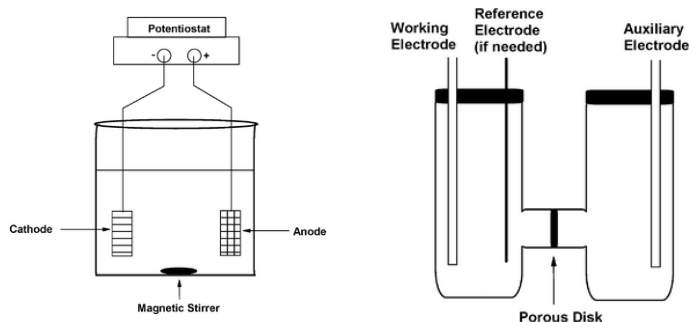


Electrochemistry is the study of chemical reactions which take place at the interface of an electrode, usually a solid metal or a semiconductor, and an ionic conductor, the electrolyte. These reactions involve electric charges moving between the electrodes and the electrolyte (or ionic species in a solution).

In short, **electrochemistry is redox chemistry**.

Refer to Electrochemistry in Organic Synthesis group meeting (2005) for experimental setup/equipment basics.

Undivided cell vs. divided cell (H-cell):



Undivided cells are more straightforward to set up (can be shot glass, beaker, round-bottom flask, etc.); both oxidation and reduction take place within the same compartment.

Divided cells require more specialized setup; advantage is that no substrate/reagent moves between compartments; substrate to be oxidized is placed in anodic compartment, while substrate to be reduced is placed in cathodic compartment.

Anode is typically graphite, platinum, etc.

Cathode is typically graphite, mercury, lead, etc.

Reaction parameters for an electrochemical reaction closely mirror those of a "normal" chemical reaction with two notable differences: the necessary electrolyte and constant current/potential experiment.

Electrolyte can be LiClO_4 , AcOH , H_2SO_4 , Brawndo™, R_4NClO_4 , R_4NBF_4 , other tetraalkyl ammonium salts.

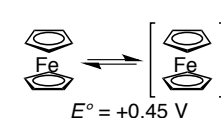
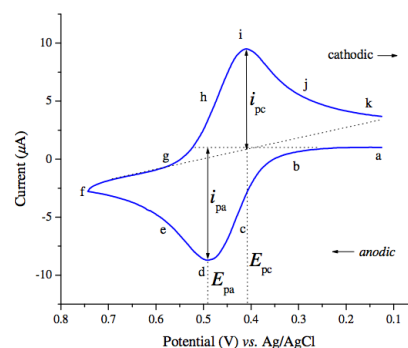
Constant potential experiments allow for selective oxidation/reduction; as reactive species is consumed, current drops, so reaction time can be much longer; requires reference electrode.

Constant current experiments allow simplified reaction setup; rate of reaction can be carefully controlled (*i.e.* slow addition of electrons).

Reference electrodes have stable and well-known electrode potentials.

Standard Hydrogen Electrode (SHE)	$E = 0.000 \text{ V}$
Saturated Calomel Electrode (SCE)	$E = 0.241 \text{ V}$
Cu/CuSO_4 electrode (CSE)	$E = 0.314 \text{ V}$
Ag/AgCl electrode	$E = 0.197 \text{ V}$

Cyclic voltammetry shows current response to changes in the working electrode's potential; useful to study redox behavior of a substrate, including whether oxidation/reduction is reversible, irreversible, or quasi-reversible.

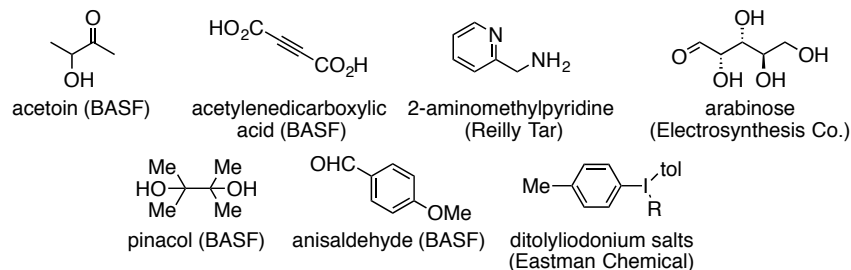


$E^\circ = +0.45 \text{ V}$
CV of ferrocene in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$; Pt working electrode, Pt-wire counter electrode, aqueous Ag/AgCl reference, scan rate = 0.10 V/s.

