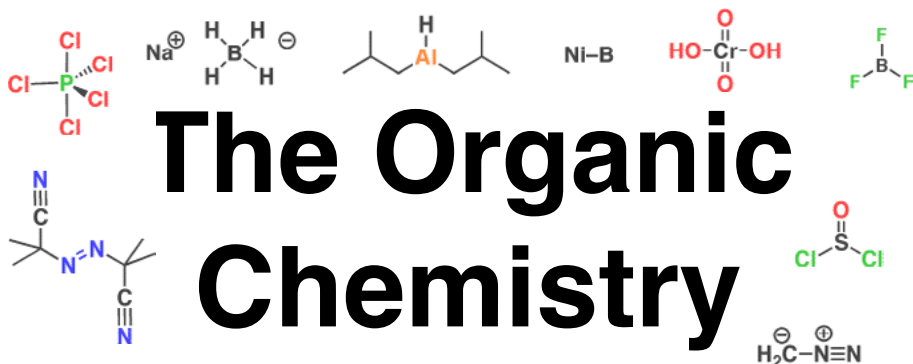
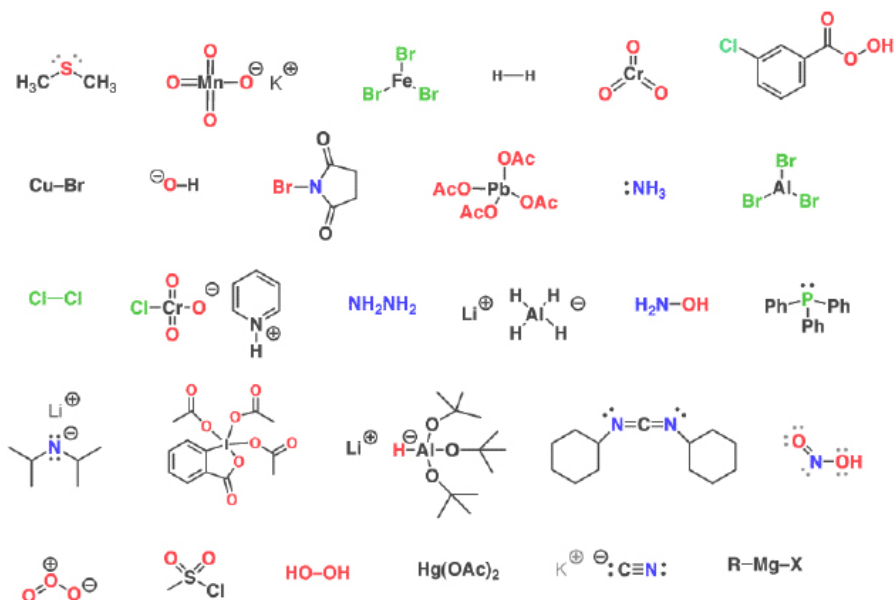




The Organic Chemistry Reagent Guide



masterorganicchemistry.com

The Organic Chemistry Reagent Guide

I'm an online organic chemistry tutor. Over the past several years I've spent over two thousand hours coaching students in organic chemistry courses. One of the most consistent complaints my students express to me is what a nightmare it is to keep track of the vast number of different reagents in their organic chemistry course. I found myself answering the same questions again and again: "What is DIBAL?", "What does DMSO do?", "What reagents can I use to go from an alcohol to a carboxylic acid?". While textbooks indeed do contain this information, the important contents can be scattered throughout a 1000+ page tome. Furthermore, online resources like Wikipedia are often not aimed at the precise needs of the student studying introductory organic chemistry.

I thought it would be useful to take all the reagents that students encounter in a typical 2-semester organic chemistry course and compile them into a big document. Hundreds of hours of work later, the result is before you: "The Organic Chemistry Reagent Guide".

This document is divided into four parts:

Part 1: Quick Index of Reagents. All the key reagents and solvents of organic chemistry on one page. In an upgrade from Version 1, this is now completely clickable.

Part 2: Reagent profiles. Each reagent (>80 in all) has its own section detailing the different reactions it performs, as well as the mechanism for each reaction (where applicable).

Part 3: Useful tables. This section has pages on common abbreviations, functional groups, common acids and bases, oxidizing and reducing agents, organometallics, reagents for making alkyl and acid halides, reagents that transform aromatic rings, types of arrows, and solvents.

Part 4: Transition-Metal Catalyzed Reactions. An increasing number of courses are including sections on olefin metathesis and palladium catalyzed carbon-carbon bond forming reactions. This goes in direct opposition to the admonishment of many professors to "don't memorize, understand!" because the necessary conceptual tools to truly understand these reactions are not provided. Nevertheless, one consistent complaint from previous versions was that these reagents and reactions were not covered. So in this edition a section on these reactions, their reagents, and the mechanisms has been included.

I would like to thank everyone who has helped with proofreading and troubleshooting, in particular Dr. Christian Drouin whose contributions were immensely valuable. I would also like to thank Dr. Adam Azman, Shane Breazeale, Dr. Tim Cernak, Tiffany Chen, Jon Constan, Mike Evans, Mike Harbus, Dr. Jeff Manthorpe, for helpful suggestions, along with countless readers who reported small errors and typos in the first edition.

The primary references used for this text are "Organic Chemistry" by Maitland Jones Jr. (2nd edition) and "March's Advanced Organic Chemistry" (5th edition).

This work is continually evolving. Although considerable effort has been expended to make this as thorough as possible, no doubt you will encounter reagents in your course that are not covered here. Please feel free to suggest reagents that can be included in future editions. Furthermore you may also find some conflicts between the material in this Guide and that in your course. Where conflicts arise, your instructor is the final authority.

Any errors in this document are my own; I encourage you to alert me of corrections by email at james@masterorganicchemistry.com

Above all, else: I hope this Guide is useful to you!

And if you have any suggestions or find mistakes, please leave [feedback](#)

Sincerely, James A. Ashenhurst, Ph.D.
 Founder, MasterOrganicChemistry.com
James@masterorganicchemistry.com
 Twitter: @jamesashchem

Guide contents copyright 2015, James A. Ashenhurst. All rights reserved. This took hundreds of hours to put together. Stealing is bad karma. Please, don't do it.

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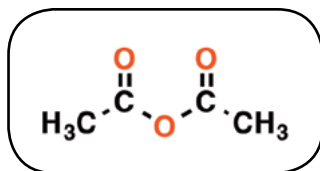
Reagents and Solvents

Ac ₂ O	Acetic Anhydride	6	HgSO ₄	Mercuric Sulfate	54
AgNO ₃	Silver Nitrate	7	HI	Hydroiodic acid	55
Ag ₂ O	Silver Oxide	8	HIO ₄	Periodic acid	57
AIBN	[2,2'-Azobis(2-methyl propionitrile)]	9	HONO	Nitrous Acid (HNO ₂)	58
AlBr ₃	Aluminum bromide	10	HNO ₃	Nitric Acid	59
AlCl ₃	Aluminum chloride	11	H ₂ O ₂	Hydrogen peroxide	60
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BH ₃	Borane	14	H ₂ SO ₄	Sulfuric acid	63
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BsCl	<i>p</i> -bromobenzene sulfonyl chloride	19	KMnO ₄	Potassium permanganate	66
CCl ₄	Carbon Tetrachloride	151	KCN	Potassium cyanide	23
CH ₂ Cl ₂	Dichloromethane	151	KO ^t Bu	Potassium <i>t</i> -butoxide	69
Cl ₂	Chlorine	20	KPhth	Potassium Phthalimide	70
CN	Cyanide ion	23	LDA	Lithium diisopropyl amide	71
CrO ₃	Chromium trioxide	24	Li	Lithium	72
CuBr	Copper (I) Bromide	26	Lindlar's Catalyst		74
CuCl	Copper (I) Chloride	27	LiAlH ₄	Lithium aluminum hydride	75
CuI	Copper (I) Iodide	28	LiAlH(O ^t Bu) ₃	Lithium tri <i>tert</i> -butoxy aluminum hydride	77
D	Deuterium	32	<i>m</i> -CPBA	<i>m</i> -chloroperoxy benzoic acid	78
DBU	1,8-Diazobicyclo undec-7-ene	133	Mg	Magnesium	80
DCC	<i>N,N'</i> -dicyclohexane carbodiimide	29	MsCl	Methanesulfonyl chloride	81
CH ₂ N ₂	Diazomethane	31	NaN ₃	Sodium azide	82
DIBAL	Di-isobutyl aluminum hydride	33	Na	Sodium	83
DMF	<i>N,N'</i> -Dimethylformamide	151	NaBH ₄	Sodium borohydride	85
DMP	Dess-Martin Periodinane	35	NaBH(OAc) ₃	Sodium triacetoxo borohydride	87
DMS	Dimethyl sulfide	30	NaCNBH ₃	Sodium cyanoborohydride	88
DMSO	Dimethyl sulfoxide	151	Na ₂ Cr ₂ O ₇	Sodium dichromate	50
Et ₂ O	Diethyl ether	151	NaH	Sodium Hydride	89
Fe	Iron	36	NaIO ₄	Sodium periodate	90
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HCl	Hydrochloric acid	48	NH ₃	Ammonia	99
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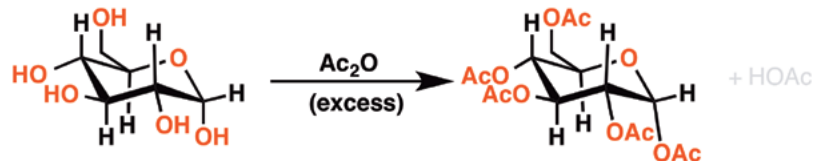
NMO	<i>N</i> -methylmorpholine		<u>End Notes</u>	
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SOBr ₂	Thionyl bromide	123		
SOCl ₂	Thionyl chloride	124		
Sn	Tin	125		
TBAF	Tetrabutyl ammonium fluoride	126		
THF	Tetrahydrofuran	151		
TMSCl	Trimethylsilyl chloride	127		
TsCl	<i>p</i> -Toluenesulfonyl chloride	128		
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Zn	Zinc	130		
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Ac₂O Acetic Anhydride

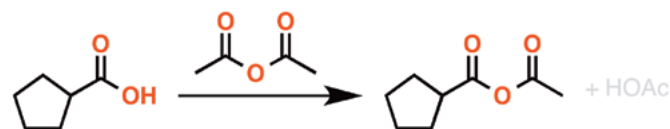


What it's used for: Converts alcohols to acetates (esters). Can be used as a temporary protecting group for alcohols, especially with sugars. Used to convert carboxylic acids to anhydrides. Can also be used in the Friedel-Crafts acylation of aromatic rings.

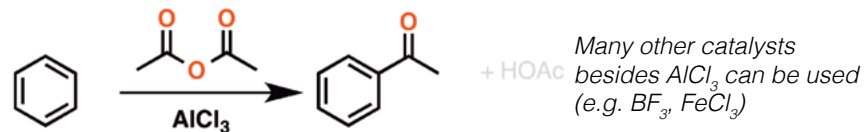
Example 1: Acetylation of alcohols



Example 2: Conversion of carboxylic acids to anhydrides

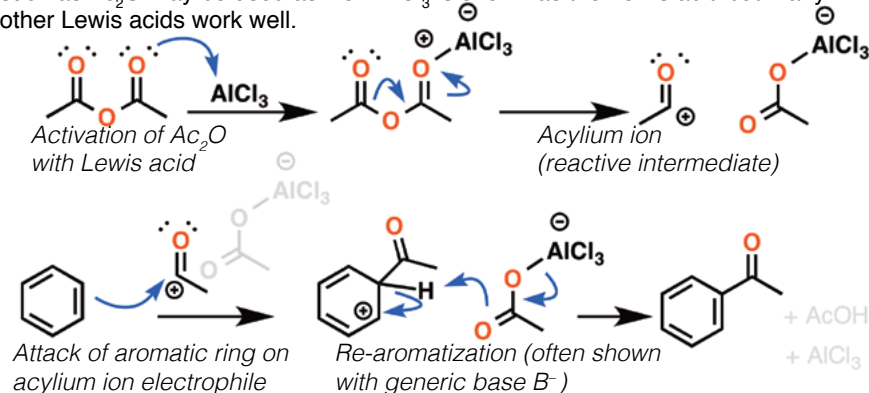


Example 3: Friedel-Crafts acylation

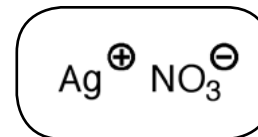


How it works: Friedel-Crafts Acylation

Acid halides are most often used for the Friedel-Crafts acylation, but anhydrides such as Ac₂O may be used as well. AlCl₃ is shown as the Lewis acid but many other Lewis acids work well.



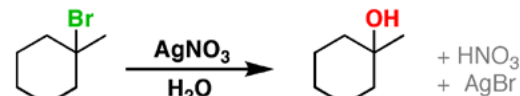
AgNO₃ Silver Nitrate



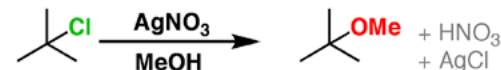
What it's used for: Silver nitrate will react with alkyl halides to form silver halides and the corresponding carbocation. When a nucleophilic solvent such as water or an alcohol is used, this can result in an S_N1 reaction. It can also react in the Tollens reaction to give carboxylic acids from aldehydes.

Similar to: AgBF₄

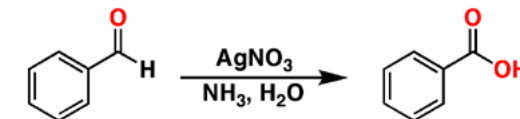
Example 1: Substitution (S_N1) conversion of alkyl halides to alcohols



Example 2: Substitution (S_N1) conversion of alkyl halides to ethers

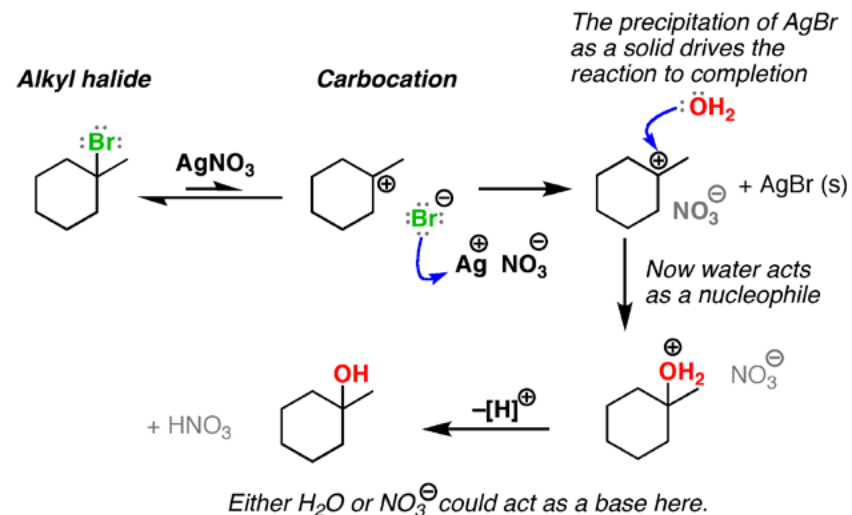


Example 3: Tollens oxidation - conversion of aldehydes to carboxylic acids

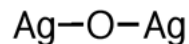


How it works: S_N1 Reaction of alkyl halides

Silver nitrate, AgNO₃, has good solubility in aqueous solution, but AgBr, AgCl, and AgI do not. Ag⁺ coordinates to the halide, which then leaves, forming a carbocation. The carbocation is then trapped by solvent (like H₂O)



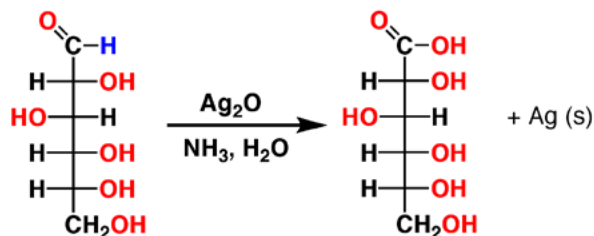
Ag₂O Silver Oxide


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What it's used for: Silver oxide is used in the Tollens reaction to oxidize aldehydes to carboxylic acids. This is the basis of a test for the presence of aldehydes, since a mirror of Ag⁰ will be deposited on the flask. It is also used as the base in the Hoffman elimination.

Similar to: [AgNO₃](#)

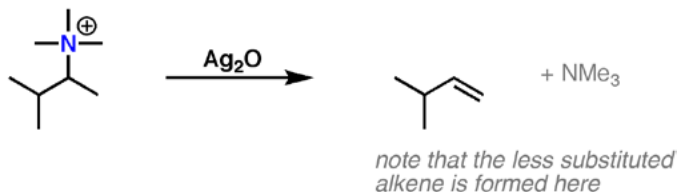
Example 1: Tollens oxidation of aldehydes to carboxylic acids



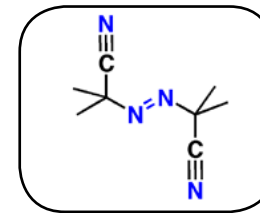
Aldehyde (open form)

This reaction is usually introduced in the context of sugar chemistry

Example 2: As the base in the Hoffmann elimination



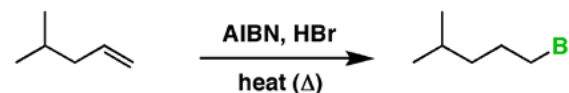
AIBN [2,2'-Azobis(2-methyl propionitrile)]



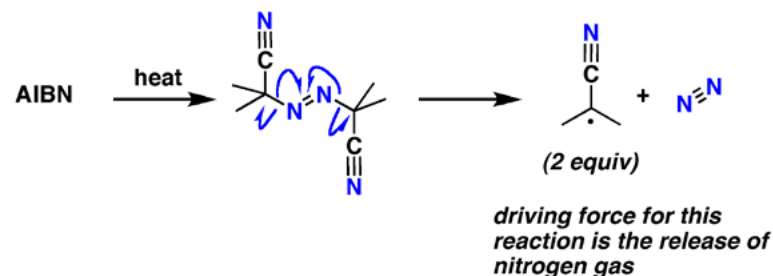
What it's used for: Free radical initiator. Upon heating, AIBN decomposes to give nitrogen gas and two free radicals.

Similar to: [RO-OR](#) ("peroxides"), benzoyl peroxide

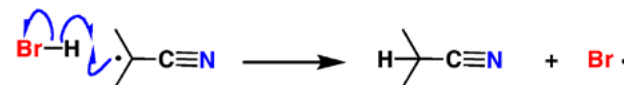
Example 1: Free-radical halogenation of alkenes



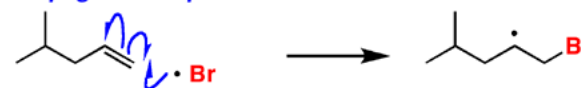
How it works: *Free-radical halogenation of alkenes*



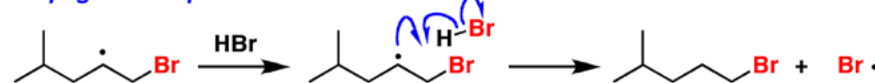
Initiation:



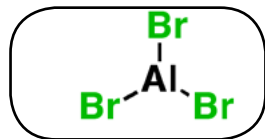
Propagation step 1:



Propagation step 2:



AlBr₃ Aluminum Bromide



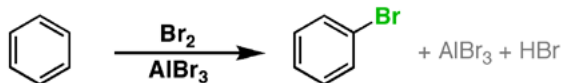
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Also known as: Aluminum tribromide

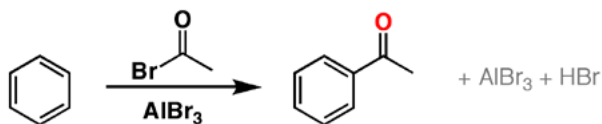
What it's used for: Lewis acid, promoter for electrophilic aromatic substitution

Similar to: FeCl₃, FeBr₃, AlCl₃

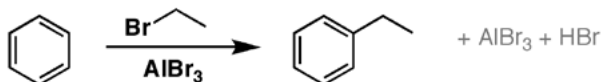
Example 1: Electrophilic bromination - conversion of arenes to aryl halides



Example 2: Friedel-Crafts acylation - conversion of arenes to aryl ketones

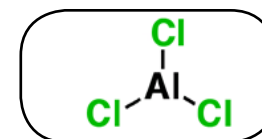


Example 3: Friedel-Crafts alkylation - conversion of arenes to alkyl arenes



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AlCl₃ Aluminum chloride

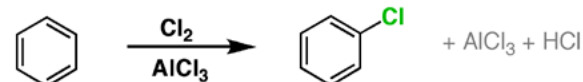


Also known as: Aluminum trichloride

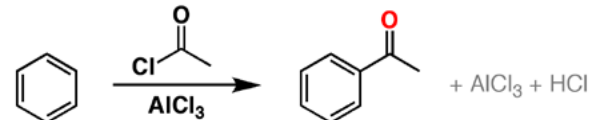
What it's used for: Aluminum chloride is a strong Lewis acid. It can be used to catalyze the chlorination of aromatic compounds, as well as Friedel-Crafts reactions. It can also be used in the Meerwein-Ponndorf-Verley reduction.

Similar to: AlBr₃, FeBr₃, FeCl₃

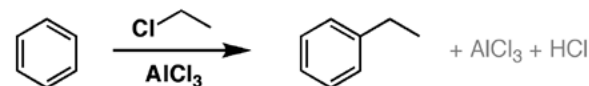
Example 1: Electrophilic chlorination - conversion of arenes to aryl halides



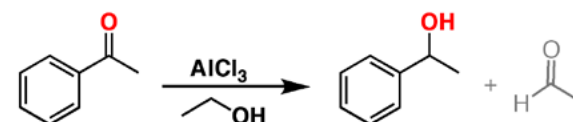
Example 2: Friedel-Crafts acylation - conversion of arenes to aryl ketones



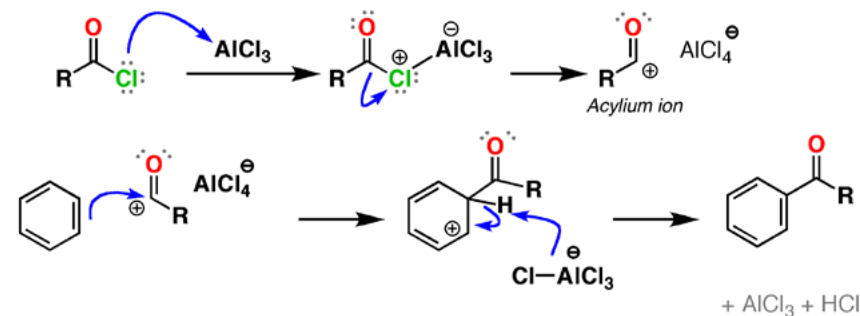
Example 3: Friedel-Crafts alkylation - conversion of arenes to alkyl arenes



Example 4: Meerwein-Ponndorf-Verley reduction - reduction of ketones and alcohols to aldehydes



How it works: *Friedel-Crafts acylation*

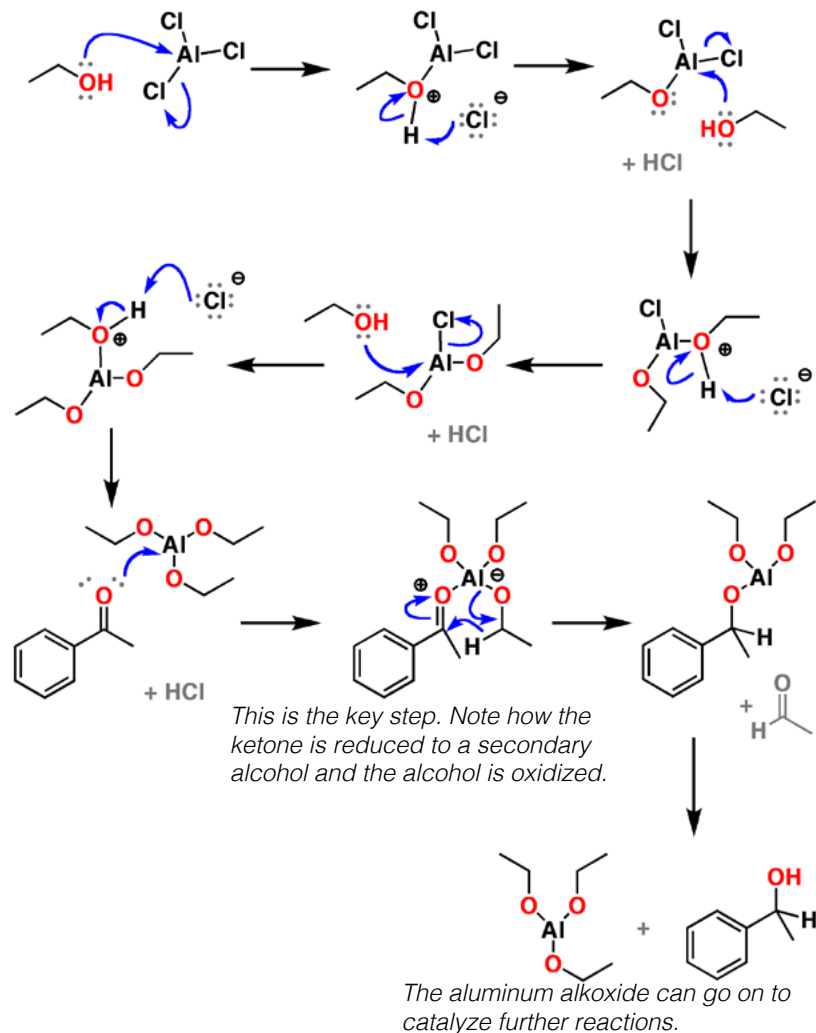


AlCl₃ (continued)

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How it works: *Meerwein-Ponndorf-Verley Oxidation*

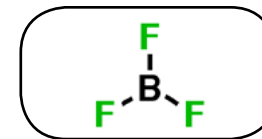
This reaction is typically run using an alcohol solvent such as ethanol or isopropanol. When AlCl₃ is added, the solvent replaces the chloro groups:



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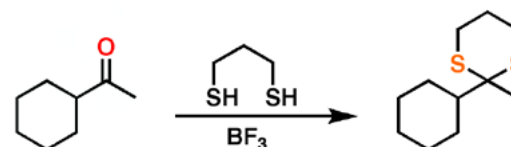
BF₃ Boron Trifluoride



What it's used for: Boron trifluoride is a strong Lewis acid. It is commonly used for the formation of thioacetals from ketones (or aldehydes) with thiols. The product is a thioacetal.

