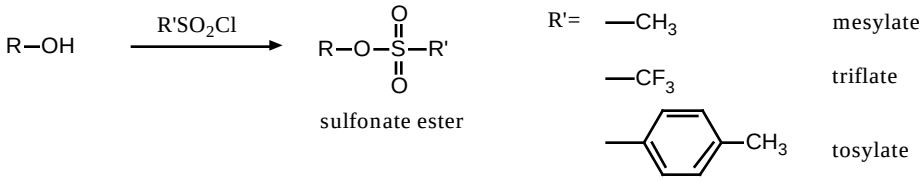
**Functional Group Interconversions**

C&S Chapter 3 #1; 2; 4a,b, e; 5a, b, d; 6a,b,c,d; 8

1 sulfonates
2 halides
3 nitriles
4 azides
5 amines
6 esters and lactones
7 amides and lactams

*Sulfonate Esters*

- reaction of an alcohols (1° or 2°) with a sulfonyl chloride

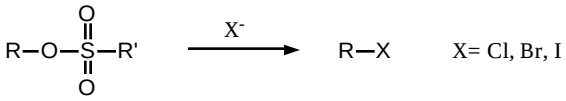


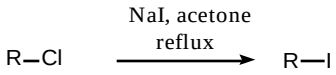

- sulfonate esters are very good leaving groups. Elimination is often a competing side reaction

*Halides*

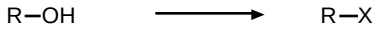
- halides are good leaving groups with the order of reactivity in $S_N2$ reactions being I>Br>Cl. Halides are less reactive than sulfonate esters, however elimination as a competing side reaction is also reduced.

- sulfonate esters can be converted to halides with the sodium halide in acetone at reflux. Chlorides are also converted to either bromides or iodides in the same fashion (Finkelstein Reaction).




- conversion of hydroxyl groups to halides: *Organic Reactions* **1983**, *29*, 1



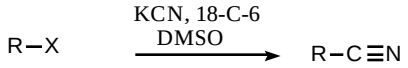

- R-OH to R-Cl
  - $SOCl_2$
  - $Ph_3P$, $CCl_4$
  - $Ph_3P$, $Cl_2$
  - $Ph_3P$, $Cl_3CCOCCl_3$

- R-OH to R-Br
  - $PBr_3$, pyridine
  - $Ph_3P$, $CBr_4$
  - $Ph_3P$, $Br_2$

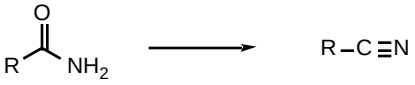
- R-OH to R-I
  - $Ph_3P$, DEAD, MeI

*Nitriles*

- displacement of halides or sulfonates with cyanide anion

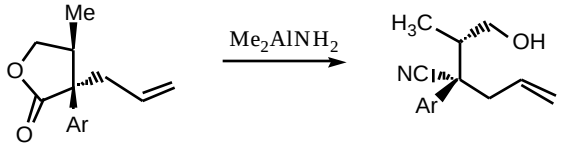



- dehydration of amides



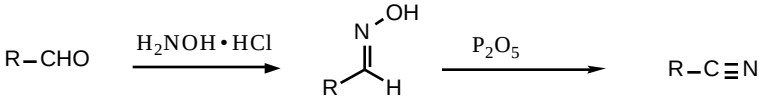

  - $POCl_3$, pyridine
  - TsCl, pyridine
  - $P_2O_5$
  - $SOCl_2$

- Reaction of esters and lactones with dimethylaluminium amide
  *TL* **1979**, 4907