Industrial electrosynthesis is widespread for production of both inorganic and organic chemicals.

Chemical	Equation	Electrodes
Aluminum	$2 \text{Al}_2\text{O}_3 + 3 \text{C} \rightarrow 4 \text{Al} + 3 \text{CO}_2$	Carbon (A), Aluminum (C)
Chlorine/NaOH	$2 \text{NaCl} + 2 \text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2 \text{NaOH}$	Ti(A), steel or Hg (C)
Fluorine	$2 \text{F}^- \rightarrow \text{F}_2 + 2 \text{e}^-$	Carbon (A), steel (C)
Ozone	$\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_3 + 2 \text{H}^+ + 2 \text{e}^-$	Vitreous carbon (A)

Aluminum and chloroalkali industries together account for > 90% of electricity used in electrolytic processes, with aluminum the largest in terms of energy usage and chloroalkali the largest in terms of tonnage.

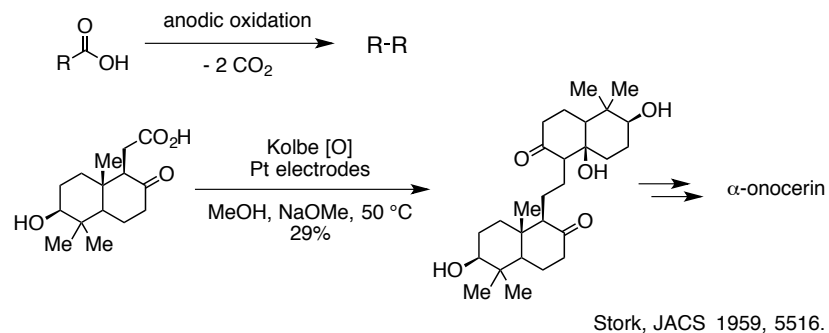