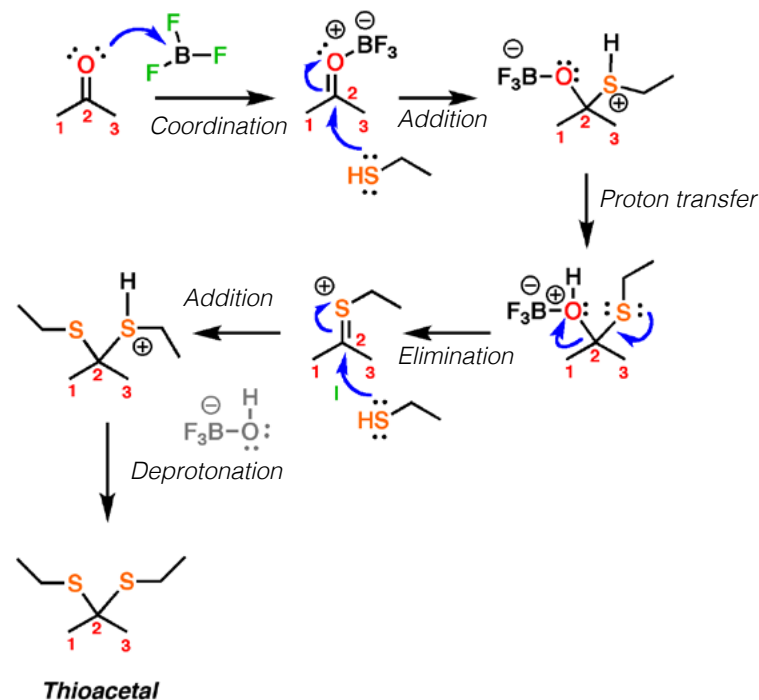
Similar to: FeCl₃, AlCl₃ (also Lewis acids)

Example 1: Conversion of ketones to thioacetals



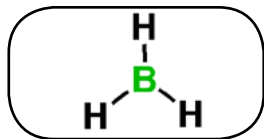
How it works: *Formation of thioacetals*

BF₃ acts as a Lewis acid, coordinating to the carbonyl oxygen and activating the carbonyl carbon towards attack by sulfur.



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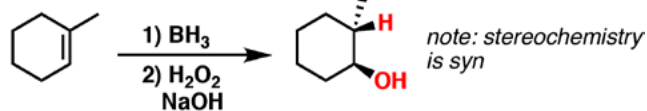
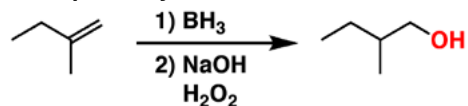
BH₃ Borane


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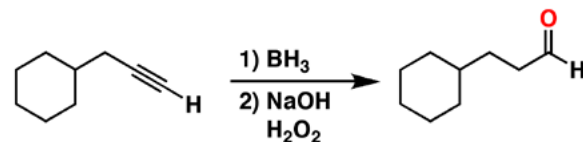
What it's used for: Borane is used for the hydroboration of alkenes and alkynes.

Similar to: B₂H₆ ("diborane"), BH₃·THF, BH₃·SMe₂, disiamylborane, 9-BBN (for our purposes, these can all be considered as "identical").

Example 1: Hydroboration reaction - conversion of alkenes to alcohols

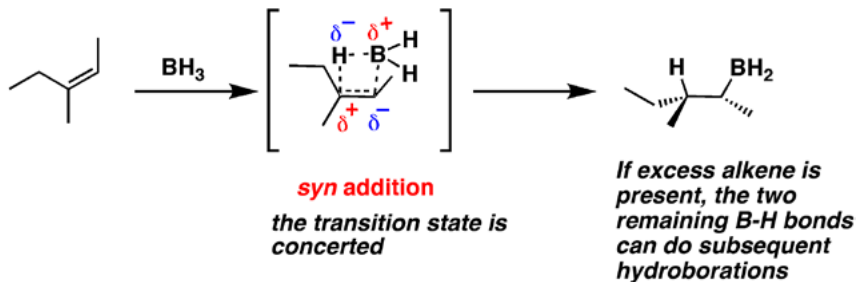


Example 2: Hydroboration reaction - conversion of alkynes to aldehydes



How it works: Hydroboration of alkenes

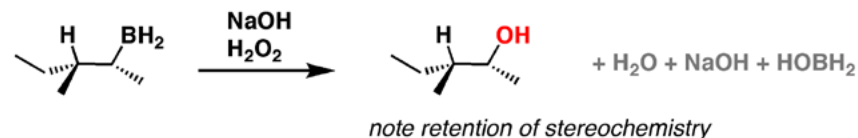
Hydroboration is notable in that the **boron adds to the less substituted end of the alkene**. This is usually referred to as "anti-Markovnikov" selectivity. The reason for the selectivity is that the **boron hydrogen bond is polarized so that the hydrogen has a partial negative charge and the boron has a partial positive charge (due to electronegativity)**. In the transition state, the **partially negative hydrogen "lines up" with the more substituted end of the double bond** (i.e. the end containing more bonds to carbon) since this will preferentially stabilize partial positive charge. The hydrogen and boron add **syn** to the double bond.


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BH₃ (continued)

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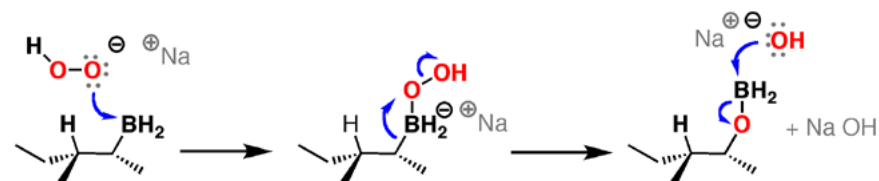
The second step of the hydroboration is an oxidation that replaces the C–B bond with a C–O bond



The first step is deprotonation of hydrogen peroxide by sodium hydroxide; this makes the peroxide ion more nucleophilic (and more reactive)

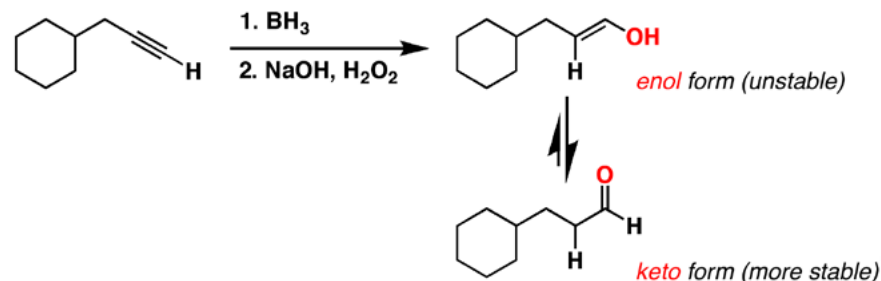


The deprotonated peroxide then attacks the boron, which then undergoes rearrangement to break the weak O–O bond. Then, hydroxide ion cleaves the B–O bond to give a deprotonated alcohol, which is then protonated by alcohol.



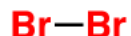
How it works: Hydroboration of alkynes

Hydroboration of alkynes forms a product called an **enol**. Through a process called **tautomerism**, the enol product is converted into its more stable constitutional isomer, the **keto** form. In the case of a terminal alkyne (one which has a C–H bond) an aldehyde is formed.


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Br₂ Bromine

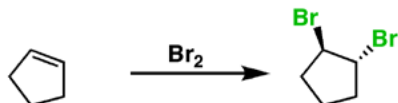
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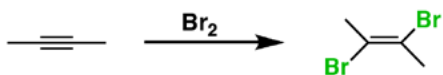
What it's used for: Bromine will react with alkenes, alkynes, aromatics, enols, and enolates, producing brominated compounds. In the presence of light, bromine will also replace hydrogen atoms in alkanes. Finally, bromine is also used to promote the Hoffmann rearrangement of amides to amines.

Similar to: NBS, Cl₂, I₂, NIS, NCS

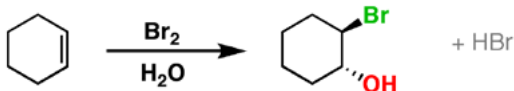
Example 1: Bromination - conversion of alkenes to vicinal dibromides



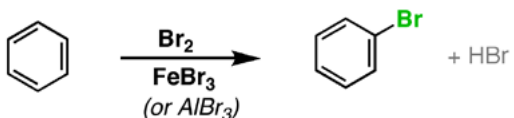
Example 2: Bromination - conversion of alkynes to vicinal dibromides



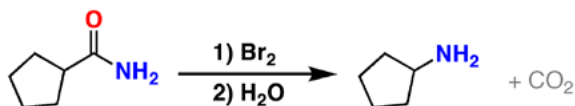
Example 3: Conversion of alkenes to halohydrins



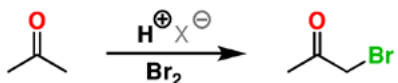
Example 4: Electrophilic bromination - conversion of arenes to aryl bromides.



Example 5: Hoffmann rearrangement - conversion of amides to amines

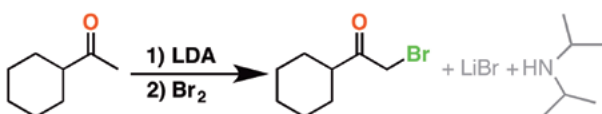


Example 6: Conversion of ketones to α-bromoketones



"HX" is just a strong acid (e.g. HBr)

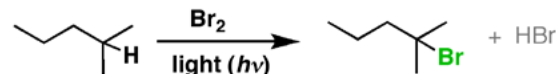
Example 7: Conversion of enolates to α-bromoketones



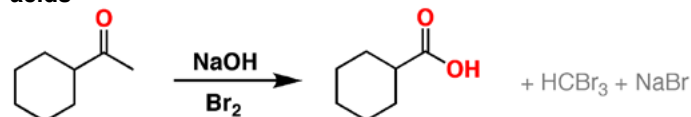
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Br₂ (continued)

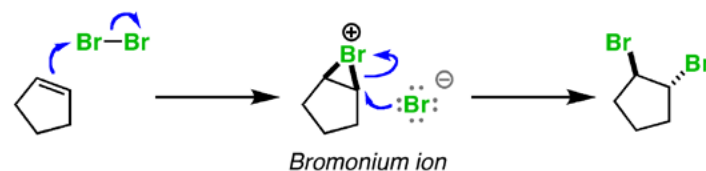
Example 8: Radical halogenation - conversion of alkanes to alkyl bromides



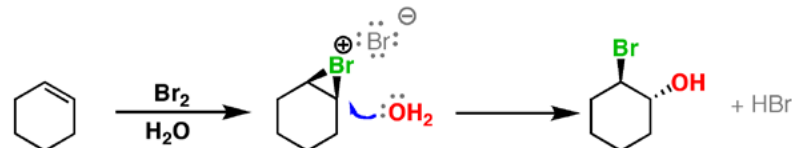
Example 9: Haloform reaction - conversion of methyl ketones to carboxylic acids



How it works: Bromination of alkenes



Treatment of an alkene with Br₂ leads to the formation of a bromonium ion, which undergoes backside attack. In the presence of a solvent that can act as a nucleophile, the halohydrin is obtained:



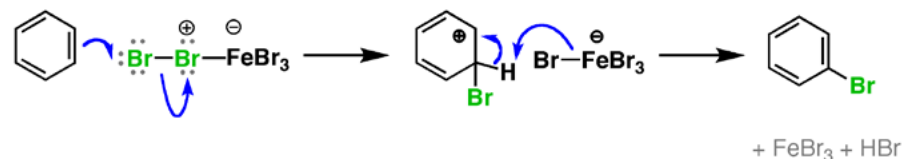
How it works: Bromination of alkenes

Bromine is made more electrophilic by a Lewis acid such as FeBr₃; it can then undergo attack by an aromatic ring, resulting in electrophilic aromatic substitution of H for Br

Step 1: Activation



Step 2: Electrophilic aromatic substitution

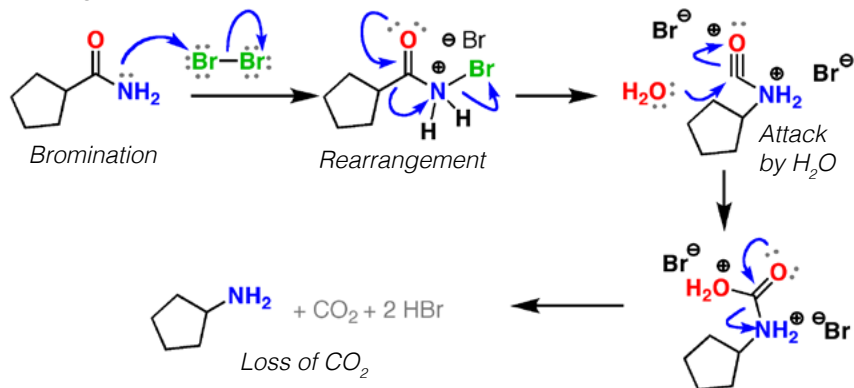


Br₂ (continued)

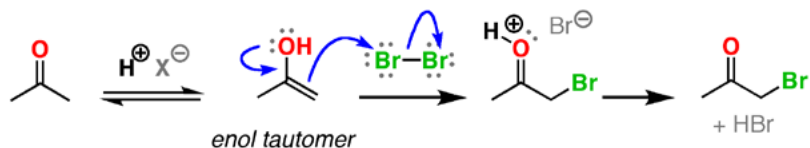
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How it works: Hoffmann Rearrangement

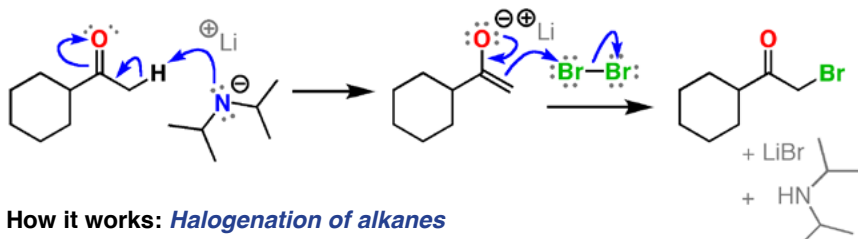
In this reaction, the lone pair on nitrogen attacks bromine, which leads to a rearrangement. Attack at the carbonyl carbon by water then leads to loss of CO₂, resulting in the formation of the free amine.



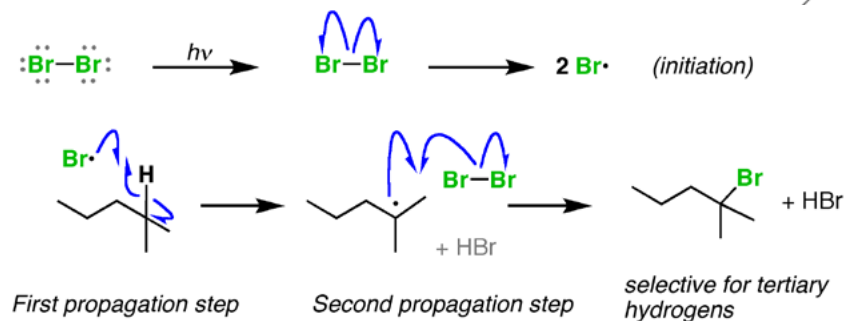
How it works: Bromination of enols



How it works: Bromination of enolates



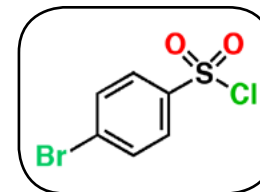
How it works: Halogenation of alkanes



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BsCl

p-bromobenzenesulfonyl chloride

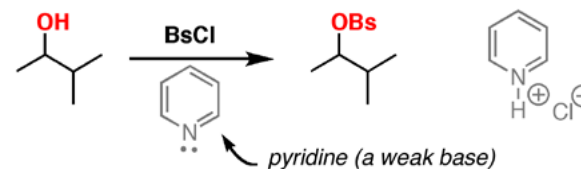


Also known as: Brosyl chloride

What it's used for: *p*-bromobenzene sulfonyl chloride (BsCl) is used to convert alcohols into good leaving groups. It is essentially interchangeable with TsCl and MsCl for this purpose.

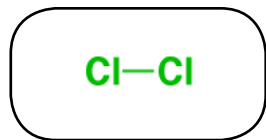
Similar to: TsCl, MsCl

Example 1: Conversion of alcohols into alkyl brosylates



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Cl₂ Chlorine

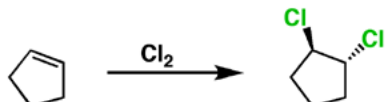


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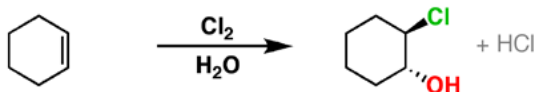
What it's used for: Chlorine is a very good electrophile. It will react with double and triple bonds, as well as aromatics, enols, and enolates to give chlorinated products. In addition it will substitute Cl for halogens when treated with light (free-radical conditions). Finally, it assists with the rearrangement of amides to amines (the Hoffmann rearrangement).

Similar to: NCS, Br₂, NBS, I₂, NIS

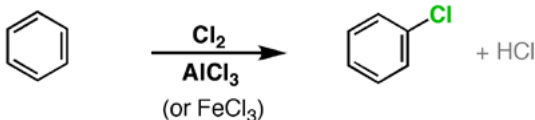
Example 1: Chlorination - conversion of alkenes to vicinal dichlorides



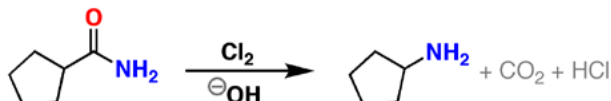
Example 2: Conversion of alkenes to chlorohydrins



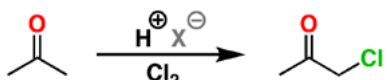
Example 3: Electrophilic chlorination - conversion of arenes to chloroarenes



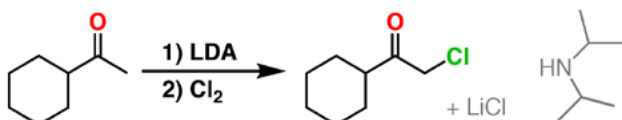
Example 4: Hoffmann rearrangement - conversion of amides to amines



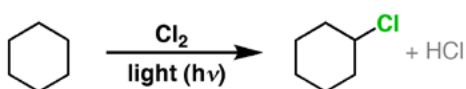
Example 5: Conversion of ketones to α-chloro ketones



Example 6: Conversion of enolates to α-chloro ketones



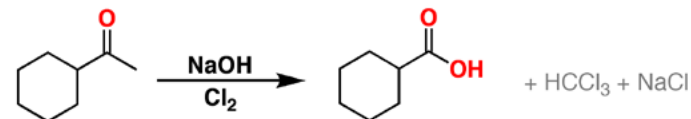
Example 7: Radical chlorination of alkanes to alkyl chlorides



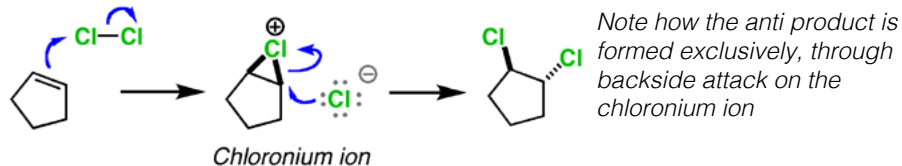
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Cl₂ (continued)

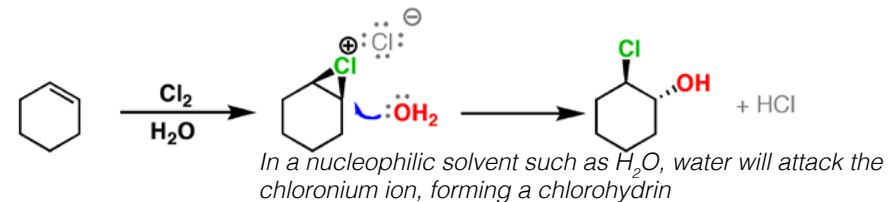
Example 8: The haloform reaction



How it works: Chlorination of alkenes



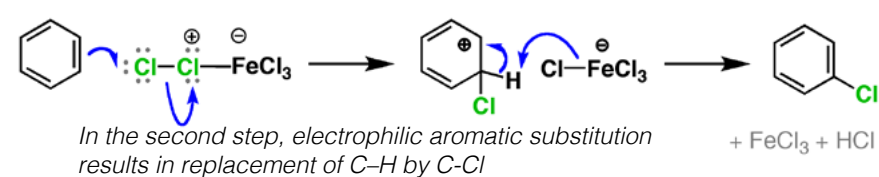
How it works: Chlorohydrin formation



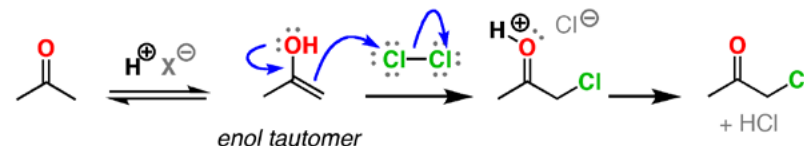
How it works: Electrophilic chlorination

Step 1: Activation
In the first step of this reaction, a Lewis acid such as FeCl₃ activates Cl₂ towards attack by the aromatic ring.

Step 2: Electrophilic aromatic substitution



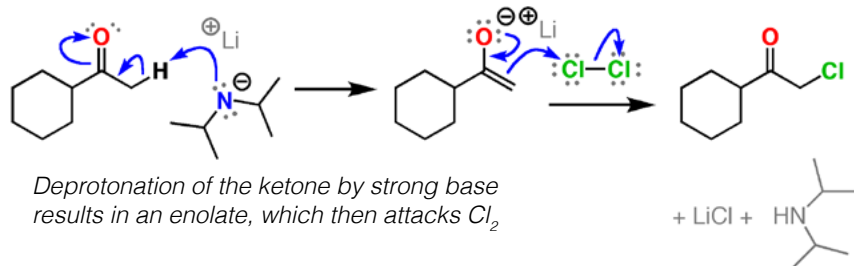
How it works: Chlorination of ketones under acidic conditions



Cl₂ (continued)

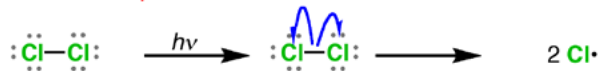
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How it works: *Chlorination of enolates*

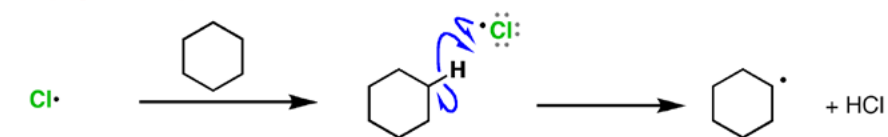


How it works: *Chlorination of alkanes*

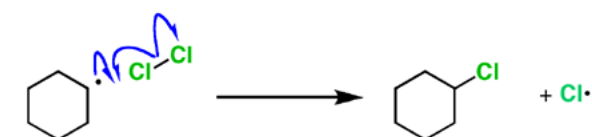
Initiation step



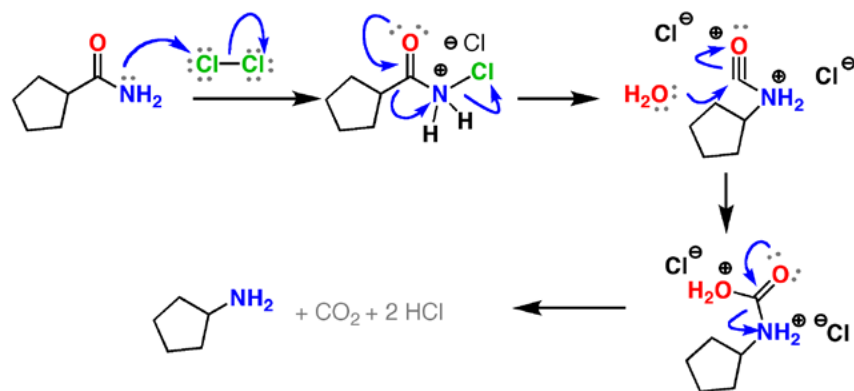
Propagation step #1



Propagation step #2



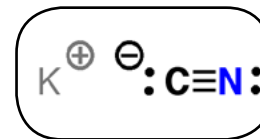
How it works: *Hoffmann Rearrangement*



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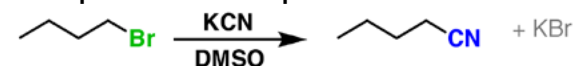
CN Cyanide ion



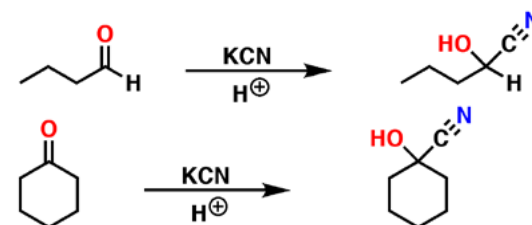
What it's used for: Cyanide ion is a good nucleophile. It can be used for substitution reactions (S_N2), for forming cyanohydrins from aldehydes or ketones, and in the benzoin condensation.

