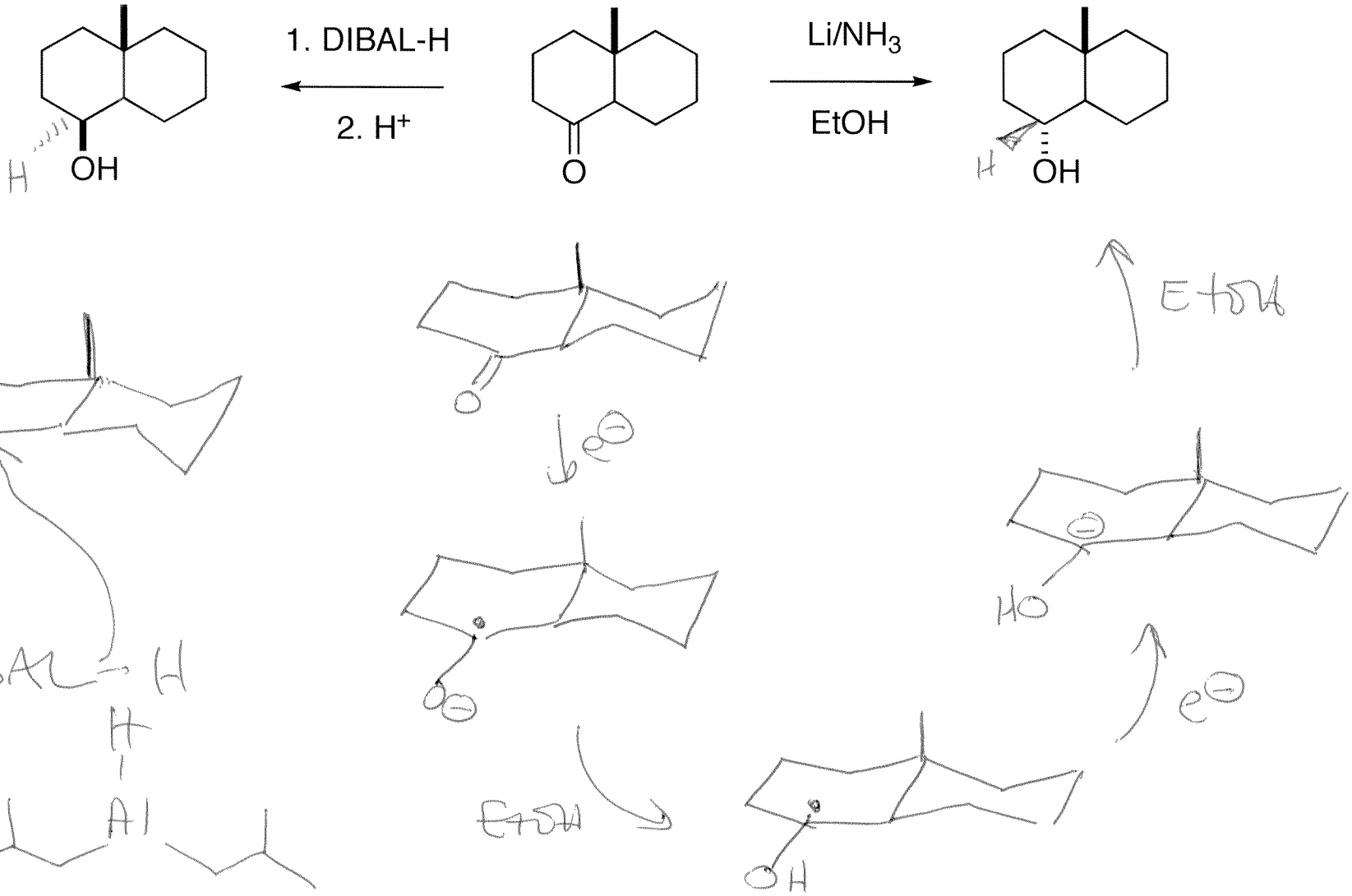
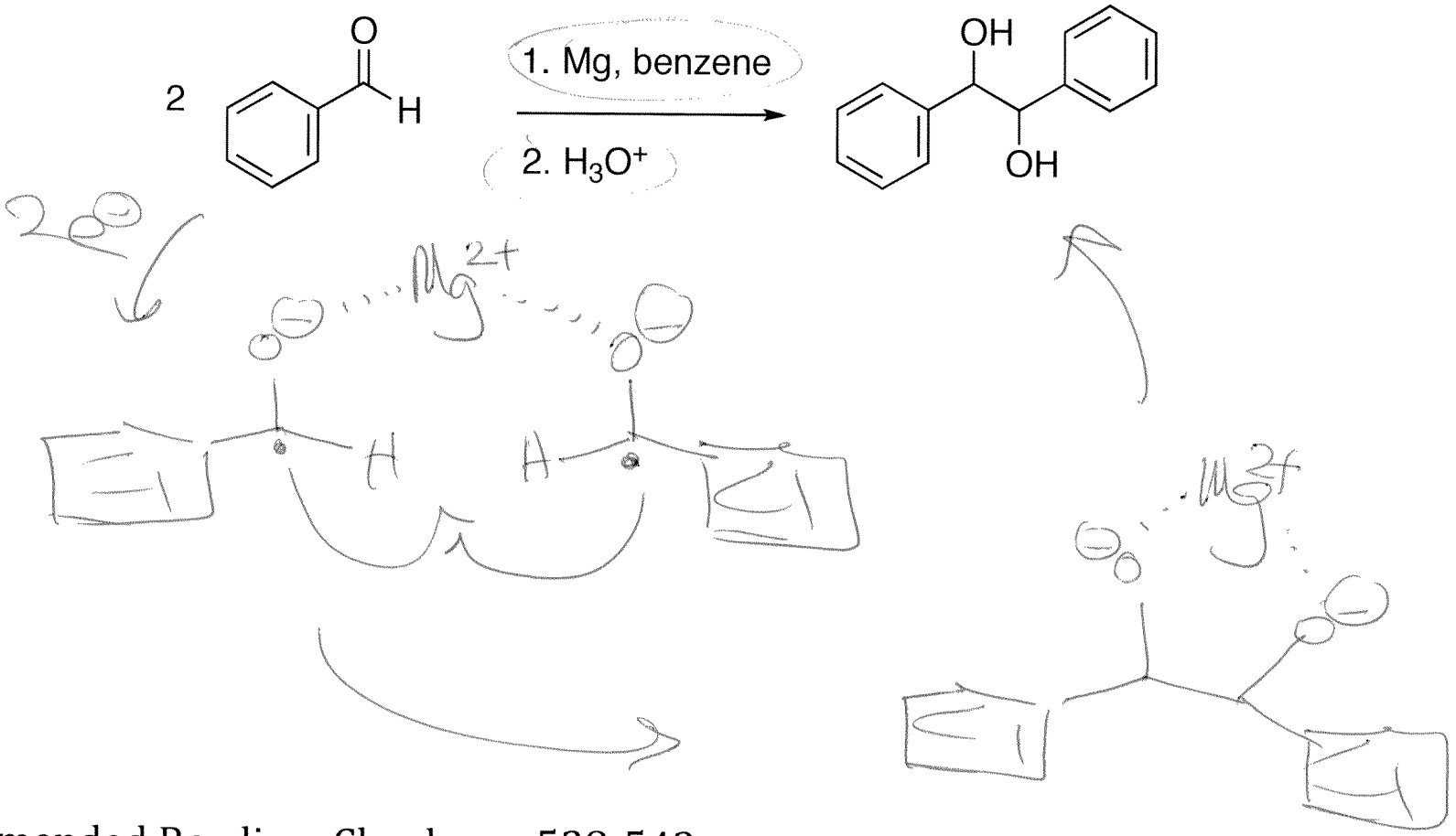
Due to the mechanism, complementary stereochemistry can be observed in these reactions with respect to those of hydride reagents.

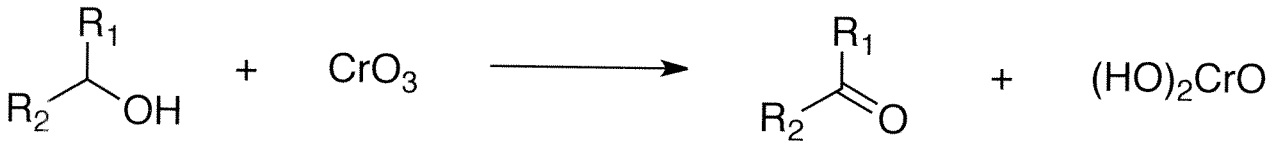


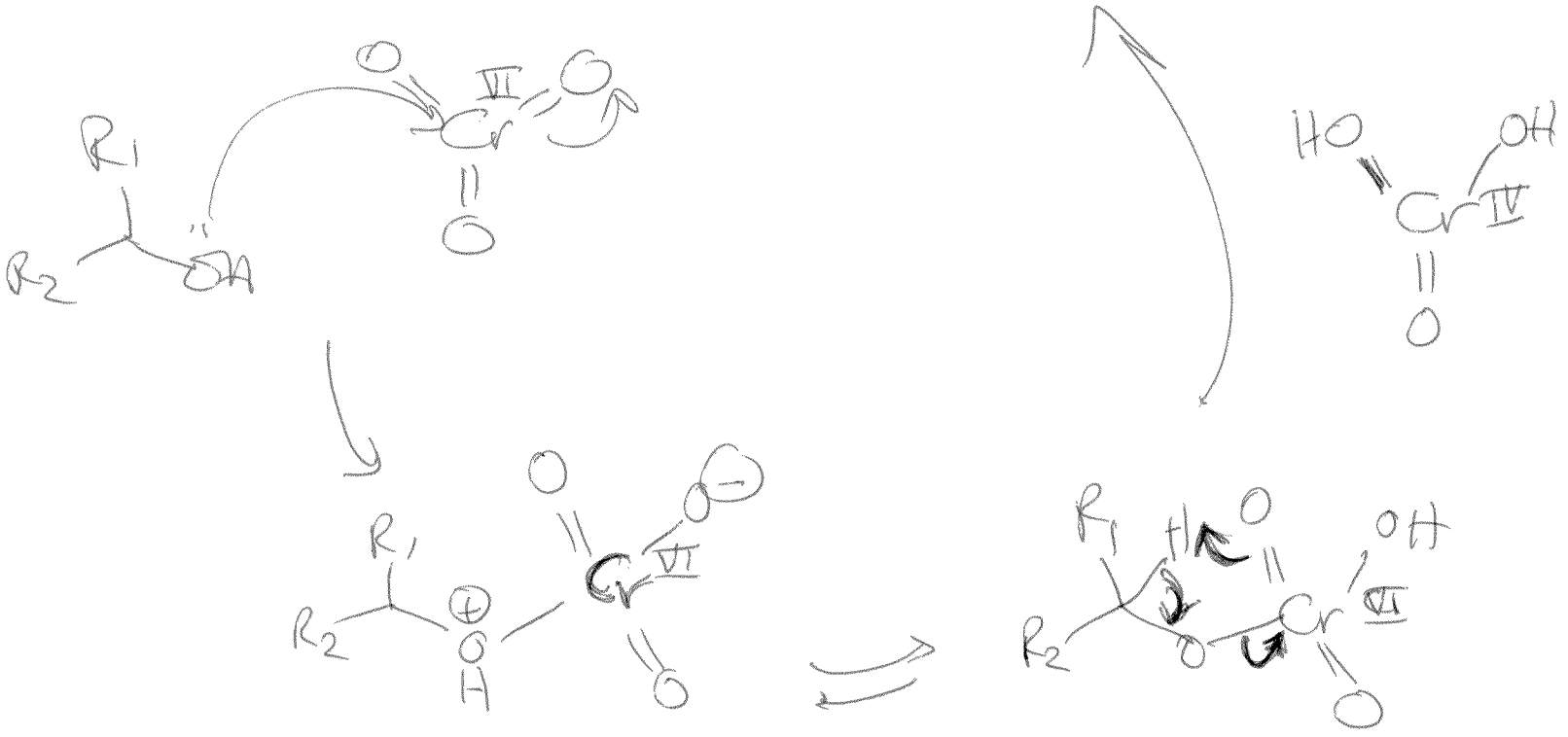
The dimerization pathway leading to C-C bond formation can be favoured by using magnesium as the reducing metal; this is referred to as a pinacol coupling.



