Organic Electrochemistry

General information: ---This is just a general survey of the types of reactions that are available via electrochemistry

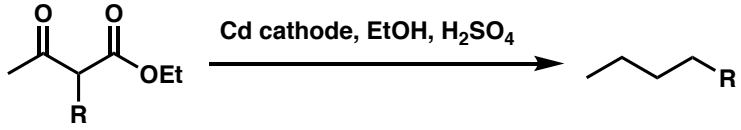
- Single electron transfer (radical intermediates)
- Protons consumed at the cathode, and generated at the anode so that a buffer will often be required to maintain constant pH
- Aprotic solvents
  - Acetonitrile: most common for oxidations
  - DMF or Acetonitrile: common for reductions
- Protic solvents
  - alcohol/water or dioxane/water mixtures
- Common anodes(oxidation site): Platinum, lead dioxide, and graphite/carbon
- Common cathodes(reduction site): Platinum, mercury, lead, cadmium and graphite/carbon
- Common electrolytes: $LiClO_4$, AcOH, Et_4NClO_4, BU_4NBF_4, and tetra alkyl ammonium salts
- Undivided cell vs. divided cell set ups depending on reactivity of product
- Cathode generally represented by (+), and Anode (-)

Named Reactions:

Kolbe Oxidation:

Kolbe, H. Justus Liebigs Ann. Chem. 1848, 69, 257
JACS, 1959, 5516
JOC, 2008, vol. 73, 17, 6888
JOC, 2011, vol. 7, 1108
TL, 2012, vol. 68, 29, 5857

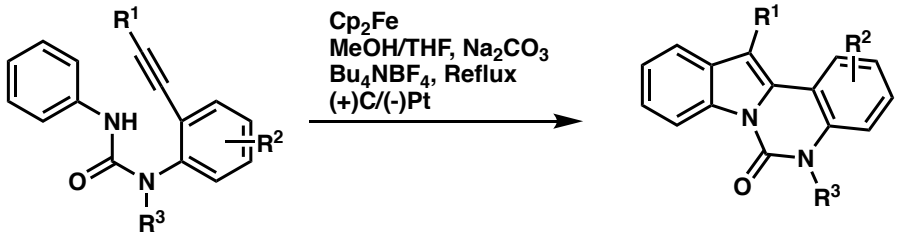
Tafel Rearrangement:



Chemische Berichte, 1912, vol. 45, p. 452

Anodic Oxidation:

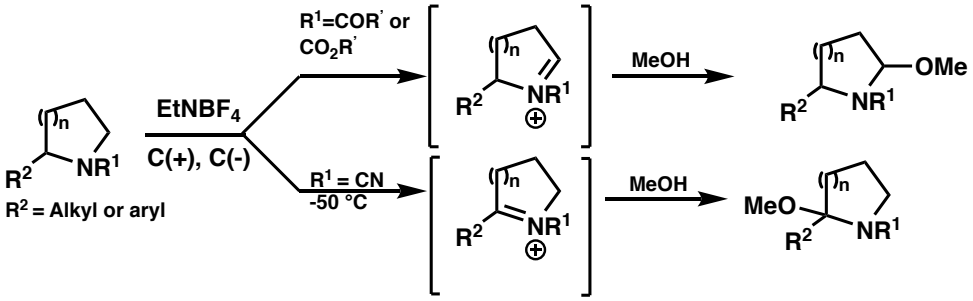
Oxidation of amides:



Angew. Chem. Int. Ed. 2016, 55, 2226

Amy Boylan

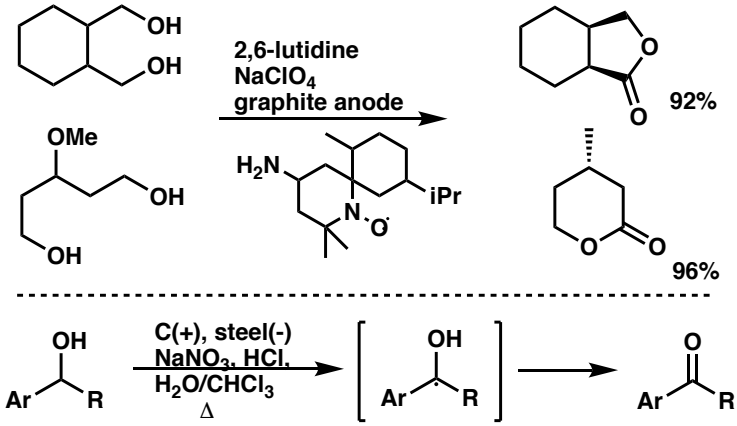
Oxidation of amines:



