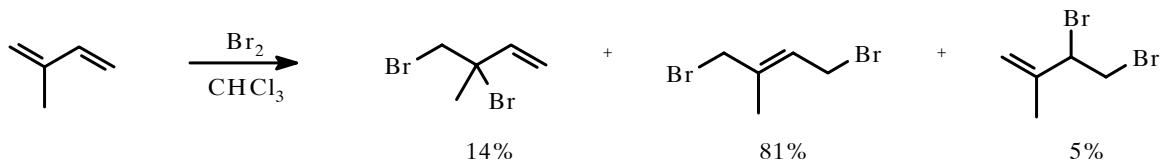




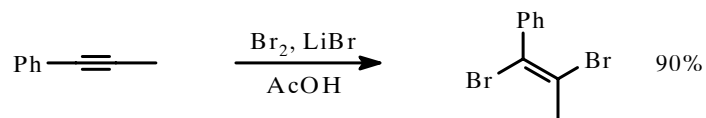
Mehanizam i stereochemija adicije



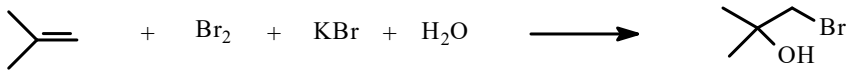
Dieni: 1,4 (dominira) + 1,2



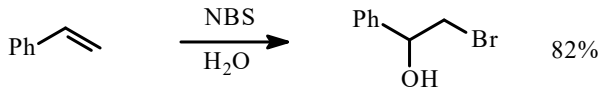
Alkini



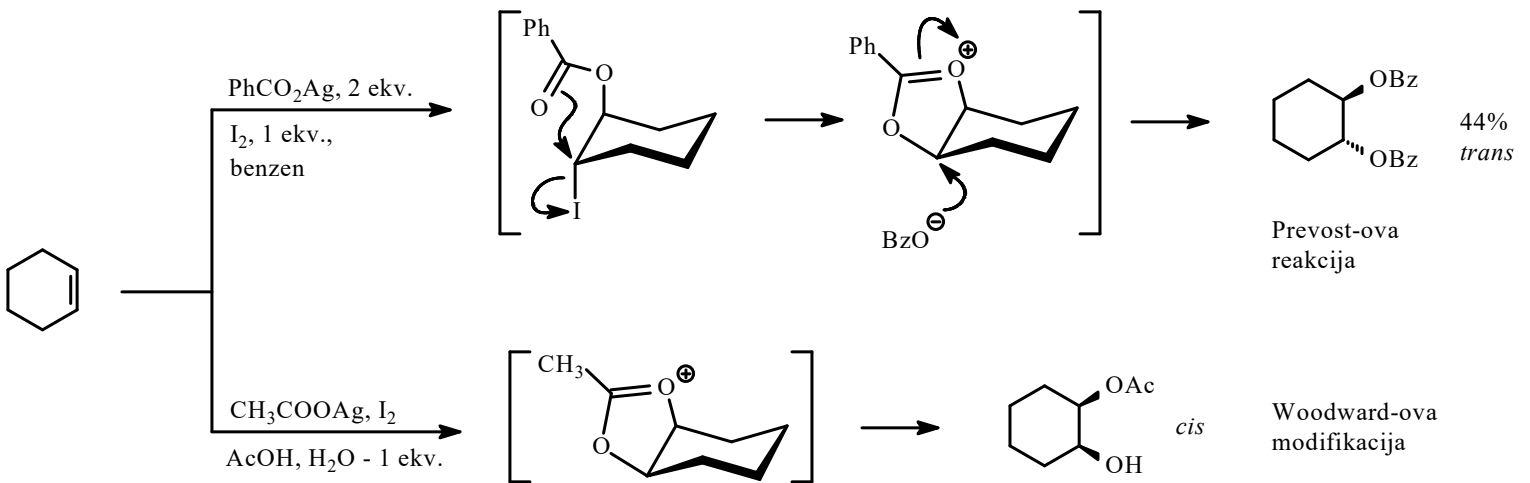
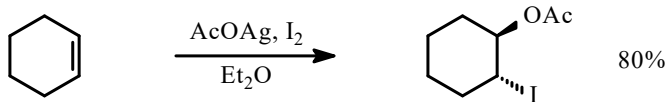
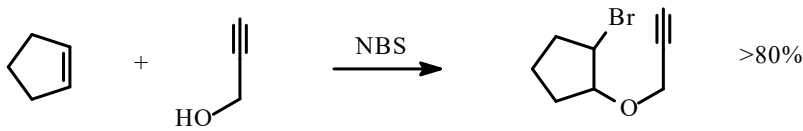
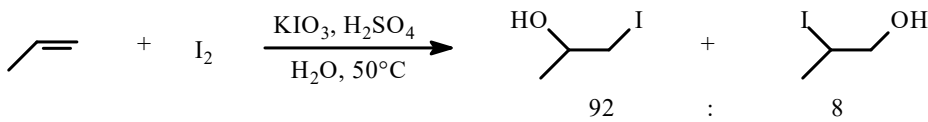
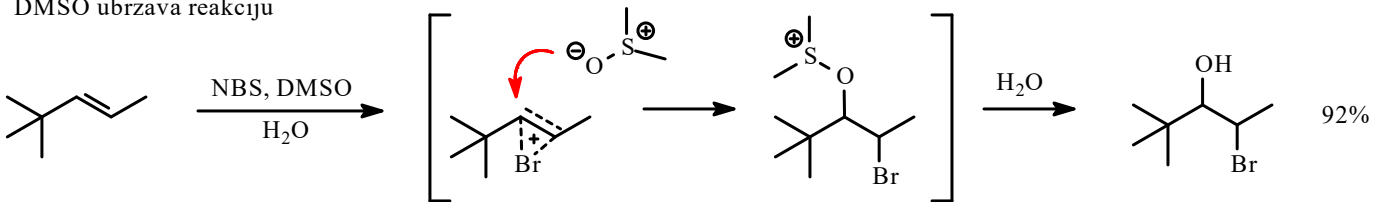
Haloeterifikovanje i slične reakcije (presretanje intermedijera)