Same as: KCN, NaCN, LiCN

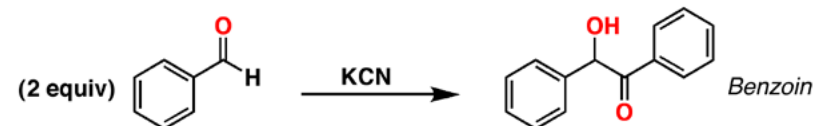
Example 1: As a nucleophile in substitution reactions



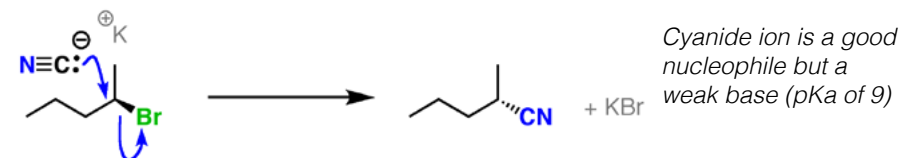
Example 2: Formation of cyanohydrins from aldehydes/ketones



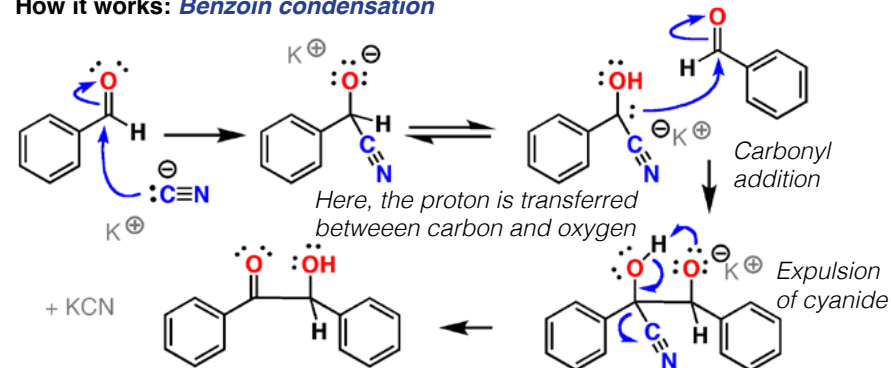
Example 3: In the benzoin condensation



How it works: *Nucleophilic substitution*

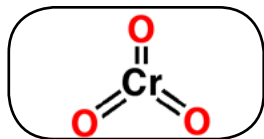


How it works: *Benzoin condensation*



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CrO₃ Chromium trioxide



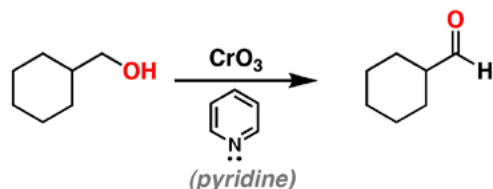
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What it's used for: CrO₃ is an oxidant. When pyridine is present, it is a mild oxidant that will oxidize primary alcohols to aldehydes. However, if water and acid are present, the aldehyde will be oxidized further to the carboxylic acid.

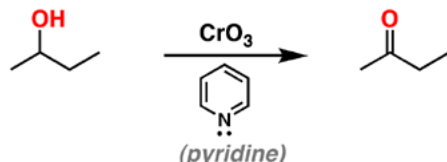
Similar to: PCC (when pyridine is added)

When aqueous acid is present, it is the same or similar to Na₂Cr₂O₇ / K₂Cr₂O₇ / Na₂Cr₂O₇ / H₂CrO₄ (and KMnO₄). **Watch out!** this reagent is the source of much confusion!

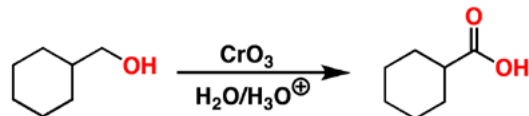
Example 1: Oxidation of primary alcohols to aldehydes (with pyridine)



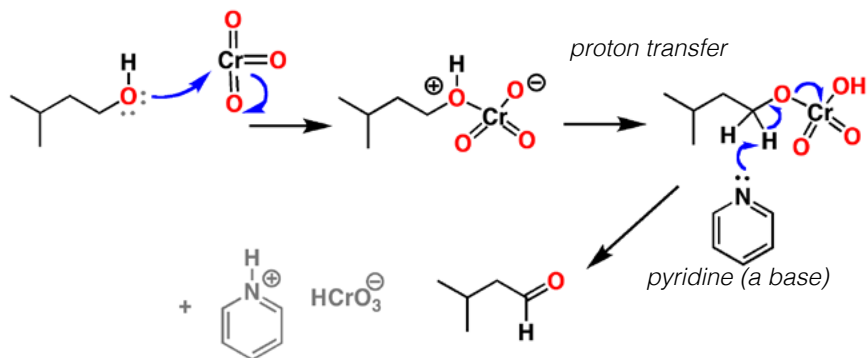
Example 2: Oxidation of secondary alcohols to ketones (with pyridine)



Example 3: Oxidation of primary alcohols to carboxylic acids



How it works: Oxidation of primary alcohols to aldehydes

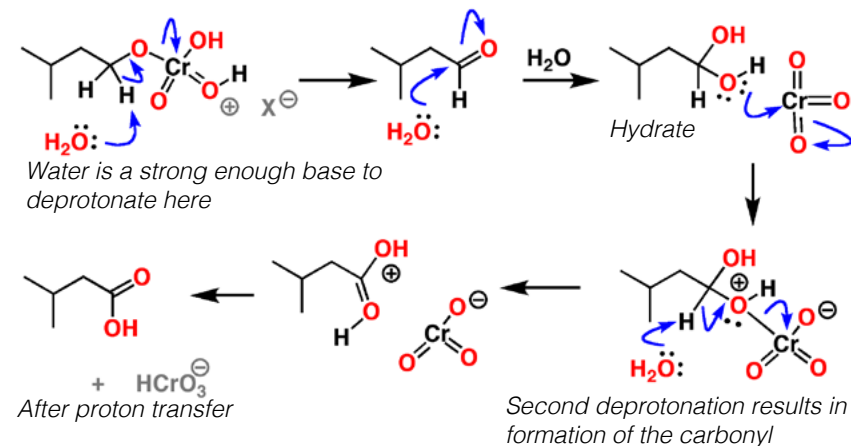


CrO₃ (continued)

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How it works: Oxidation of primary alcohols to carboxylic acids

When water is present the aldehyde will form the hydrate, which will be further oxidized to the carboxylic acid.



CuBr

Copper (I) Bromide

Cu-Br

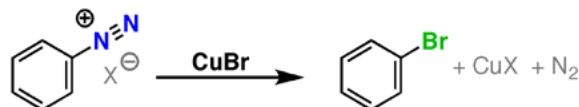
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Also known as: Cuprous bromide

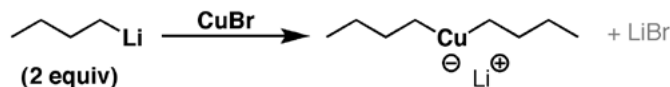
What it's used for: Reacts with aromatic diazonium salts to give aromatic bromides. Also used to make organocuprates (Gilman reagents).

Similar to: Copper(I) cyanide (CuCN), [Copper\(I\) chloride](#), [Copper\(I\) iodide](#)

Example 1: Formation of aryl bromides from aryl diazonium salts



Example 2: Formation of organocuprate reagents (Gilman reagents)

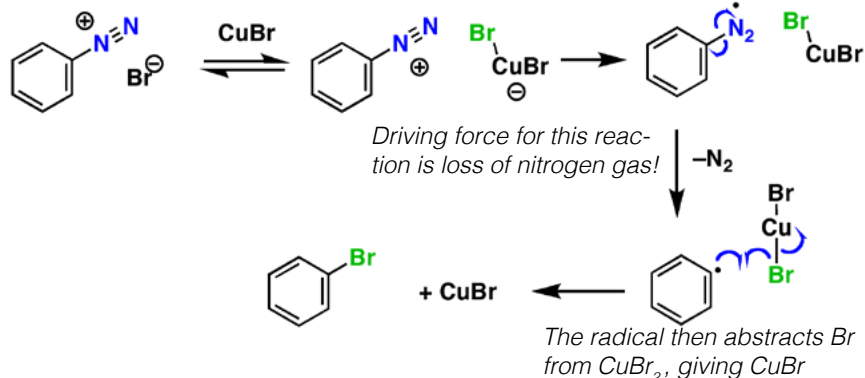


How it works: [Formation of aryl bromides](#)

Not perfectly understood!

It is known that this reaction occurs through a free radical process. Here is a suggested mechanism:

Donation of an electron by Cu(I) to give Cu(II)



CuCl

Copper (I) Chloride

Cu-Cl

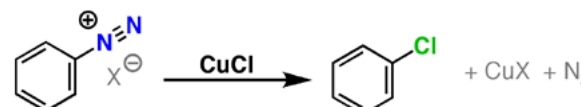
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Also known as: Cuprous chloride

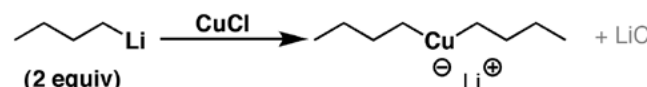
What it's used for: Reacts with aromatic diazonium salts to give aryl chlorides; also used to form organocuprates (Gilman reagents) from organolithium salts.

Similar to: Copper(I) cyanide (CuCN), [Copper bromide](#), [Copper iodide](#)

Example 1: Formation of aryl chlorides from diazonium salts



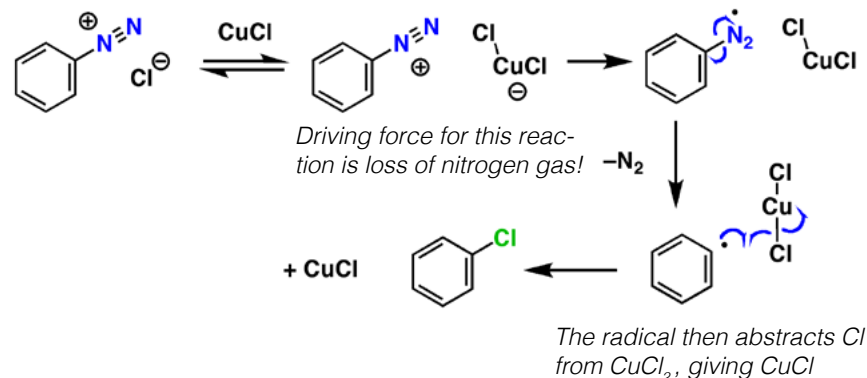
Example 2: Formation of organocuprates (Gilman reagents)



How it works: [Formation of aryl chlorides from aryl diazonium salts](#)

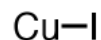
Not perfectly understood, although proceeds through a free radical process. Suggested mechanism:

Donation of an electron by Cu(I) to give Cu(II)



CuI

Copper (I) Iodide

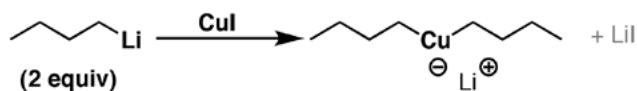

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Also known as: Cuprous iodide

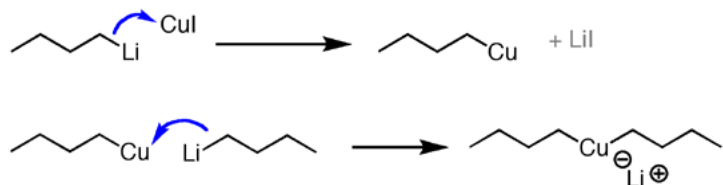
What it's used for: Reacts with alkyllithium reagents to form dialkyl cuprates

Similar to: [CuBr](#), [CuCN](#), [CuCl](#)

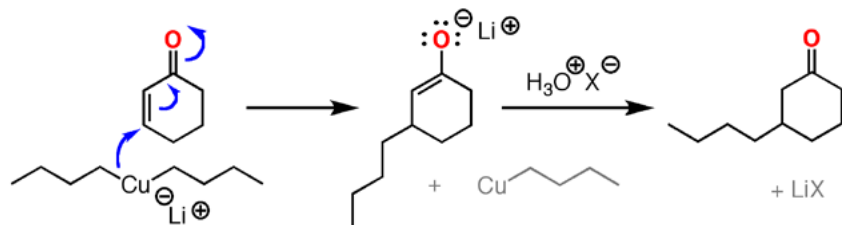
Example 1: Formation of dialkyl cuprates (Gilman reagents)



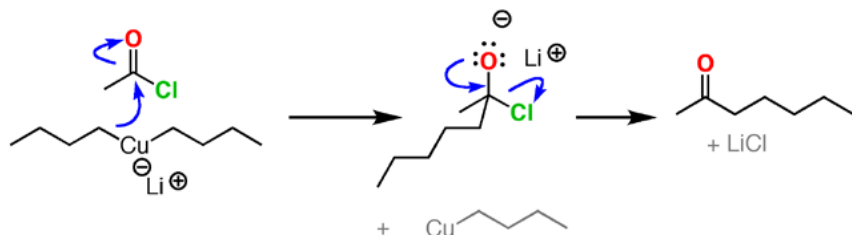
How it works: *Formation of organocuprates*



Cuprates can be used to do conjugate additions [1,4 addition]:

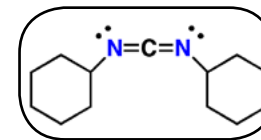


They will also add to acyl halides to give ketones:


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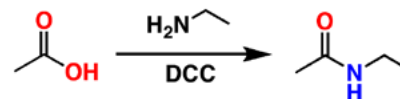
DCC

N,N'-dicyclohexane carbodiimide



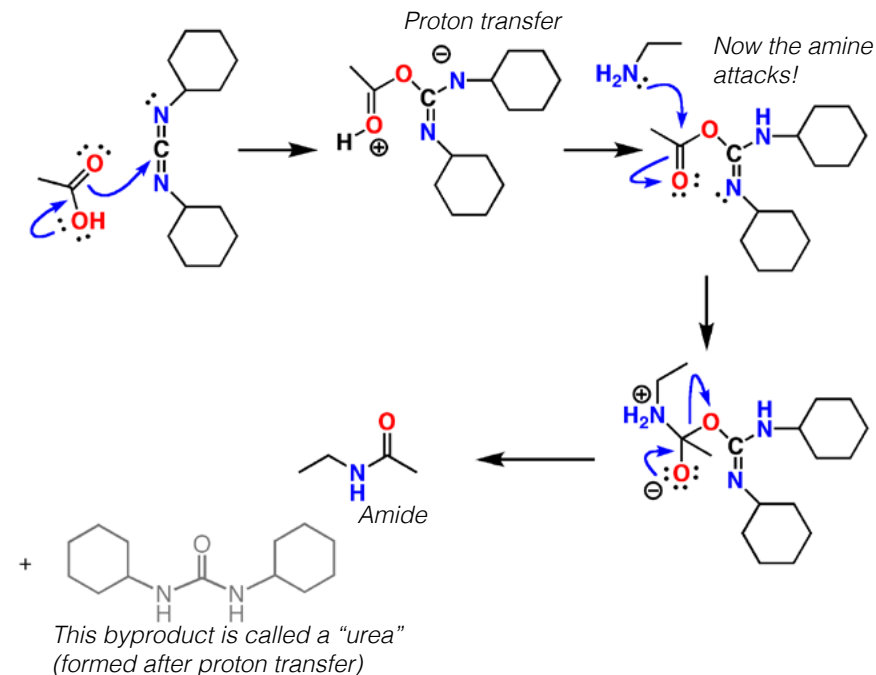
What it's used for: DCC is primarily used for the synthesis of amides from amines and carboxylic acids. It is, essentially, a dehydration reagent (removes water)

Example 1: Formation of amides from carboxylic acids and amines



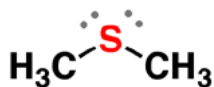
How it works: *Formation of amides from carboxylic acids and amines*

The first step is attack of the carbon on the imide by the oxygen on the carboxylic acid.


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DMS

Dimethyl sulfide



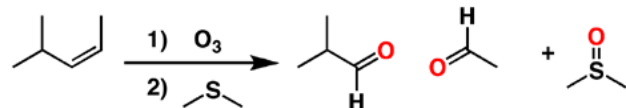
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Also known as: Me₂S, methyl sulfide

What it's used for: Used in the "reductive workup" of ozonolysis, to reduce the ozonide that is formed. DMS is oxidized to dimethyl sulfoxide (DMSO) in the process.

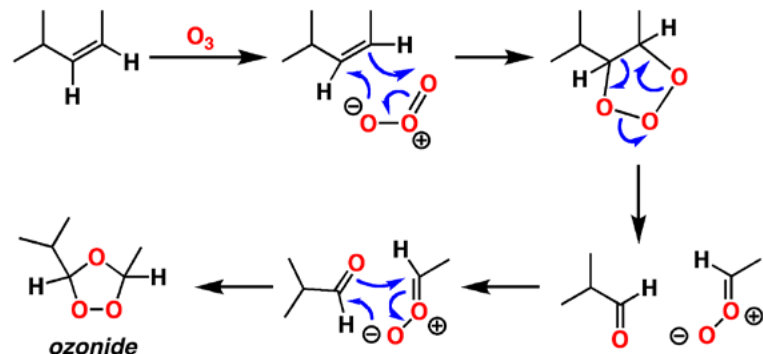
Similar to: Zn (in the reductive workup for ozonolysis)

Example 1: Reductive workup for ozonolysis

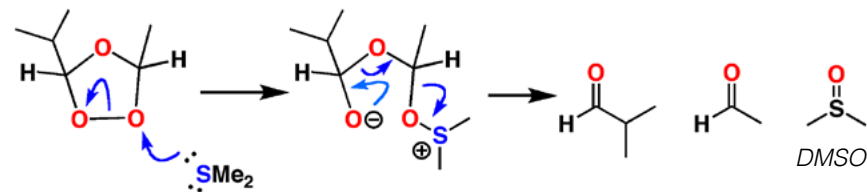


How it works: *Reductive workup for ozonolysis*

The first step is formation of an ozonide by treating an alkene with O₃



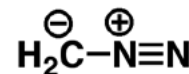
In the second step, the ozonide is treated with DMS, which results in reduction of the ozonide and formation of dimethyl sulfoxide (DMSO)



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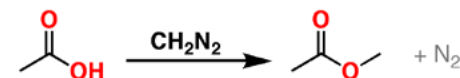
CH₂N₂

Diazomethane

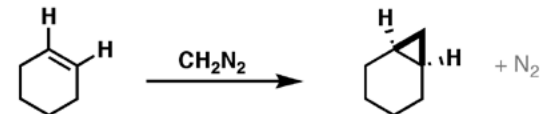


What it's used for: Diazomethane is used for three main purposes: 1) to convert carboxylic acids into methyl esters, and 2) in the Wolff rearrangement, as a means to extend carboxylic acids by one carbon, and 3) for cyclopropanation of alkenes.

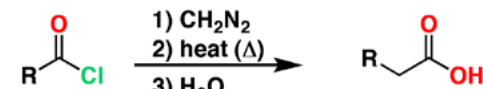
Example 1: Conversion of carboxylic acids to methyl esters



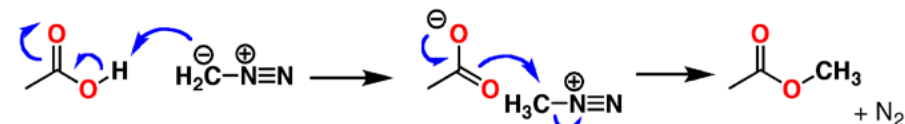
Example 2: Cyclopropanation of alkenes



Example 3: In the Wolff Rearrangement

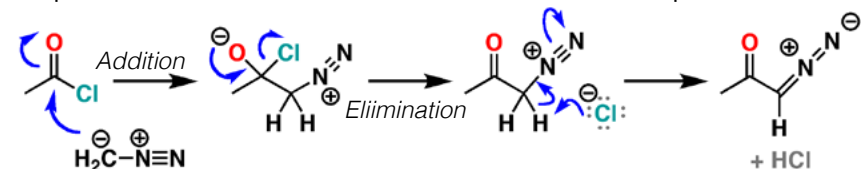


How it works: *Formation of methyl esters*

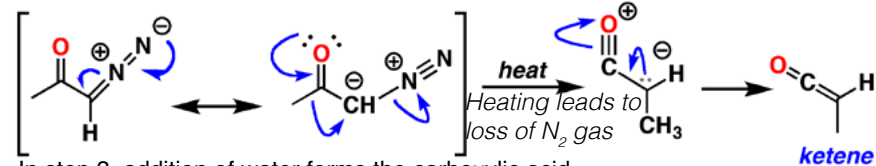


How it works: *Wolff Rearrangement*

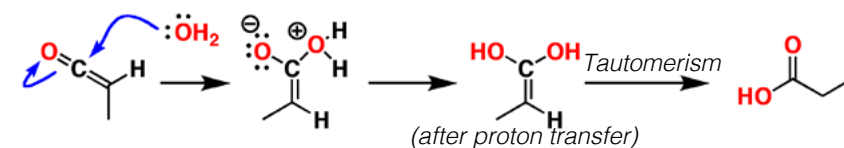
Step 1 is addition of diazomethane to the acid chloride and displacement of Cl.



Step 2 is heat, which initiates the rearrangement, forming a ketene.



In step 3, addition of water forms the carboxylic acid.



D Deuterium

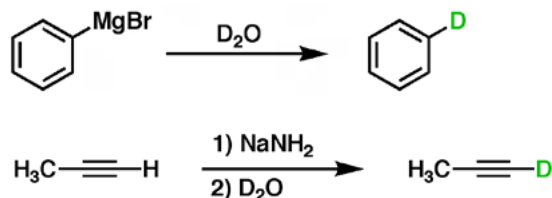
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"D"
e.g. D₂O

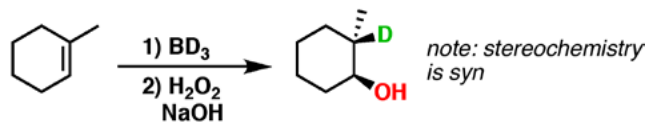
Also known as: "heavy hydrogen"

What it's used for: Deuterium is the heavy isotope of hydrogen, having an atomic weight of two. Deuterium has essentially the same reactivity as hydrogen, but due to the different magnetic properties of the nucleus, it can be differentiated from hydrogen in ¹H NMR. Deuterium analogs of hydrogen-containing reagents can therefore be useful in introducing deuterium as a "label" for examining stereochemistry and mechanisms.

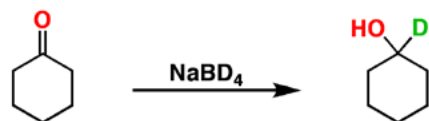
Example 1: Deuterium reagents as acids



Example 2: Hydroboration of alkenes



Example 3: Reduction of ketones

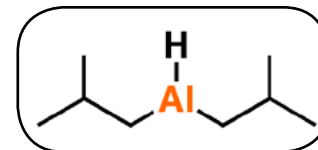


How it works: Deuterium as a reagent

For examples of the mechanisms, see the section for the corresponding hydrogen reagents.

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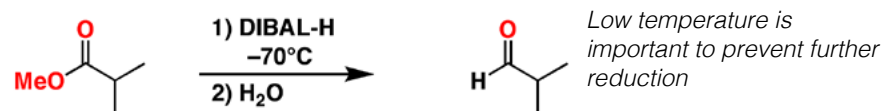
DIBAL Di-isobutyl aluminum hydride



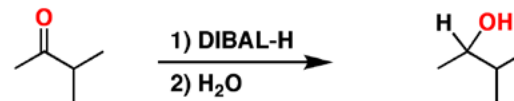
What it's used for: Strong, bulky reducing agent. It is most useful for the reduction of esters to aldehydes: unlike LiAlH₄, it will not reduce the aldehyde further unless an extra equivalent is added. It will also reduce other carbonyl compounds such as amides, aldehydes, ketones, and nitriles.

Similar to: LiAlH₄ (LAH), LiAlH(Ot-Bu)₃

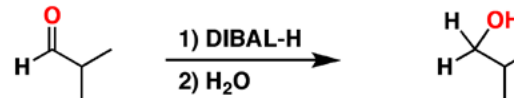
Example 1: Reduction of esters to aldehydes



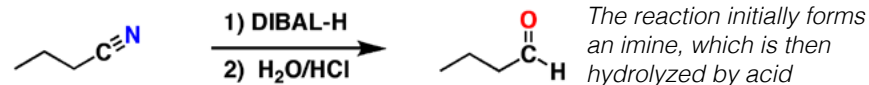
Example 2: Reduction of ketones to secondary alcohols



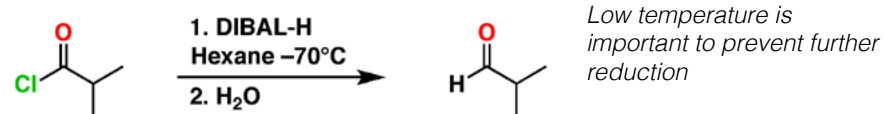
Example 3: Reduction of aldehydes to primary alcohols



Example 4: Reduction of nitriles to aldehydes



Example 5: Reduction of acyl halides to aldehydes

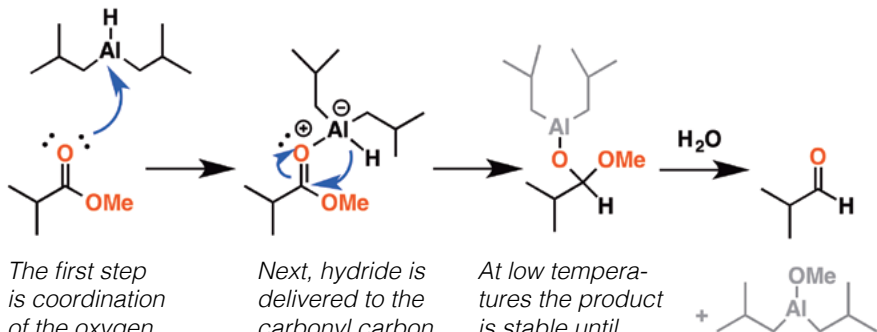


DIBAL (continued)

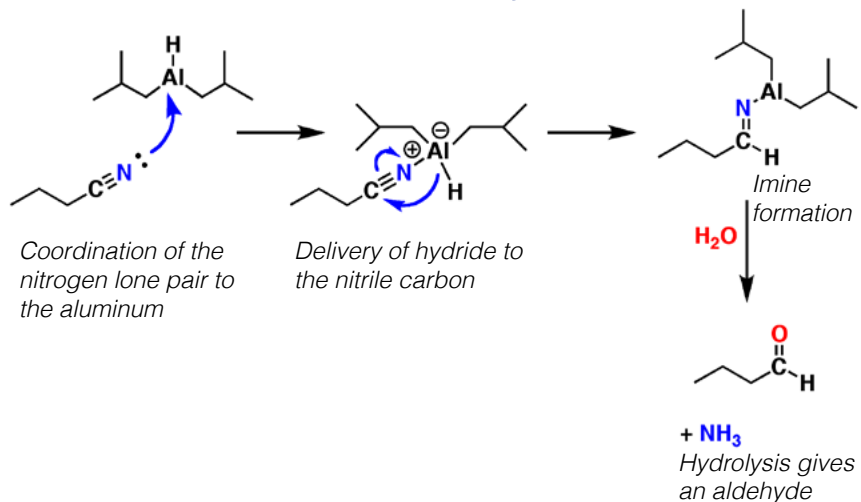
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How it works: *Reduction of esters to aldehydes*

With its bulky isobutyl groups, DIBAL is more sterically hindered than LiAlH_4 . If the temperature is kept low, DIBAL can reduce an ester to an aldehyde without subsequent reduction to the alcohol.