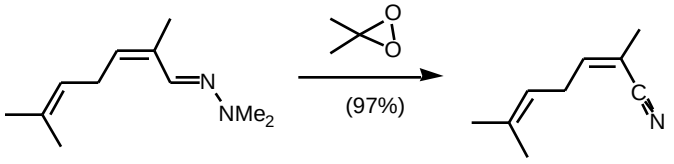



*JOC* **1987**, *52*, 1309

- Dehydration of oximes

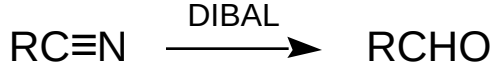



- Oxidation of hydrazones



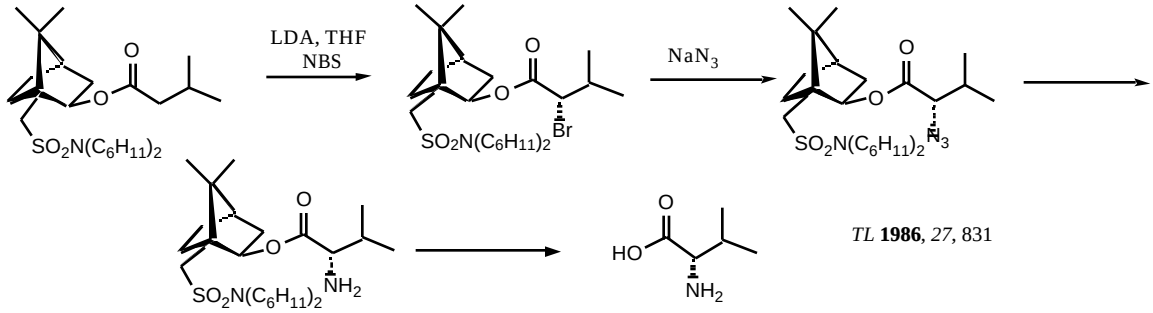

*Tetrahedron Lett.* **1998**, *39*, 2009

- Reduced to aldehydes with DIBAL.



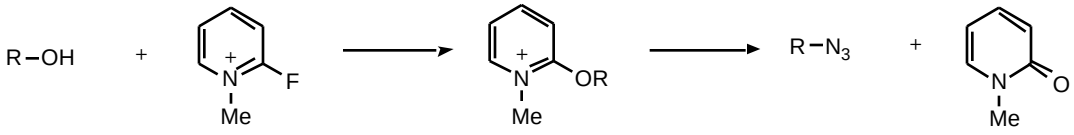
*Azides*

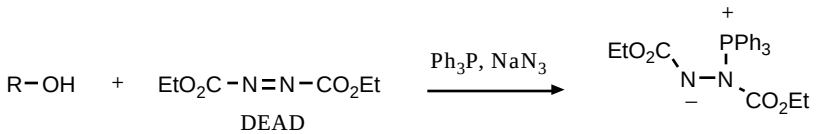
- displacement of halides and sulfonates with azide anion

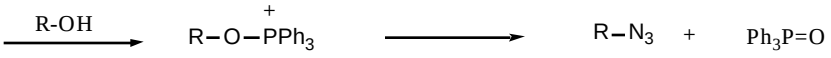



*TL* **1986**, *27*, 831

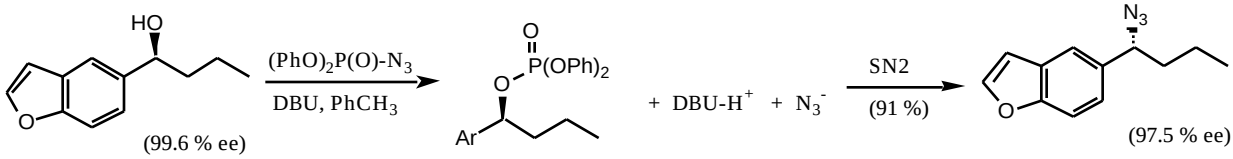
- activation of the alcohol



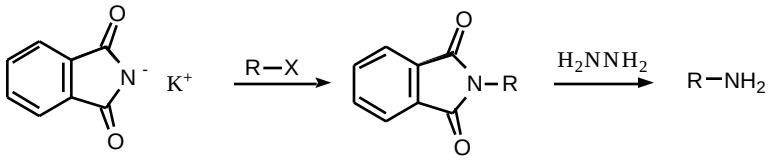

*JOC* **1993**, *58*, 5886



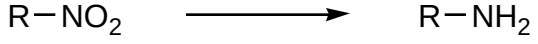

- Photolyzed to aldehydes

*Amines*

- Gabriel Synthesis

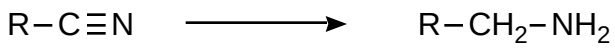



- reduction of nitro groups



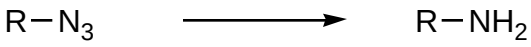

$H_2$, Pd / C
Al(Hg), $H_2O$
$NaBH_4$
$LiAlH_4$
Zn, Sn or Fe and HCl
$H_2NNH_2$
sodium dithionite