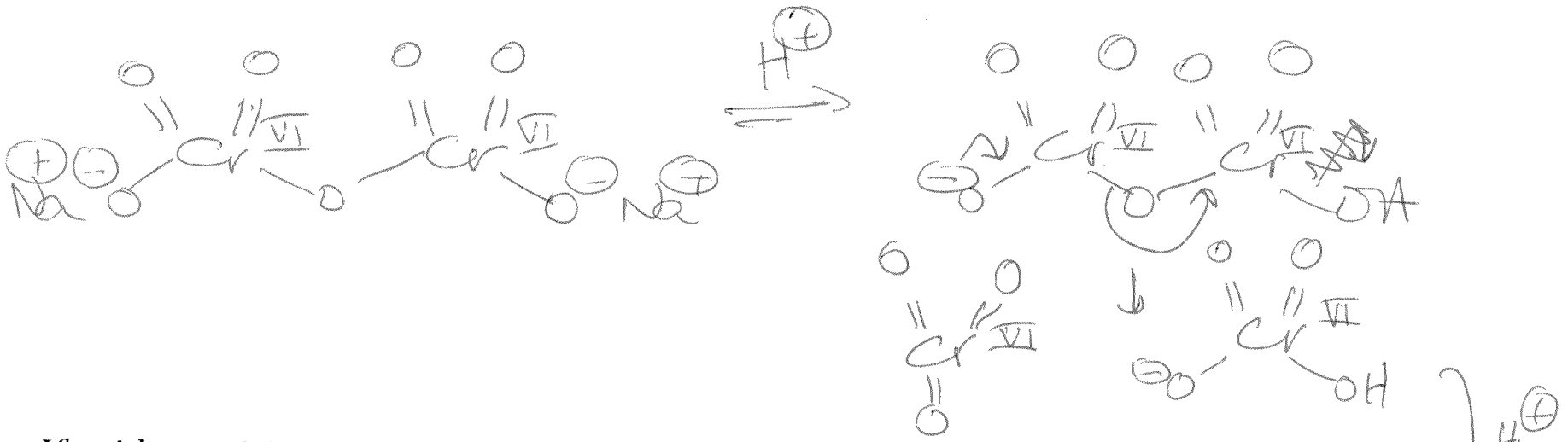
Recommended Reading: Clayden p. 528-543

Let's now talk a little bit about oxidations. In organic II you learn about chromium reagents, in particular.

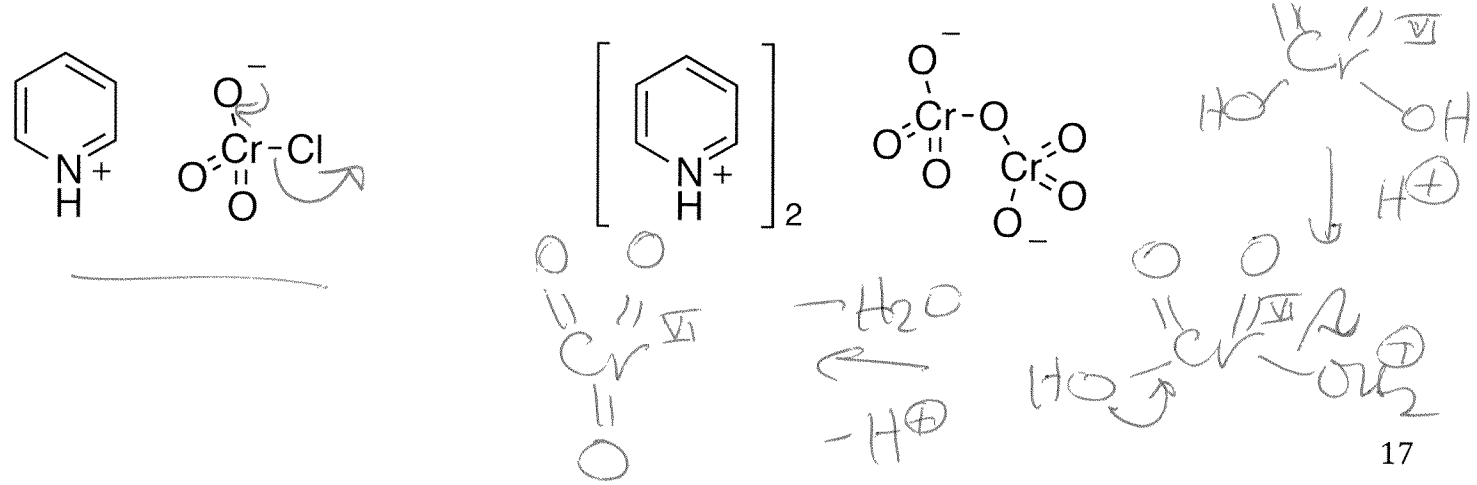




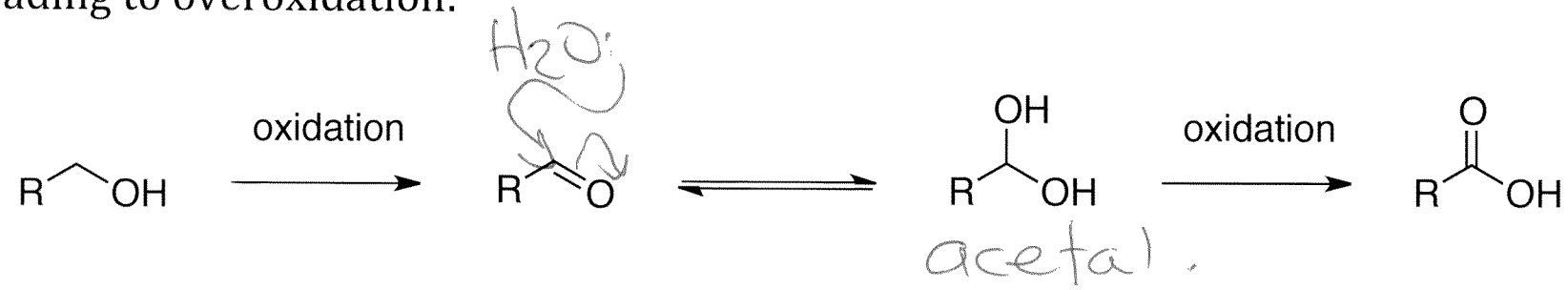
The common version of this reaction is the "Jones oxidation", which employs $Na_2Cr_2O_7$ in a sulfuric acid/acetone mixture.



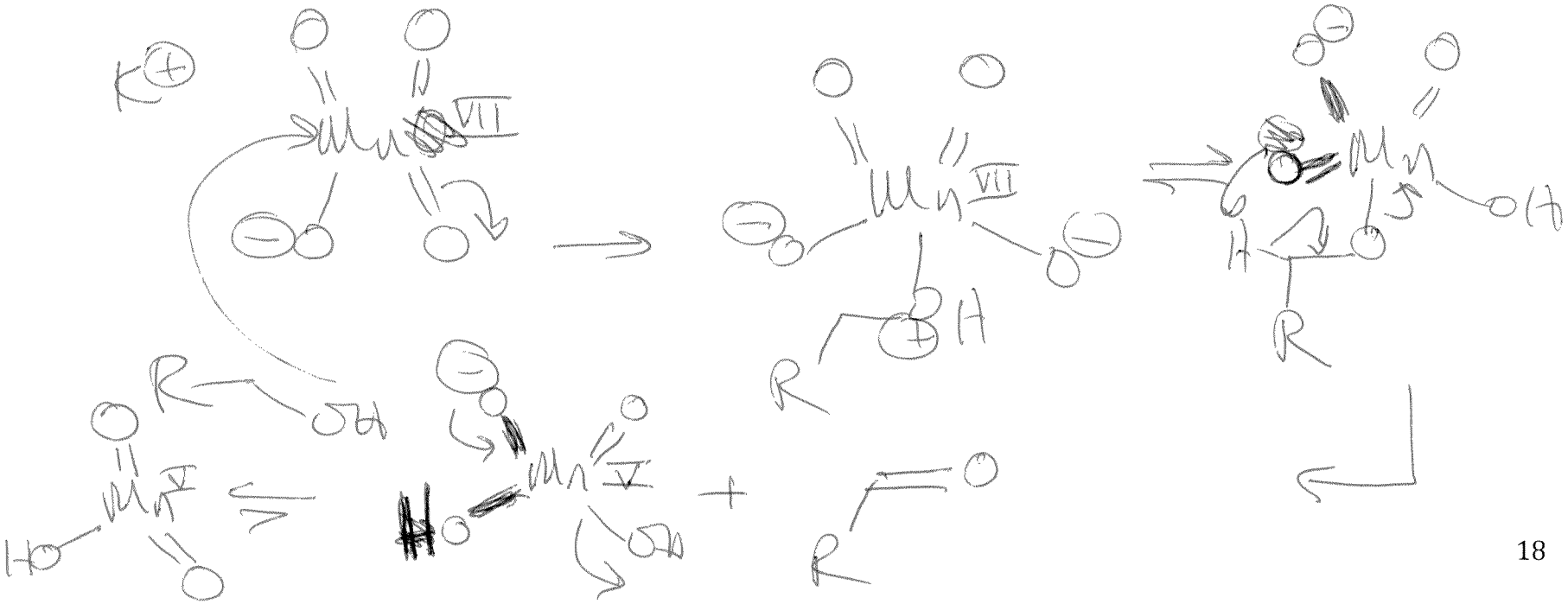
If acid-sensitive groups are found on in the substrate, pyridinium chlorochromate (PCC) or pyridinium dichromate (PDC) can be used as a source of CrO_3.



Chromium (and many other) oxidations are difficult to control in water, usually leading to overoxidation:

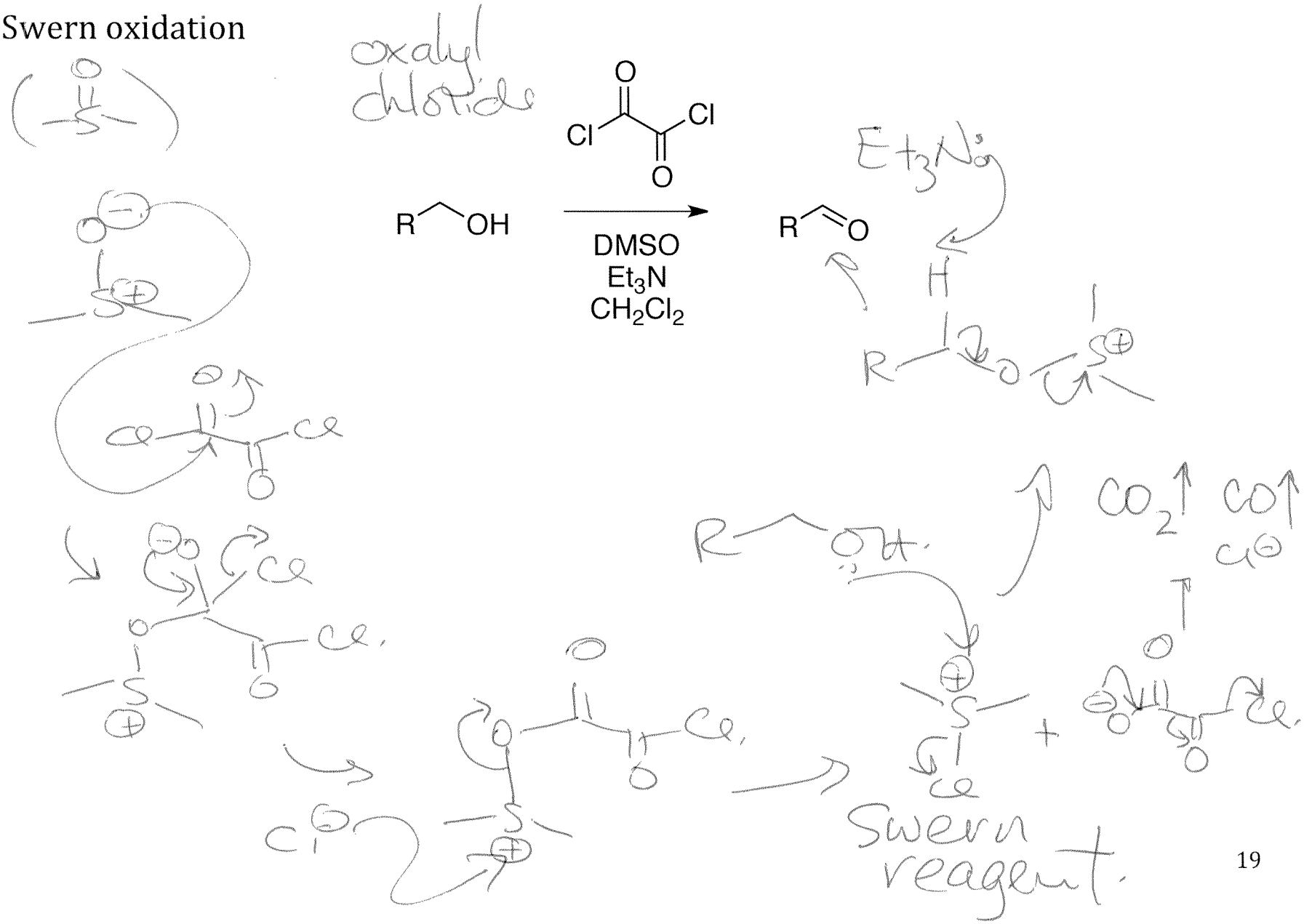


This is great if you want the acid, but not so good if you want the aldehyde. Another common reagent for obtaining the acid from the alcohol which follows the same mechanism as for CrO_3 is $KMnO_4$:

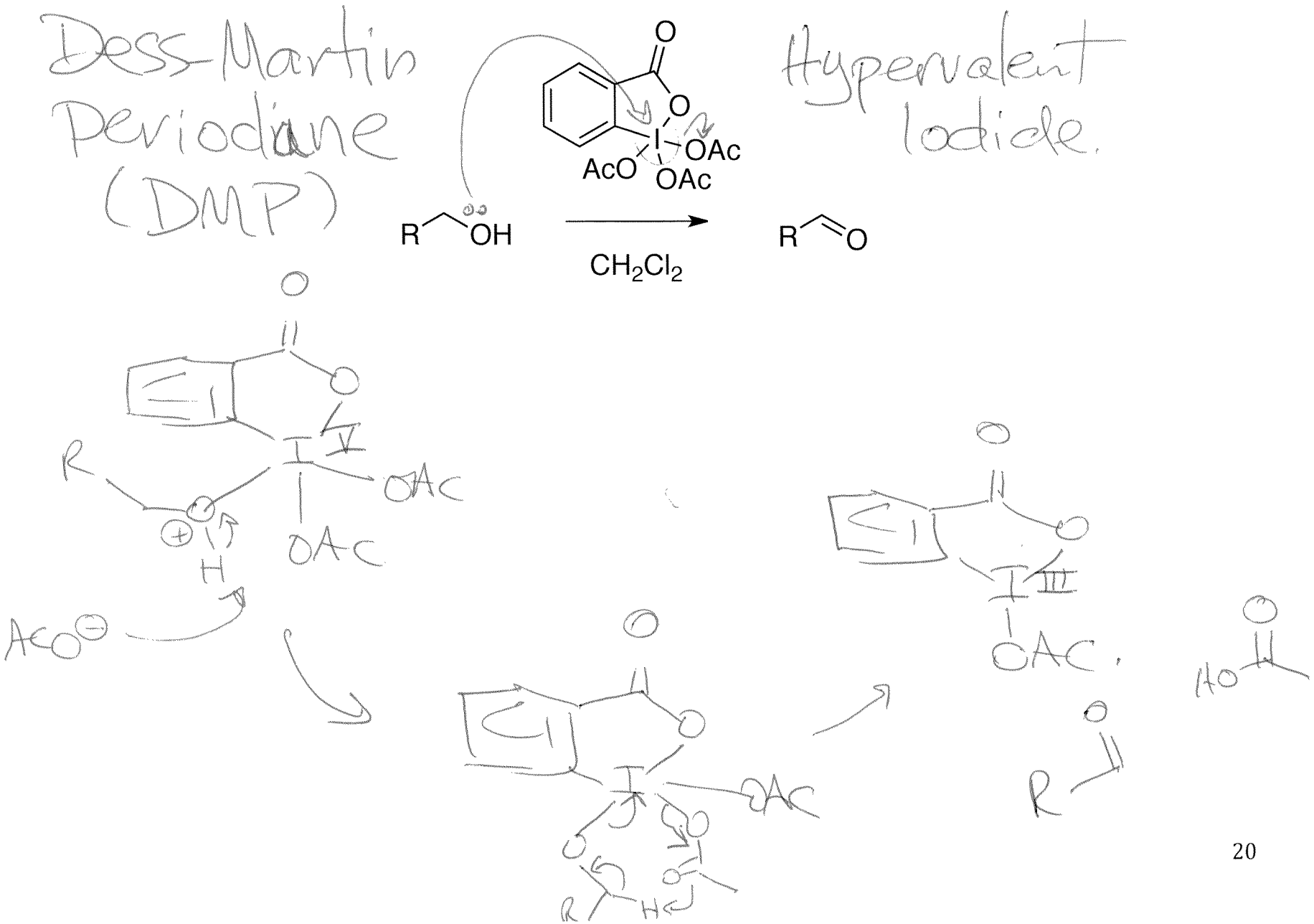


Some selective methods to oxidize alcohols to aldehydes are:

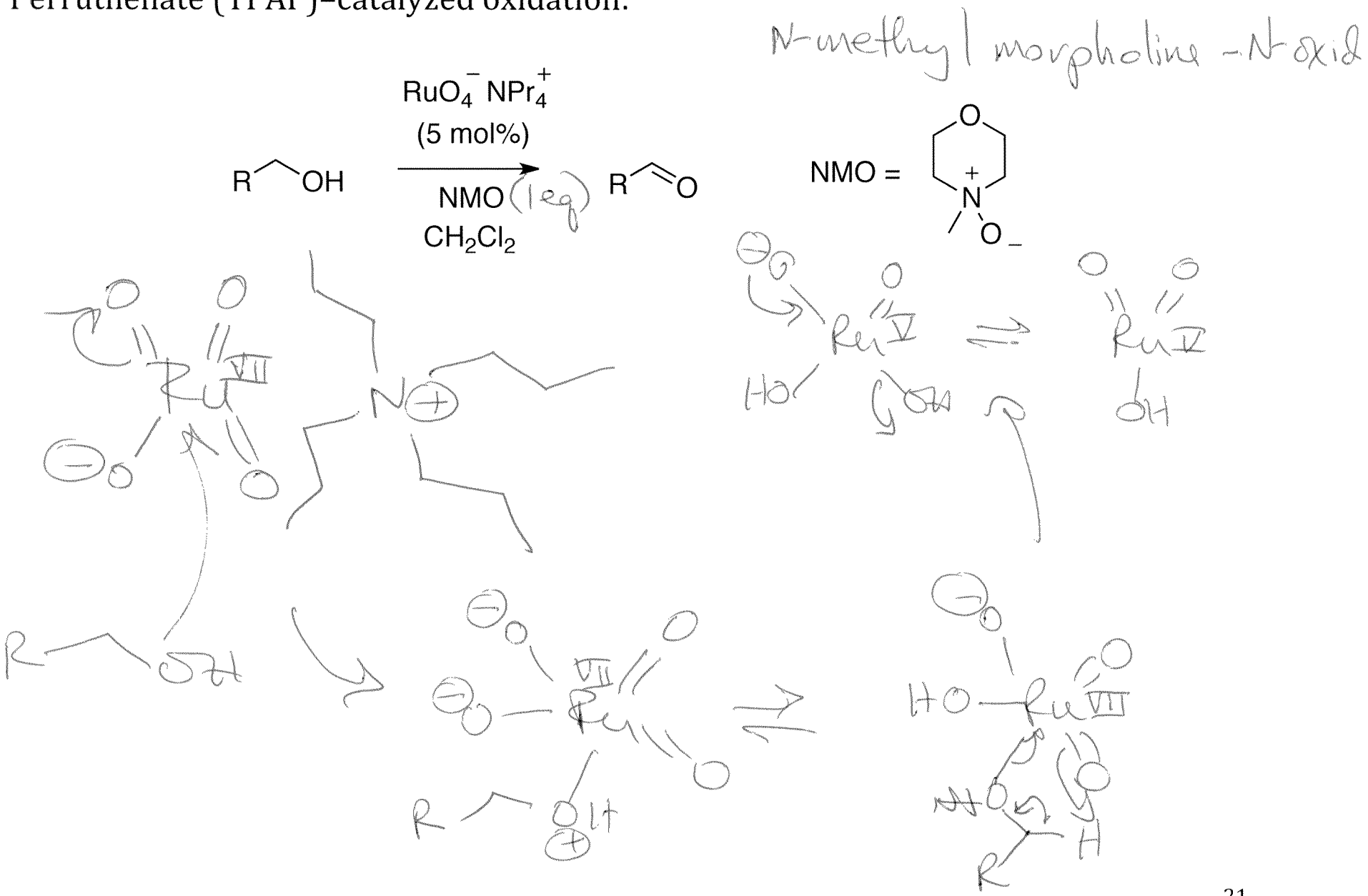
Swern oxidation

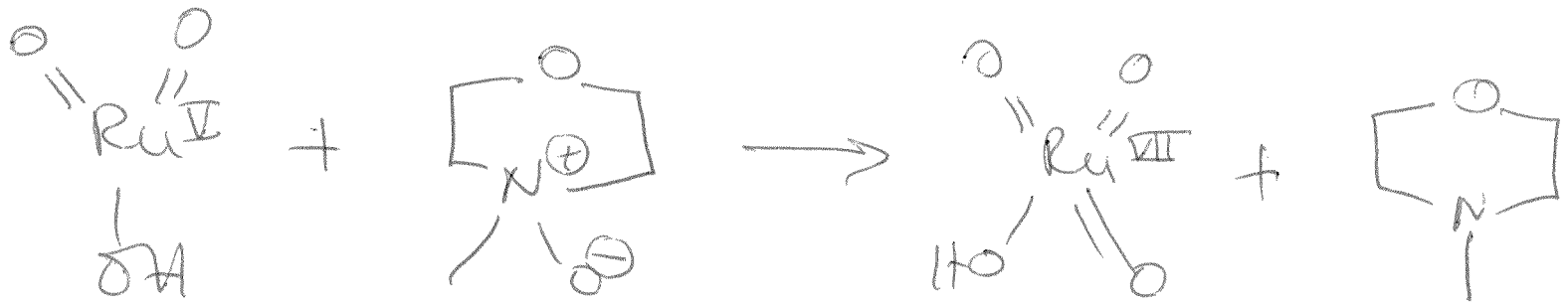


Dess-Martin oxidation



Perruthenate (TPAP)–catalyzed oxidation:



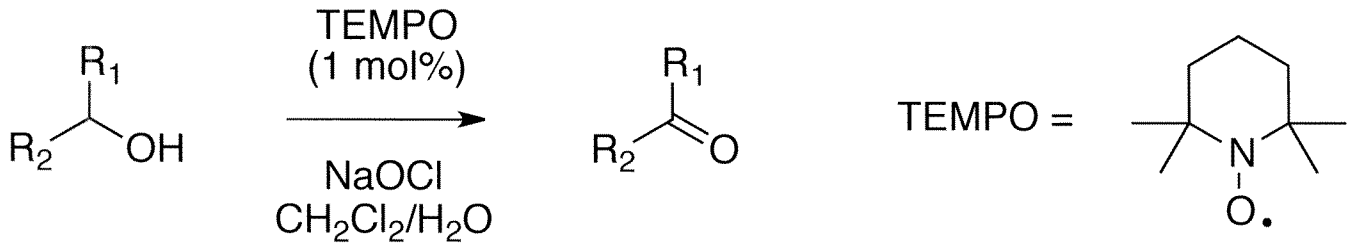


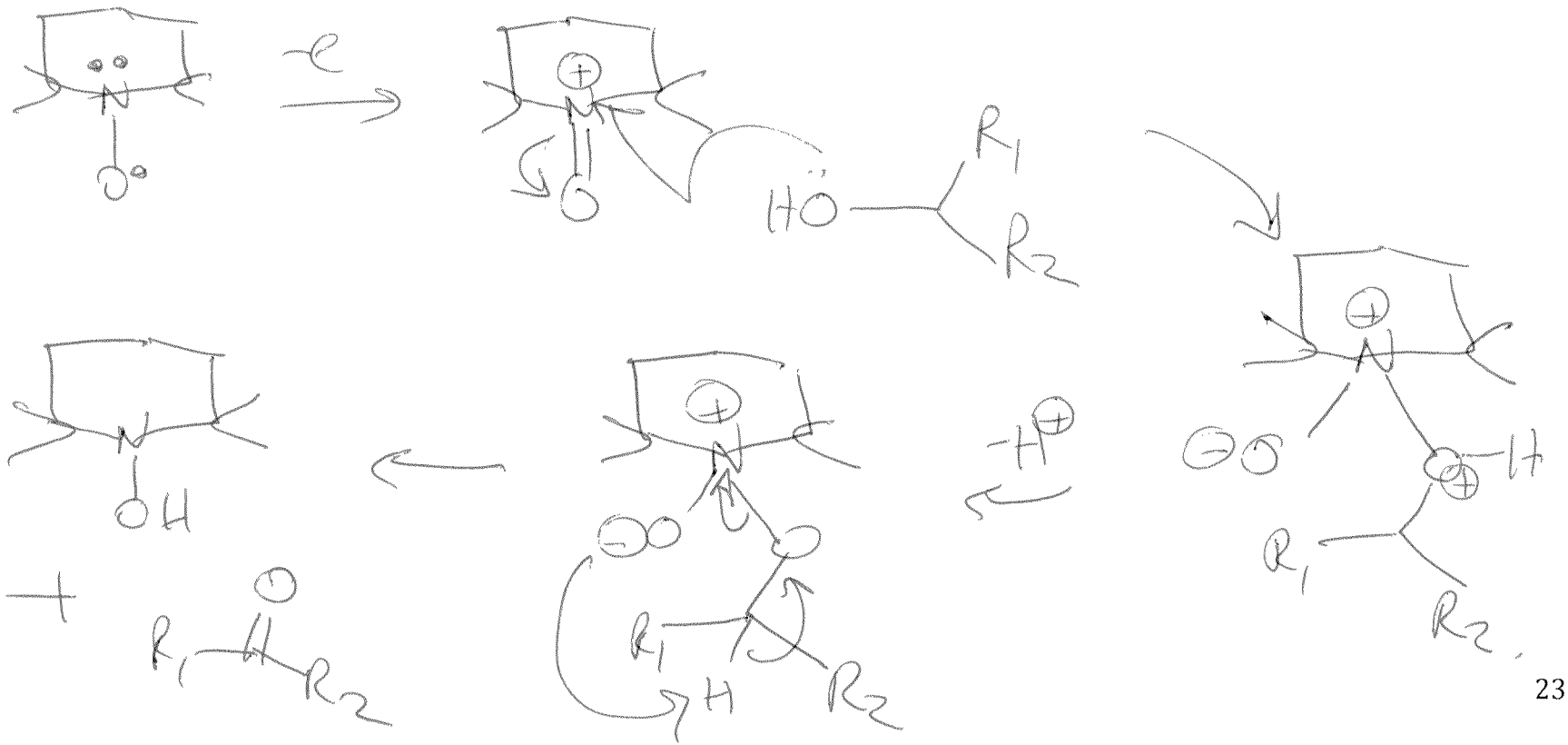
STOICHIOMETRIC OXIDANT.

CATALYTIC OXIDANT.

All three of these methods can also be used for secondary alcohols to ketones.

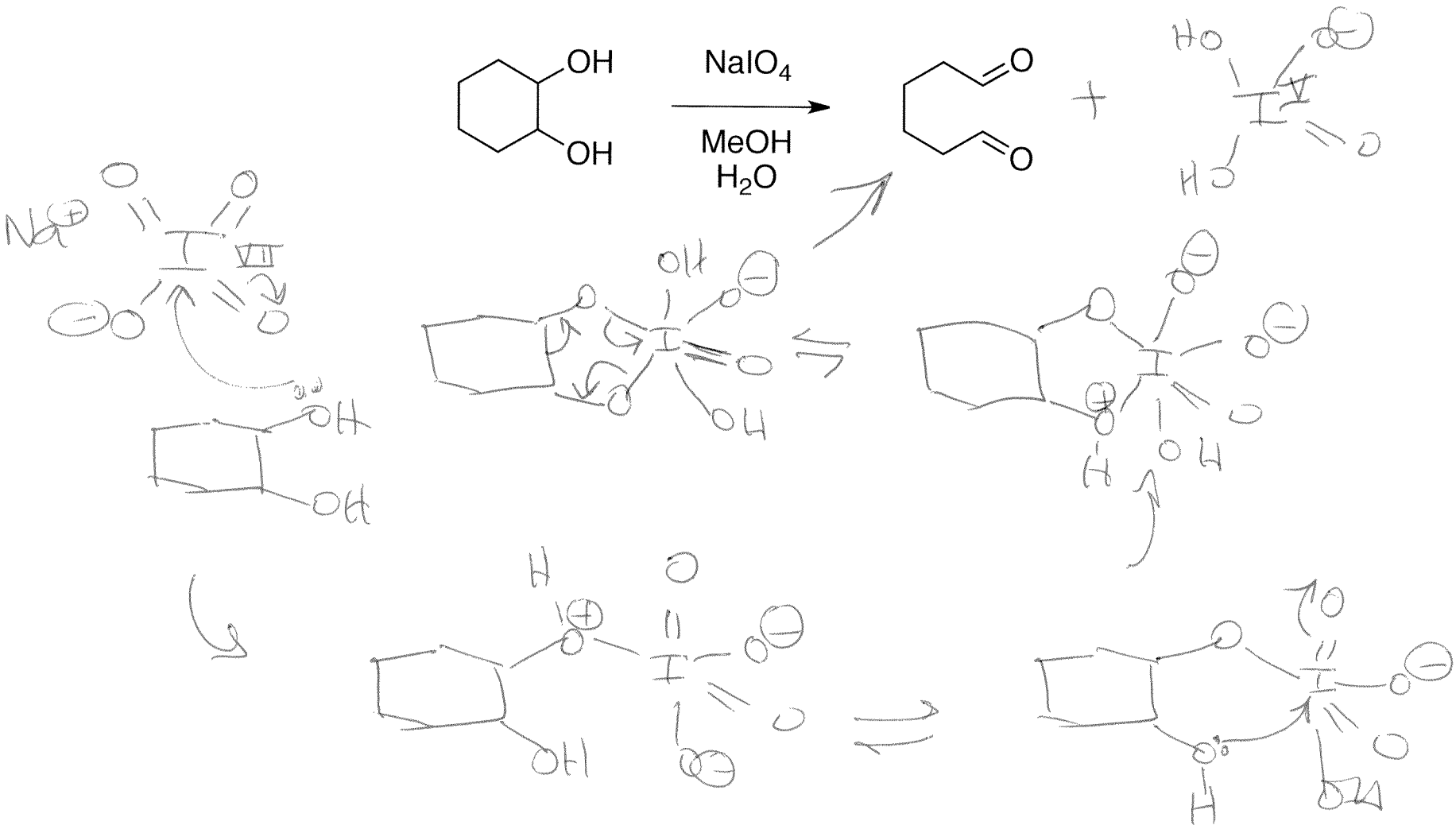
Another "organic" oxidation for this purpose employs the persistent free radical TEMPO:



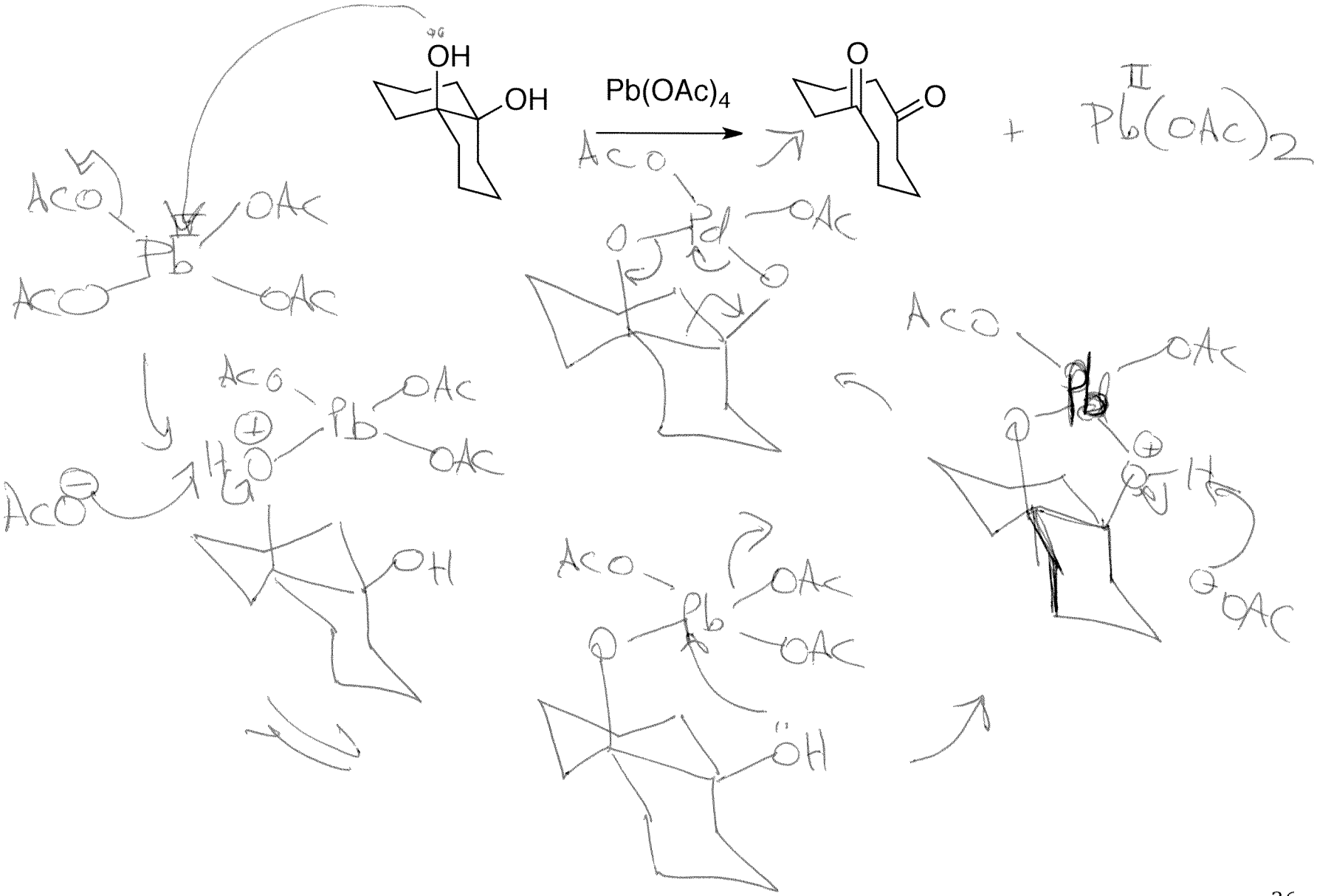


(NaOCl + H2O ⟶ NaOH + HOCl)

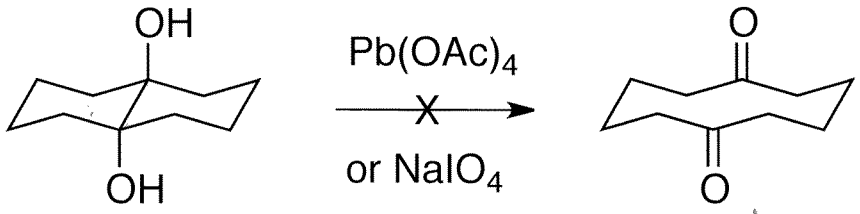
Since vicinol diols (a.k.a glycols) figure so prominently in natural products, methods to specifically oxidize them have been extensively developed over the years. In these reactions, the oxidation occurs with cleavage of the carbon-carbon bond!