*regioselectivity can be reversed in this Shono-type oxidation

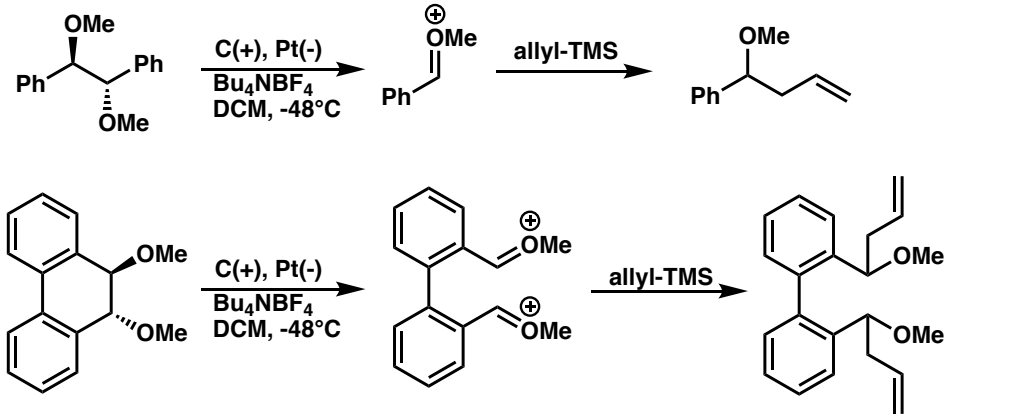
JOC, 2008, 75, 680

Oxidation of alcohols:



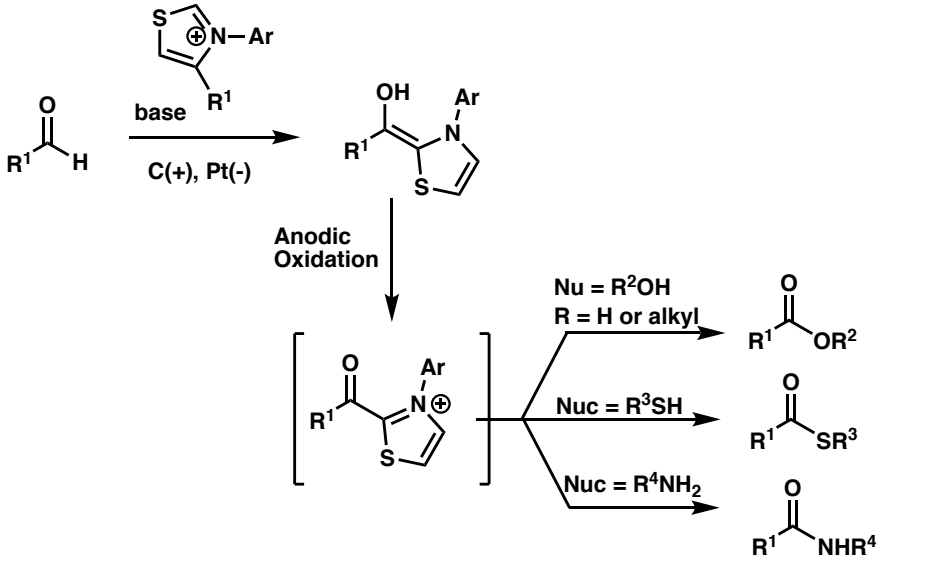
JACS, 2015, 137, 16179

Electrochemical formation of oxocarbenium:



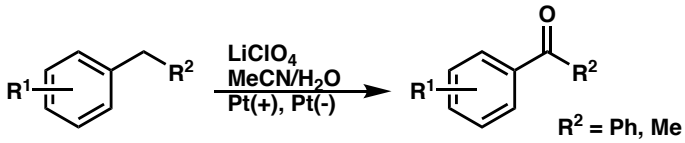
JACS, 2005, 127, 6930

Oxidation of aldehydes:



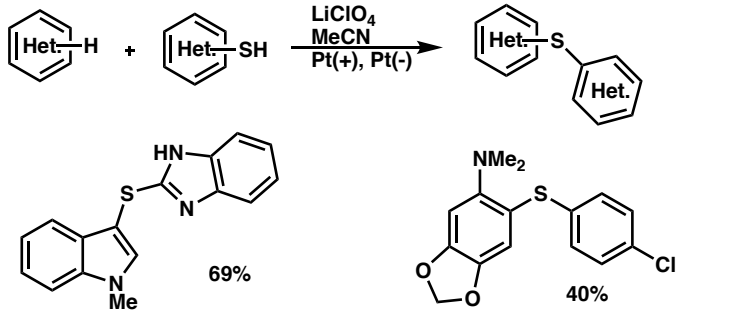
JACS, 2012, 134, 12374

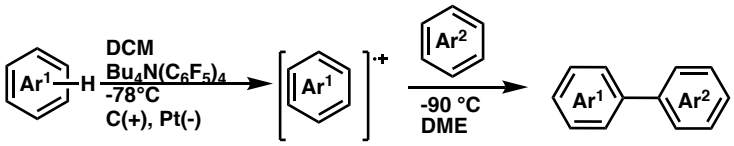
Benzylic functionalization:

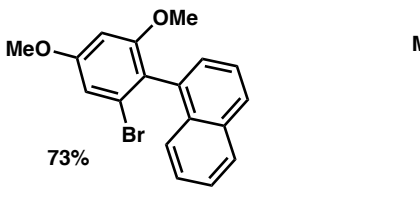


Chem. Eur. J. 2013, 19, 5542

Oxidation of the arene nucleus



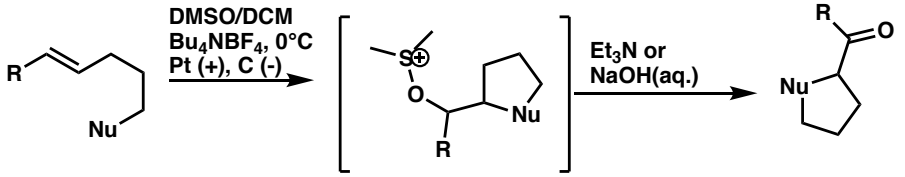


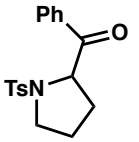


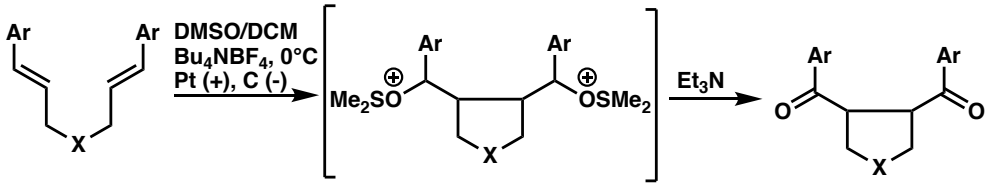
J. App. Electrochem. 2003, 33, 52

Curr. Org, Chem. 2004, 8, 113

Olefin oxidation:



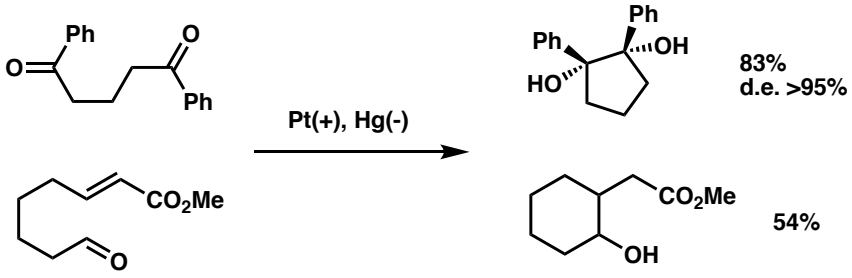


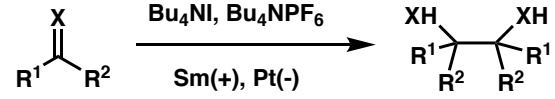


OL, 2007, 9, 5633
Org. Biomol. Chem. 2013, 11, 3322

Cathodic Reductions:

Aldehyde and ketone reduction:

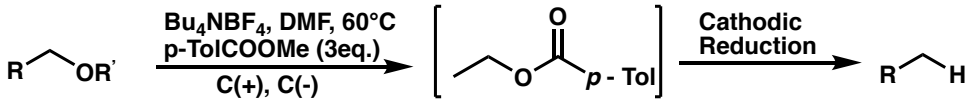




X= O, N-Ph
R^1= Aryl
R^2= H, Me

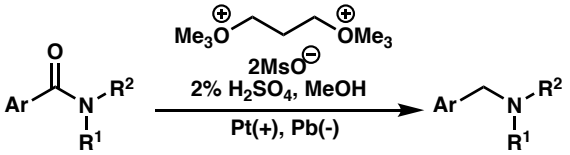
Euro. J. Org. Chem. 2003, 2919
Synlett 2000, 1119
Electrochemistry, 2011, 79, 447

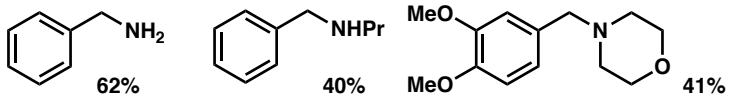
Ester reduction:



OL, 2011, 13, 406

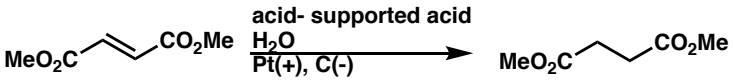
Amide reduction:

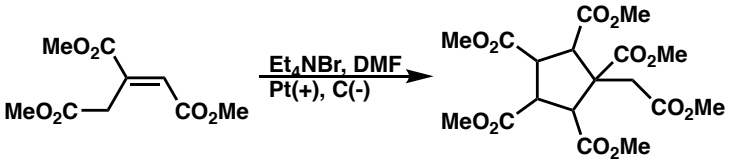


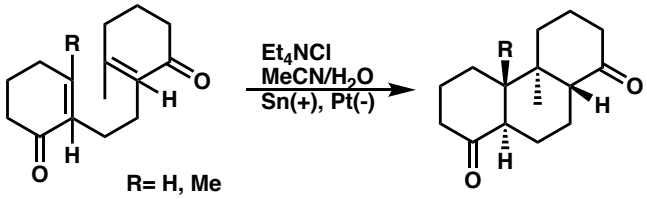


Eur. J. Org. Chem. 2014, 5144

Olefin reduction:

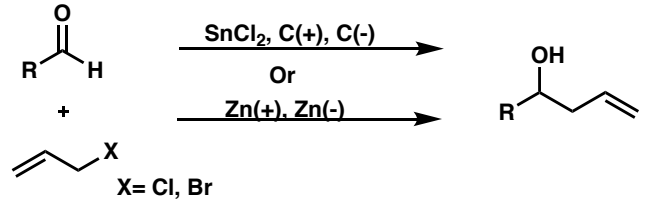


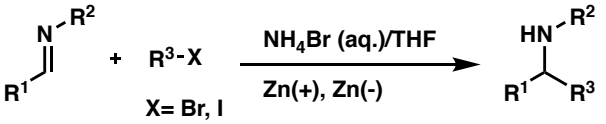


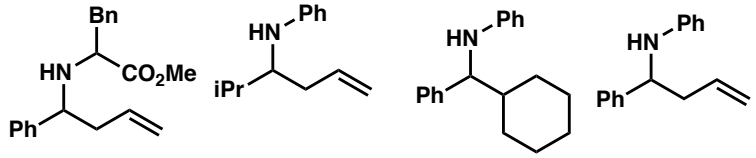


Electrochemistry, 2013, 81, 371
Electrochem. Commun. 2016, 73, 46
J. Electroanal. Chem. 2001, 507, 2

Alkyl halide reduction:







Angew. Chem. Int. Ed. 2001, 40, 3399
Agnew. Chem. Int. Ed. 2011, 50, 924
Synthesis, 2002, 2002, 533