Electroorganic Chemistry

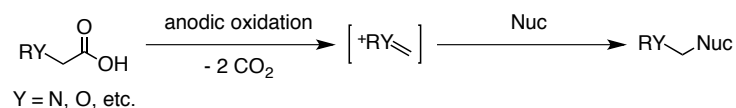
Brandon Rosen

8 November 2014

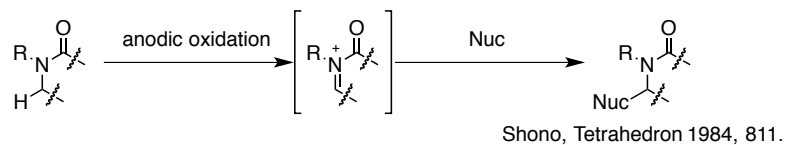
Kolbe Oxidation



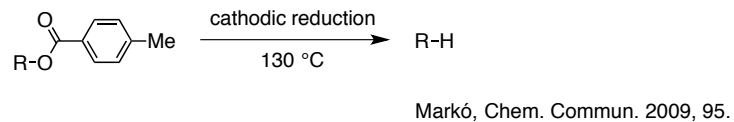
Non-Kolbe Oxidation



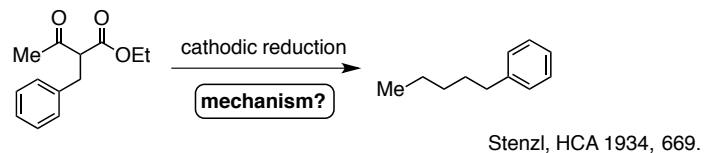
Shono Oxidation



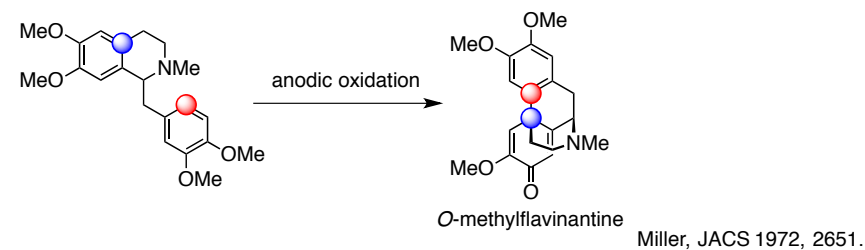
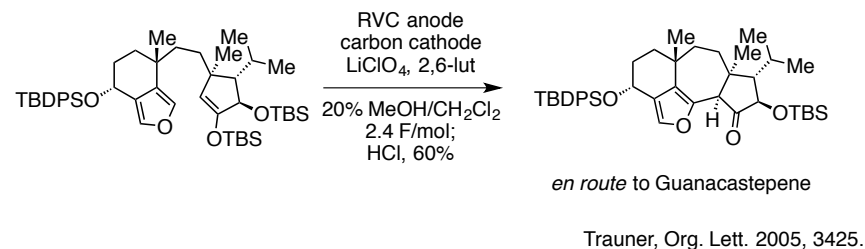
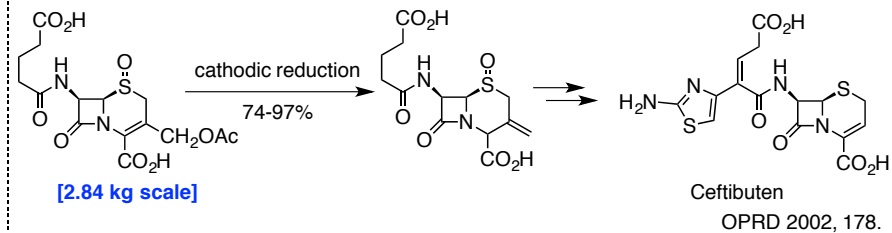
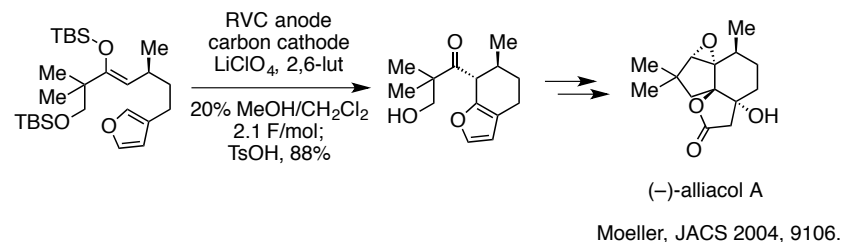
Markó-Lam Reduction



Tafel Rearrangement

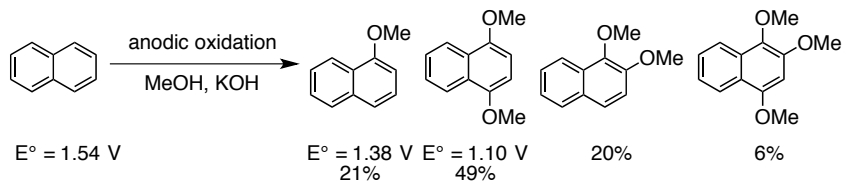
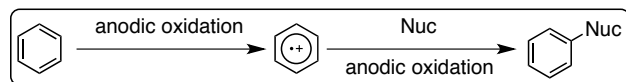


Electrochemical transformations have featured prominently in total synthesis.



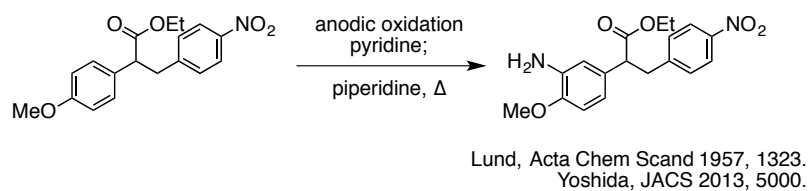
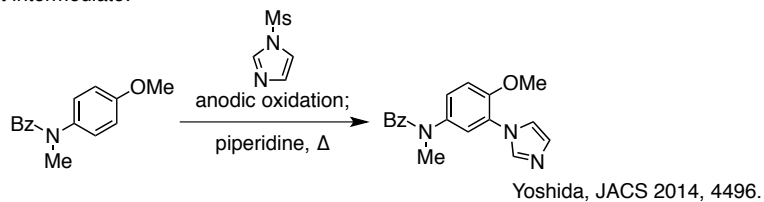
Direct C(sp²)-H Functionalization

Strategy I: Oxidation of arene.