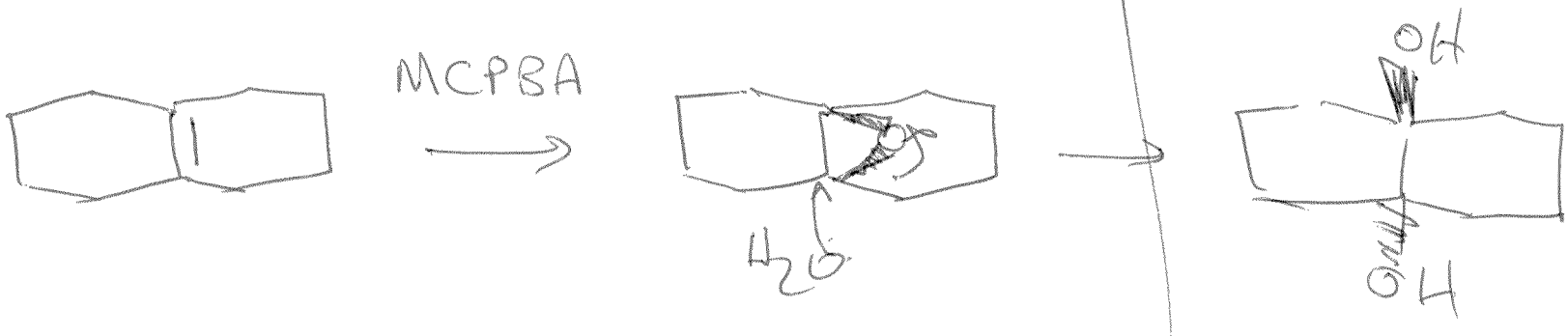
Related to this is oxidation with $Pb(OAc)_4$:



… however because of the mechanism, *anti* diols are problematic!

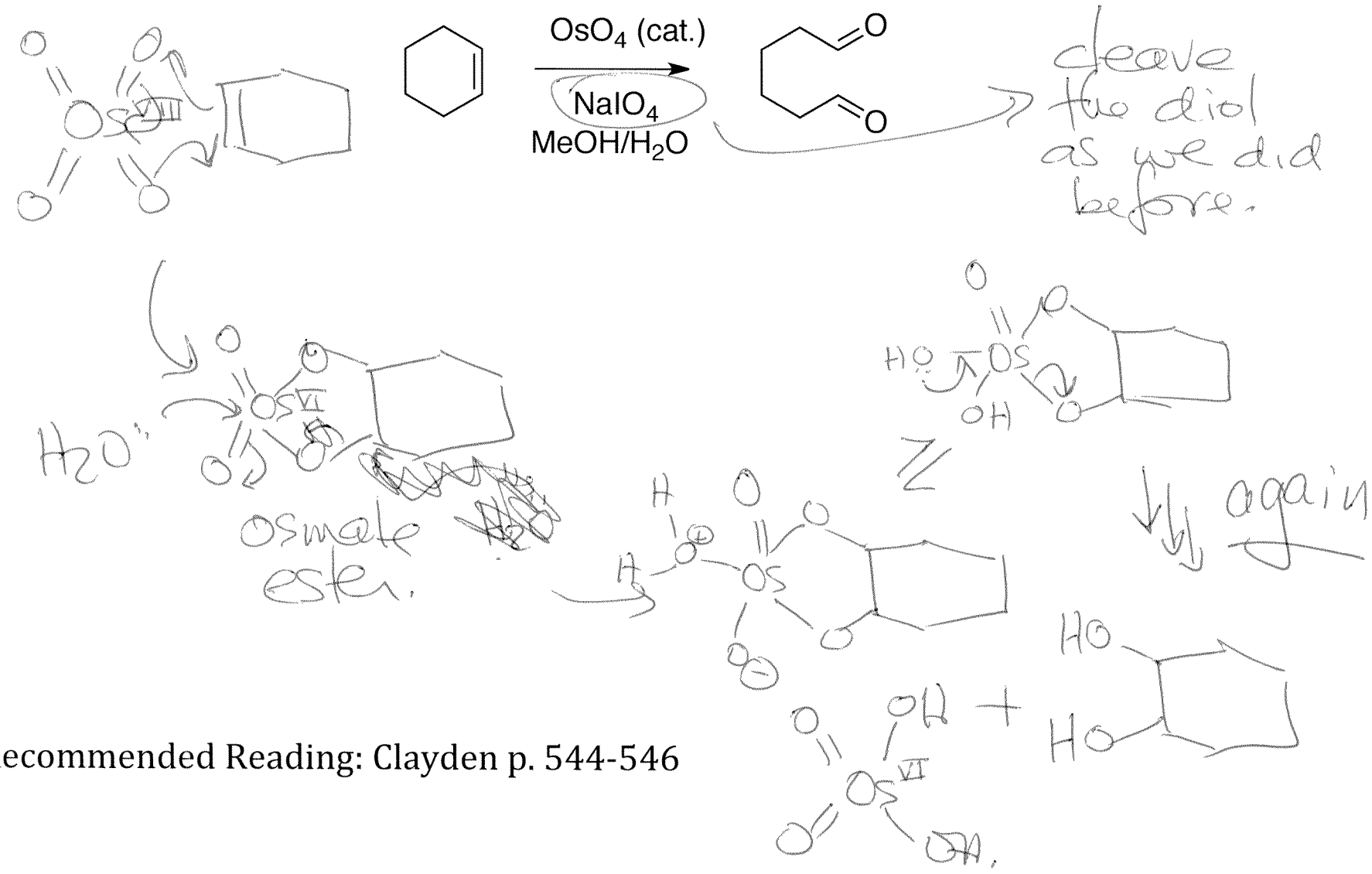


And, *anti* diols are most common! Think of how we might synthesize them:



Is there another way to do get to the dicarbonyl compound via an oxidative cleavage?

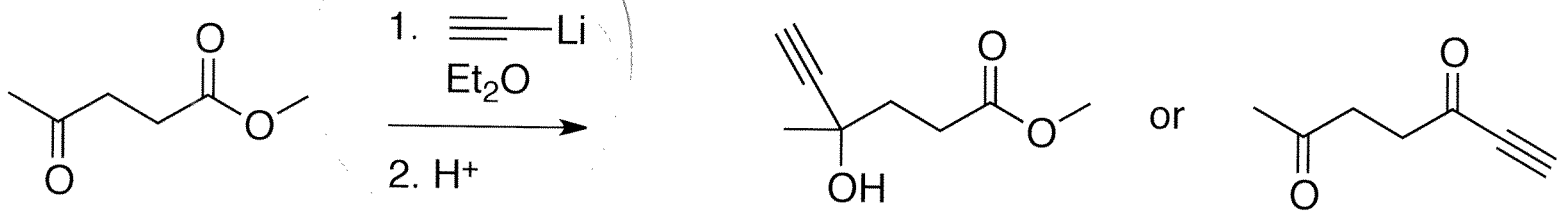
The same transformation can be accomplished with catalytic osmium tetroxide:



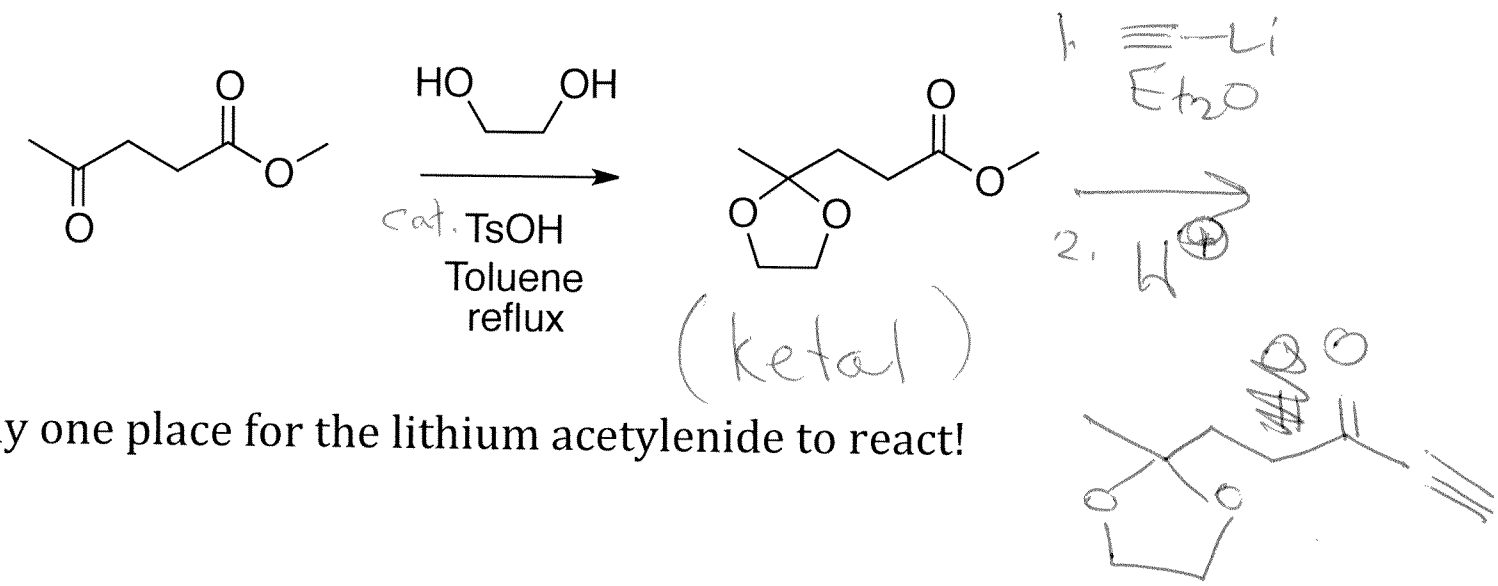
Recommended Reading: Clayden p. 544-546

Protecting Groups: a strategy employed to manipulate the least reactive group.

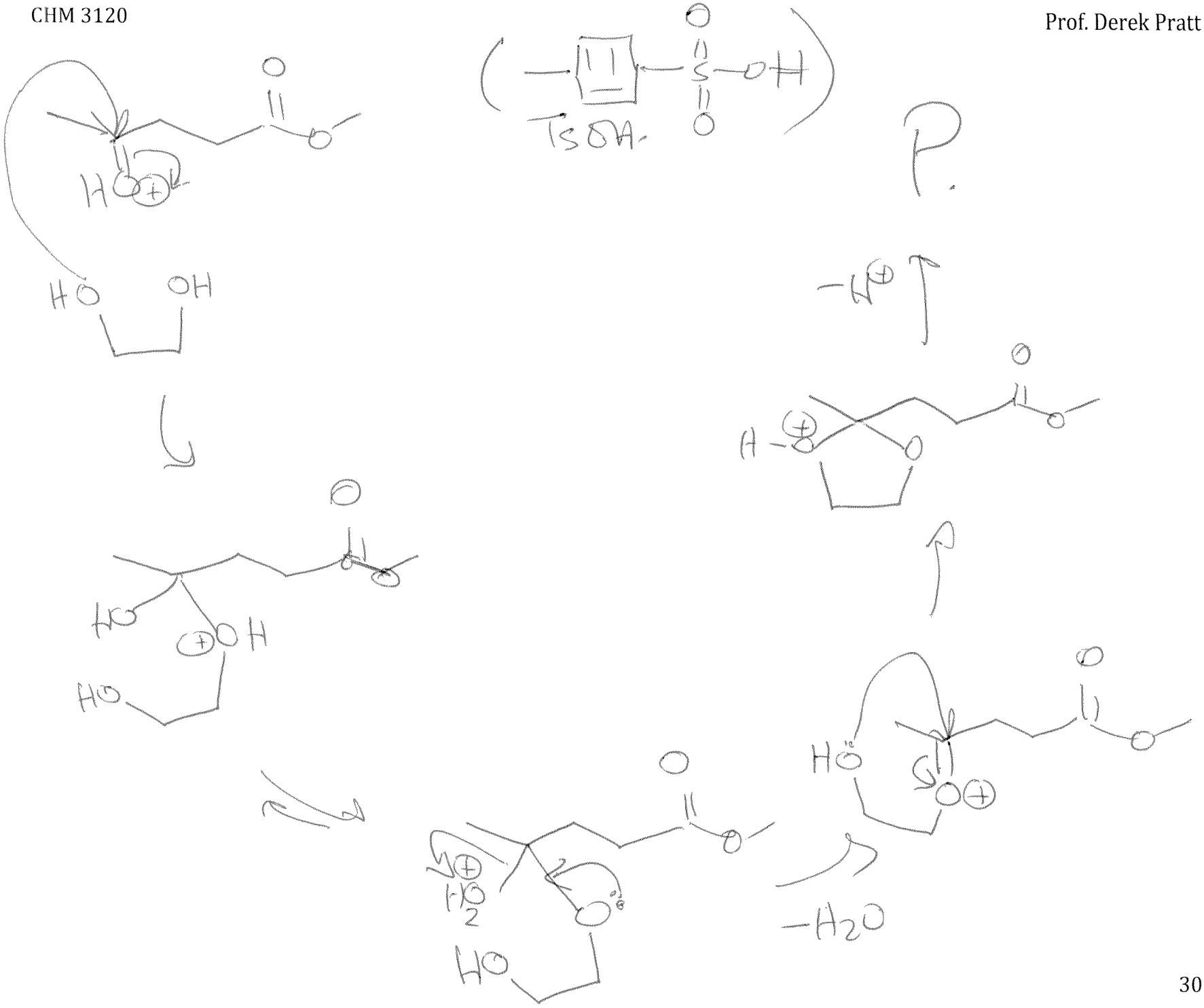
Remember this example?