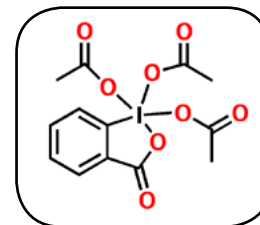
How it works: *Conversion of nitriles to aldehydes*



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DMP Dess-Martin Periodinane



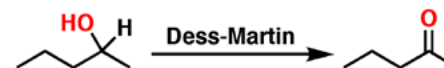
What it's used for: Dess-Martin periodinane is an oxidizing agent. It will oxidize primary alcohols to aldehydes without going to the carboxylic acid (similar to PCC). It will also oxidize secondary alcohols to ketones.

Similar to: PCC, CrO_3 with pyridine

Example 1: Oxidation - conversion of primary alcohols to aldehydes

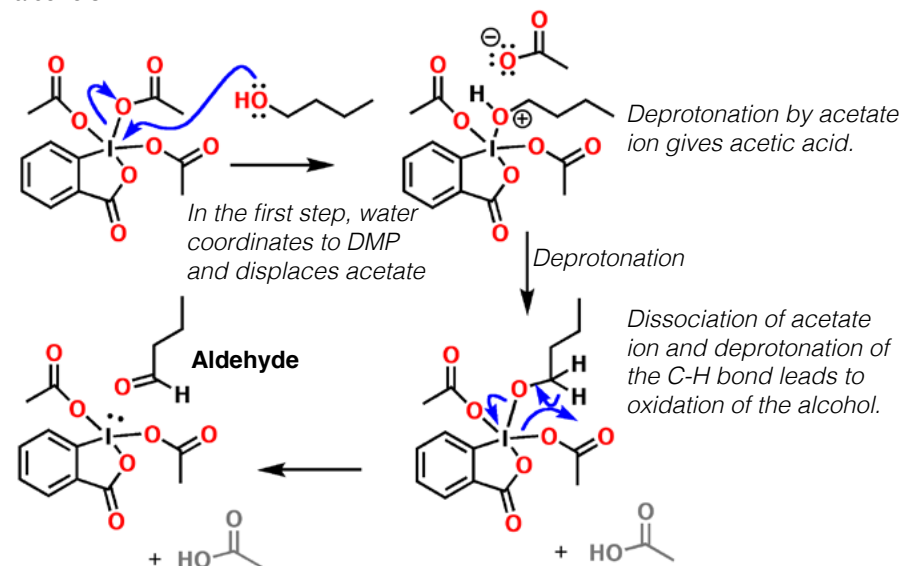


Example 2: Oxidation - conversion of secondary alcohols to ketones



How it works: *Oxidation of alcohols*

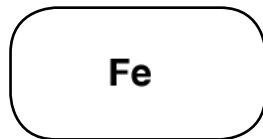
The mechanism for oxidation of alcohols by Dess-Martin periodinane is almost never covered in introductory textbooks. However it is included here in the interests of completeness. Mechanism is the same for primary and secondary alcohols.



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Fe

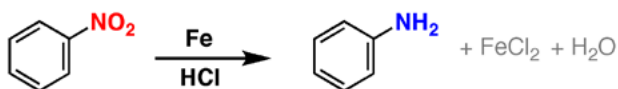
Iron


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What it's used for: Iron metal (Fe) will reduce nitro groups to amines in the presence of a strong acid such as HCl.

Similar to: Tin (Sn), zinc (Zn)

Example 1: Reduction: conversion of nitro groups to primary amines



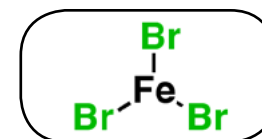
How it works: *Reduction of nitro groups*

The mechanism for this reaction is complex and proceeds in multiple steps. It likely proceeds similarly to that drawn in the section for tin.

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FeBr₃

Iron (III) Bromide

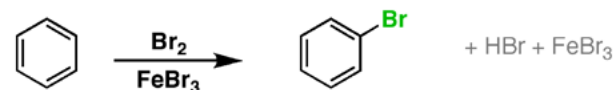


Also known as: Ferric bromide, iron tribromide

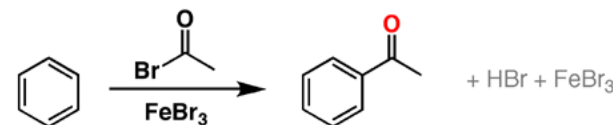
What it's used for: Lewis acid, promoter for electrophilic aromatic substitution

Similar to: AlBr₃, AlCl₃, FeCl₃

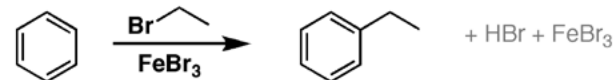
Example 1: Electrophilic bromination - conversion of arenes to aryl bromides



Example 2: Friedel-Crafts acylation - conversion of arenes to aryl ketones

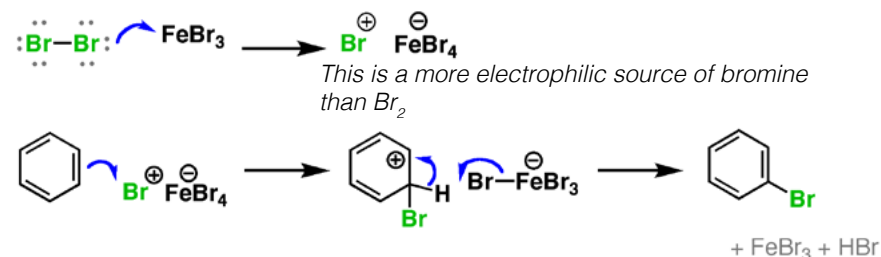


Example 3: Friedel-Crafts alkylation - conversion of arenes to alkyl arenes

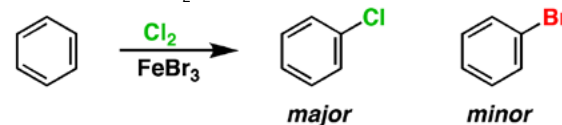


How it works: *Electrophilic bromination*

FeBr₃ is a Lewis acid that can coordinate to halogens. In doing so it increases their electrophilicity, making them much more reactive.



Trivia: FeBr₃ can also be used for chlorination, but FeCl₃ is more often used. The reason is that small amounts of halide scrambling can occur when FeBr₃ is used with Cl₂

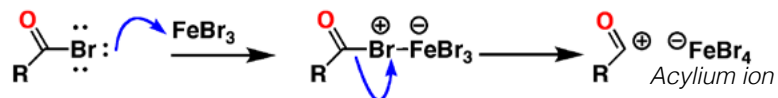


FeBr₃ (continued)

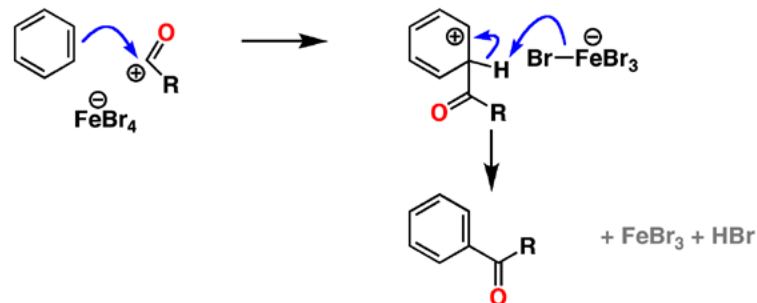
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How it works: *Friedel-Crafts Acylation*

Coordination of the Lewis acid FeBr₃ to the Br of the acid halide makes Br a better leaving group, facilitating formation of the carbocation ("acylium ion" in this case).



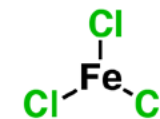
Next, attack of the aromatic ring upon the carbocation followed by deprotonation gives the aryl ketone.



A similar process operates for the Friedel-Crafts alkylation (not pictured)

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FeCl₃ Iron (III) chloride

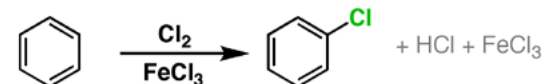


Also known as: Ferric chloride, iron trichloride

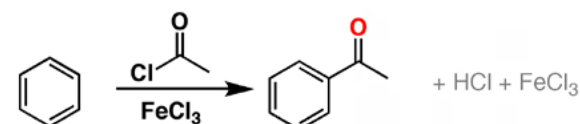
What it's used for: Iron (III) chloride (ferric chloride) is a Lewis acid. It is useful in promoting the chlorination of aromatic compounds with Cl₂ as well as in the Friedel-Crafts alkylation and acylation reactions.

Similar to: AlCl₃, AlBr₃, FeBr₃

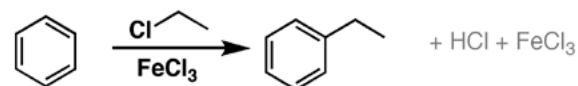
Example 1: Electrophilic chlorination - conversion of arenes to aryl chlorides



Example 2: Friedel-Crafts acylation - conversion of arenes to aryl ketones



Example 3: Friedel-Crafts alkylation: conversion of arenes to alkylarenes



How it works:

See sections on AlCl₃ and FeBr₃ - FeCl₃ works in exactly the same way.

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Grignard Reagents



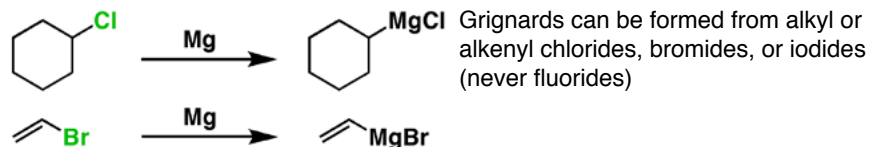
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Also known as: Organomagnesium reagents

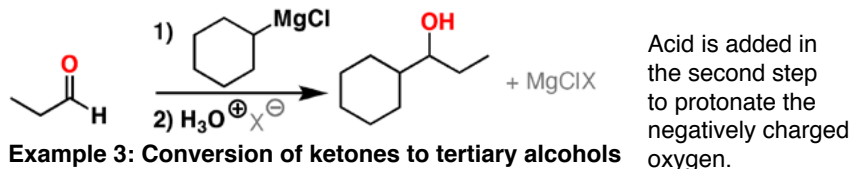
What it's used for: Extremely good nucleophile, reacts with electrophiles such as carbonyl compounds (aldehydes, ketones, esters, carbon dioxide, etc.) and epoxides. In addition Grignard reagents are very strong bases and will react with acidic hydrogens.

Similar to: Organolithium reagents (R-Li)

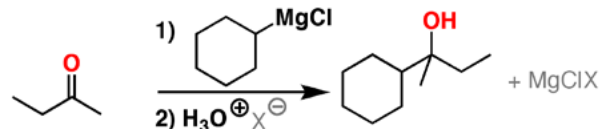
Example 1: Conversion of alkyl or alkenyl halides to Grignard reagents



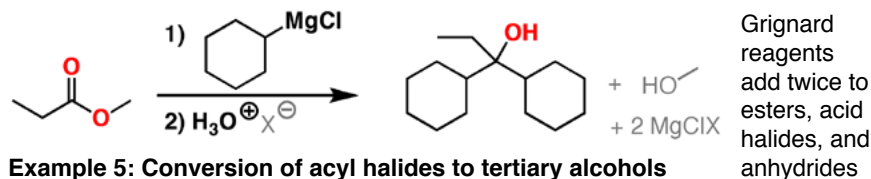
Example 2: Conversion of aldehydes to secondary alcohols



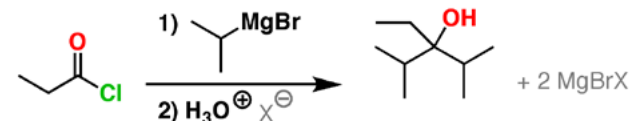
Example 3: Conversion of ketones to tertiary alcohols



Example 4: Conversion of esters to tertiary alcohols



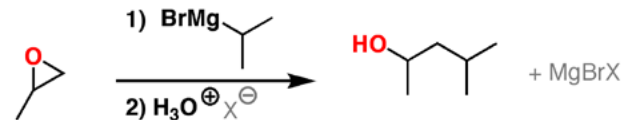
Example 5: Conversion of acyl halides to tertiary alcohols



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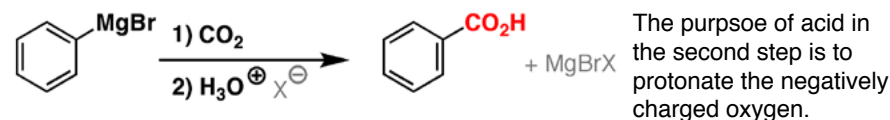
Grignard reagents
(continued)

Example 6: Reaction with epoxides

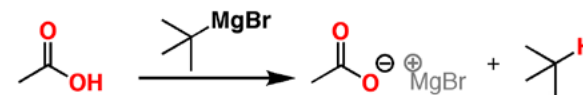


Grignard reagents add to the less substituted end of epoxides

Example 7: Reaction with carbon dioxide



Example 8: Reaction with acidic hydrogens

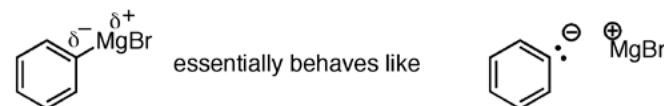


This can be used to introduce deuterium:

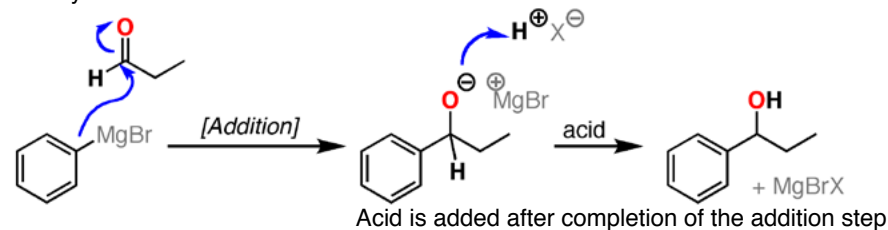


How it works: Addition to aldehydes and ketones

Grignard reagents are extremely strong nucleophiles. The electrons in the C-Mg bond are heavily polarized towards carbon



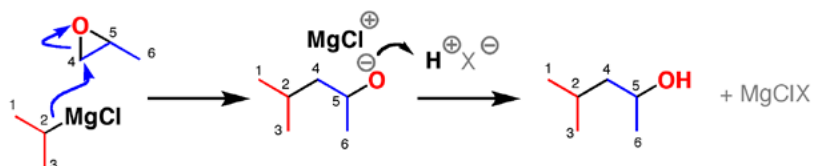
Therefore, Grignard reagents will react well with electrophiles such as aldehydes and ketones.



Grignard Reagents (continued)

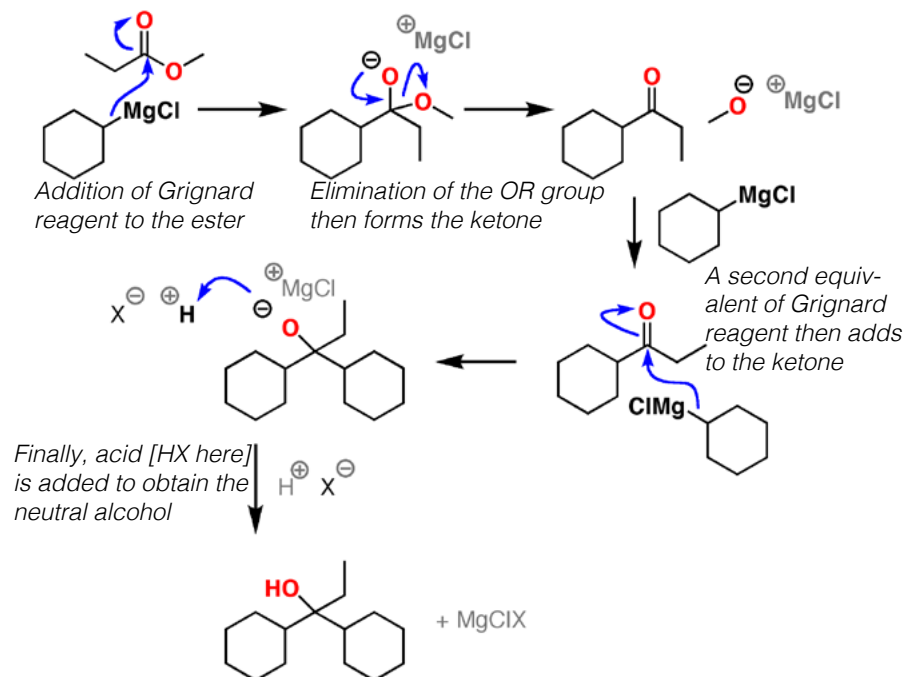
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How it works: *Addition to epoxides*



How it works: *Addition to esters*

These proceed through a two step mechanism: addition followed by elimination. Acid is added at the end to obtain the alcohol.



The same mechanism operates for acid halides and anhydrides.

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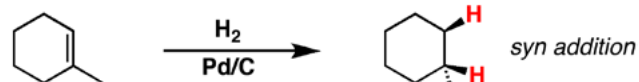
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H₂ Hydrogen

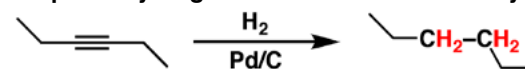


What it's used for: Hydrogen gas is used for the reduction of alkenes, alkynes, and many other species with multiple bonds, in concert with catalysts such as Pd/C and Pt.

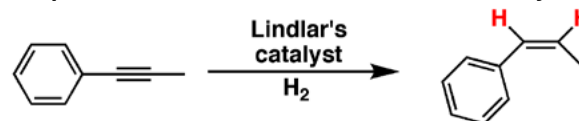
Example 1: Hydrogenation - conversion of alkenes to alkanes



Example 2: Hydrogenation - conversion of alkynes to alkanes



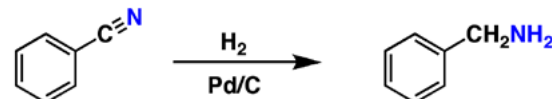
Example 3: Lindlar reduction - conversion of alkynes to alkenes



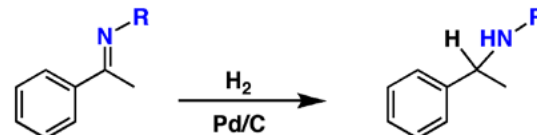
Example 4: Reduction - conversion of nitro groups to primary amines



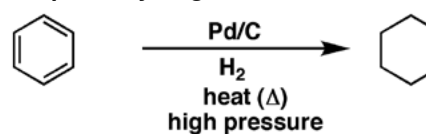
Example 5: Hydrogenation - conversion of nitriles to primary amines



Example 6: Hydrogenation - conversion of imines to amines



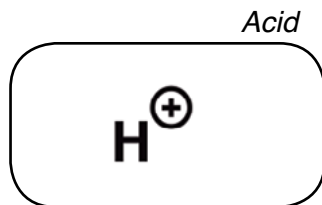
Example 7: Hydrogenation - conversion of arenes to cycloalkanes



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Anhydrous Acid



Also known as: “proton”, “proton source”, “anhydrous acid”

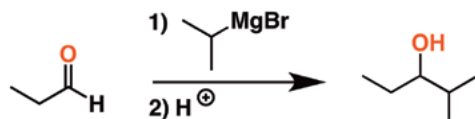
What it's used for: H^+ is a shorthand term for “anhydrous acid”. There is actually no such reagent as “ H^+ ”, because positive charge never exists without a negative counter-ion. The term H^+ is a common shorthand referring to a generic acid where the identity of the negatively charged “spectator ion” is not important and no water is present.

Similar to: Sulfuric acid (H_2SO_4), tosic acid (TsOH) and phosphoric acid H_3PO_4 are all equivalent to “ H^+ ”. See these sections for specific examples.

There are too many uses of anhydrous acid to hope to be comprehensive here. Three illustrative examples are given.

Example 1: Acid workup

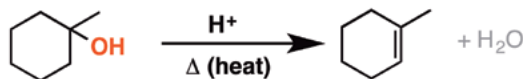
Many reactions form anions, particularly on oxygen, and acid workup serves to protonate the anion and deliver a neutral compound. Often seen after addition of Grignard, organolithium reagents, and reducing agents to carbonyls



Equivalent to H_3O^+ in this case.

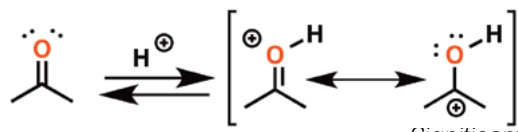
Example 2: To make neutral species into better leaving groups

Certain functional groups (alcohols, ethers, amines) become better leaving groups when protonated to give their conjugate acid. H^+ (as shorthand for H_2SO_4 , TsOH , or H_3PO_4) can help to promote substitution and elimination reactions that fail under neutral conditions



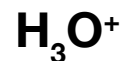
Example 3: To make carbonyls more electrophilic (more reactive towards nucleophiles)

Protonation of carbonyl oxygens makes the attached carbonyl carbon more reactive towards nucleophiles. This is because the resonance form with a positive charge on carbon makes a more significant contribution to the hybrid than in the unprotonated molecule.

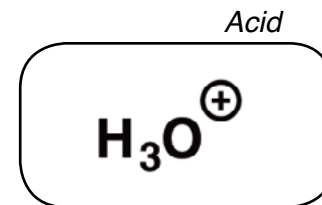


Protonation of a carbonyl oxygen by H^+ is a key step in many reactions

Significant resonance form – very reactive carbon!



Aqueous acid



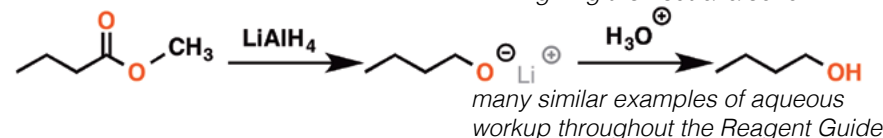
Also known as: Hydronium ion

What it's used for: Too general a “reagent” to be comprehensively covered here. H_3O^+ is a generic term for “aqueous acid”, omitting the negative counter-ion (which generally does not participate in reactions). Broadly speaking, aqueous acid is used for many hydrolysis reactions, as well as when a reaction requires “acid workup”.

Equivalent to: $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$, $\text{H}_2\text{O}/\text{H}_3\text{PO}_4$

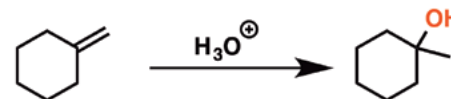
Aqueous acid protonates the negatively charged alkoxide, giving the neutral alcohol

Example 1: Acidic workup



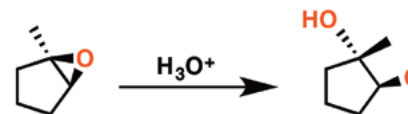
many similar examples of aqueous workup throughout the Reagent Guide

Example 2: Hydration of alkenes to give alcohols



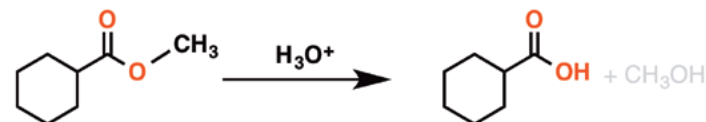
An equivalent reagent here would be $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$

Example 3: Opening of epoxides to give trans diols



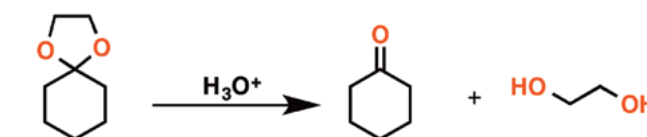
Reaction proceeds through protonation of oxygen followed by attack of water at most substituted position

Example 4: Hydrolysis of esters to give carboxylic acids



Amides, nitriles, imines, and enamines can also be hydrolyzed by aqueous acid.

Example 5: Hydrolysis of acetals to give ketones



HBr

Hydrobromic acid

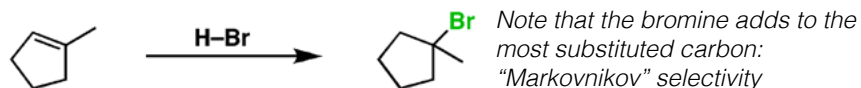


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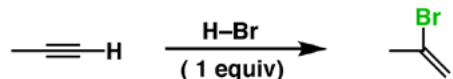
What it's used for: Hydrobromic acid is a strong acid. It can add to compounds with multiple bonds such as alkenes and alkynes. It can also react with primary, secondary, and tertiary alcohols to form alkyl bromides.