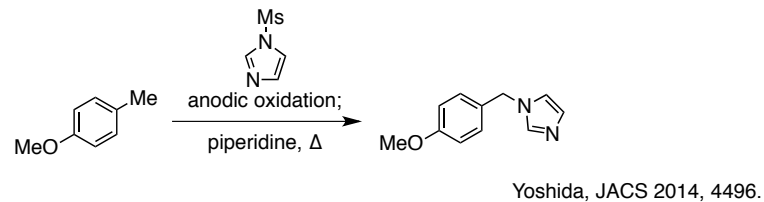


Fritz, *Electrochim Acta* 1976, 1099.

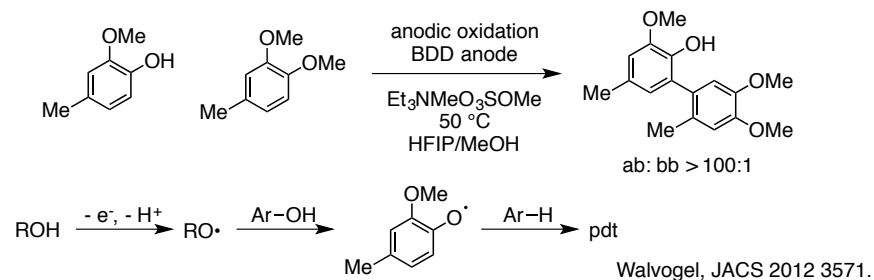
Overoxidation of ptd common problem; one solution is to prepare an electrooxidatively inert intermediate:



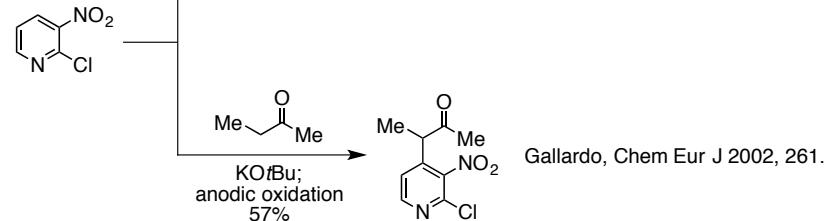
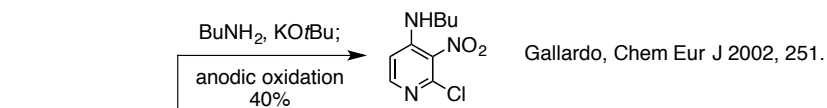
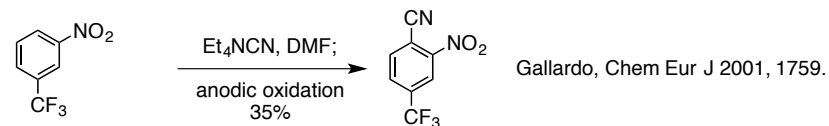
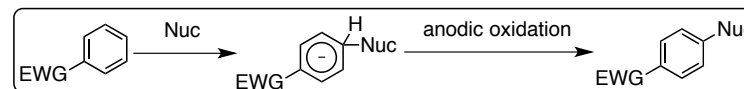
Benzylic functionalization often takes place alongside (or in preference to) arene functionalization; innate reactivity of substrate dictates ptd:



Indirect oxidation:



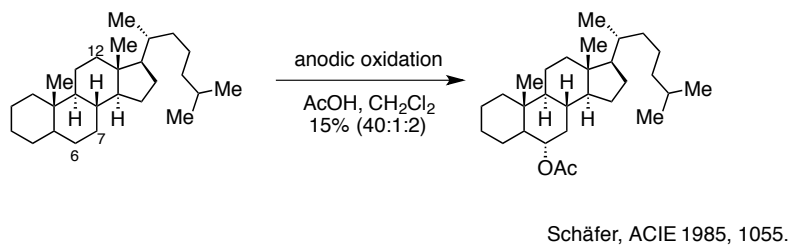
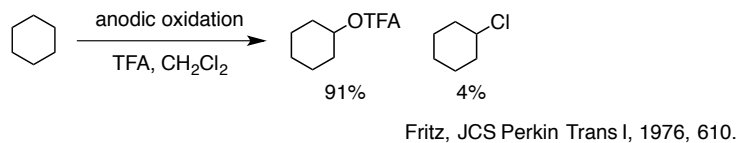
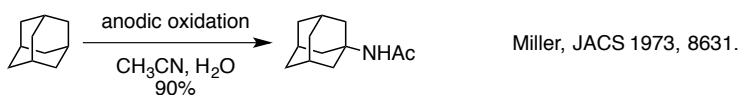
Strategy II: Oxidation of Meisenheimer complex.



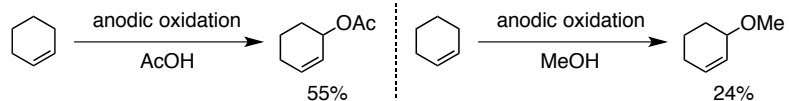
For a review on nucleophilic functionalization of arenes by electrochemical methods, see: Petrosyan, *Russian Chemical Reviews* 2013, 747.

Direct C(sp³)-H Functionalization

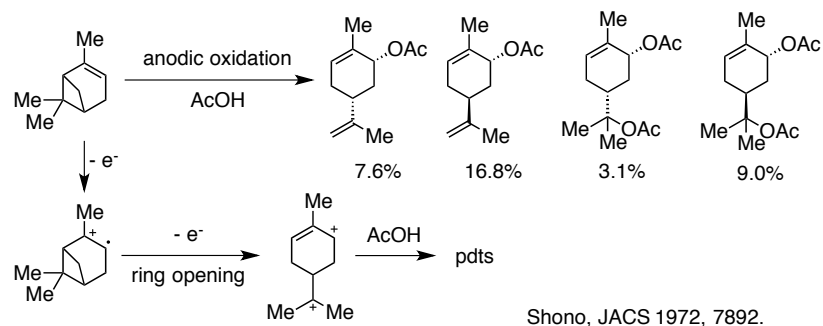
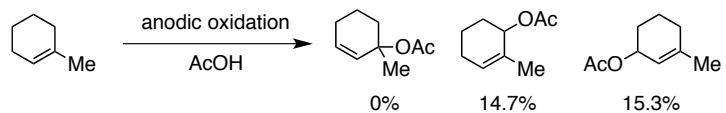
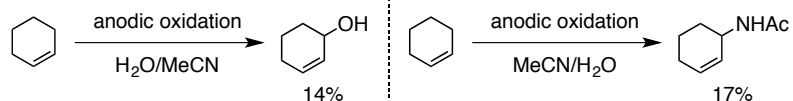
Fully saturated systems



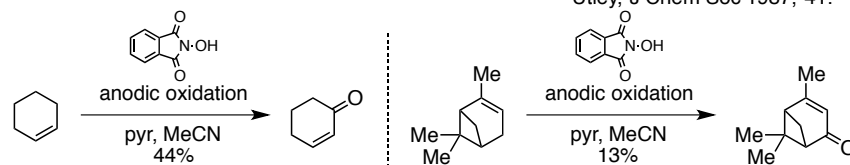
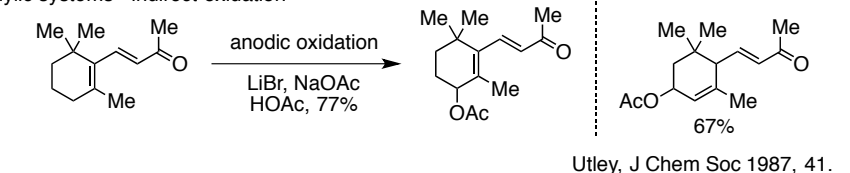
Allylic systems - direct oxidation