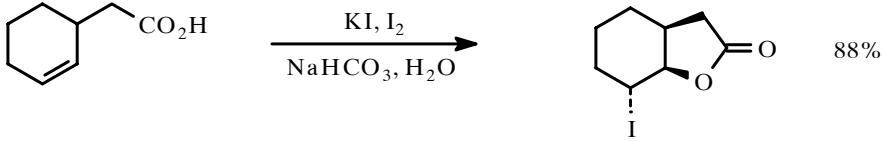
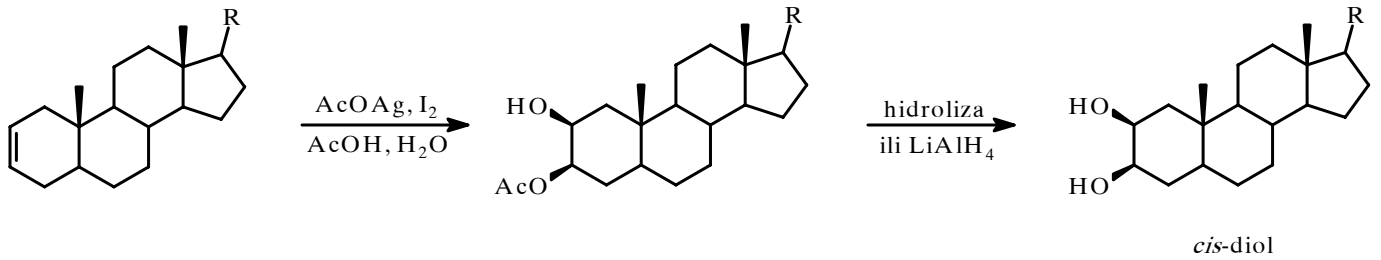


Drugi izvori "pozitivnog" halogena: NBS, HClO, Ca(OCl)<sub>2</sub>,...