Similar to: HCl, HI

Example 1: Hydrohalogenation - conversion of alkenes to alkyl bromides



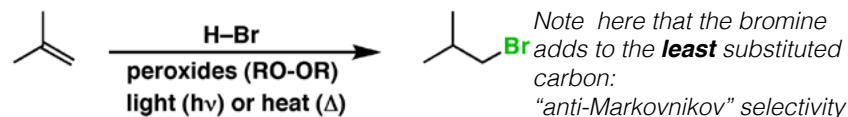
Example 2: Hydrohalogenation - conversion of alkynes to alkenyl bromides



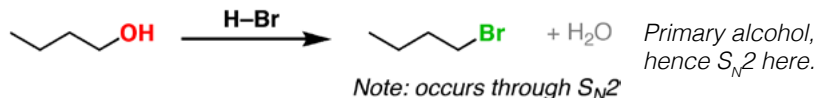
Example 3: Hydrohalogenation - conversion of alkynes to geminal dibromides



Example 4: Free-radical addition - conversion of alkenes to alkyl bromides



Example 5: Conversion of alcohols to alkyl bromides (S_N2)

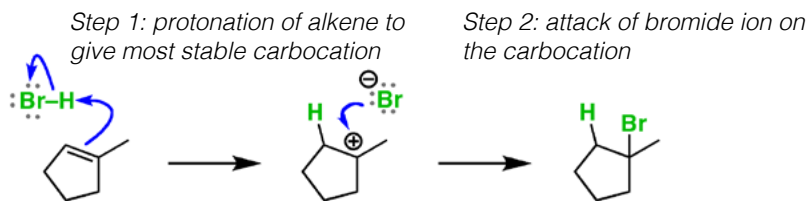


Example 6: Conversion of alcohols to alkyl bromides (S_N1)



Note: occurs through S_N1

How it works: Addition to alkenes



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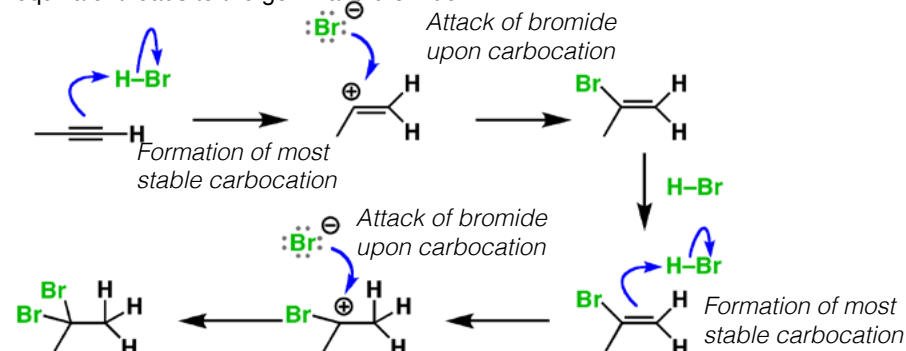
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HBr

(continued)

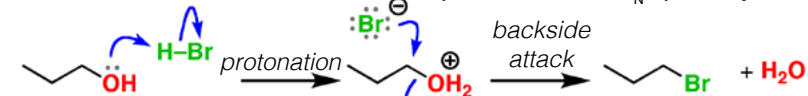
How it works: Addition to alkynes

Addition of 1 equivalent of HBr will lead to a vinyl bromide; addition of a second equivalent leads to the geminal dibromide

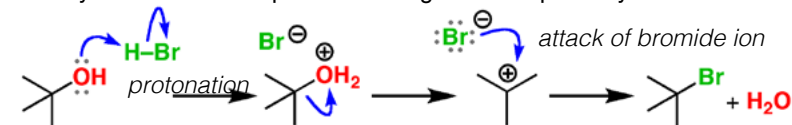


How it works: Formation of alkyl bromides from alcohols

Protonation of OH by HBr makes a good leaving group (H_2O). When a stable carbocation cannot be formed, the reaction proceeds via an S_N2 pathway:

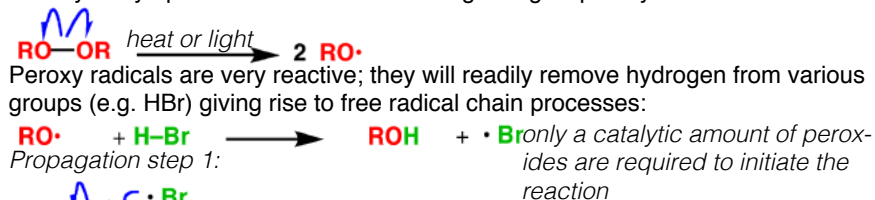


Tertiary alcohols tend to proceed through an S_N1 pathway:



How it works: Free radical addition of HBr to alkenes

Peroxides (general formula RO-OR) have a weak O-O bond and will fragment homolytically upon treatment with heat or light to give peroxy radicals:

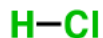


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HCl

Hydrochloric acid

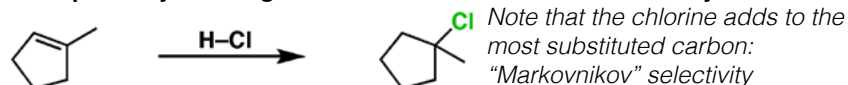
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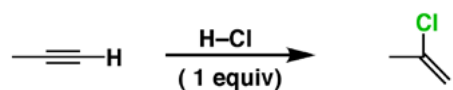
What it's used for: Hydrochloric acid is a strong acid. As a reagent, it can react with multiple bonds in alkenes and alkynes, forming chlorinated compounds. It can also convert alcohols to alkyl chlorides.

Similar to: HBr, HI

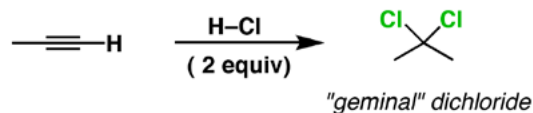
Example 1: Hydrohalogenation - conversion of alkenes to alkyl chlorides



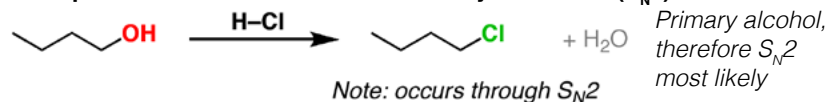
Example 2: Hydrohalogenation - conversion of alkynes to alkenyl chlorides



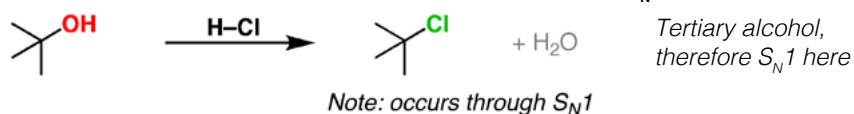
Example 3: Hydrohalogenation - conversion of alkynes to geminal dichlorides



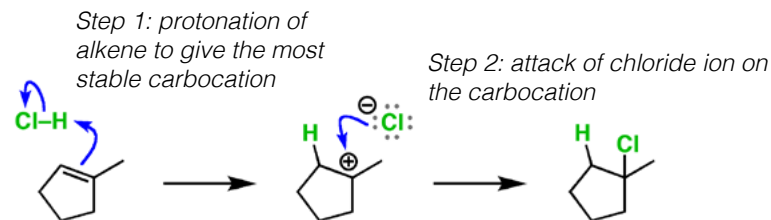
Example 4: Conversion of alcohols to alkyl chlorides (S_N2)



Example 5: Conversion of alcohols to alkyl chlorides (S_N1)



How it works: Addition to alkenes



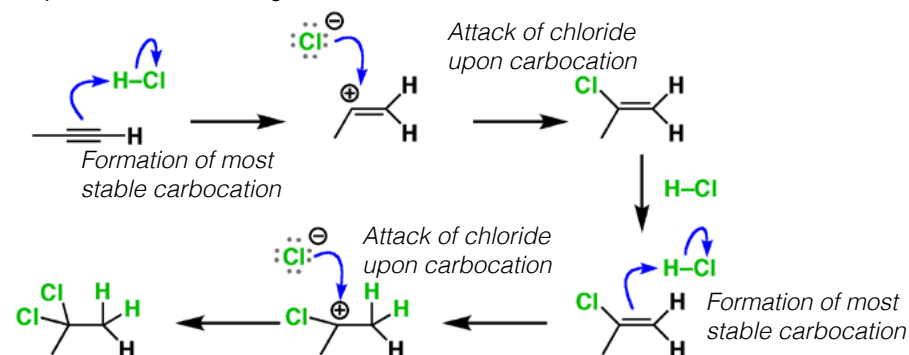
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HCl

(continued)

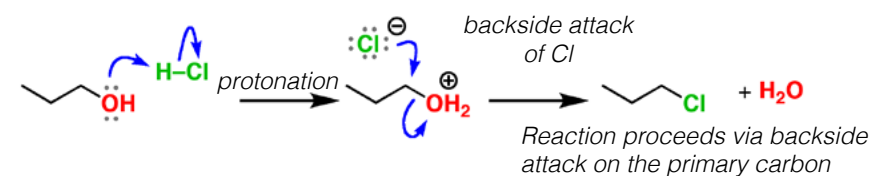
How it works: Addition to alkynes

Addition of 1 equivalent of HBr will lead to a vinyl bromide; addition of a second equivalent leads to the geminal dibromide

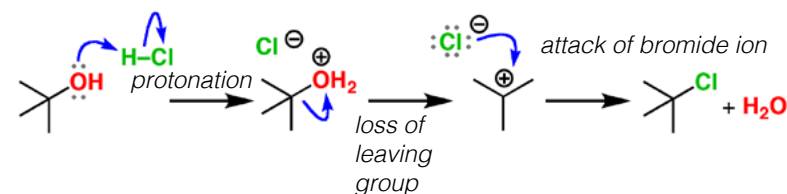


How it works: Formation of alkyl chlorides from alcohols

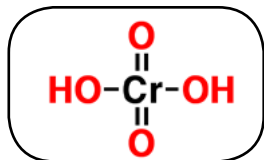
Protonation of OH by HCl makes a good leaving group (H_2O). When a stable carbocation cannot be formed, the reaction proceeds via an S_N2 pathway:



In situations where a more stable carbocation can be formed (e.g. with tertiary alcohols), the reaction proceeds via S_N1 :



H₂CrO₄ Chromic acid



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Also known as: Chromic acid is often formed in solution by adding acid to salts of chromate or dichromate. Examples:

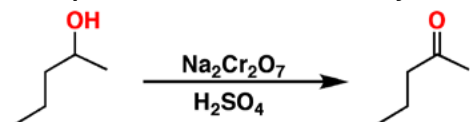
K₂Cr₂O₇ / H₃O⁺, Na₂Cr₂O₇ / H₃O⁺, NaCrO₄ / H₃O⁺, KCrO₄ / H₃O⁺, CrO₃ / H₃O⁺

All of these conditions are equivalent to H₂CrO₄. So is the "Jones Reagent"

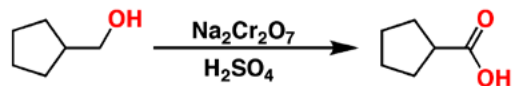
What it's used for: Chromic acid is a strong oxidizing agent. It will oxidize secondary alcohols to ketones and primary alcohols to carboxylic acids.

Similar to: KMnO₄

Example 1: Oxidation of secondary alcohols to give ketones

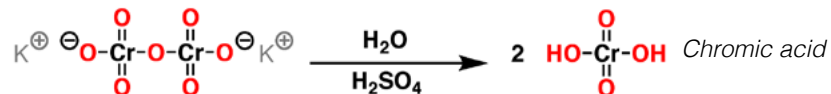


Example 2: Oxidation of primary alcohols to give carboxylic acids

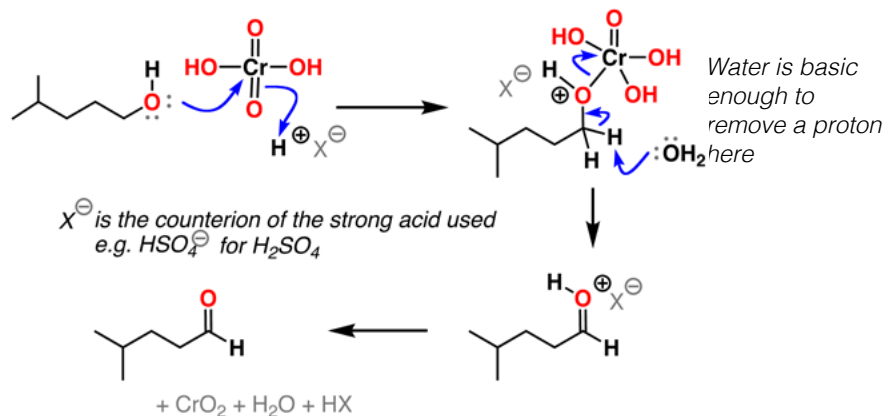


How it works: Oxidation of alcohols

Aqueous acidic conditions convert sodium or potassium dichromate into chromic acid, which is the active oxidant here.



Chromic acid is then attacked by oxygen. Deprotonation of the C-H bond results in oxidation of the alcohol.

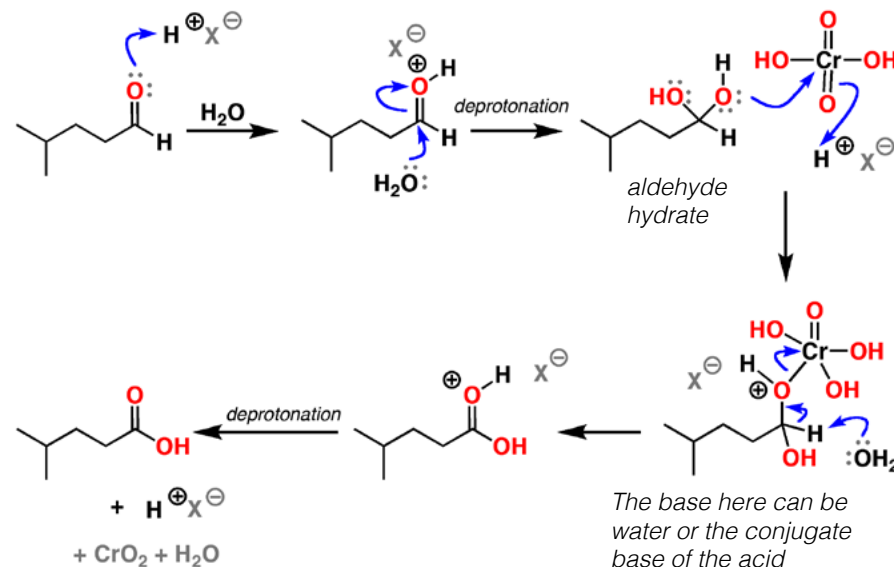


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H₂CrO₄ (continued)

How it works: Oxidation of aldehydes to carboxylic acids



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Hg(OAc)₂ Mercuric Acetate

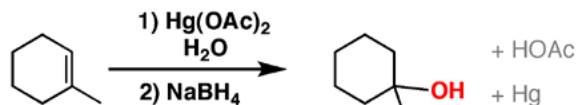


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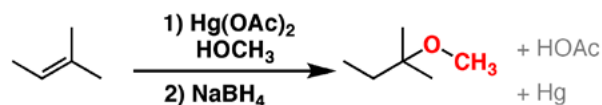
What it's used for: Mercuric acetate is a useful reagent for the oxymercuration of alkenes and alkynes. It makes double bonds more reactive towards nucleophilic attack by nucleophiles such as water and alcohols. The mercury is removed by using NaBH₄ (or H₂SO₄ in the case of addition to alkynes).

Similar to: HgSO₄, Hg(OTFA)₂ is a related reagent (TFA = trifluoroacetate)

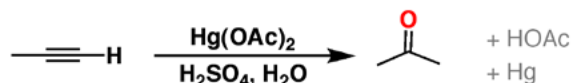
Example 1: Oxymercuration - conversion of alkenes to alcohols



Example 2: Oxymercuration - conversion of alkenes to ethers



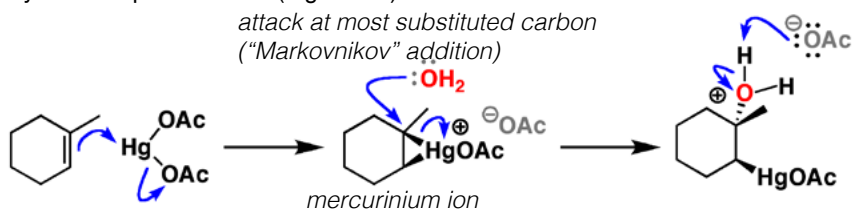
Example 3 - Oxymercuration - conversion of alkynes to ketones



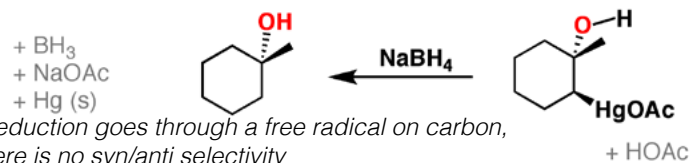
How it works: Oxymercuration of alkenes

In the oxymercuration reaction, an alkene reacts with mercuric acetate to give a 3-membered ring containing mercury (a "mercurinium ion"). This is then attacked by a nucleophilic solvent (e.g. water) at the most substituted carbon

attack at most substituted carbon
("Markovnikov" addition)



NaBH₄ converts the C-Hg bond to a C-H bond



The result of the oxymercuration reaction is a Markovnikov addition of water to an alkene. After treatment with NaBH₄, solid mercury (0) is obtained.

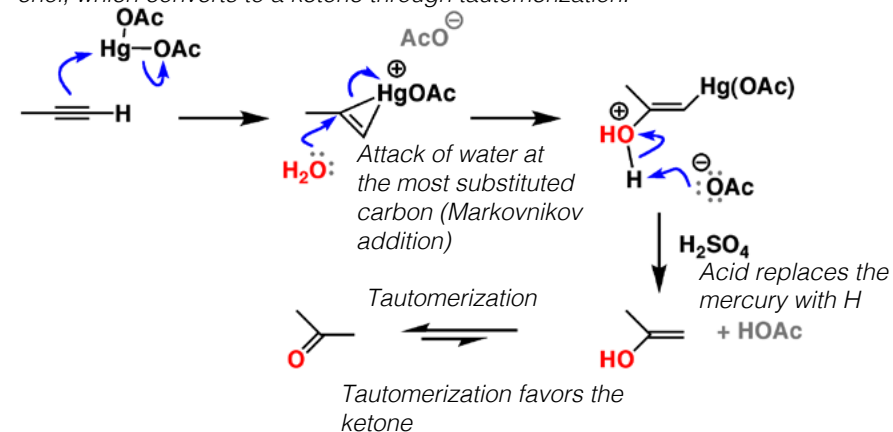
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Hg(OAc)₂ (continued)

How it works: Oxymercuration of alkynes

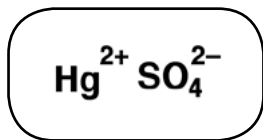
Treatment of an alkyne with Hg(OAc)₂ and water leads to the formation of an enol, which converts to a ketone through tautomerization.



Trivial detail: since mercury is liberated as Hg²⁺, this process is catalytic in mercury.

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HgSO₄ Mercuric Sulfate



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What it's used for: Mercuric sulfate is a Lewis acid. In the presence of aqueous acid ("H₃O⁺" or H₂SO₄/H₂O) it will perform the oxymercuration of alkynes to ketones.

Similar to: Mercuric acetate (Hg(OAc)₂)

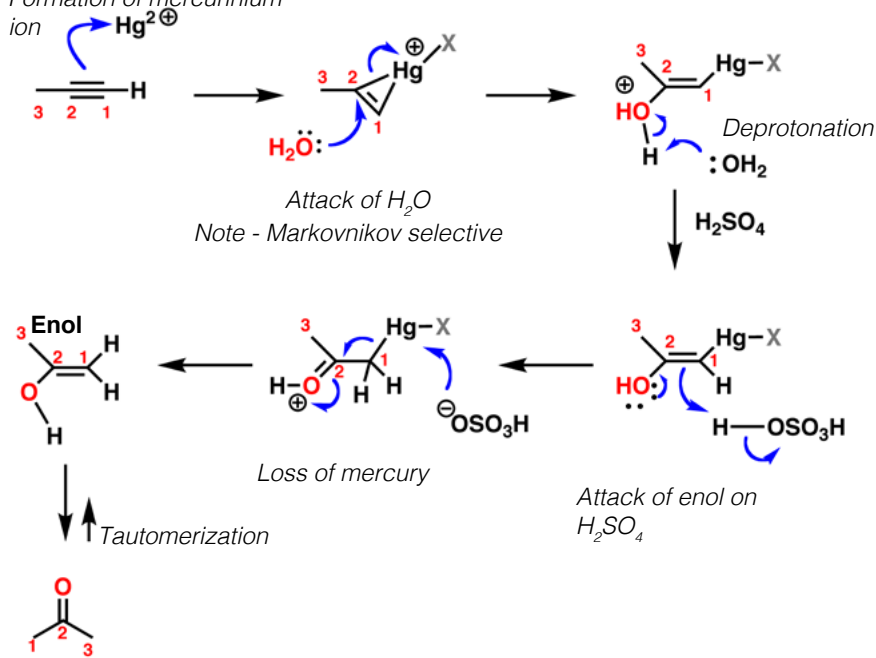
Example 1: Oxymercuration - conversion of alkynes to ketones



How it works: *Oxymercuration of alkynes*

Oxymercuration of alkynes occurs through attack of the alkyne PI bond on Hg²⁺, followed by attack of water, protonation/demercuration, and tautomerization of the resulting enol to give the ketone.

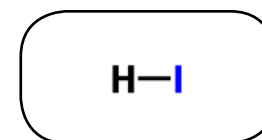
Formation of mercurinium ion



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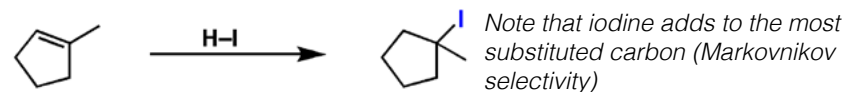
HI Hydroiodic acid



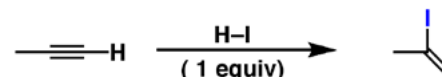
What it's used for: Hydroiodic acid is a strong acid. As a reagent it can add hydrogen and iodine across compounds with multiple bonds such as alkenes and alkynes. It is also useful for the cleavage of ethers and the conversion of alcohols to alkyl halides.

Similar to: HBr, HCl

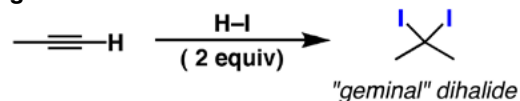
Example 1: Hydrohalogenation - conversion of alkenes to alkyl iodides



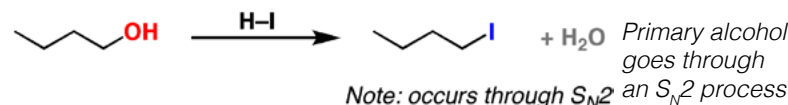
Example 2: Hydrohalogenation - conversion of alkynes to alkenyl iodides



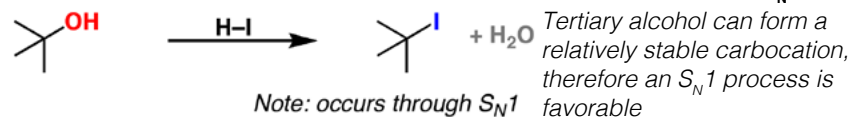
Example 3: Hydrohalogenation - double addition of HI to alkynes to give geminal diiodides



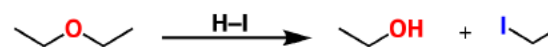
Example 4: Substitution - conversion of alcohols to alkyl iodides (S_N2)



Example 5: Substitution - conversion of alcohols to alkyl iodides (S_N1)

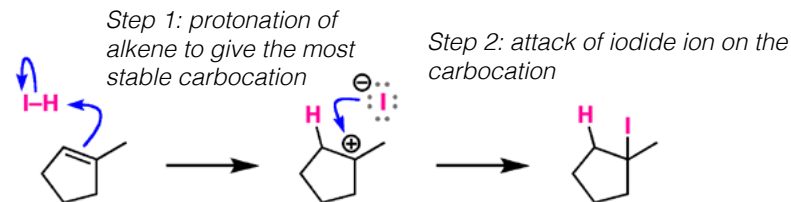


Example 6: Conversion of ethers to alcohols and alkyl iodides



How it works: *Addition to alkenes*

In the first step, the alkene is protonated to give the more substituted carbon, followed by attack of the iodide ion to give the alkyl iodide.

