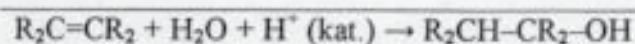
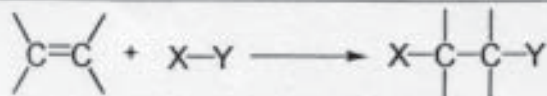
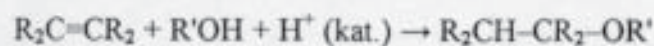


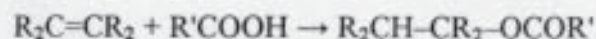
Nekatere tipične sintezno pomembne polarne adicije



adicija vode (sinteza alkoholov)



adicija alkoholov (sinteza etrov)



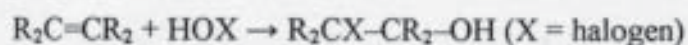
adicija kislin (sinteza estrov)



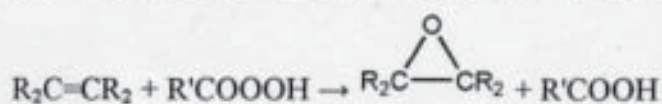
hidrohalogeniranje



halogeniranje

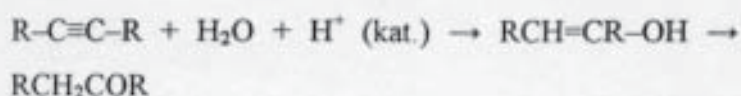


sinteza halohidrinov

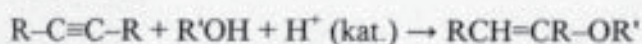


adicija peroksi kislin (epoksidacija):

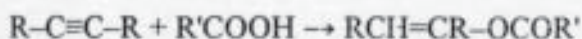
sinteza epoksidov (oksiranov)



adicija vode na acetilene: sinteza karbonilnih spojin



adicija alkoholov na alkinе: sinteza enoletrov



adicija kislin na acetilene: sinteza enol estrov

Tipična organska topila in njihova polarnost

| Nepolarna aprotična topila | * | Polarna aprotična topila | * | Protična topila | * |
|----------------------------|-----|-----------------------------|----|------------------------|------|
| heksan | 1.9 | piridin | 12 | ocetna kislina | 6.1 |
| CCl ₄ | 2.2 | aceton | 21 | trifluorocetna kislina | 8.6 |
| benzen | 2.3 | nitrobenzen | 35 | <i>t</i> -butanol | 12.5 |
| eter | 4.3 | nitrometan | 36 | etanol | 24.5 |
| kloroform | 4.8 | <i>N,N</i> -dimetilformamid | 37 | metanol | 32.7 |
| tetrahidrofuran | 7.6 | dimetilsulfoksid | 47 | voda | 78 |

* vrednost dielektrične konstante

Tipični nukleofili so (razvrstitev po padajoči nukleofilnosti):

a) anioni: $\text{RS}^- > \text{HOO}^- > \text{CN}^- > \text{HO}^- > \text{RO}^- > \text{ArO}^- \sim \text{Br}^- \sim \text{N}_3^- > \text{Cl}^- \sim \text{RCOO}^- > \text{F}^-$.

(ostali primeri: HS^- , $\text{R}-\text{C}\equiv\text{C}^-$, S_2^{2-} , OCN^- , SCN^- , $(\text{ROOC})_2\text{CH}^-$, Br^- , I^- , BH_4^- , AlH_4^- , NO_2^- , R_3C^-)

b) brez naboja: $\text{R}_3\text{N} \sim \text{NH}_2\text{NH}_2 \sim \text{NH}_2\text{OH} > \text{NH}_3$.

(ostali primeri: RNH_2 , R_2NH , R_3N , H_2O , ROH , H_2S , RSH , R_2S , R_3P)

Približno zaporedje lahko izstopajočih skupin:

$\text{CF}_3\text{SO}_2\text{O}- > \text{p-NO}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{O}- > \text{p-Me-C}_6\text{H}_4\text{-SO}_2\text{O}- > \text{I} > \text{Br} > ^+\text{OH}_2 > \text{Cl}$

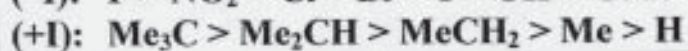
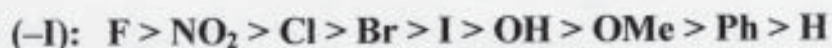
Skupine, ki težje izstopajo:

$\text{F}-$, R_3N^+- , $\text{ArCOO}-$, $-\text{CN}$, $\text{RS}-$, $\text{RO}-$, $\text{HO}-$, $\text{R}_2\text{N}-$, $\text{H}_2\text{N}-$

