(1) KMnO$_4$, OH$^-$, Δ (2) H$_3$O$^+$

LiAlH$_4$

(1) LiAlH(Ot-Bu)$_3$, Et$_2$O
(2) H$_2$O

$$R-\overset{\overset{O}{\|}}{C}-Cl$$

SOCl$_2$

$$R-CH_2-OH \quad \xrightarrow{\text{Cr}^{+6}} \quad R-\overset{\overset{O}{\|}}{C}-H$$

A. NaBH$_4$
B. LiAlH$_4$

A. (1) KMnO$_4$, OH$^-$, Δ (2) H$_3$O$^+$
B. (1) Ag(NH$_3$)$_2{}^+$ / NH$_3$ (2) H$_3$O$^+$
C. (1) Ag$_2$O, OH$^-$ (2) H$_3$O$^+$
D.   OsO$_4$
E. $R-\overset{\overset{O}{\|}}{C}-O-OH$ (Bayer-Villager Rxn)
F.   Cr^{+6}

$$R-\overset{\overset{O}{\|}}{C}-OH$$

$$R-\overset{\overset{O}{\|}}{C}-O-R'$$

(1) DIBAL-H, hexane
(2) H$_2$O

$$R-C\equiv N$$

(1) DIBAL-H, hexane
(2) H$_2$O

(1) R'MgBr

(2) H$_3$O$^+$

(Grignard Rxn)

$$R-\overset{\overset{OH}{|}}{\underset{\underset{R'}{|}}{C}}-H$$

(R may be H)

R'OH

H$^+$ or OR$^-$

(Acetal Rxn)

$$R-\overset{\overset{OR''}{|}}{\underset{\underset{OR'}{|}}{C}}-H \quad \longleftarrow \quad R-\overset{\overset{OH}{|}}{\underset{\underset{OR'}{|}}{C}}-H$$

OH
|
R–CH–R'

O
‖
R–O–C–R'

OH
|
R–C–R'
|
R"

Assuming R has greatest migaratory aptitude
H > phenyl > 3° > 2° > 1° > methyl
(Baeyer-Villager Rxn)

O
‖
R"–C
O–OH

A. LiAlH$_4$
B. NaBH$_4$

H$_2$CrO$_4$

(1) R"MgBr
(2) H$_3$O$^+$ (Grignard Rxn)

O
‖
R–C–R'

C=C

(1) O$_3$
(2) Zn, H$_2$O

AlCl$_3$
Friedel-Crafts Acylation onto Benzene
(where R' is Aryl)

O
‖
R–C–Cl   +   ⬡

R–Br (1) Li, Et$_2$O / (2) Cu I   R$_2$–CuLi

O
‖
R–C–Cl

R$_2$CuLi

(1) X$_2$ / NaOH
(2) H$_3$O$^+$
where R' is CH$_3$

O
‖
R–C–OH   +   CHX$_3$

R–C≡N

A. (1) R'-MgX   (2) H$_3$O$^+$ (Grignard Rxn)
B. (1) R'-Li   (2) H$_3$O+

(where R' is CH$_3$)

H
|
R–C=C–H
|
OH

HgSO$_4$
H$_2$SO$_4$ / H$_2$O

R–C≡C–H

R—C(=O)—Cl

A. $SOCl_2$
 ($-SO_2$, HCl)

B. PCl_3
 ($-H_3PO_3$)

C. PCl_5
 ($-POCl_3$, HCl)

$RCOO^-$
 ($-Cl^-$)

Pyridine, R'OH
 ($-pyrH^+Cl^-$)

NHR'R" excess
 ($-NH_2R'R"^+Cl^-$)

OH^-/H_2O
 ($-Cl^-$)

H_2O
 ($-H^+Cl^-$)

R—C(=O)—O—C(=O)—R

R'OH
 ($-RCOOH$)

NHR'R"
 ($-RCOOH$)

H_2O

R—C(=O)—O—R'

NHR'R"
 ($-R'OH$)

OH^-/H_2O
 ($-R'OH$)

R'OH, H+
 ($-H_2O$)

H+/H2O
 ($-R'OH$)

A. NHR'R", Δ ($-H_2O$) *poor
B. NHR'R", DCC
 ($-N,N'$-Dicyclohexylurea)

R—C(=O)—N(R')(R")