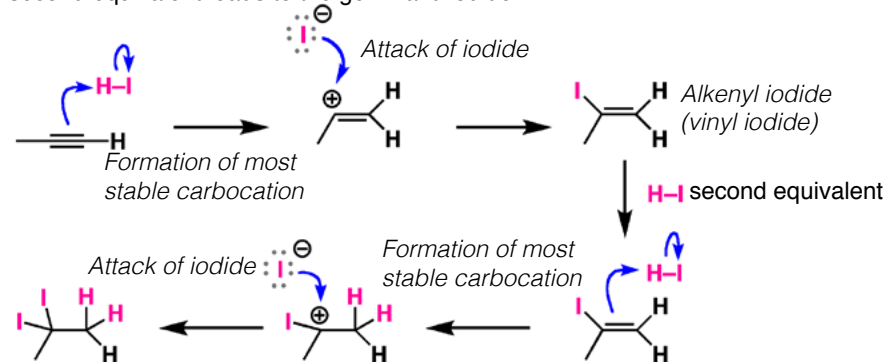


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HI (continued)

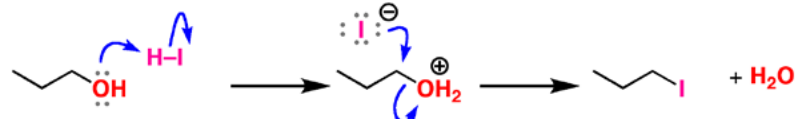
How it works: Addition to alkynes

Addition of 1 equivalent of HI will lead to an alkenyl iodide; addition of a second equivalent leads to the geminal diiodide

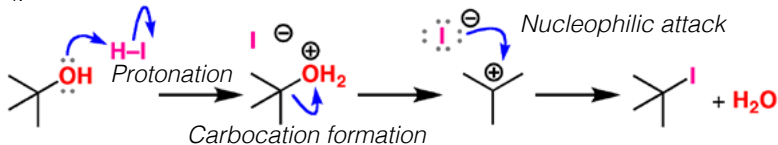


How it works: Conversion of alcohols to alkyl iodides

Protonation converts OH to a better leaving group (H_2O). $\text{S}_\text{N}2$ dominant for primary

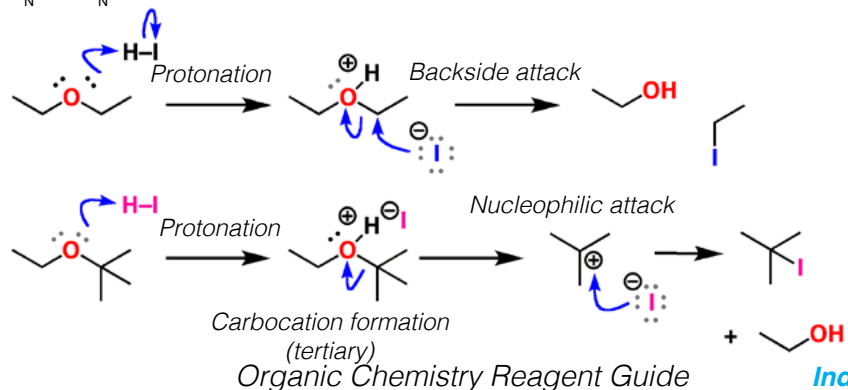


$\text{S}_\text{N}1$ dominates when a relatively stable carbocation can form:

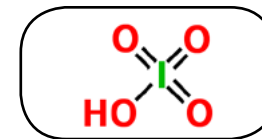


How it works: Cleavage of ethers

Depending on the structure of the ether, cleavage can occur either through $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$



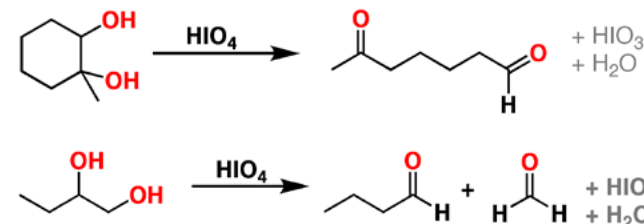
HIO_4 Periodic acid



What it's used for: Periodic acid is a strong oxidizing agent. It is most commonly used for the oxidative cleavage of 1,2-diols (vicinal diols) to give aldehydes and ketones.

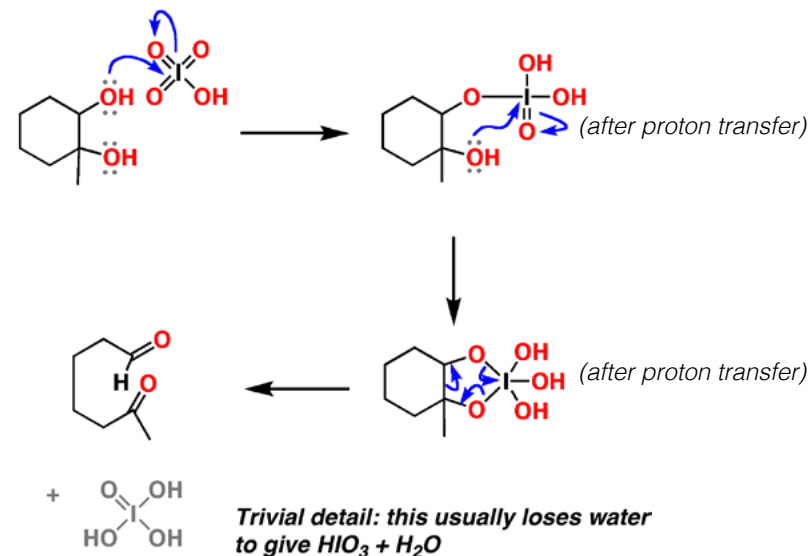
Similar to: Sodium periodate (NaIO_4), Lead (IV) acetate [$\text{Pb}(\text{OAc})_4$]

Example 1: Cleavage of diols to give aldehydes/ketones



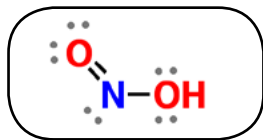
How it works: Cleavage of diols to give aldehydes/ketones

Periodic acid is a strong oxidizing agent. Similar to $\text{Pb}(\text{OAc})_4$, it can cleave 1,2-diols (vicinal diols) to give the corresponding aldehydes or ketones.



Notice how iodine starts in the (VII) oxidation state and goes to (V) (it has been reduced)

HONO Nitrous Acid

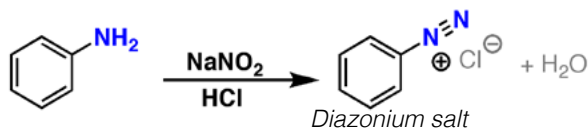


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Also known as: HNO_2 . Equivalent to $\text{NaNO}_2 / \text{H}_2\text{SO}_4$ or $\text{NaNO}_2 / \text{HCl}$

What it's used for: Nitrous acid is primarily used to convert aromatic amines to diazonium salts, which can be converted into many different compounds via the Sandmeyer reaction. It can also be made from NaNO_2 if a strong acid such as H_2SO_4 or HCl is added.

Example 1: Conversion of aromatic amines to diazonium salts

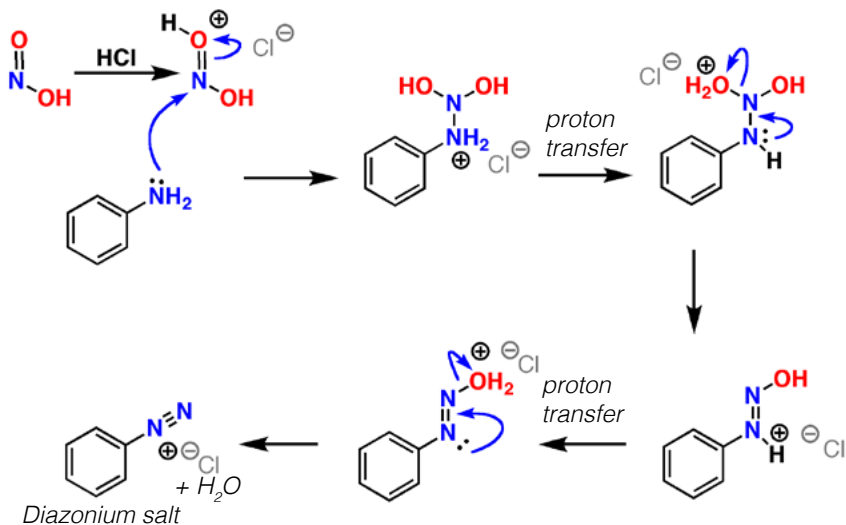


Note: other acids beside HCl can be used as the acid here (such as H_2SO_4)

How it works: Formation of diazonium salts

Nitrous acid reacts with aromatic amines to form diazonium salts. The reaction is greatly assisted by strong acids such as HCl or H_2SO_4

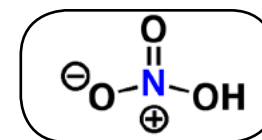
Acid activates the $\text{N}=\text{O}$ bond toward attack by the amine



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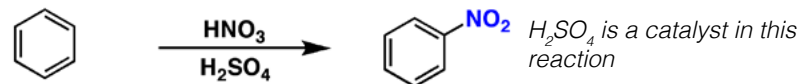
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HNO_3 Nitric Acid

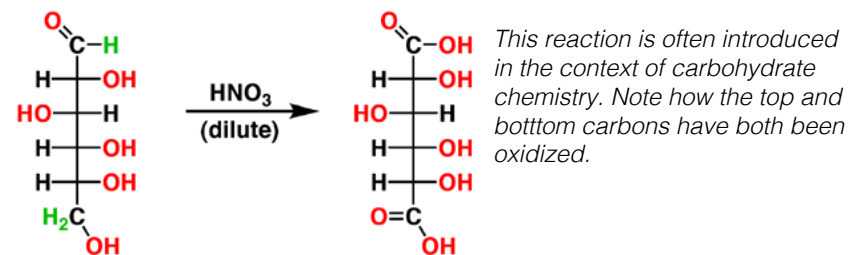


What it's used for: A strong acid, HNO_3 is used as a reagent in the addition of NO_2 to aromatic compounds ("nitration"). It will also oxidize primary alcohols and aldehydes to carboxylic acids.

Example 1: Nitration - conversion of arenes to nitroarenes

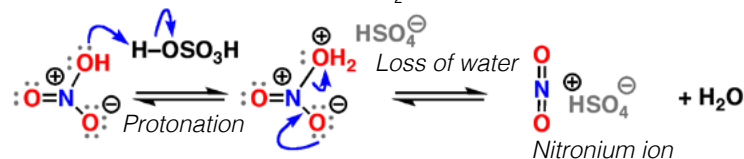


Example 2: Oxidation - conversion of aldehydes/primary alcohols to carboxylic acids

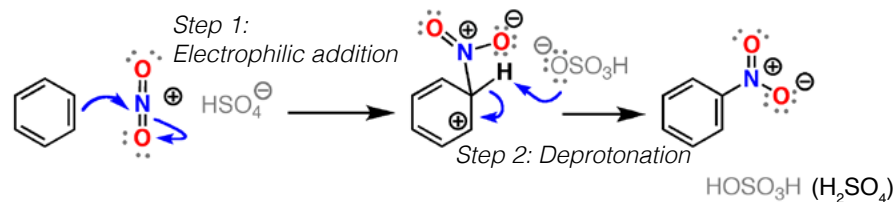


How it works: Nitration of aromatics

In the presence of a strong acid such as H_2SO_4 , HNO_3 is protonated and loses water to form the nitronium ion (NO_2^+), a very reactive electrophile.



The NO_2^+ is then attacked by the aromatic ring to give a carbocation, which is then deprotonated to restore aromaticity. H_2SO_4 is regenerated which can then go on to react with another equivalent of HNO_3 (it is a catalyst here).



Note that acid is regenerated here; it acts as a catalyst in this reaction.

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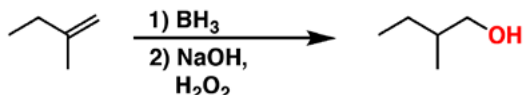
H₂O₂ Hydrogen peroxide



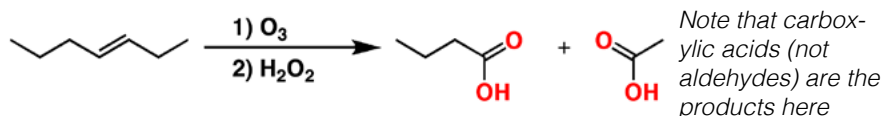
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What it's used for: Hydrogen peroxide is used as an oxidant in the hydroboration of alkenes and alkynes, converting the C-B bond into a C-O bond. It is also used in the oxidative workup of ozonolysis, converting aldehydes into carboxylic acids.

Example 1: As an oxidant in the hydroboration reaction

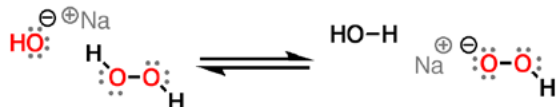


Example 2: For oxidative workup in ozonolysis

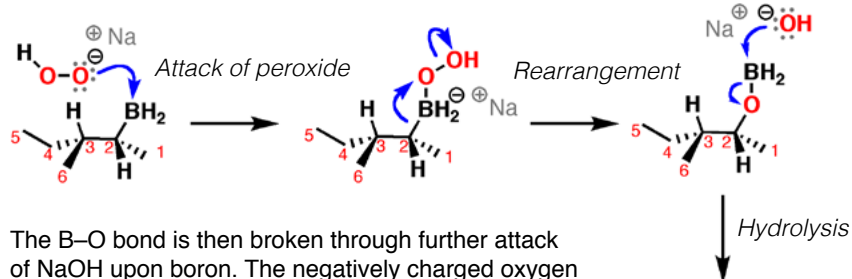


How it works: Hydroboration of alkenes

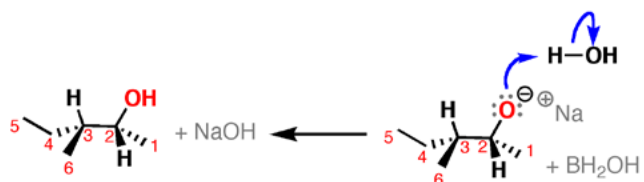
Hydrogen peroxide is used in concert with the strong base NaOH. Deprotonation of H₂O₂ gives its conjugate base, which is a more reactive nucleophile:



The peroxide ion then attacks boron. In the key step a rearrangement occurs, breaking the weak (138 kJ/mol) O-O bond.



The B-O bond is then broken through further attack of NaOH upon boron. The negatively charged oxygen ("alkoxide") is eventually protonated by water.



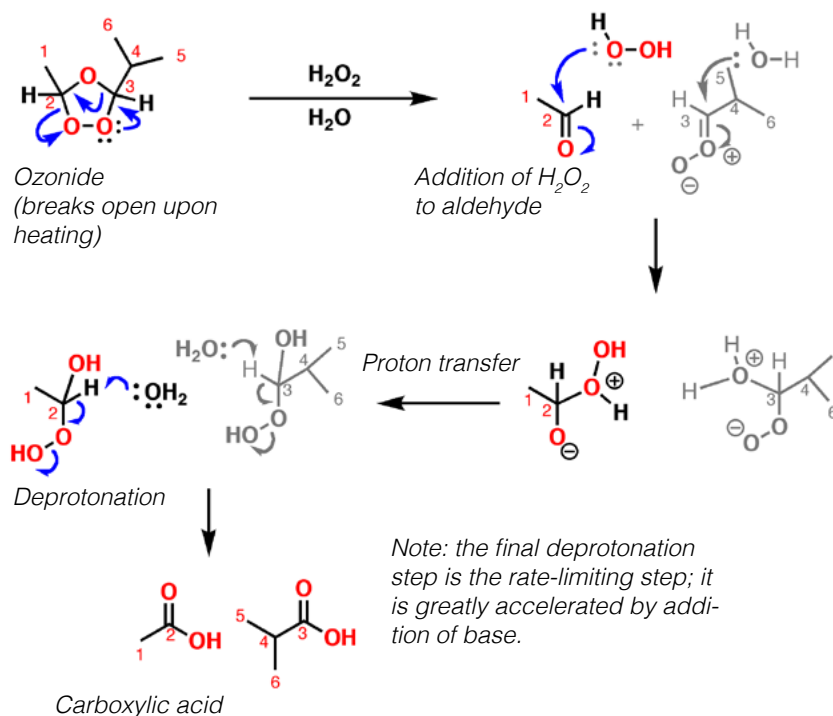
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H₂O₂ (continued)

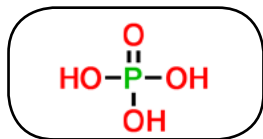
How it works: Oxidative workup for ozonolysis

Hydrogen peroxide can oxidize aldehydes to carboxylic acids. This is the basis for "oxidative workup" of the ozonolysis reaction, where the aldehyde is treated with aqueous H₂O₂ (minor note: addition of a base such as NaOH speeds up this reaction)



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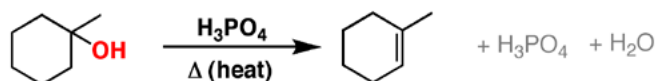
H_3PO_4 Phosphoric acid


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What it's used for: Phosphoric acid is a moderately strong acid. The conjugate acid of H_3PO_4 is a poor nucleophile, so phosphoric acid is an excellent acid to use for elimination reactions.

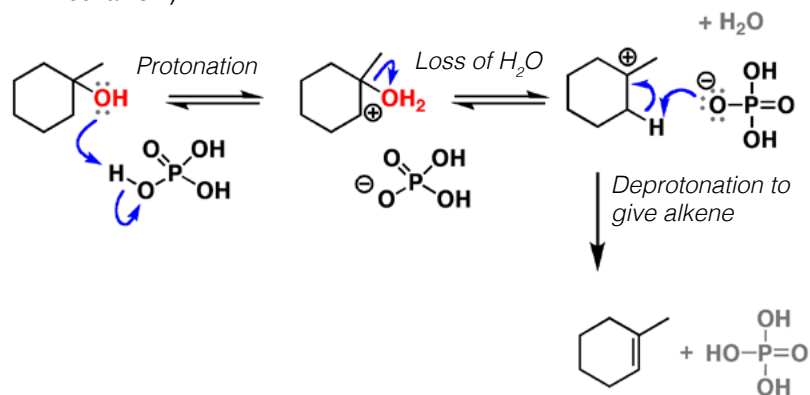
Similar to: Sulfuric acid (H_2SO_4), tosic acid (TsOH)

Example 1: Elimination of alcohols to give alkenes

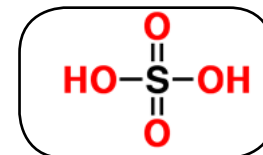


How it works: *Elimination of alcohols to give alkenes*

Protonation of the alcohol by phosphoric acid makes OH into a good leaving group (H_2O) which departs to give a carbocation. Deprotonation of the carbon adjacent to the carbocation leads to an alkene (this is an E1 mechanism).


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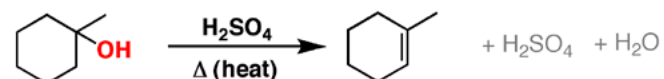
H_2SO_4 Sulfuric acid



What it's used for: Sulfuric acid, known to alchemists as "oil of vitriol" is a strong acid ($\text{pK}_a -3.0$). It is particularly useful for elimination reactions since its conjugate base [HSO_4^-] is a very poor nucleophile. It finds use in many other reactions as a general strong acid.

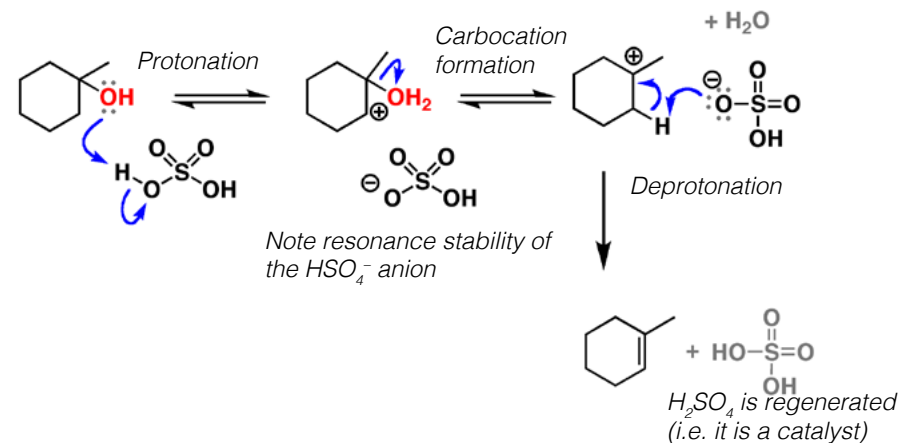
Similar to: *p*-toluenesulfonic acid (TsOH)

Example 1: Elimination – conversion of alcohols to alkenes



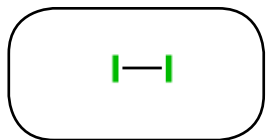
How it works: *Elimination of alcohols*

Protonation of the alcohol forms its conjugate acid [an "oxonium ion"], which has a much better leaving group (H_2O) than the alcohol (HO^-). Loss of water results in the formation of a carbocation. The resonance stabilized HSO_4^- anion is a poor nucleophile, and tends not to add to the carbocation (unlike HBr and HCl for example). Deprotonation, either by HSO_4^- or by water, leads to formation of the alkene and regeneration of acid.



As with many reactions that pass through carbocations, rearrangements can occur in situations where a more stable carbocation can form through a hydride or alkyl shift.

I₂ Iodine

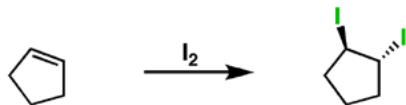


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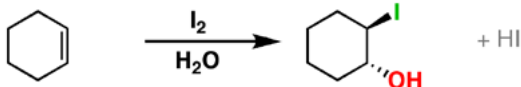
What it's used for: Iodine is an excellent electrophile due to the weak I-I bond (approx 151 kJ/mol [36 kcal/mol]). It reacts with carbon-carbon multiple bonds such as alkenes and alkynes, along with other nucleophiles. It is also used in the iodoform reaction.

Similar to: *N*-iodo succinimide (NIS) performs many of the same reactions.

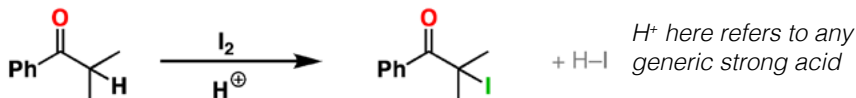
Example 1: Iodination - conversion of alkenes to vicinal diiodides



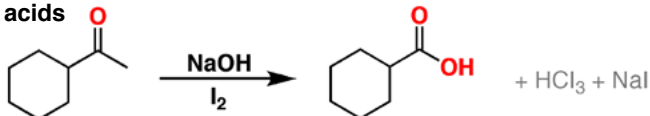
Example 2: Conversion of alkenes to iodohydrins



Example 3: Conversion of ketones to α-iodo ketones

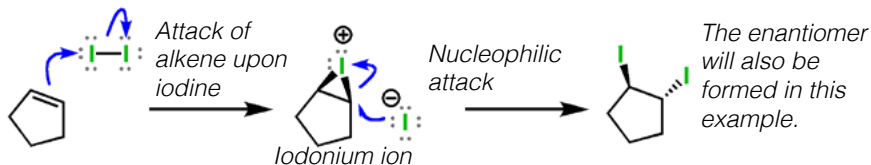


Example 4: Iodoform reaction - conversion of methyl ketones to carboxylic acids

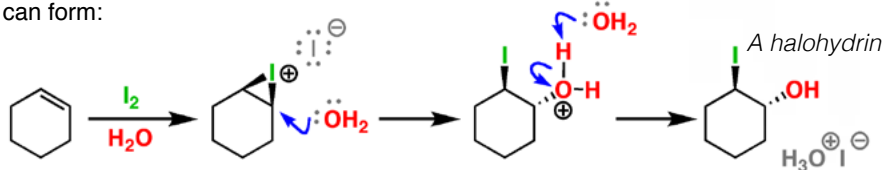


How it works: Iodination of alkenes

Treatment of an alkene with I₂ leads to formation of an iodonium ion, which undergoes backside attack by iodide ion to give the trans product.



When a nucleophilic solvent such as H₂O or an alcohol is present, halohydrins can form:



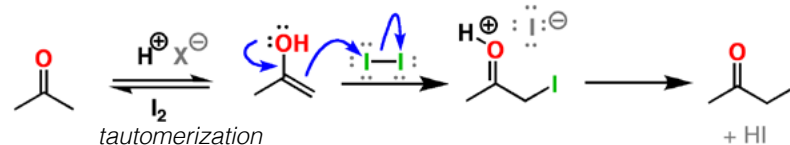
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Iodine (continued)

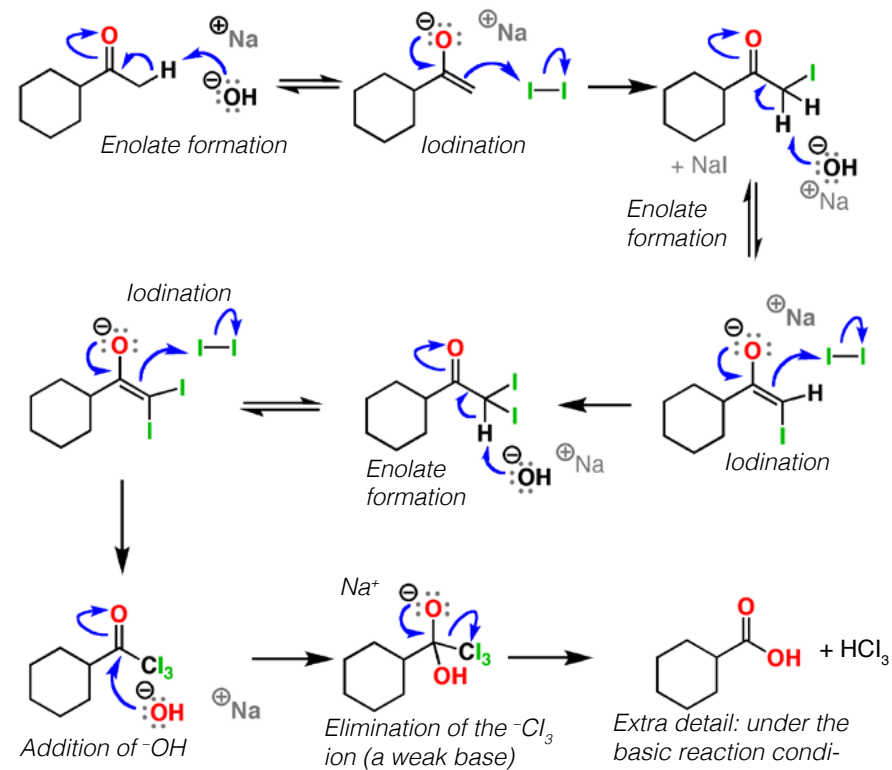
How it works: Iodination of ketones

Treatment of ketones with acid ["HX"] catalyzes keto-enol tautomerization. Attack of iodine by the enol tautomer followed by deprotonation gives the iodinated ketone.