- reduction of nitriles



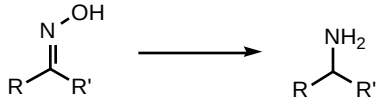
$H_2$, $PtO_2$ / C
$B_2H_6$
$NaBH_4$
$LiAlH_4$
$AlH_3$
Li, $NH_3$

- reduction of azides



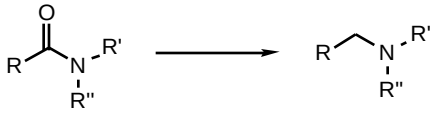
$H_2$, Pd / C
$B_2H_6$
$NaBH_4$
$LiAlH_4$
Zn, HCl
$(RO)_3P$
$Ph_3P$
thiols

- reduction of oximes (from aldehydes and ketones)



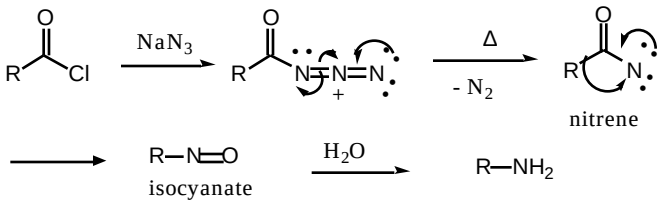
$H_2$, Pd / C
Raney nickel
$NaBH_4$, $TiCl_4$
$LiAlH_4$
Na(Hg), AcOH

- reduction of amides



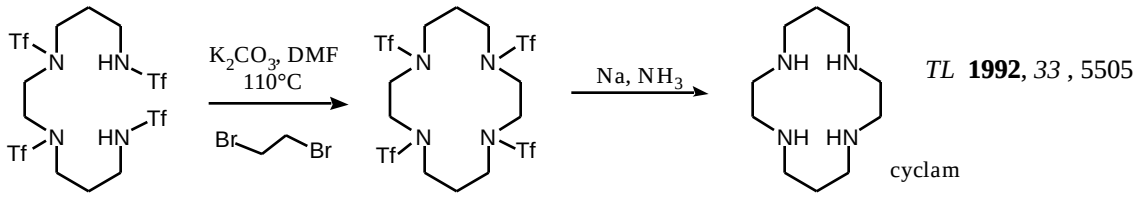
$H_2$, Pd / C
$B_2H_6$
$NaBH_4$, $TiCl_4$
$LiBH_4$
$LiAlH_4$
$AlH_3$

- Curtius rearrangement



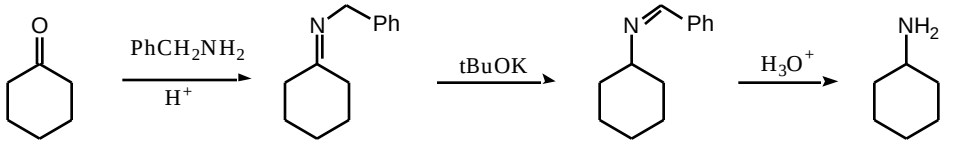
- reductive aminations of aldehydes and ketones
  - Borsch Reaction
  - Eschweiler-Clark Reaction

- alkylation of sulfonamides




*TL* **1992**, *33* , 5505

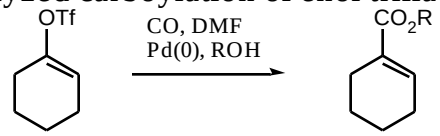
- transamination




*Can. J. Chem.* **1970**, *48*, 570

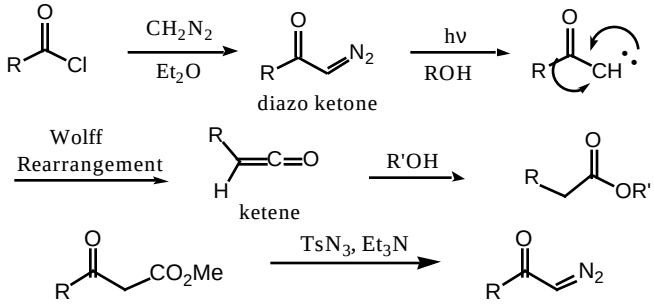
*Esters and Lactones*

- Reaction of alcohols with "activated acids"
- Baeyer-Villigar Reaction *Organic Reactions* **1993**, *43*, 251
- Pd(0) catalyzed carboylation of enol triflates

