

Oxidation States, Hydrogenation, And Hydrogenolysis

from chapter(s) _____ in the recommended text

A. Introduction

B. Oxidation States In Organic Chemistry

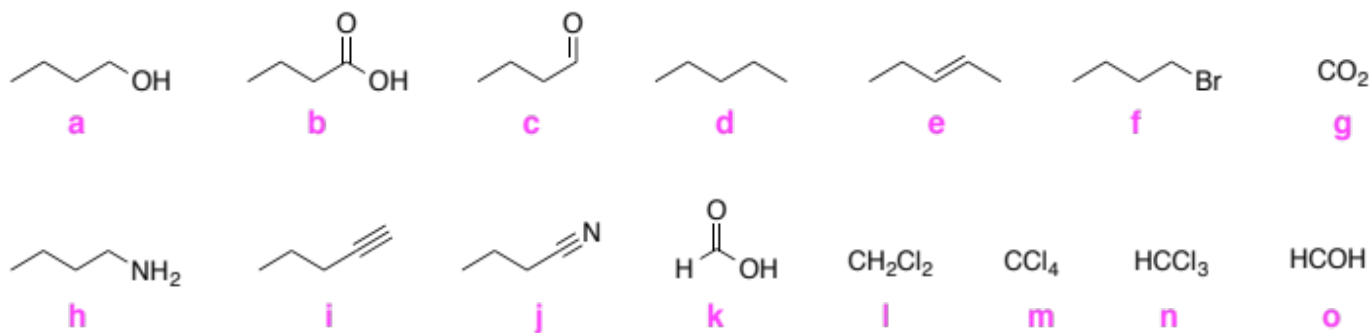
Reduction is *addition* of electrons from the substrate, and *loss* from the reducing agent. Oxidation is *e⁻addition* from the oxidizing agent and *loss* from the substrate.