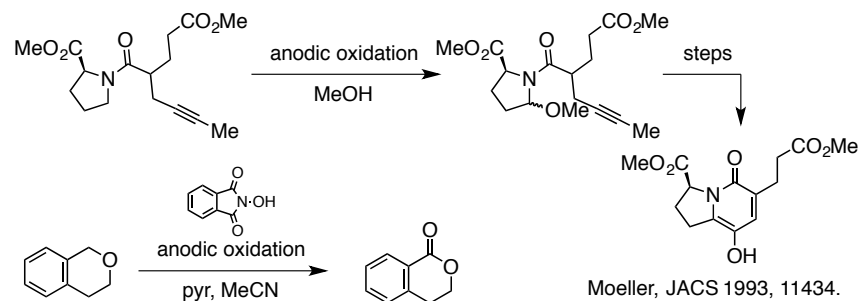
Additional ring rearrangement pdt isolated.



Allylic systems - indirect oxidation

Masui, Chem Pharm Bull 1983, 4209.
Masui, Chem Pharm Bull 1985, 4798.

Oxidation adjacent to heteroatoms

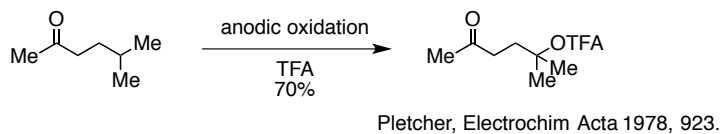


Masui, Chem Pharm Bull 1983, 4209.

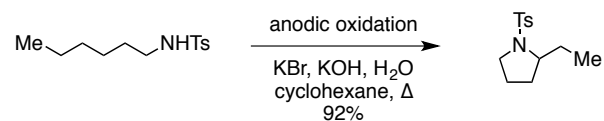
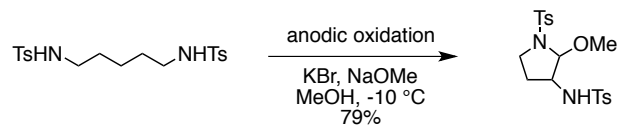
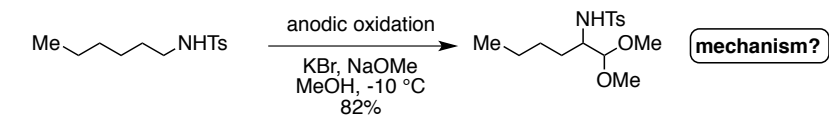
For a review on reactions of alkenes induced by electrochemical oxidation, see:
Ogibin, Russian Chemical Reviews 2001, 543.

Direct C(sp³)-H Functionalization

Carbonyl oxidation

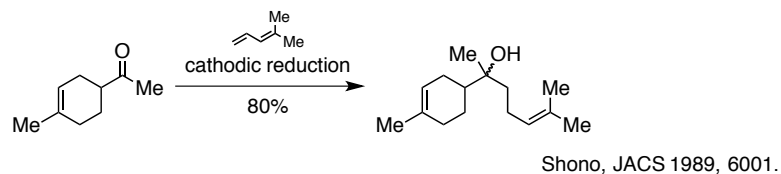
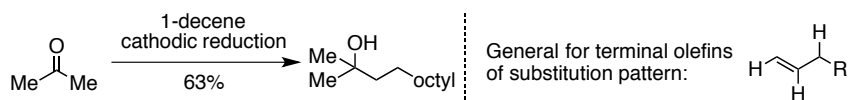
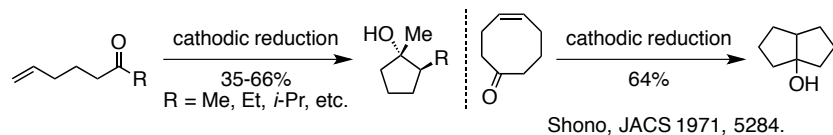