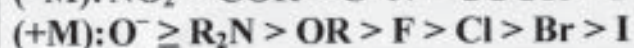
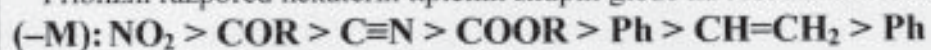
Sposobnost privlačenja elektronov nekaterih tipičnih skupin (v padajočem zaporedju):



Približni razpored nekaterih tipičnih skupin glede na induktivni efekt (v padajočem zaporedju):



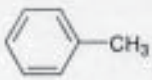
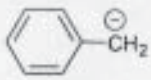






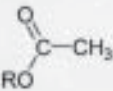
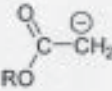
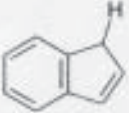
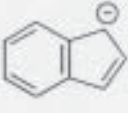




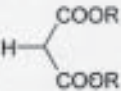
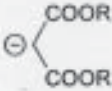


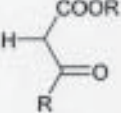
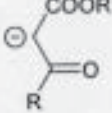


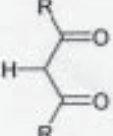
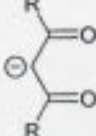
Približni razpored nekaterih tipičnih skupin glede na resonančni efekt (v padajočem zaporedju):














Razporeditev substituentov glede na njihove vplive:

| +M in +I | +M in -I | -M in -I |
|---|---|---|
| Me-, Et-, Me ₂ CH-, Me ₃ C-, itd. (alkil-) | RCONH-, RCOO-, NH ₂ , NR ₂ , F, Cl, Br, I, Ph, OH, OR | RCO-, CN, CF ₃ , CCl ₃ , NO ₂ , R ₃ N ⁺ |

pKa vrednosti značilnih organskih spojin

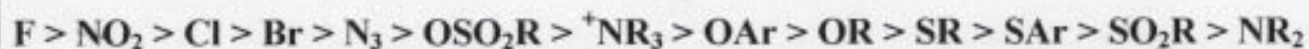
| Spojina ("kislina") | Anion | pKa (v vodi) |
|---|---|--------------|
| (ciklo)alkil-H | (ciklo)alkil ⁻ | ~50 |
|  |  | ~40 |
|  |  | ~40 |
|  |  | ~40 |
|  |  | ~40 |
| HC≡C-H | HC≡C ⁻ | ~25 |
| N≡C-CH3 | N≡C-CH2 ⁻ | ~25 |
|  |  | ~24 |
|  |  | ~20 |
|  |  | ~19-20 |
| R3C-O-H R = H, alkil | R3C-O ⁻ R = H, alkil | ~16-17 |
|  |  | ~16 |
| H-O-H | H-O ⁻ | 15.74 |
| Me-O-H | Me-O ⁻ | 15.2 |
|  |  | ~13 |
|  |  | ~12 |
|  |  | ~11 |
|  |  | ~10 |
|  |  | ~9 |
| N≡C-H | N≡C ⁻ | 9.2 |

Tipične elektrofilne aromatske substitucije

| Nastanek elektrofila | Elektrofil | Ime reakcije | Primer pretvorbe |
|---|---|-------------------------------|---|
| $2\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4 + \text{H}_2\text{O}$ | NO_2^+ | nitriranje |  |
| $\text{HNO}_3 + \text{H}^+ \rightarrow \text{NO}^+ + \text{H}_2\text{O}$ | NO^+ | nitroziranje |  |
| $\text{X}_2 + \text{MX}_n \rightarrow \delta^+ \text{X}_2 \cdots \delta^- \text{MX}_n$ | $\delta^+ \text{X}_2 \cdots \delta^- \text{MX}_n$ | halogeniranje |  |
| $\text{H}_2\text{S}_2\text{O}_7 \rightarrow \text{H}_2\text{SO}_4 + \text{SO}_3$ | SO_3 | sulfoniranje |  |
| $\text{RSO}_2\text{-X} + \text{MX}_n \rightarrow \text{R}^{\delta+} \text{SO}_2\text{-X} \cdots \delta^- \text{MX}_n$ | $\text{R}^{\delta+} \text{SO}_2\text{-X} \cdots \delta^- \text{MX}_n$ | halosulfoniranje |  |
| $\text{R}_3\text{C-X} + \text{MX}_n \rightarrow \text{R}_3\text{C}^+ + \text{MX}_{n+1}$ | R_3C^+ | alkiliranje |  |
| $\text{R-X} + \text{MX}_n \rightarrow \delta^+ \text{R-X} \cdots \delta^- \text{MX}_n$ | $\delta^+ \text{R-X} \cdots \delta^- \text{MX}_n$ | alkiliranje |  |
| $\text{R}_2\text{C=O} + \text{H}^+ \rightarrow \text{R}_2\text{C=OH}^+$ | $\text{R}_2\text{C=OH}^+$ | hidroksialkiliranje |  |
| $\text{RCO-X} + \text{MX}_n \rightarrow \text{RCO}^+ + \text{MX}_{n+1}$ | RCO^+ | aciliranje |  |
| $\text{RCO-X} + \text{MX}_n \rightarrow \text{R}^{\delta+} \text{CO-X} \cdots \delta^- \text{MX}_n$ | $\text{R}^{\delta+} \text{CO-X} \cdots \delta^- \text{MX}_n$ | aciliranje |  |
| $\text{ArNH}_2 + \text{HNO}_2 + \text{H}^+ \rightarrow \text{Ar-N}_2^+ + 2\text{H}_2\text{O}$ | Ar-N_2^+ | pripremanje diazonijevih soli |  |