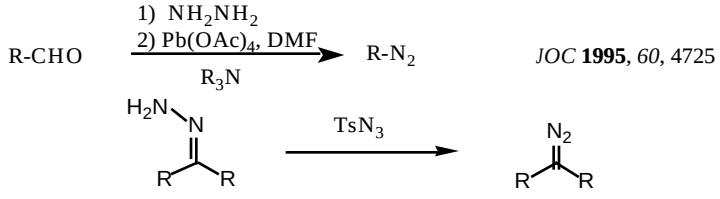



*TL* **1985**, *26* , 1109

- Arndt-Eistert Reaction *Angew. Chem. Int. Ed. Engl.* **1975**, *15*, 32.

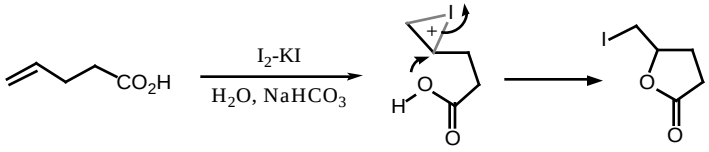


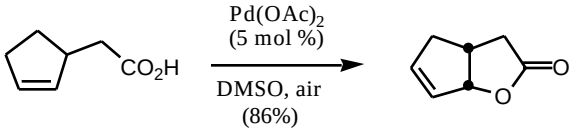

- Diazoalkanes: carbene precursors




*JOC* **1995**, *60*, 4725

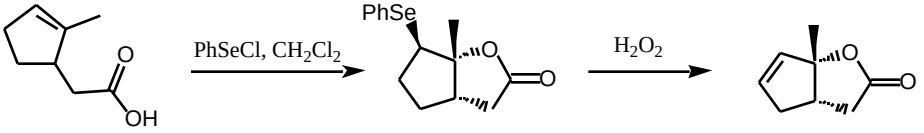
- Halo Lactonizations review: *Tetrahedron* **1990**, *46* , 3321





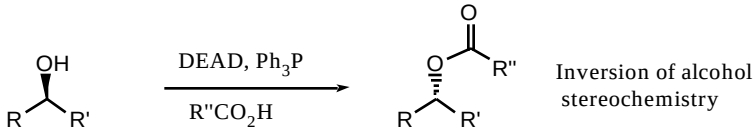

*JOC* **1993**, *58*, 5298

- Selenolactonization




*JACS* **1985**, *107* , 1148

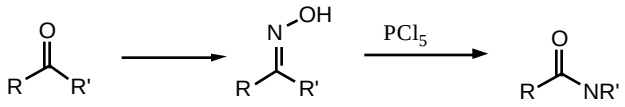
- Mitsunobu Reaction *Synthesis* **1981** , 1; *Organic Reactions*, **1991**, *42*, 335
  Mechanism: *JACS* **1988**, *110* , 6487



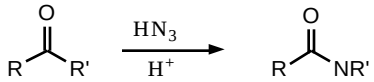

Inversion of alcohol stereochemistry

*Amides and Lactams*

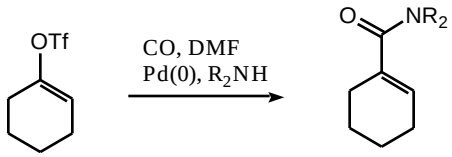
- reaction of an "activated acid" with amines
- Beckman Rearrangement *Organic Reactions* **1988**, *35*, 1



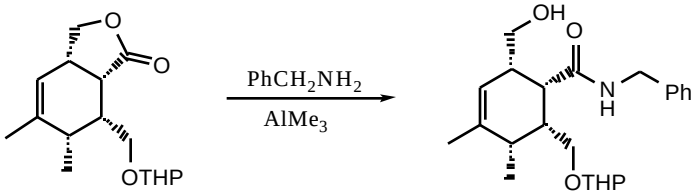

- Schmidt rearrangement




- others




*TL* **1985**, *26* , 1109




*TL* **1977**, 4171

-Weinreb amide *Tetrahedron Lett.* **1981**, *22*, 3815