Misc. oxidation

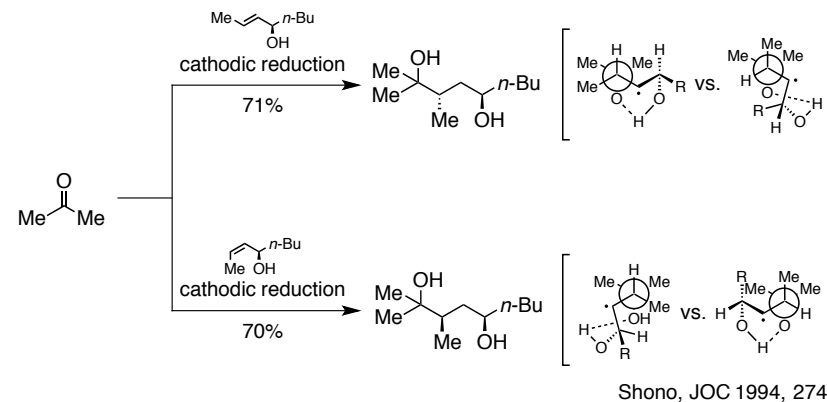


Shono, *Tet Lett* 1986, 6083.
Shono, *JACS* 1990, 2368.

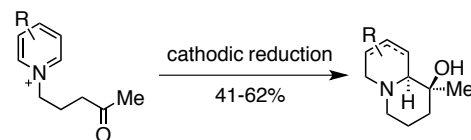
Carbonyl Reductive Couplings



Uniquely active allylic alcohols



Addition to heterocycles

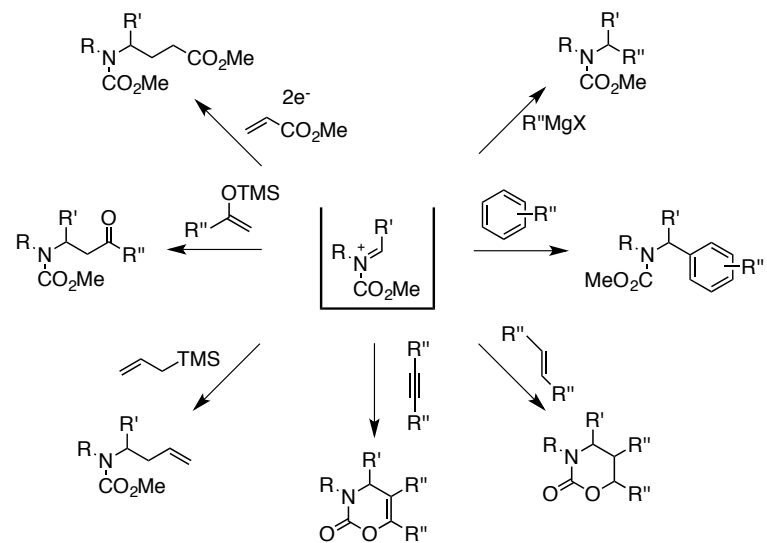
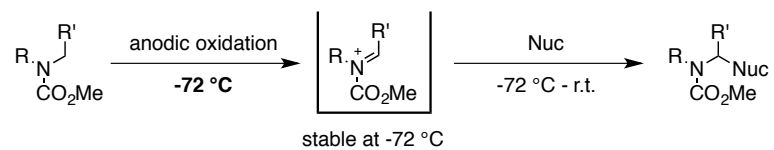
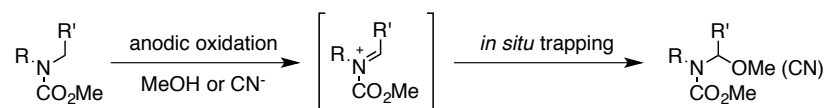


• Intermolecular requires large excess of ketone

Schäfer, *ACIE* 1995, 2007.

Cation Pool Method

Low-temperature electrolysis technique allows for the generation and accumulation of highly reactive species.



Yoshida, Chem Rev 2008, 2265.