more

less

less

more



lowest oxidation state

d

one level higher

a, e, f, h

one more level higher

c, i, l, o

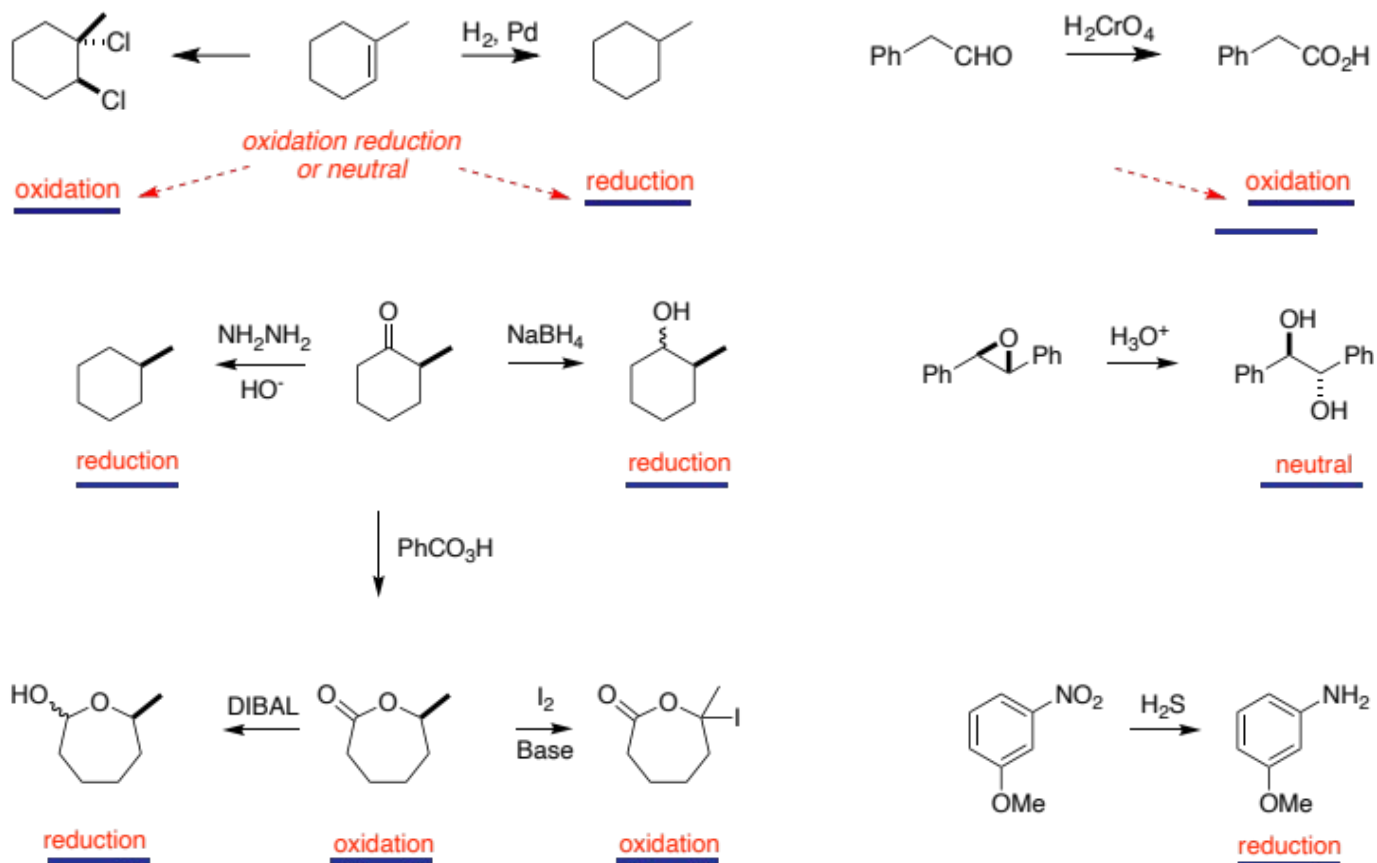
still another level higher

b, j, k, n

highest oxidation state

g, m

Cyclohexane is at a *higher* oxidation state than hexane.



C. Addition Of H₂

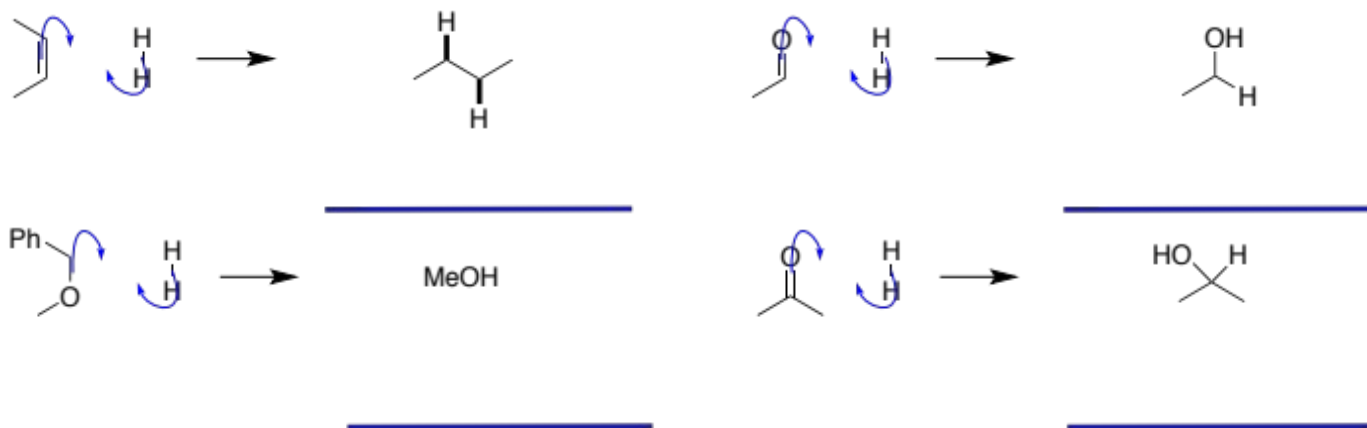
Hydrogenation And Hydrogenolysis

Hydrogenation involves addition of H₂ across an unsaturated bond without cleaving

Hydrogenolysis involves addition of H₂ across a single bond with cleavage.

Addition of hydrogen to an alkene or an aldehyde can be thought of as proceeding via: (i) *homolytic* cleavage of H₂

Hydrogenolysis is closer to a *radical* mechanism, than a *ionic* one.