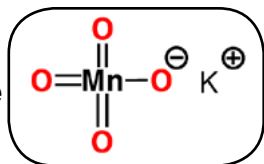
How it works: The haloform reaction

Methyl ketones treated with strong base (e.g. NaOH) form enolates, which attack iodine. After complete replacement of H by I, the -CI₃ ion can then be displaced from the ketone, giving a carboxylic acid.



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KMnO₄ Potassium permanganate

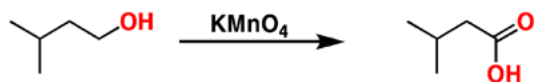


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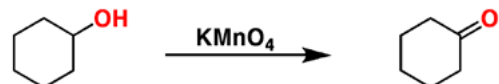
What it's used for: This strong oxidizing agent will oxidize primary alcohols (and aldehydes) to carboxylic acids, secondary alcohols to ketones, form diols from alkenes, and oxidatively cleave carbon-carbon bonds. It will also oxidize C-H bonds adjacent to aromatic rings.

Similar to: K₂Cr₂O₇, OsO₄, O₃

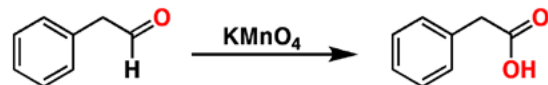
Example 1: Oxidation - conversion of primary alcohols to carboxylic acids



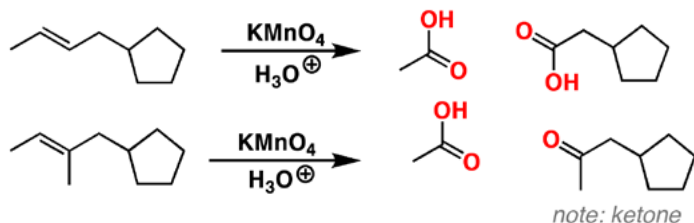
Example 2: Oxidation - conversion of secondary alcohols to ketones



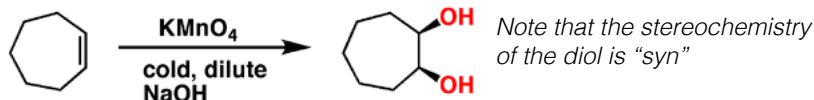
Example 3: Oxidation - conversion of aldehydes to carboxylic acids



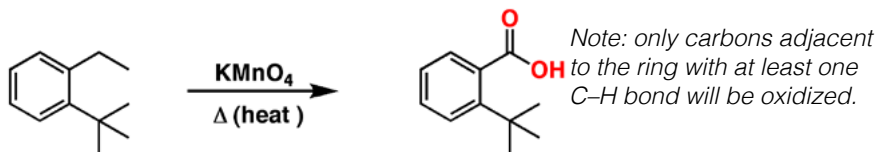
Example 4: Oxidative cleavage - conversion of alkenes to ketones / carboxylic acids



Example 5: Dihydroxylation - conversion of alkenes to vicinal diols



Example 6: Oxidation - conversion of alkylaromatics to carboxylic acids

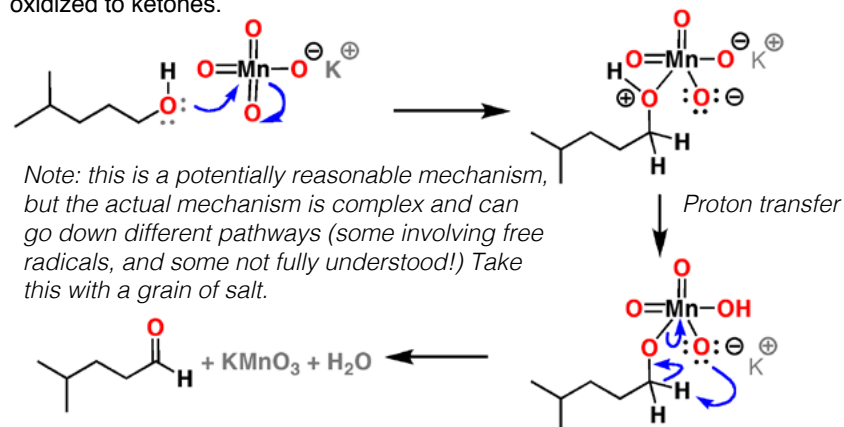


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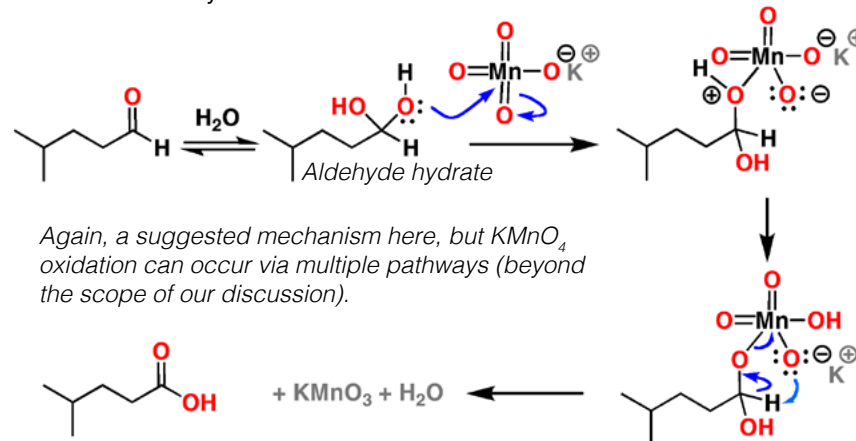
KMnO₄ (continued)

How it works: Oxidation of primary and secondary alcohols

Primary alcohols are oxidized to carboxylic acids; secondary alcohols are oxidized to ketones.

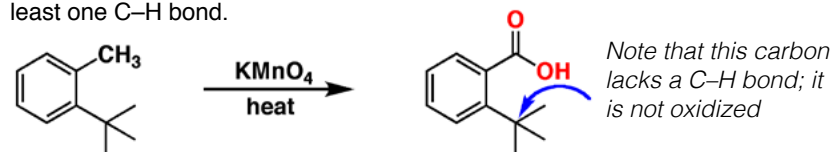


Aldehydes are not stable under these reaction conditions and will be further oxidized to carboxylic acids



How it works: Oxidation of aromatic side chains

The mechanism for side chain oxidation is complex (involves free radicals) and not completely understood. It requires that the carbon adjacent to the arene have at least one C-H bond.

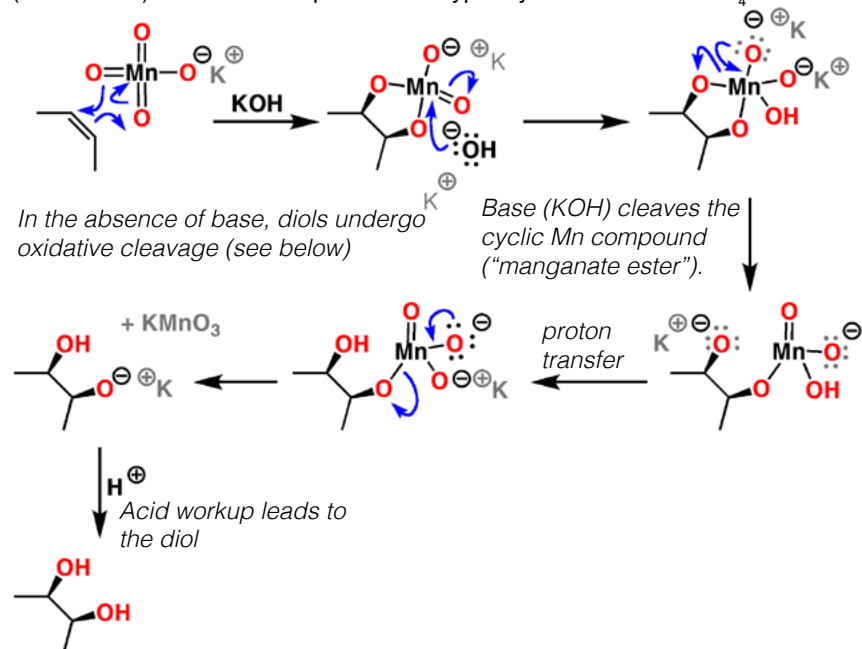


KMnO₄ (continued)

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How it works: Dihydroxylation of alkenes

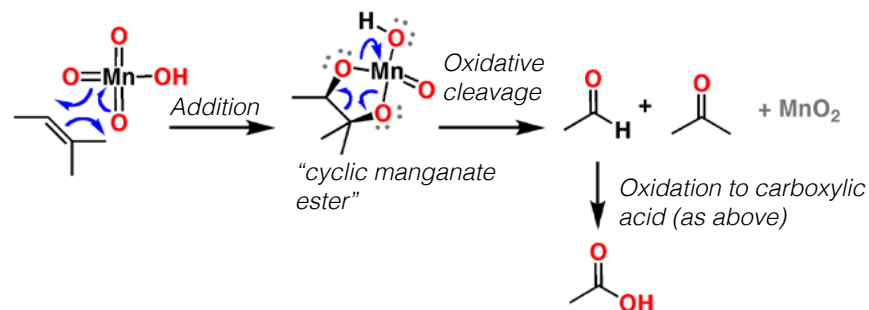
Under cold, dilute basic conditions, KMnO₄ will convert alkenes into 1,2-diols (vicinal diols). Yields for this process are typically lower than for OsO₄.



How it works: Oxidative cleavage of alkenes

Under acidic conditions vicinal diols undergo oxidative cleavage.

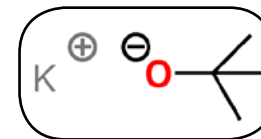
KMnO₄ is protonated to give HMnO₄ and adds to the alkene as above:



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KOt-Bu Potassium *t*-butoxide

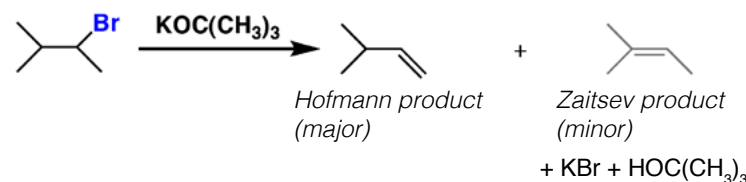


Also known as: KOC(CH₃)₃, potassium tert-butoxide

What it's used for: Potassium *t*-butoxide is a strong, sterically hindered base. The prototypical "bulky base", it is useful in elimination reactions for forming the less substituted "non-Zaitsev" [sometimes called "Hofmann"] alkene product.

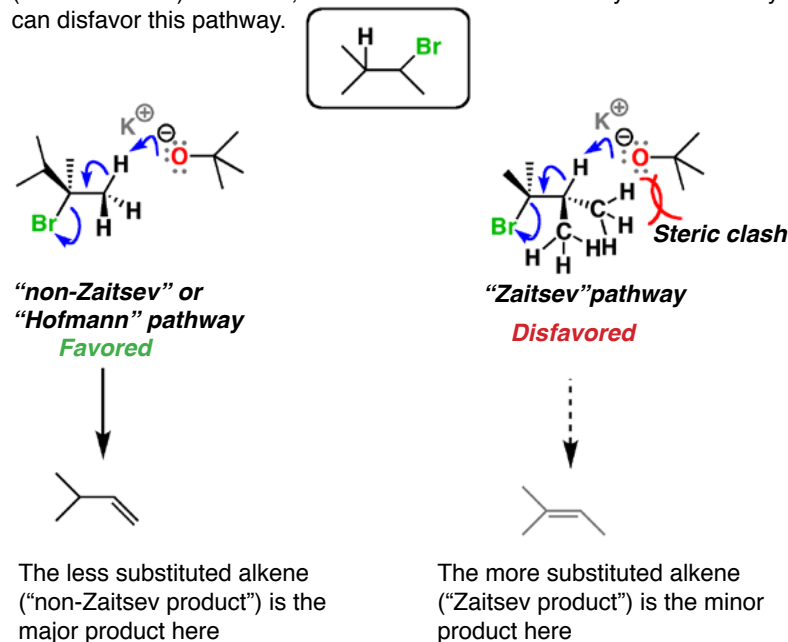
Similar to: Essentially identical to NaOtBu and LiOtBu [these are all treated as the same here]. Lithium diisopropyl amide (LDA) is a stronger bulky base.

Example 1: Elimination - conversion of alkyl halides to alkenes ("non-Zaitsev" or "Hofmann" alkene products)



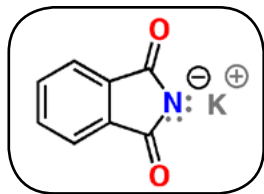
How it works: Formation of "non-Zaitsev" elimination products

Elimination reactions generally favor formation of the more substituted alkene ("Zaitsev's rule"). However, steric clash between the bulky base and alkyl groups can disfavor this pathway.



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KPhth Potassium Phthalimide

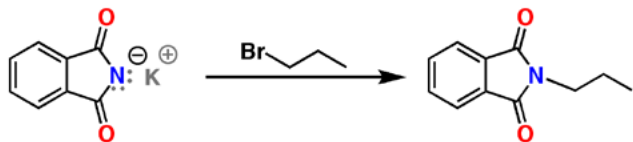


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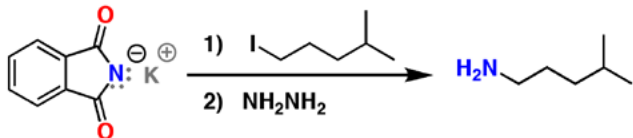
Also known as: phthalimide ion

What it's used for: Sodium (or potassium) phthalimide is a nitrogen-containing nucleophile used in the Gabriel synthesis. Potassium phthalimide reacts with alkyl halides to form a C–N bond, which is then cleaved by treatment with hydrazine to give a primary amine.

Example 1: Substitution - formation of alkyl phthalimides from alkyl halides

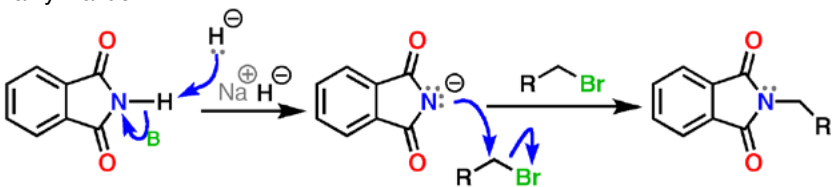


Example 2: Conversion of phthalimides to primary amines (after cleavage with NH_2NH_2)



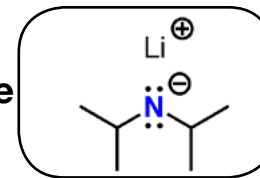
How it works: *Substitution reaction*

In the reaction below, a strong base (NaH) is used to deprotonate phthalimide to give the conjugate base, which then performs an $\text{S}_{\text{N}}2$ reaction on a primary alkyl halide.



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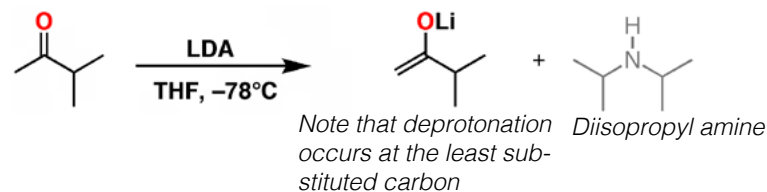
LDA Lithium diisopropyl amide



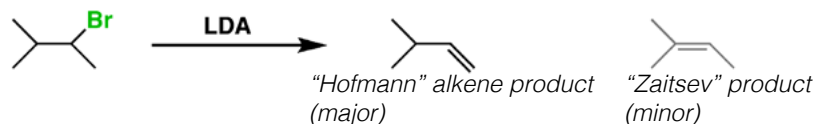
What it's used for: LDA is a strong, bulky, non-nucleophilic base. It is the reagent of choice for selectively removing a proton from the least hindered carbon next to a ketone. It can also be used to form the "Hofmann" product in elimination reactions.

Similar to: NaNH_2 (in strength), KOt-Bu (in size)

Example 1: Conversion of ketones to enolates

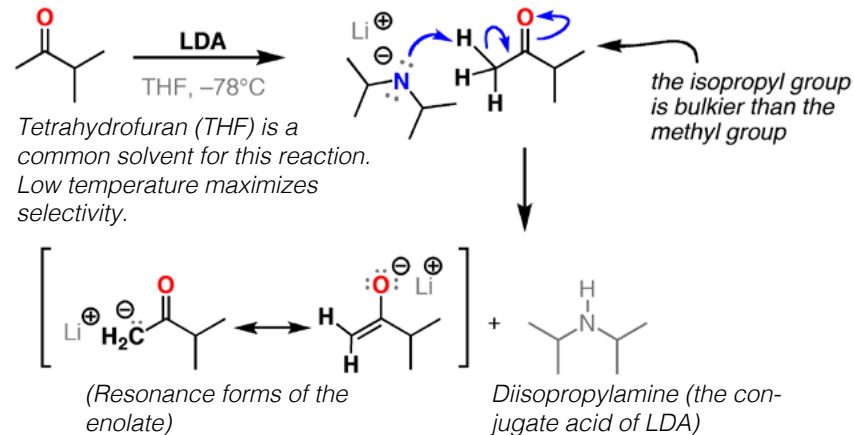


Example 2: Elimination of alkyl halides to give "Hofmann" alkenes



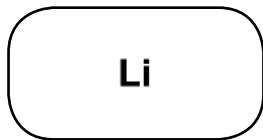
How it works: *Formation of less substituted enolates ("kinetic" enolates)*

The bulky isopropyl groups of LDA make it a highly selective base for removing a proton from the less hindered α -carbon of the ketone.



Li

Lithium

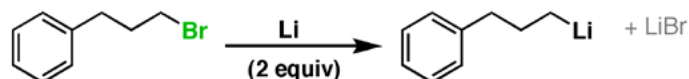


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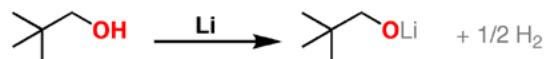
What it's used for: Lithium is a reducing agent. It will convert alkyl halides to alkyl lithium compounds. It is similar to (although a weaker reducing agent than) sodium and potassium. It will also form H_2 when treated with alcohols, giving lithium alkoxides.

Similar to: Sodium (Na), Potassium (K)

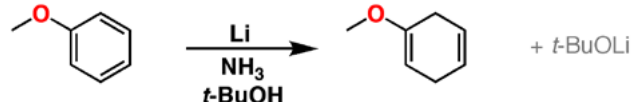
Example 1: Conversion of alkyl halides to alkyllithiums



Example 2: Conversion of alcohols to alkoxides

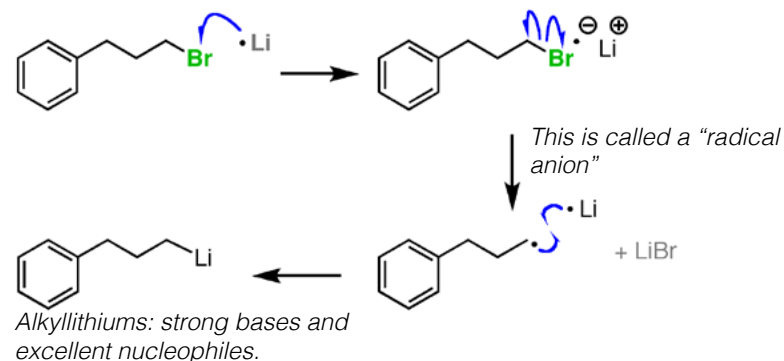


Example 3: Birch reduction - conversion of arenes to dienes



How it works: Formation of organolithium reagents

Like all alkali metals, lithium readily gives up its single valence electron. When treated with an alkyl halide, it will form an alkyl lithium species. Two equivalents of lithium are required for this reaction.



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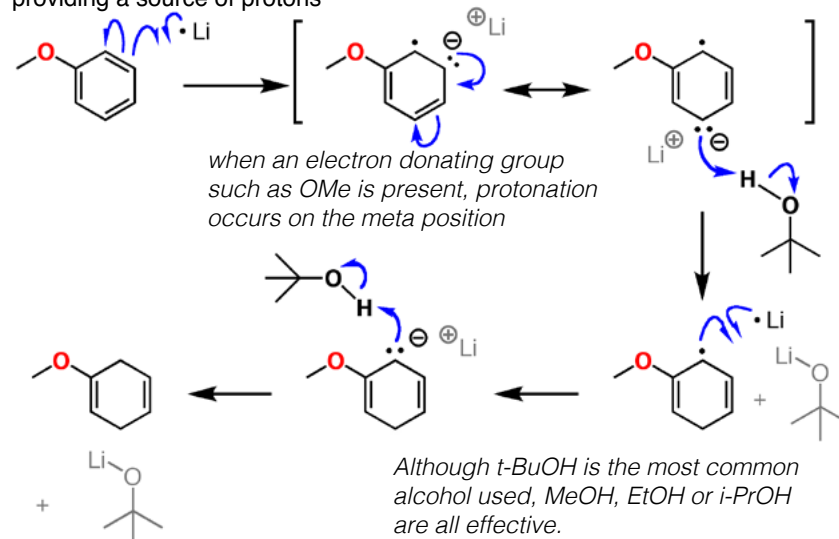
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Li

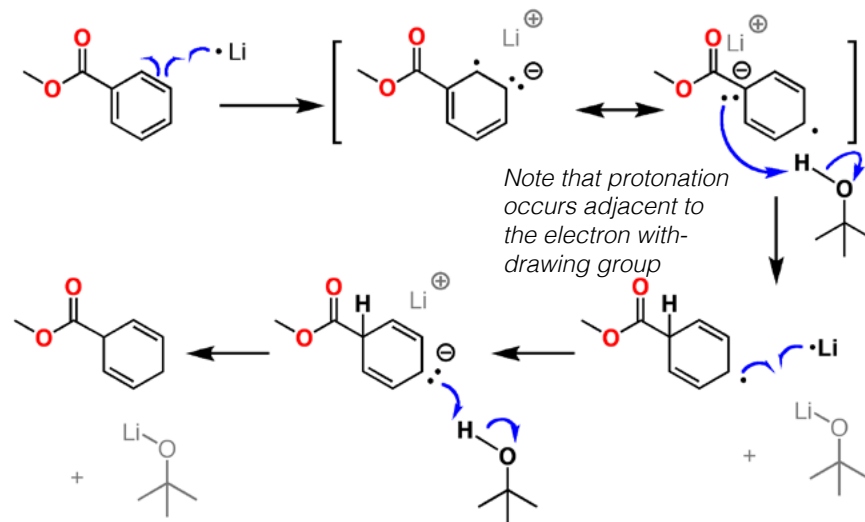
(continued)

How it works: Birch reduction

The Birch reduction is a useful way of obtaining dienes from aromatic groups. Ammonia (NH_3) is the usual solvent with small amounts of an alcohol such as t-BuOH providing a source of protons



When electron withdrawing substituents are present, protonation occurs on the carbon adjacent to the electron withdrawing group



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Lindlar's Catalyst



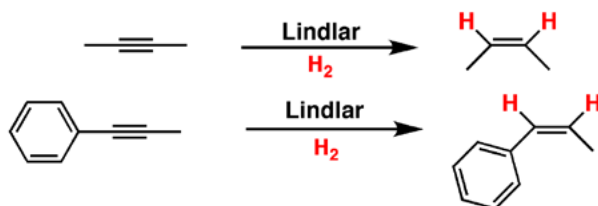
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Also known as: Poisoned catalyst, Pd-CaCO₃

What it's used for: Lindlar's catalyst is a poisoned palladium metal catalyst that performs partial hydrogenations of alkynes in the presence of hydrogen gas (H₂). It always gives the *cis* alkene, in contrast to Na/NH₃ which gives *trans*.

Similar to: Nickel boride (Ni₂B), palladium on barium sulfate, Pd-CaCO₃-quinoline

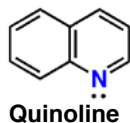
Example 1: Lindlar reduction - conversion of alkynes to alkenes



How it works: Partial hydrogenation

Other than its lower activity when compared with non-poisoned metal catalysts, Lindlar's catalyst behaves in all ways similar to other heterogeneous metal catalysts such as Pd/C, Pt, Ni, etc. (see these separately). The alkyne and hydrogen are adsorbed on to the metal surface and delivered in *cis* fashion.

Sometimes the aromatic amine quinoline is used, which assists the selectivity of the reaction and prevents the formation of alkanes.

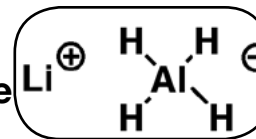


It is thought that the role of Pb (lead) is to reduce the amount of H₂ adsorbed, while quinoline helps to prevent the formation of unwanted byproducts.

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Lithium aluminum hydride

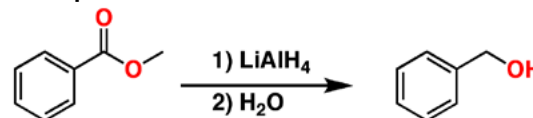


Also known as: LAH

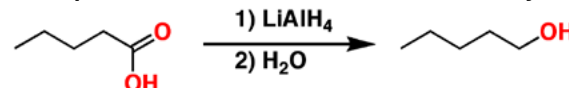
What it's used for: Lithium aluminum hydride is a very strong reducing agent. It will reduce aldehydes, ketones, esters and carboxylic acids to alcohols, amides and nitriles to amines, and open epoxides to give alcohols.