DMSO ubrzava reakciju

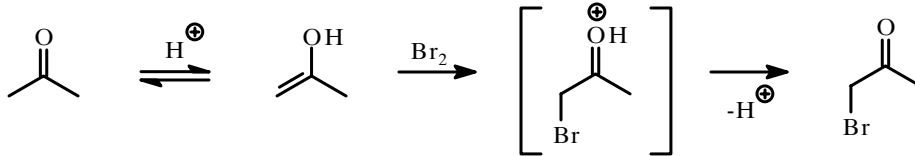




### 3) Halogenovanje karbonilnih jedinjenja

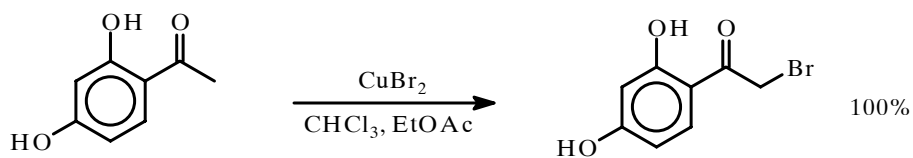
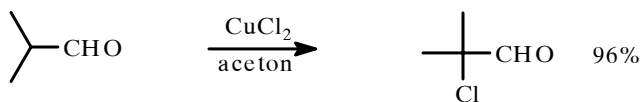
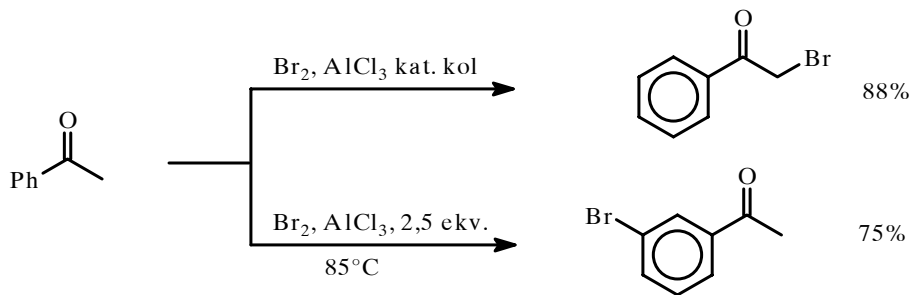
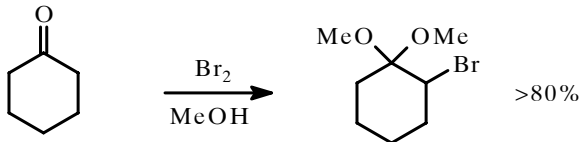
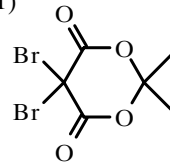
- kiselo katalizovano
- bazno katalizovano

Kiselo katalizovano

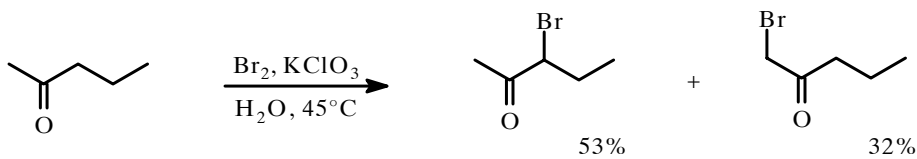


Reagensi: X<sub>2</sub> / rastvarač (AcOH, CHCl<sub>3</sub>, DMF, MeOH, EtOH)

Pored X<sub>2</sub> koriste se još i SO<sub>2</sub>Cl<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, PyrHBr•Br<sub>2</sub>,