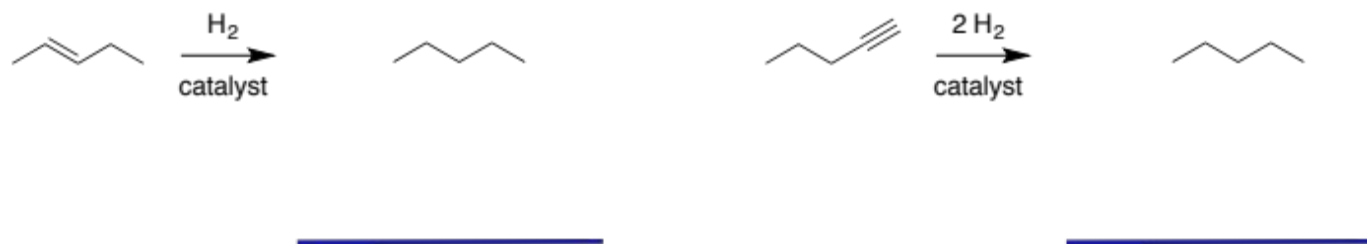


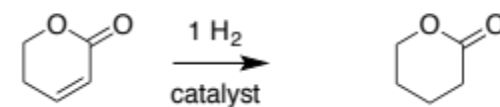
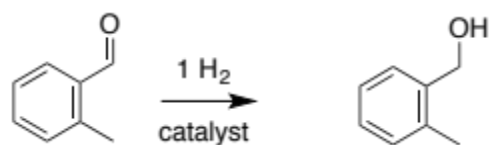
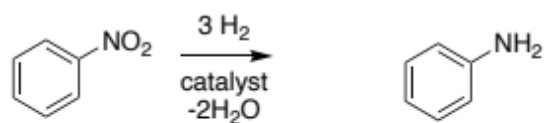
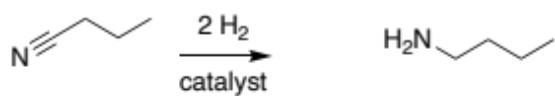
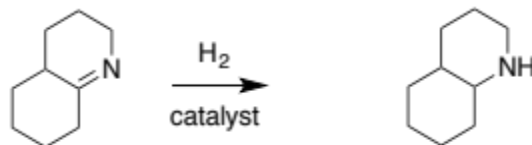
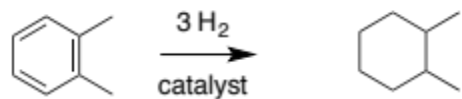
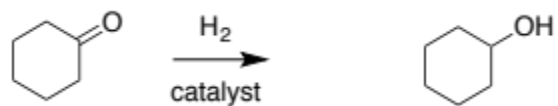
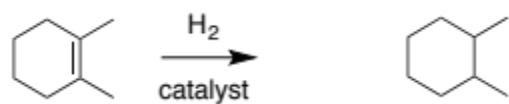
hydrogen adds to are inclined to *stabilize* a single electron.

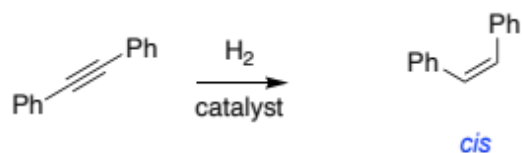
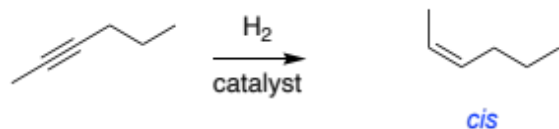
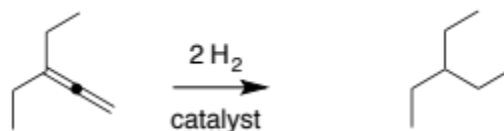
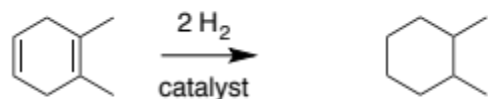
hydrogenolysis of benzyl ethers favorable, because the *benzyl* radical is stabilized by resonance.

Aromatic aldehydes, ketones, and esters are *more* easily hydrogenated than similar aliphatic

D. Hydrogenation

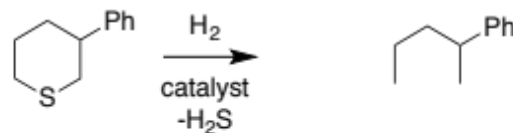
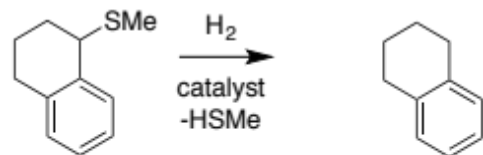


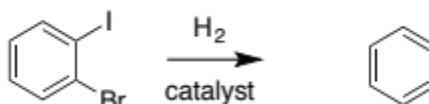
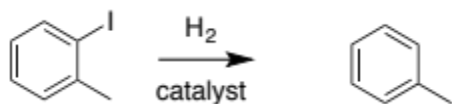
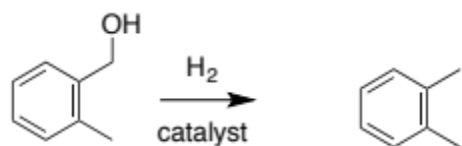