Nukleofilne aromatske substitucije

Razvrstitev izstopajočih skupin glede na lahkoto izstopanja:



Nekatere sintezno pomembne substitucije na diazonijevih soleh

| Reakcija | Produkt |
|---|--|
| $\text{Ar-N}_2^+\text{X}^- + \text{Cu}_2\text{X}_2 \rightarrow \text{Ar-X}$ | Ar-X ($\text{X} = \text{Cl}, \text{Br},$) |
| $\text{Ar-N}_2^+\text{X}^- + \text{HBF}_4 \rightarrow \text{Ar-N}_2^+\text{BF}_4^- \rightarrow \text{Ar-F}$ | Ar-F |
| $\text{Ar-N}_2^+\text{X}^- + \text{NaI} \rightarrow \text{Ar-I}$ | Ar-I |
| $\text{Ar-N}_2^+\text{X}^- + \text{AcONa} + \text{Ar}'\text{-H} \rightarrow \text{Ar-Ar}'$ | $\text{Ar-Ar}'$ |
| $\text{Ar-N}_2^+\text{X}^- + \text{KHS} \rightarrow \text{Ar-SH}$ | Ar-SH |
| $\text{Ar-N}_2^+\text{X}^- + \text{Na BH}_4 \rightarrow \text{Ar-H}$ | Ar-H |
| $\text{Ar-N}_2^+\text{X}^- + \text{H}_2\text{O} \rightarrow \text{Ar-OH}$ | Ar-OH |
| $\text{Ar-N}_2^+\text{X}^- + \text{ROH} \rightarrow \text{Ar-OR}$ | Ar-OR |

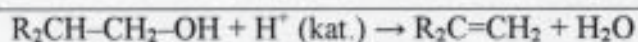
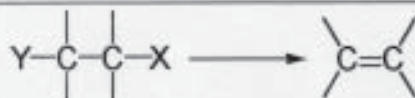
Značilni primeri sintetsko pomembnih alifatskih nukleofilnih substitucij



$X = \text{-halogen, -OSO}_2\text{R}', \text{-OP(OR)}_2, \text{-}\overset{\oplus}{\text{O}}\text{H}_2, \text{itd.}$

| Nukleofil | Produkt | Nukleofil | Produkt |
|---|--------------------------------|--|--|
| HO^- | ROH (alkohol) | $\text{R}'\text{C}\equiv\text{C}^-$ | $\text{R}'\text{C}\equiv\text{CR}$ (alkin) |
| $\text{R}'\text{O}^-$ | $\text{R}'\text{OR}$ (eter) | $\text{R}'\text{R}''\text{R}'''\text{C}^-$ | $\text{R}'\text{R}''\text{R}'''\text{C}-\text{R}$ (nova C-C vez) |
| $\text{R}'\text{COO}^-$ | $\text{R}'\text{COOR}$ (ester) | NH_3 | RNH_2 (amin) |
| HS^- | RSH (tiol) | R_3N | $\text{R}_3\text{R}'\text{N}^+ \text{X}^-$ (amonijeva sol) |
| $\text{R}'\text{S}^-$ | $\text{R}'\text{SR}$ (tioeter) | R_3P | $\text{R}_3\text{R}'\text{P}^+ \text{X}^-$ (fosfonijeva sol) |
| X^- ($\text{X} = \text{F, Cl, Br, I}$) | RX (halid) | NH_2NH_2 | RNHNNH_2 (hidrazin) |
| N_3^- | RN_3 (azid) | AgNO_2 | RNO_2 (nitro spojina) |
| NC^- | RCN (nitril) | $\text{R}'\text{MgBr}$ | $\text{R}'-\text{R}$ (alkan) |