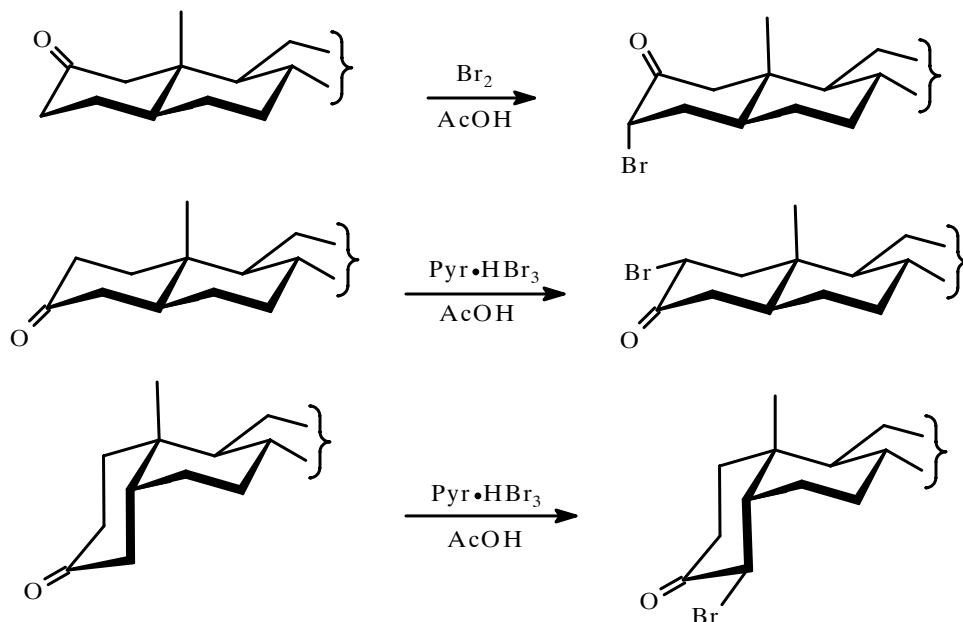




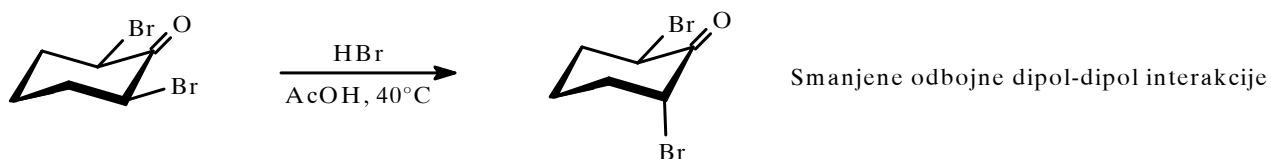


Stereohemija halogenovanja derivata cikloheksanona:

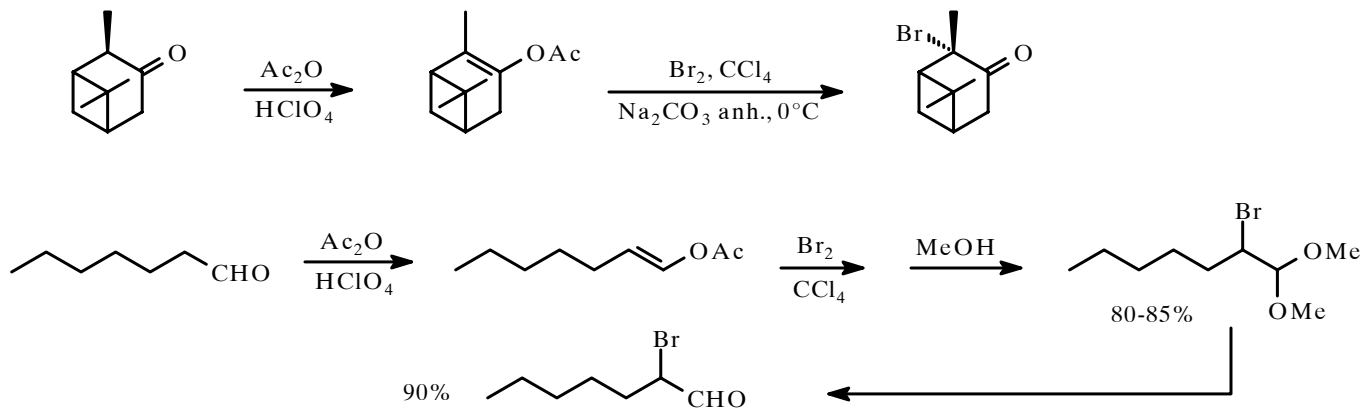
- \* ukoliko je moguće - aksijalni napad
- \* uticaj 1,3-diaksijalnih interakcija