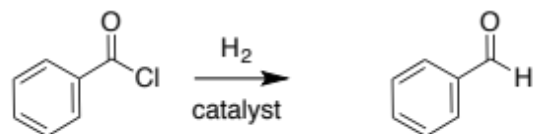
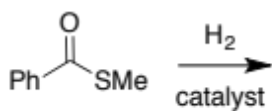
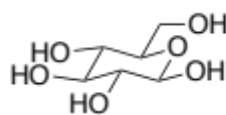
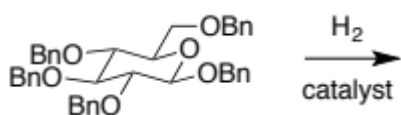
E. Hydrogenolysis

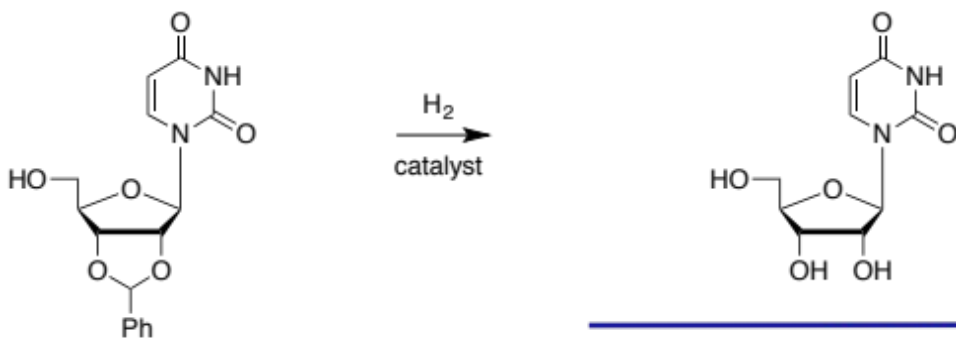
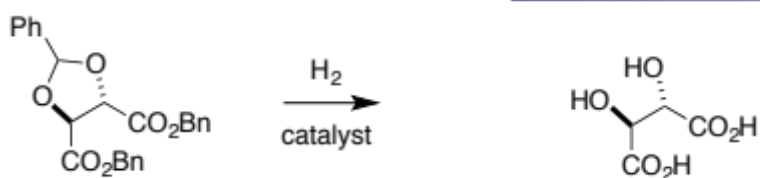
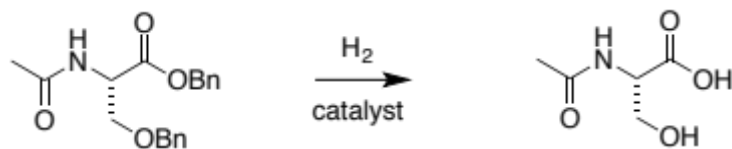
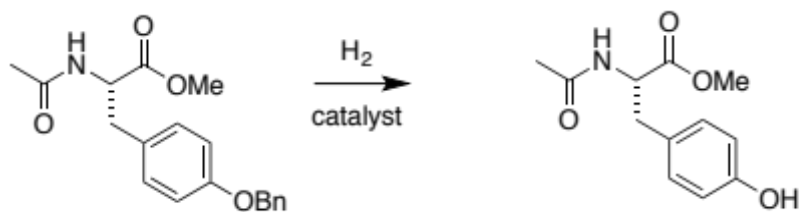
Hydrogenolysis refers to addition across *single* bonds.



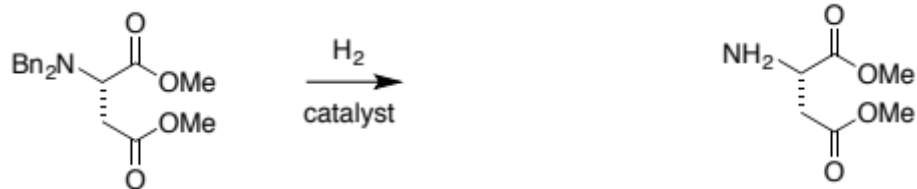


Note: further hydrogenolysis of these products to alcohols is possible, and these may undergo hydrogenolysis to toluene.