OH^-/H_2O
 ($-NHR'R"$)

R—C(=O)—O⁻

H+/H2O
 ($-NH_2R'R"^+$)

P_4O_{10}, Δ
 ($-H_2O$)

R—C(=O)—OH

H_3O^+/H_2O, Δ
 ($-NH_4^+$)

R—C≡N

OH^-/H_2O
 ($-NH_3/OH^-$)

A. NaOH ($-H_2O$)
B. $NaHCO_3$ ($-H_2O$, CO_2)

Copyright © 1998 Karl J. Miller

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[\text{(--NaCl)}]{\text{NaN}_3} R-\overset{\overset{\displaystyle O}{\|}}{C}-N_3 \xrightarrow[\text{(--N}_2\text{)}]{\Delta} R-N=C=O \xrightarrow[\text{(--CO}_2\text{)}]{\text{H}_2\text{O}}$$

$$R-Br \xrightarrow[\text{EtOH}]{\text{NaN}_3} R-N=N=N \quad \begin{array}{l}\textbf{A.} \;\; \text{Na / EtOH} \\ \textbf{B.} \;\; \text{LiAlH}_4\end{array}$$

$$\text{NH}_3 \xrightarrow[\text{(2) OH}^-]{\text{(1) R—X}}$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\text{NH}_2 \qquad \begin{array}{l}\textbf{A.} \;\; \text{(1) LiAlH}_4 \text{ / Et}_2\text{O} \\ \quad\;\;\text{(2) H}_2\text{O} \\ \textbf{B.} \;\; \text{Br}_2\text{ , NaOH / H}_2\text{O} \\ \quad\;\; \text{(--CO}_3^{-2}\text{, 2 NaBr, 2 Na}^+\text{, 2 H}_2\text{O)}\end{array} \qquad \longrightarrow \text{RNH}_2$$

$$R^*-C\equiv N \quad \begin{array}{l}\textbf{A.} \;\; \text{H}_2\text{ / Ni , 140°C} \\ \textbf{B.} \;\; \text{LiAlH}_4\end{array}$$

$$R^*-\overset{\overset{\displaystyle N-OH}{\|}}{C}-H \quad \begin{array}{l}\textbf{A.} \;\; \text{Na / EtOH} \\ \textbf{B.} \;\; \text{LiAlH}_4\end{array} \qquad R^*-C = R$$

$$\text{Ar}-\text{NO}_2 \quad \begin{array}{l}\textbf{A.} \;\; \text{H}_2\text{ / Catalyst} \\ \textbf{B.} \;\; \text{(1) Fe / HCl} \\ \quad\;\;\text{(2) OH}^-\end{array} \quad \text{Ar}-\text{NH}_2 \xrightarrow[\text{(0-5°C)}]{\text{HONO}} \text{Ar}-\text{N}_2^+$$

$$\xrightarrow{\text{Cu}_2\text{O, Cu}^{2+}\text{, H}_2\text{O}} \text{Ar}-\text{OH}$$
$$\xrightarrow{\text{CuCl}} \text{Ar}-\text{Cl}$$
$$\xrightarrow{\text{CuBr}} \text{Ar}-\text{Br}$$
$$\xrightarrow{\text{CuCN}} \text{Ar}-\text{C}\equiv\text{N}$$
$$\xrightarrow{\text{KI}} \text{Ar}-\text{I}$$
$$\xrightarrow{\text{(1) HBrF}_4 \;\;\text{(2) }\Delta} \text{Ar}-\text{F}$$
$$\xrightarrow{\text{H}_3\text{PO}_2} \text{Ar}-\text{H}$$

where "Ar" is Aryl

$$\text{Ar}-(\text{NO}_2)_2 \xrightarrow[\text{EtOH}]{\text{H}_2\text{S, NH}_3} \text{Ar}-(\text{NH}_2)(\text{NO}_2)$$

$$R-CH_2CO_2H \ + \ X_2 \ \xrightarrow{P_4} \ R-CH_2CO_2H \ + \ HX$$

$$X_2 \ = \ Cl_2 \ or \ Br_2$$

when n=2, a γ-lactone; when n=3, a δ-lactone

when n=2, a γ-lactam; when n=3, a δ-lactam

Gabriel Synthesis