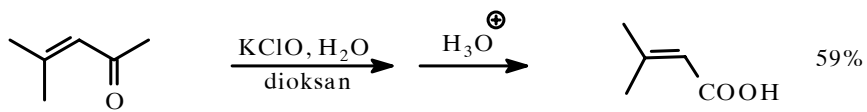
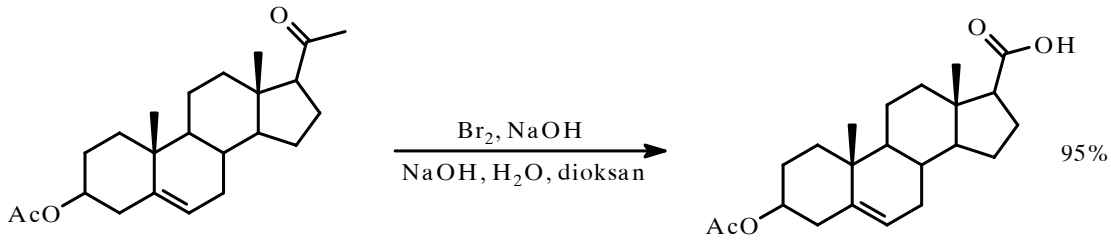
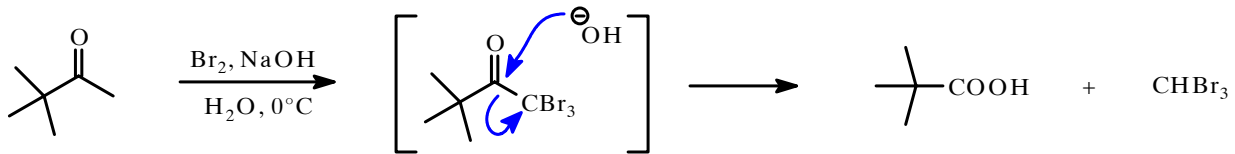
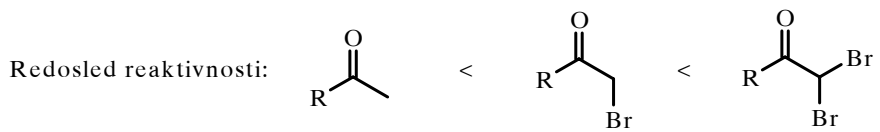
Elektronski efekti: izomerizacija



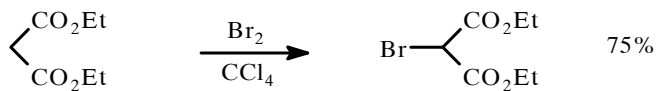
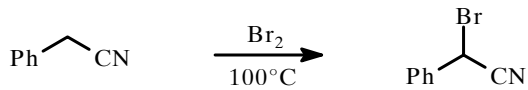
Indirektno: preko enol-acetata



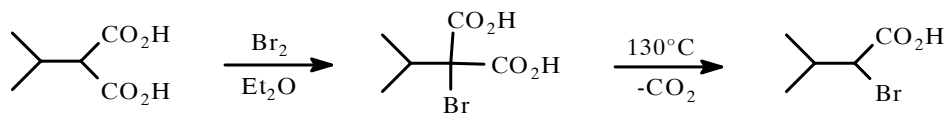
Bazno katalizovano halogenovanje karbonilnih jedinjenja (haloformska reakcija)



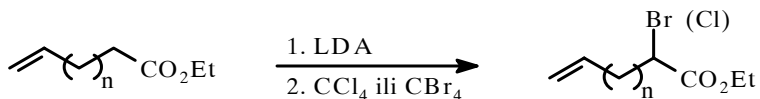
Halogenovanje ostalih metilenski aktivnih jedinjenja (estri, nitrili, kiseline i dr.)