Nekatere tipične sintezno pomembne eliminacije



dehidriranje alkoholov



dehidrohalogeniranje



dehalogeniranje



piroliza estrov



piroliza kvarternih amonijevih soli

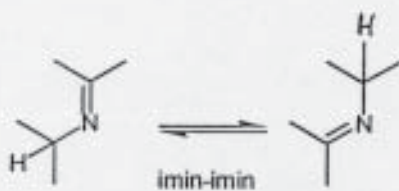
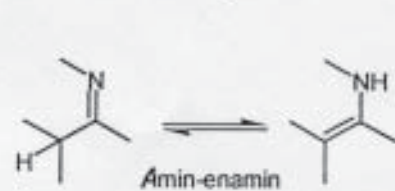
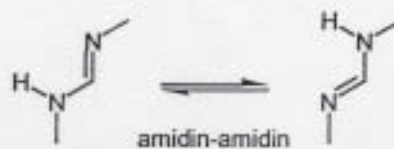
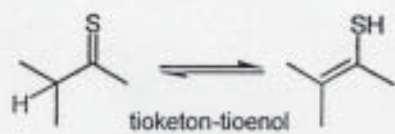
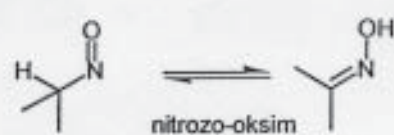


dehidriranje aldoksimov



dehidriranje primarnih amidov

Primeri prototropnih izomerizacij organskih spojin



Kislosti substituiranih očetnih kislin (vpliv induktivnega efekta substituenta na kislost COOH skupine)

| kislina | pK _a | kislina | pK _a |
|---------------------------|-----------------|--|-----------------|
| CH₃COOH | 4.74 | CH ₃ CH ₂ COOH | 4.87 |
| ClCH ₂ COOH | 2.86 | CH ₃ CH ₂ CH ₂ COOH | 4.82 |
| Cl ₂ CHCOOH | 1.26 | CH ₃ OCH ₂ COOH | 3.54 |
| Cl ₃ CCOOH | 0.64 | CH ₂ =C-CH ₂ COOH | 4.35 |
| F ₃ CCOOH | 0.23 | CH≡C-CH ₂ COOH | 3.32 |
| N≡C-CH ₂ COOH | 2.46 | ClCH ₂ CH ₂ CH ₂ COOH | 4.52 |

Kislosti para substituiranih benzojskih kislin (vpliv resonančnega efekta substituenta na kislost COOH skupine)

| kislina | pK _a | kislina | pK _a |
|---------------------------------------|-----------------|---|-----------------|
| C₆H₅COOH | 4.20 | Br-C ₆ H ₄ COOH | 3.97 |
| Me-C ₆ H ₄ COOH | 4.38 | N≡C-C ₆ H ₄ COOH | 3.55 |
| Et-C ₆ H ₄ COOH | 4.35 | HO-C ₆ H ₄ COOH | 4.57 |
| F-C ₆ H ₄ COOH | 4.14 | MeO-C ₆ H ₄ COOH | 4.47 |
| Cl-C ₆ H ₄ COOH | 3.97 | O ₂ N-C ₆ H ₄ COOH | 3.42 |

Bazičnost nekaterih aminov (vpliv induktivnega efekta substituentov na bazičnost dušikovega atoma)

| amin | pK _b | amin | pK _b |
|-----------------------|-----------------|----------------------------------|-----------------|
| NH₃ | 4.76 | EtNH ₂ | 3.36 |
| MeNH ₂ | 3.38 | Et ₂ NH | 3.06 |
| Me ₂ NH | 3.27 | Me ₃ CNH ₂ | 3.32 |
| Me ₃ N | 4.21 | | |

pK_a vrednosti nekaterih para substituiranih anilinijskih ionov (vpliv resonančnega efekta substituentov na bazičnost dušikovega atoma)

| anilinijski ion | pK _a | anilinijski ion | pK _a |
|---|-----------------|--|-----------------|
| H-C₆H₄-NH₃⁺ | 4.60 | Cl-C ₆ H ₄ -NH ₃ ⁺ | 3.98 |
| Me-C ₆ H ₄ -NH ₃ ⁺ | 5.10 | Br-C ₆ H ₄ -NH ₃ ⁺ | 3.86 |
| MeO-C ₆ H ₄ -NH ₃ ⁺ | 5.34 | N≡C-C ₆ H ₄ -NH ₃ ⁺ | 1.74 |
| F-C ₆ H ₄ -NH ₃ ⁺ | 4.65 | O ₂ N-C ₆ H ₄ -NH ₃ ⁺ | 1.00 |