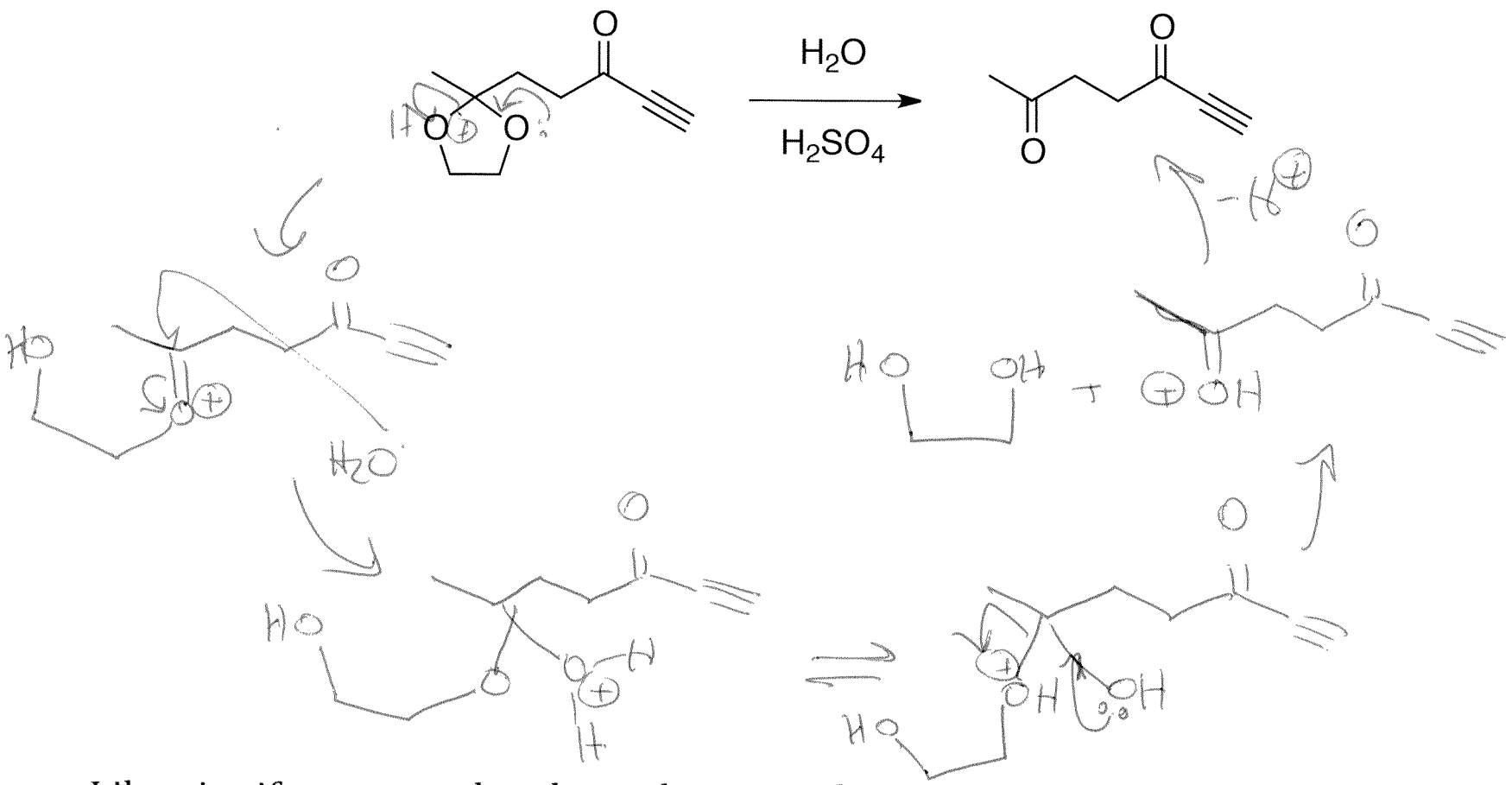
If, before we subject the γ-ketoester to these reaction conditions, we did this reaction:



Now there is only one place for the lithium acetylenide to react!


TsOH
P.
HO
OH
$-H_2O$

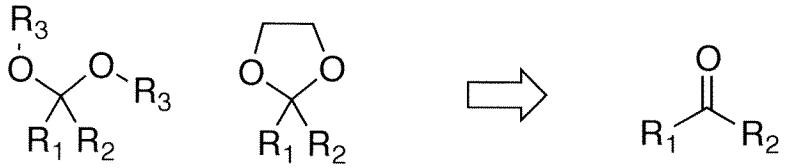
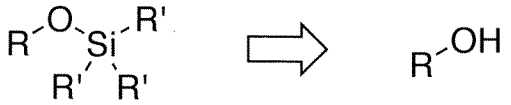
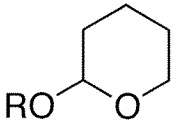
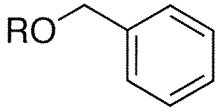
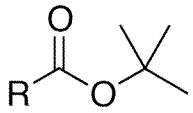
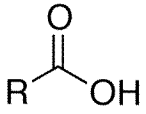
We can then remove the acetal to recover the ketone:

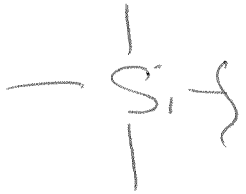


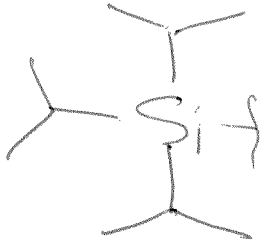
Likewise if we wanted to do a selective reduction of the ester in the "presence" of the ketone.

Common Protecting Groups (for O)

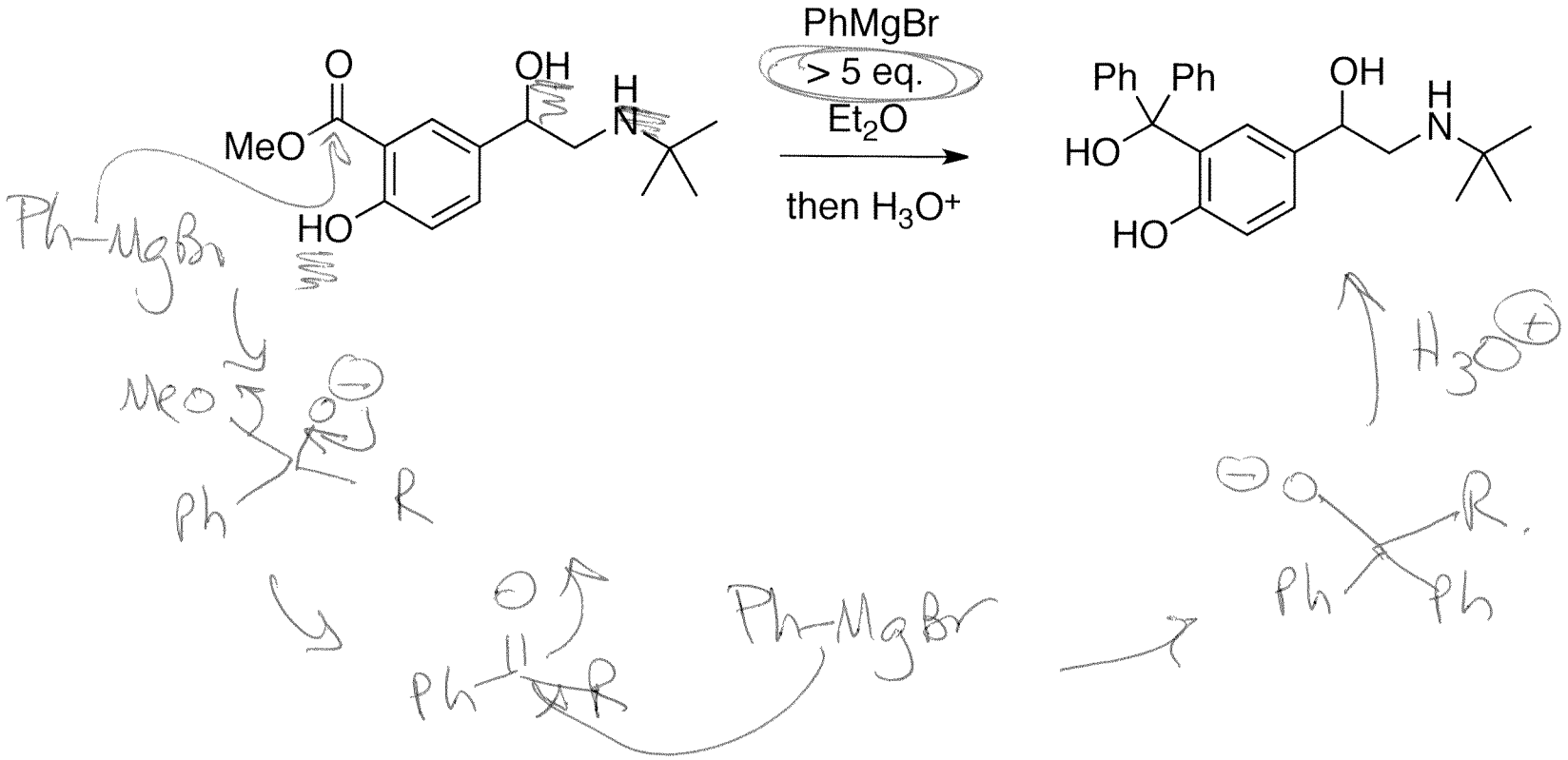
acetals, ketals

acetal			protects aldehydes, ketones from nucleophiles, bases
silyl ether		R–OH	protects alcohols (phenols, enols, hemiacetals, etc.) from electrophiles, C- and N- nucleophiles, bases
tetrahydropyranyl (THP) acetal		R–OH	protects alcohols from strong bases
benzyl ether		R–OH	protects alcohols from almost everything
t-butyl ester			protects acids from nucleophiles, bases