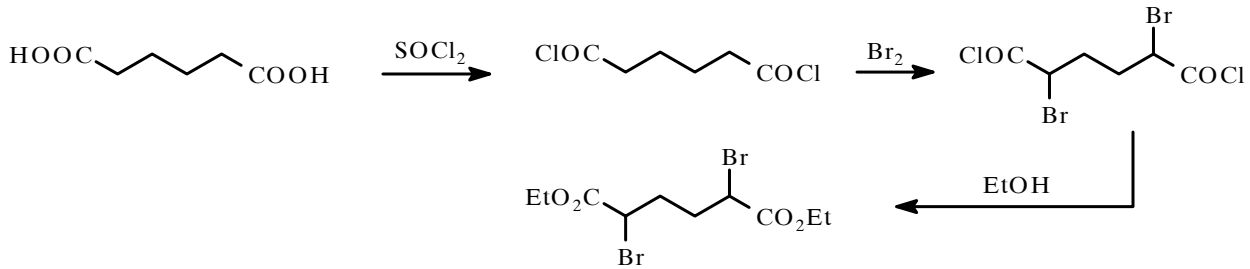
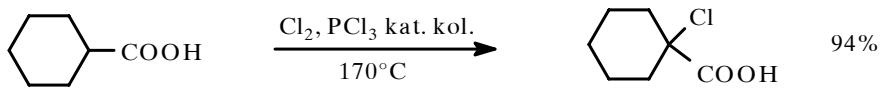
Monoestri ne reaguju  $\rightarrow$  indirektan način



Direktno: preko enolata



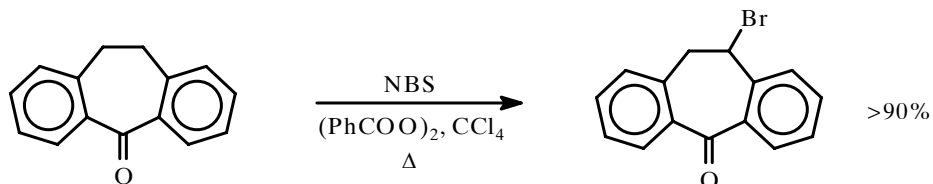
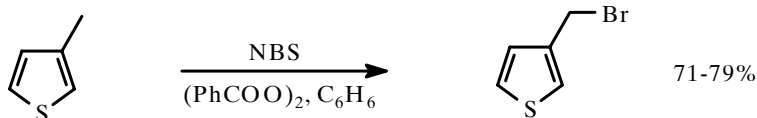
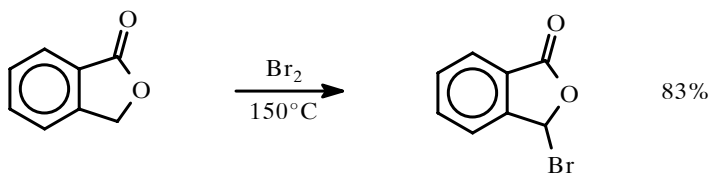
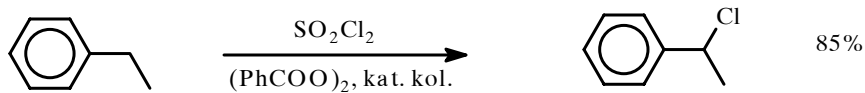
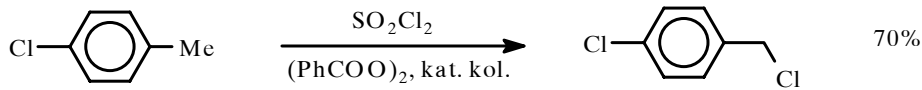
$\alpha$ -Halogenovanje kiselin: Hell-Wolhardt-Zelinski reakcija



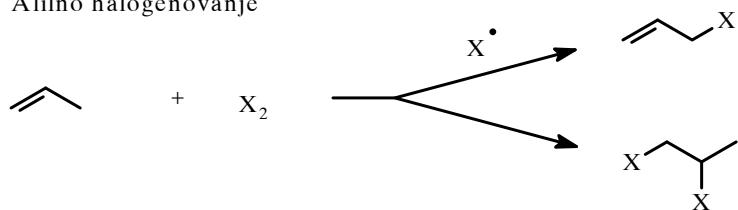
4) Alilno i benzilno halogenovanje

- \* najčešće radikalni
- \* reagensi:  $\text{SO}_2\text{Cl}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , NBS, *t*-BuOCl
- \* Br je selektivniji od Cl