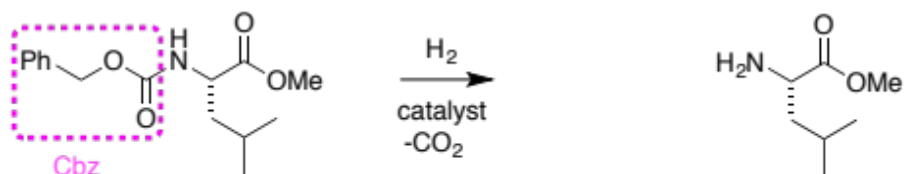


does not reduce the base



It tends to be *harder* to remove benzyl groups from amines than from alcohols

benzyl group is connected to the oxygen of a carbamate, *ie* benzyloxycarbonyl or *Cbz*.



F. Double Bond Equivalents

convert ethene and ethyne into ethane requires *1* and *2* molecules of H_2

Conversion of benzene to hexane would require *4* molecules of H_2

For hydrocarbons containing n carbon atoms, the DBE *can* be calculated

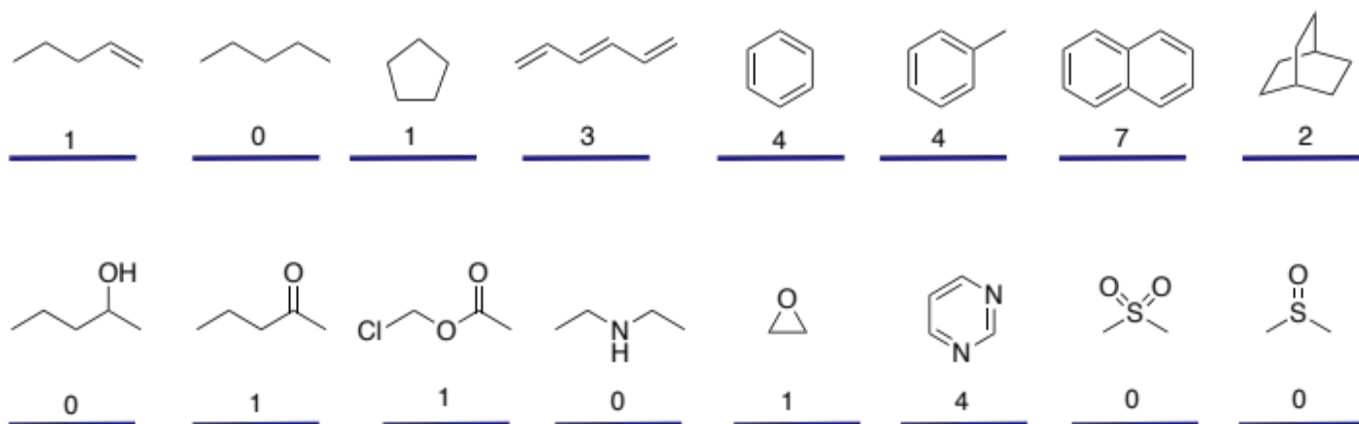
halogenated hydrocarbons containing n carbon atoms, *can* be calculated by replacing the halogen atoms

DBEs of acetone and *cis*-1,2-cyclohexandiol are **1** and **1**, respectively.

may be ignored to calculate the DBE, eg acetone C_3H_6O may be considered to be C_3H_6 . (*True*, check

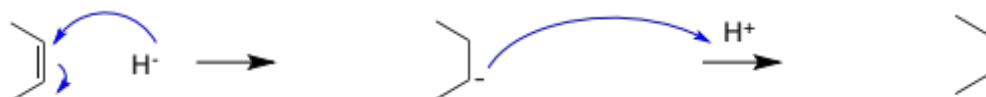
DBEs of 3-aminopropene and pyridine are **1** and **4**

calculating the DBE, eg ethylamine C_2H_7N (DBE = **0**) may be considered to be C_3H_6 . (*True*, check

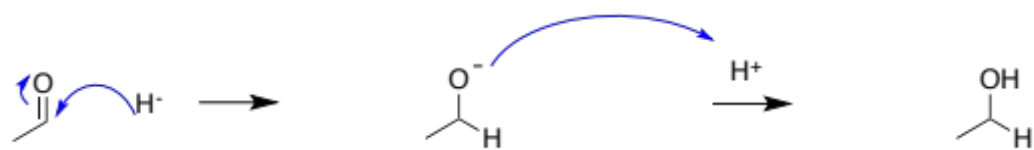


They *do not* apply when calculating unsaturation between two atoms not including carbon but addition of O and S obviously changes oxidation state but *does not* change DBEs.

G. Hydridic Reductions



hard



easy