TMS = 

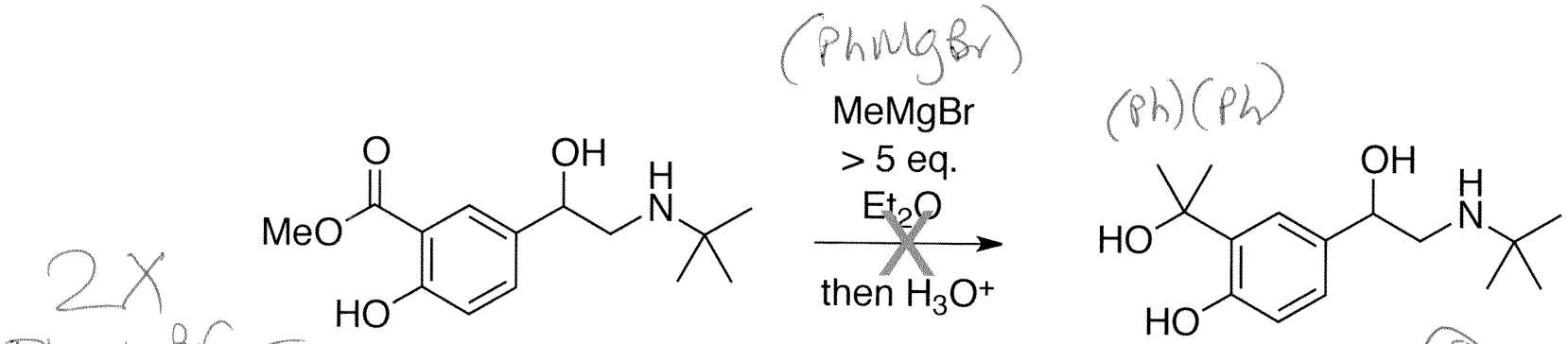
TIPS = 

Sometimes we can get around using protecting groups simply by sacrificing an excess of reagent:

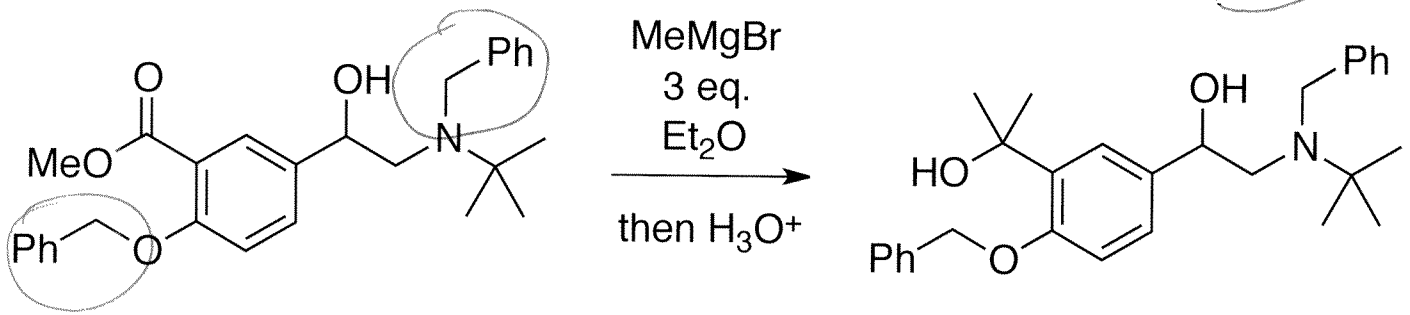


This must be balanced against the cost (in time, material) to protect and deprotect…

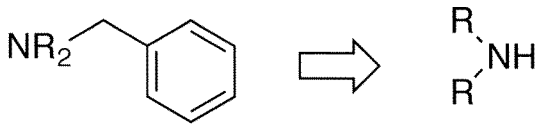
And… sometimes it doesn't work!

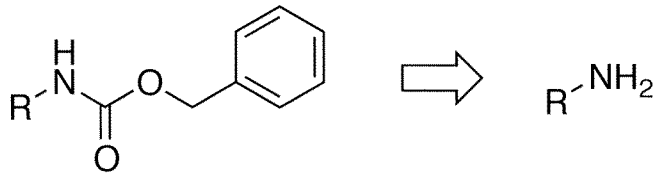


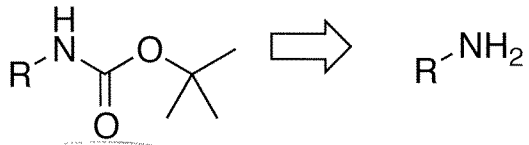
Partial protection, on the other hand, works very well in this case:

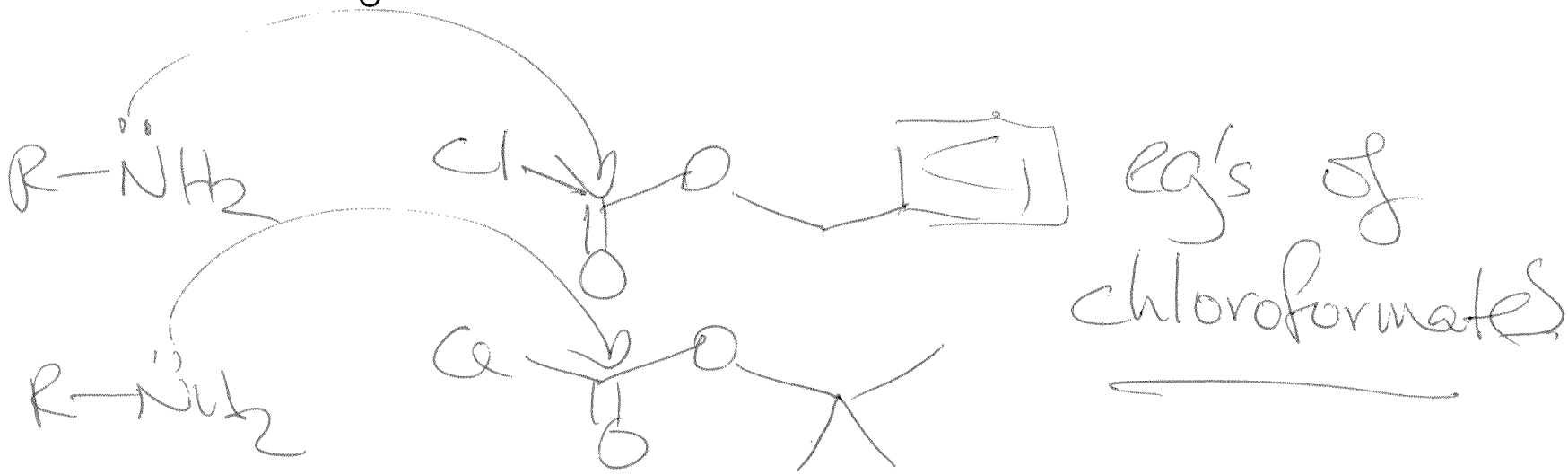


N-benzyl is one of several common protecting groups for amines:

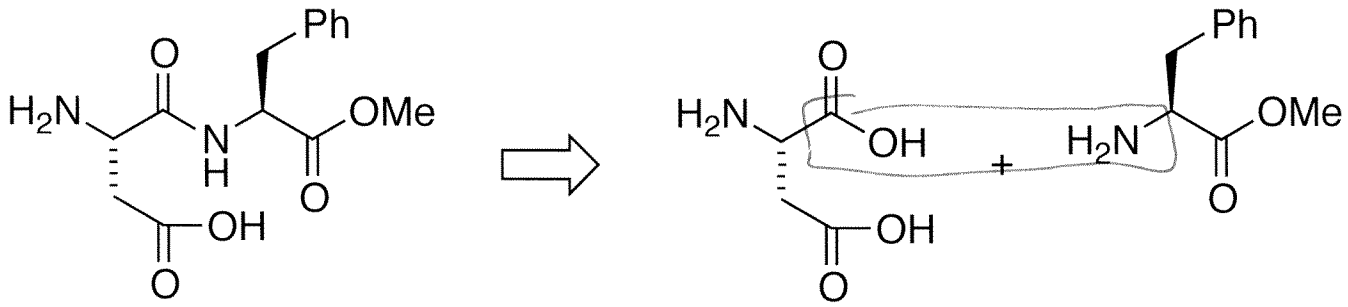
benzyl amine  protects secondary amines from electrophiles, bases

benzyl carbamate  protects amines from electrophiles

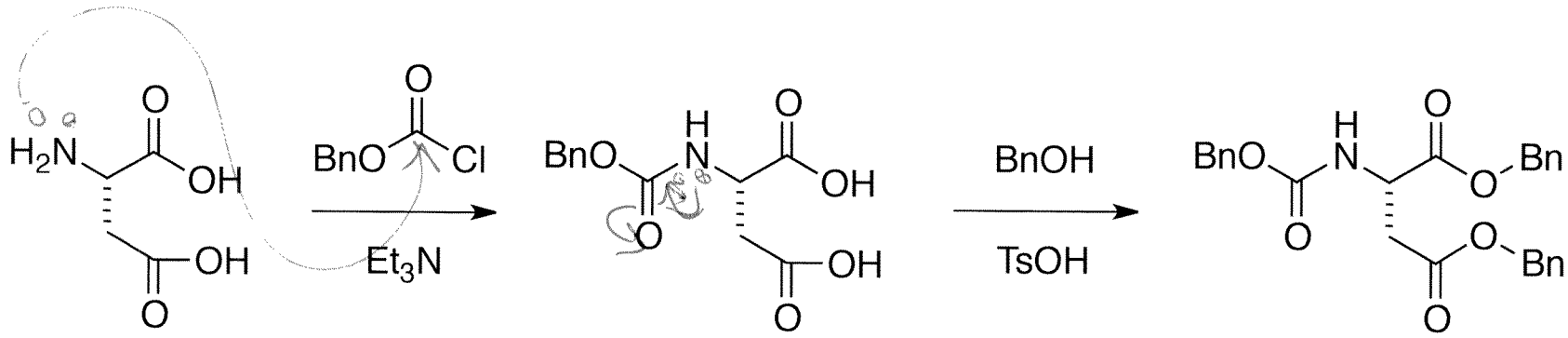
t-butyl carbamate  protects amines from electrophiles



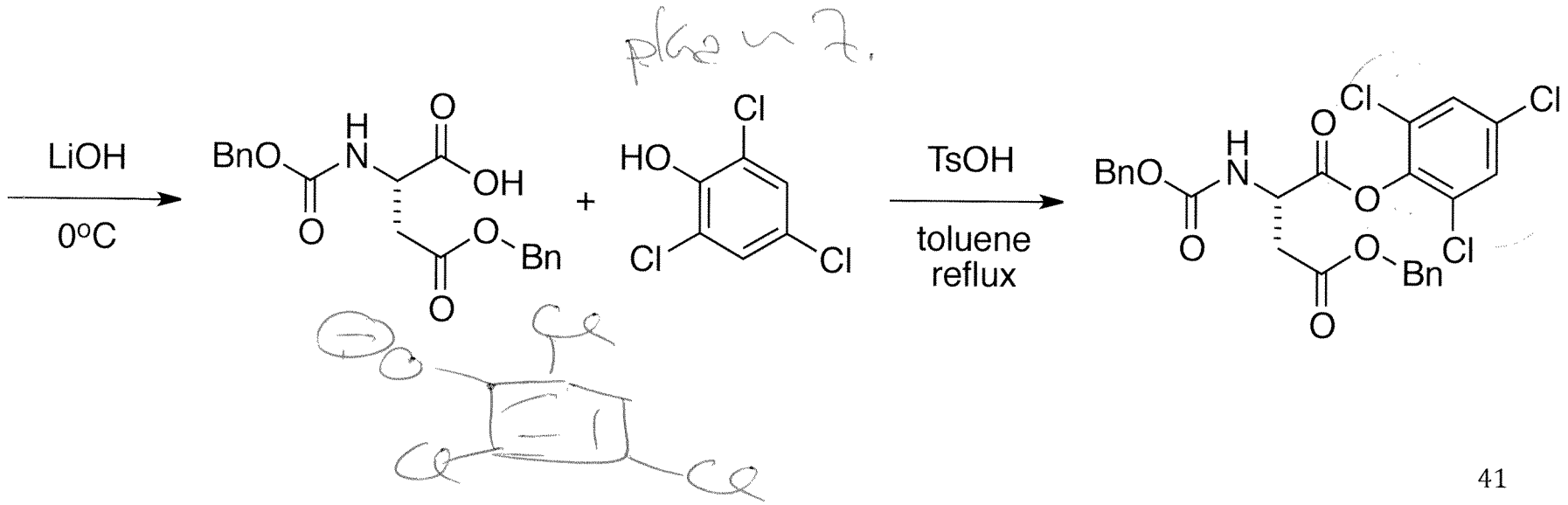
Consider the synthesis of aspartame from its constituent amino acids:



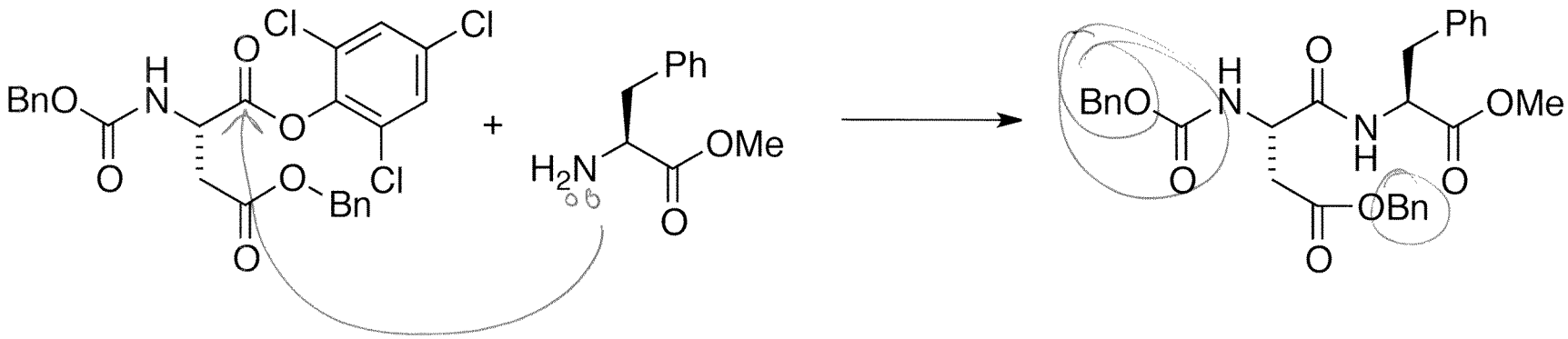
In order to ensure that we make the desired amide bond, we need to make use of protecting groups.