Benzilno halogenovanje - slobodno-radikalni mehanizam



### Alilno halogenovanje

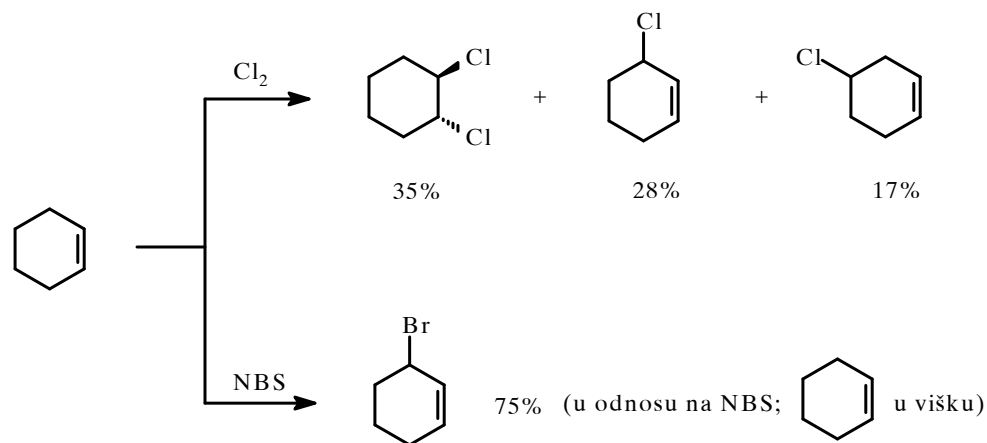


Uticaj koncentracije  $X_2$   
(treba da bude niska)

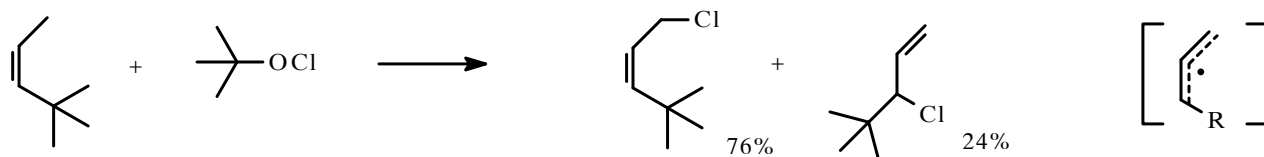
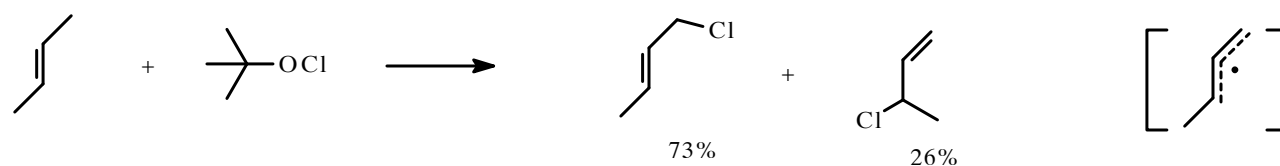
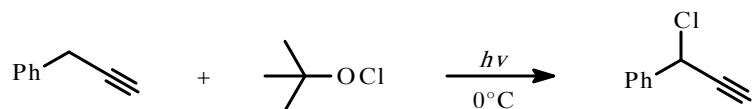
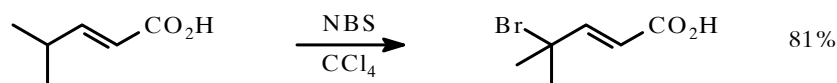
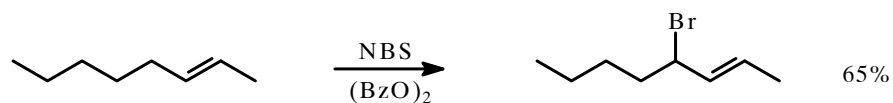
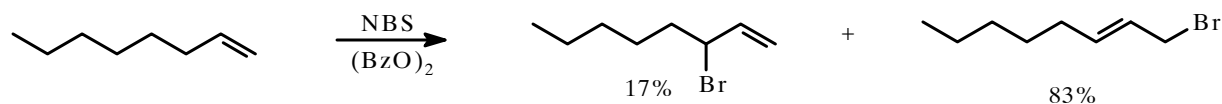
\* Redosled reaktivnosti alilnih položaja: *tert* > *sec* > *prim*

\* Br bolji od Cl

\* -I grupe usporavaju apstrakciju H



NBS/ $CCl_4$ : reagens koji omogućava nisku koncentraciju  $Br_2$



$\omega$ -Halo-ketoni