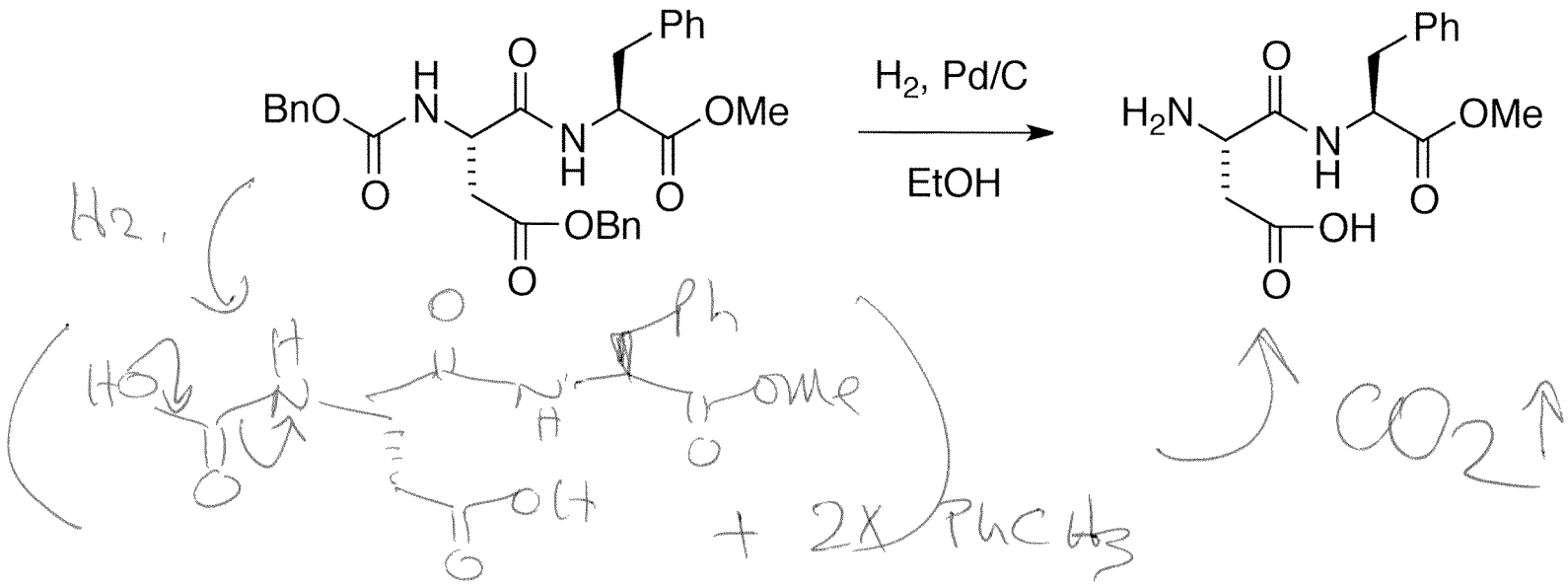
A selective hydrolysis and activation of the carboxylic acid gets us ready...



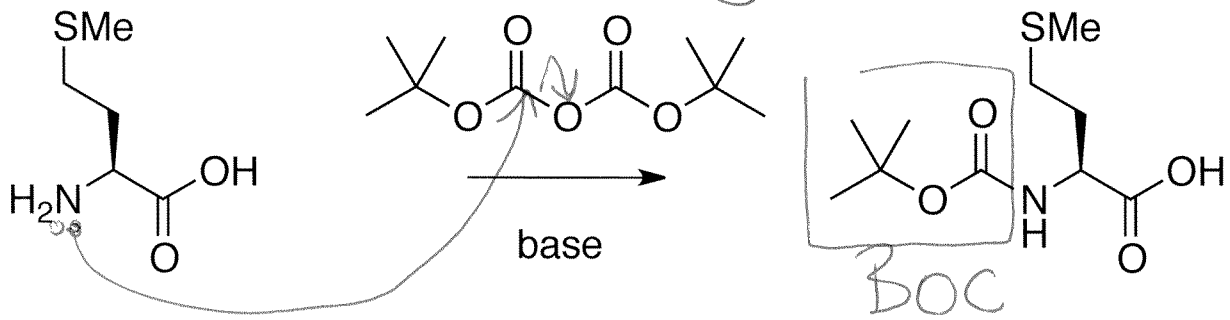
Finally, we are ready to make our amide bond:



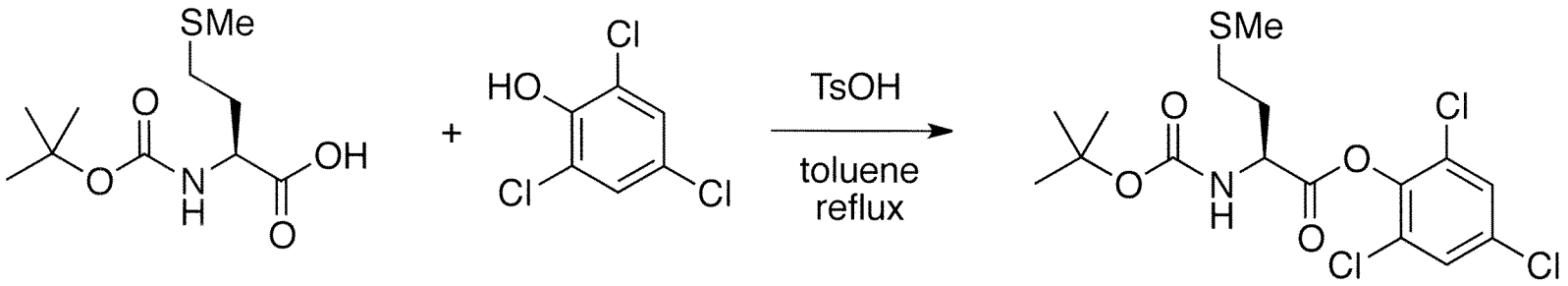
and then remove the protecting groups:

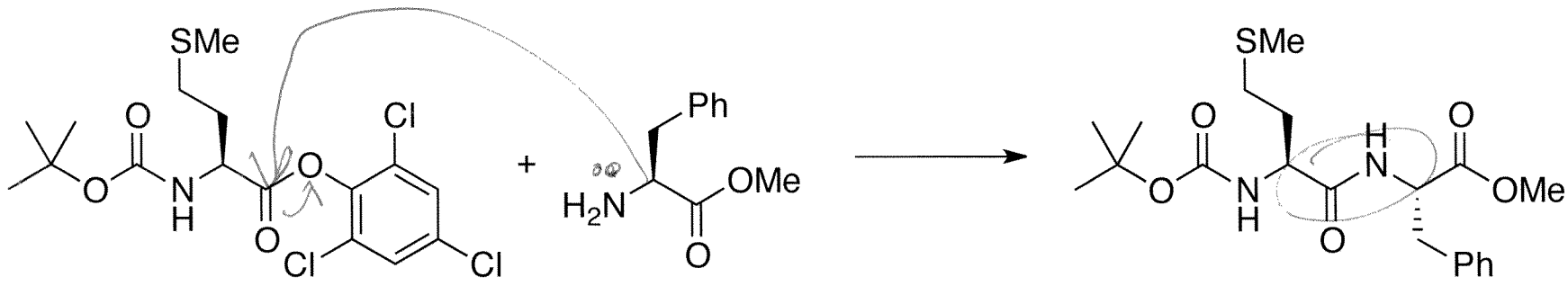


Perhaps the most versatile protecting group for an amine is the 'Boc' group. It is generally installed via the anhydride, for example in the protection of methionine:

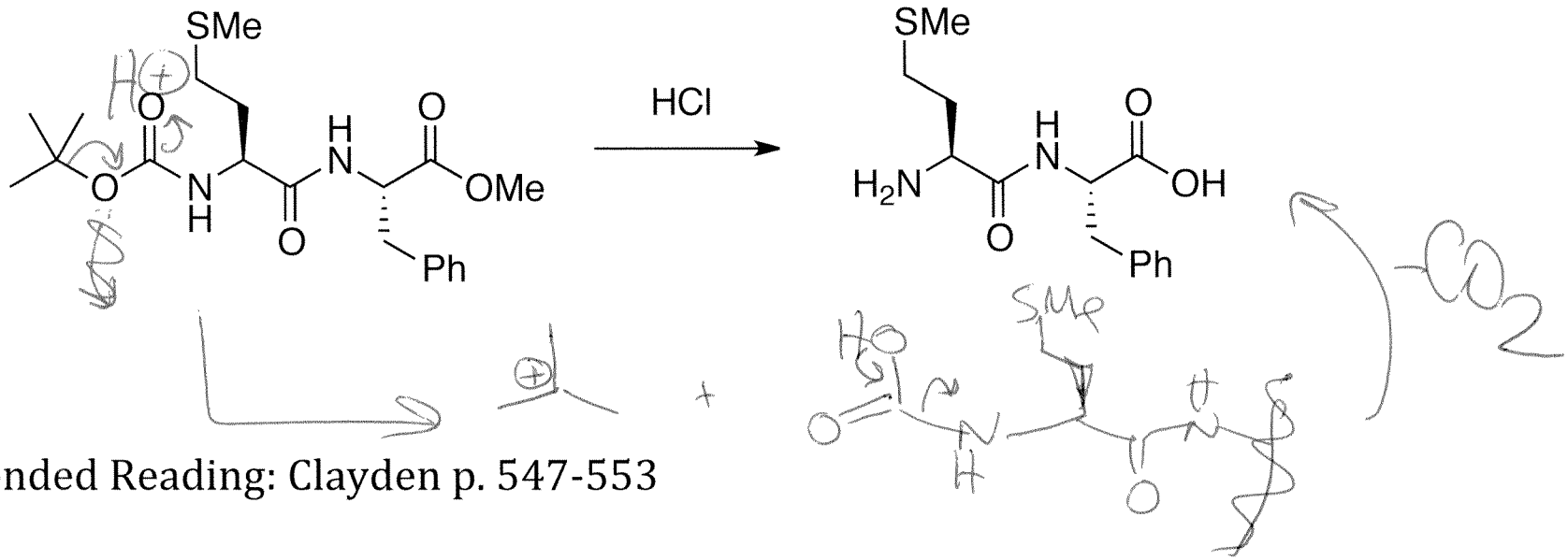


The carboxylic acid can now be activated for amide bond formation:





Boc groups are removed with dilute acid:



Recommended Reading: Clayden p. 547-553