Similar to: NaBH₄, DIBAL, LiAlH(Ot-Bu)₃

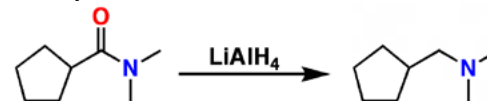
Example 1: Reduction - conversion of esters to primary alcohols



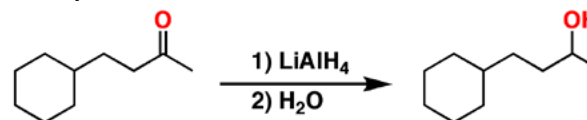
Example 2: Reduction - conversion of carboxylic acids to primary alcohols



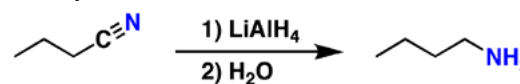
Example 3: Reduction - conversion of amides to primary amines



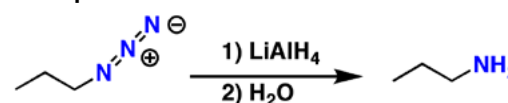
Example 4 - Reduction - conversion of ketones to secondary alcohols



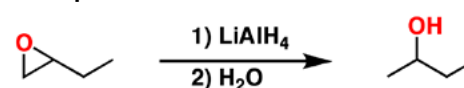
Example 5 - Reduction - conversion of nitriles to primary amines



Example 6 - Reduction - conversion of azides to primary amines



Example 7 - Reduction - conversion of epoxides to alcohols (ring opening)



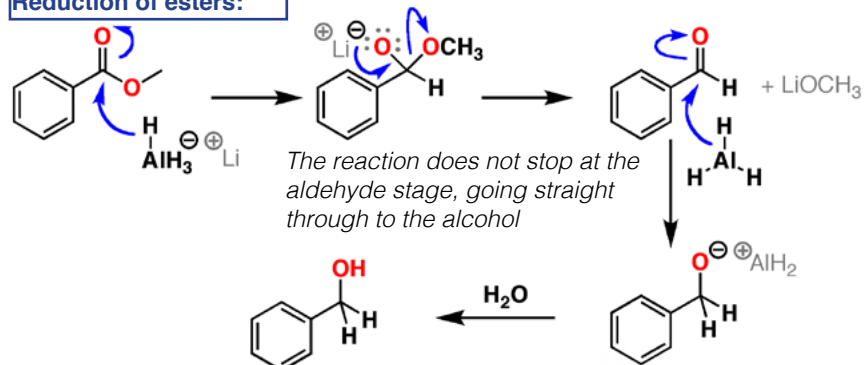
LiAlH₄ (continued)

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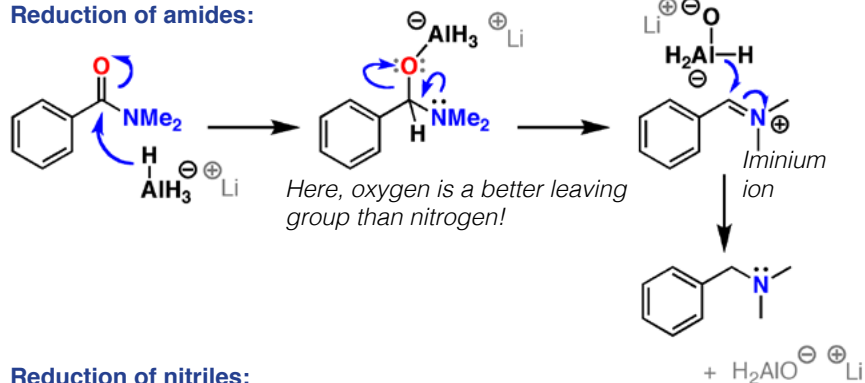
How it works: *Reduction of esters, amides, and nitriles*

Lithium aluminum hydride is a very strong reducing agent capable of reacting with a wide variety of functional groups. It is generally not possible to control reactions of LiAlH₄ so that they “stop” part of the way; reactions of esters go straight to alcohols, for instance.

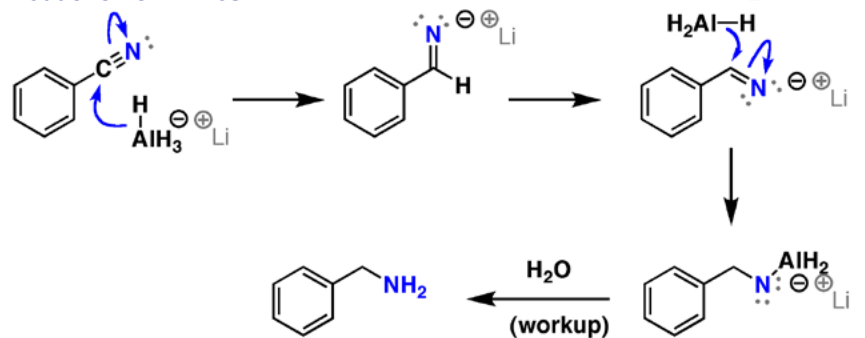
Reduction of esters:



Reduction of amides:



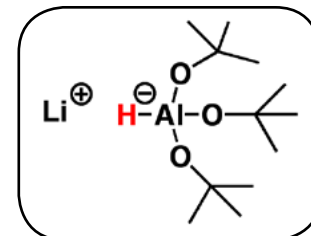
Reduction of nitriles:



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LiAlH(Ot-Bu)₃ Lithium tri tert-butoxy aluminum hydride

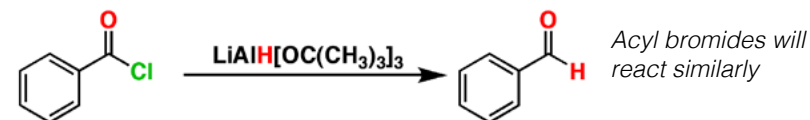


Also known as: LiAlH[OC(CH₃)₃]₃

What it's used for: Strong, bulky reducing agent. Less reactive than LiAlH₄, it will convert acyl halides to aldehydes.

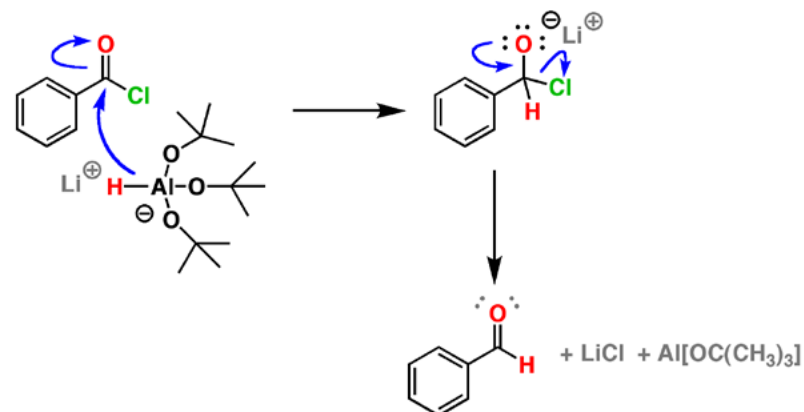
Similar to: NaBH₄, DIBAL, LiAlH₄

Example 1: Reduction of acyl halides to aldehydes

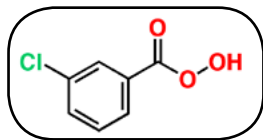


How it works: *Reduction of acyl chlorides*

The mechanism for this reaction is similar to LiAlH₄. So long as only one equivalent is used, the aldehyde will not be reduced further to the alcohol.

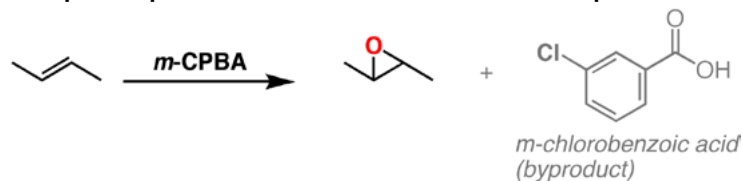
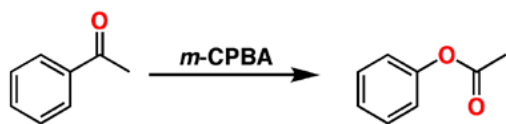


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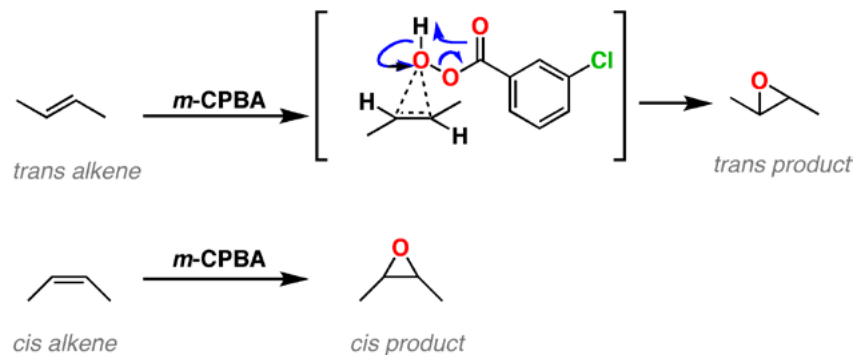
m-CPBA**m-chloroperoxybenzoic acid**[Index](#)

What it's used for: mCPBA (sometimes written MCPBA) is an oxidizing agent. It sees use in two main ways. First, it is used to transform alkenes into epoxides. Secondly, it will react with ketones to form esters in the Baeyer-Villiger reaction.

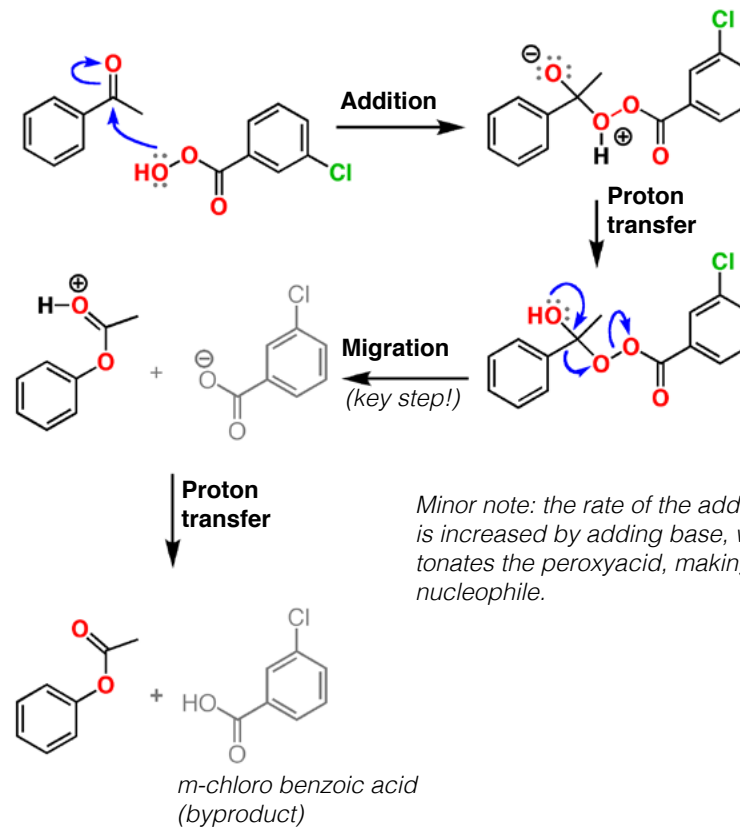
Similar to: Peroxyacetic acid [$\text{CH}_3\text{CO}_3\text{H}$], trifluoroperoxyacetic acid [$\text{CF}_3\text{CO}_3\text{H}$] and any generic peroxyacid [RCO_3H or RCOOOH]

Example 1: Epoxidation - conversion of alkenes to epoxides**Example 2: Baeyer-Villiger reaction - conversion of ketones to esters****How it works: Epoxidation of alkenes**

Treatment of alkenes with mCPBA leads to the formation of epoxides through a concerted transition state. The reaction is completely stereospecific: trans alkenes and cis alkenes give stereoisomeric products.

[Index](#)**m-CPBA****(continued)****How it works: Baeyer-Villiger reaction**

In the Baeyer-Villiger reaction, m-CPBA adds to a ketone to form a tetrahedral intermediate. In the key step, the carbon migrates to oxygen, breaking the weak O—O bond and leading to the formation of an ester.

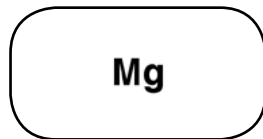


Minor note: the rate of the addition reaction is increased by adding base, which deprotonates the peroxyacid, making it a better nucleophile.

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Mg

Magnesium



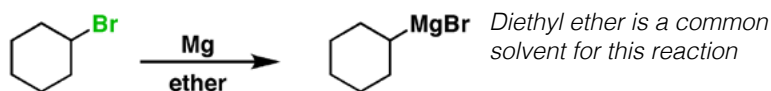
Index

Also known as: Mg^0 , Mg(s)

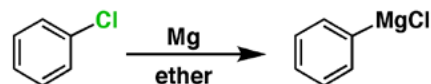
What it's used for: Magnesium metal is used for the formation of Grignard reagents from alkyl and alkenyl halides. A common solvent for these reactions are ethers, such as diethyl ether (Et_2O).

Similar to: Lithium (in the formation of alkyllithium reagents), Na, K

Example 1: Conversion of alkyl halides to Grignard reagents

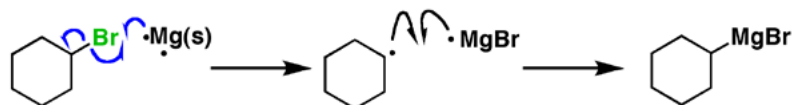


Example 2: Conversion of alkenyl halides to Grignard reagents



How it works: Formation of Grignard reagents

Although the mechanism for Grignard formation is generally not given in textbooks, formation of Grignard reagents goes through a radical process.

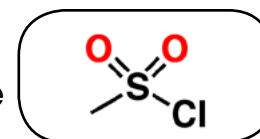


Here, magnesium donates a single electron to Br, which forms a radical anion. Homolytic fragmentation of the C-Br bond leads to a free radical, which recombines with $\text{MgBr}^\bullet$ to give the Grignard reagent.

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MsCl

Methanesulfonyl chloride

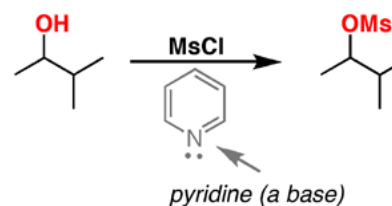


Also known as: Mesyl chloride

What it's used for: Methanesulfonyl chloride converts alcohols into good leaving groups. It behaves essentially identically to TsCl for this purpose.

Similar to: p-toluenesulfonyl chloride (TsCl)

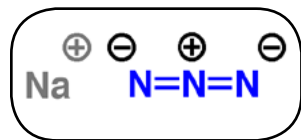
Example 1: Conversion of alcohols to alkyl mesylates



It is common to use a weak base (pyridine in this example) to react with the HCl that is formed as a byproduct of this reaction. This helps the reaction proceed to completion.

The resulting alkyl sulfonates ("mesylates") are excellent leaving groups in substitution and elimination reactions. For mechanisms and examples, see the section on TsCl .

NaN₃ Sodium azide

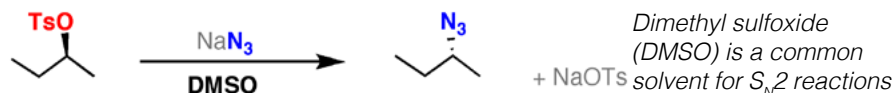


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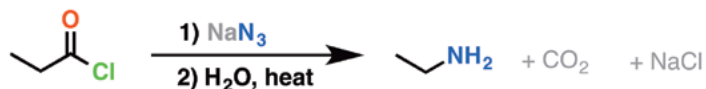
What it's used for: Sodium azide is a good nucleophile that readily participates in S_N2 reactions. Alternatively the sodium or lithium salt of azide ion can be used, but sodium is the most common.

Similar to: LiN₃, KN₃

Example 1: Substitution reaction - conversion of alkyl halides to alkyl azides

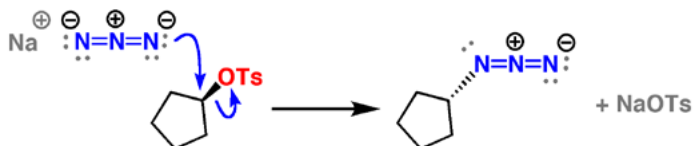


Example 2: Curtius rearrangement - acyl halides to amines



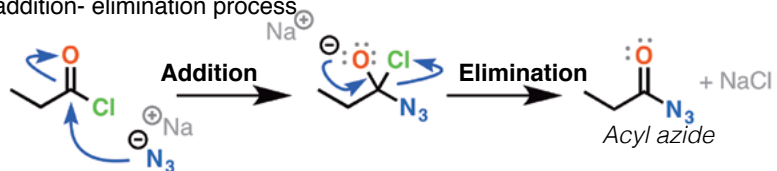
How it works: Nucleophilic substitution

Sodium azide is the conjugate base of the weak acid HN₃ (pK_a = 4.7). It is an excellent nucleophile that happens to be a weak base; reactions using N₃⁻ will have very little competition from elimination pathways.

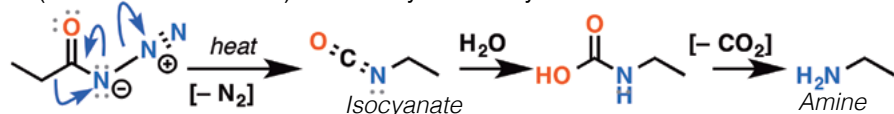


How it works: Curtius rearrangement

Sodium azide reacts with the acyl halide to form an acyl azide via a two step addition- elimination process.



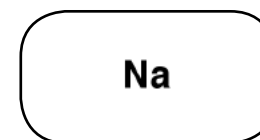
Upon heating, the neighboring carbon migrates to nitrogen in a 1,2-shift, leading to loss of N₂ and formation of an isocyanate. Addition of water to the isocyanate (mechanism not shown) followed by decarboxylation leads to an amine.



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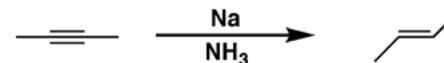
Na Sodium



What it's used for: Sodium is a very strong reducing agent. It will reduce alkynes to alkenes (trans-alkynes, specifically). It will form hydrogen gas when added to alcohols, resulting in alkoxides. It will also reduce aromatic groups to alkenes (the Birch reduction).

Similar to: Lithium (Li), potassium (K)

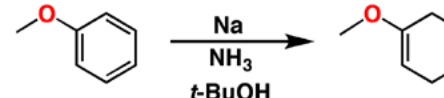
Example 1: Reduction - conversion of alkynes to trans alkenes



Example 2: Conversion of alcohols to alkoxides

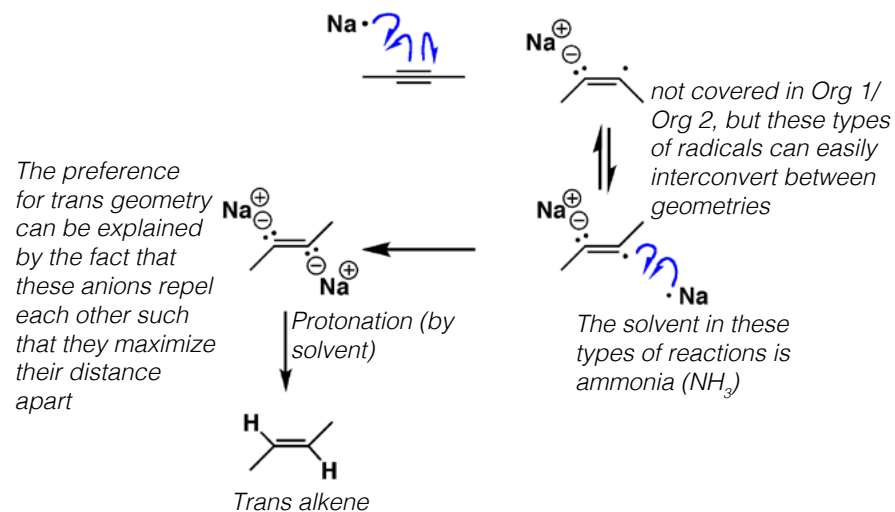


Example 3: Birch reduction - conversion of arenes to dienes



How it works: Reduction of alkynes to trans-alkenes

Sodium metal has an extremely low ionization energy and will readily give up its electron.



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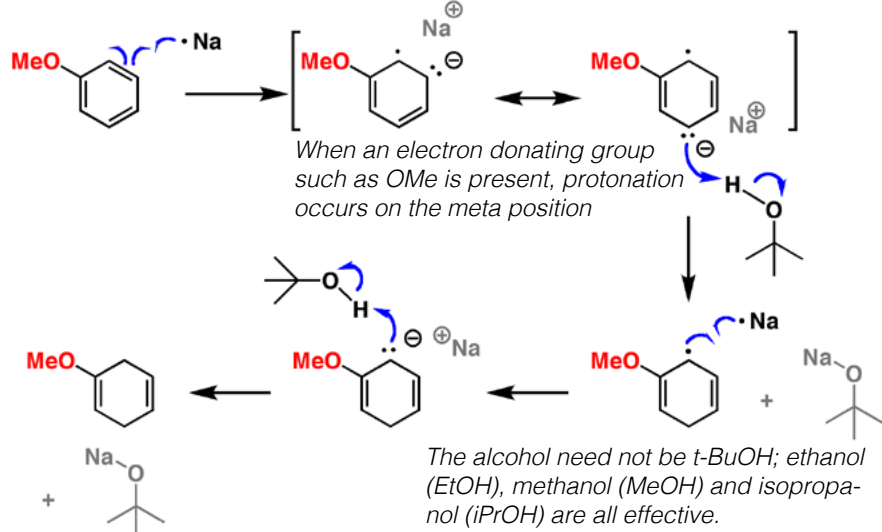
Na

(continued)

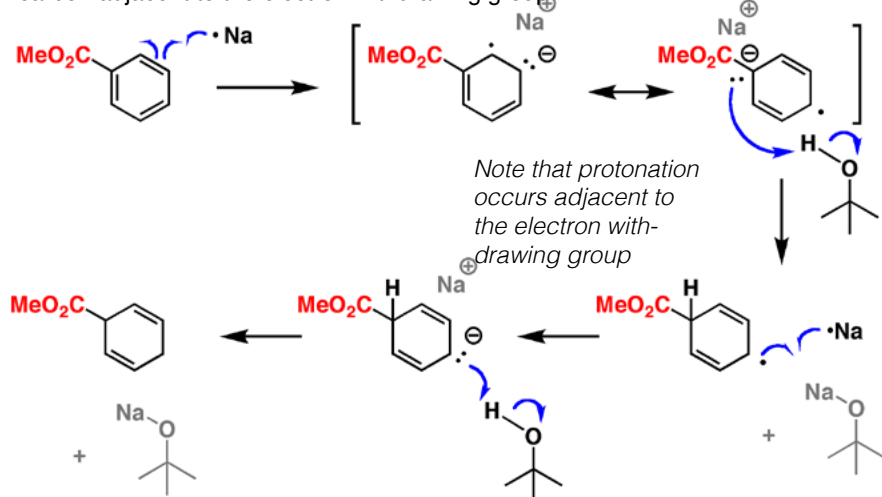
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How it works: The Birch Reduction

The Birch reduction is a method for transforming aromatic rings into dienes. The products obtained depend on the substituent. Electron donating groups provide products where the alkene is attached to the electron donating group (enol ethers):



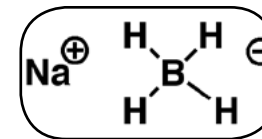
When electron withdrawing substituents are present, protonation occurs on the carbon adjacent to the electron withdrawing group



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NaBH₄

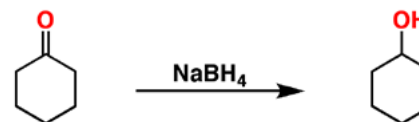
Sodium borohydride



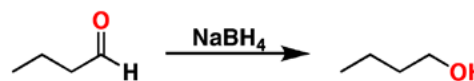
What it's used for: Sodium borohydride is a reagent mainly used for the reduction of ketones and aldehydes (it will also reduce acid halides). It is also used in the oxymercuration of alkenes, to replace mercury with H.

Similar to: Lithium aluminum hydride (LiAlH₄) but less reactive. Also similar to other reducing agents such as NaCNBH₃, DIBAL, LiAlH(Ot-Bu)₃, etc.

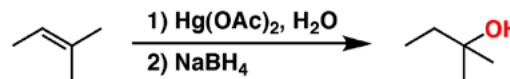
Example 1: Reduction - conversion of ketones to secondary alcohols



Example 2: Reduction of aldehydes to primary alcohols

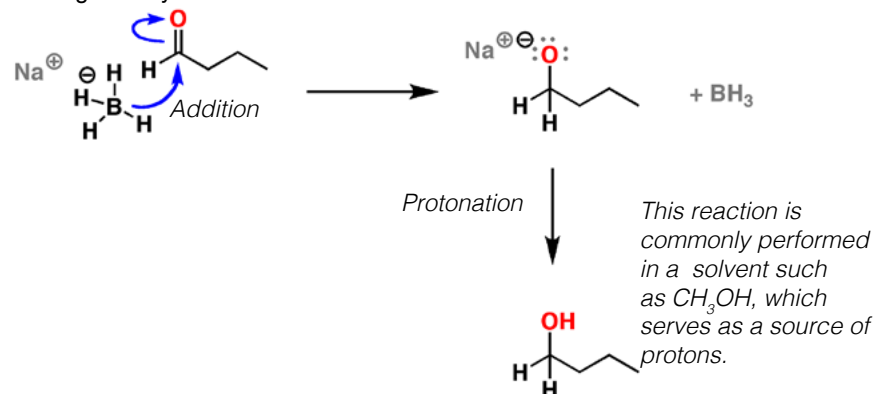


Example 3: Oxymercuration - conversion of alkenes to alcohols



How it works: Reductions of aldehydes and ketones

Sodium borohydride is a good reducing agent. Although not as powerful as LiAlH₄, it is very effective for the reduction of aldehydes and ketones to alcohols. It will generally not reduce esters or amides.

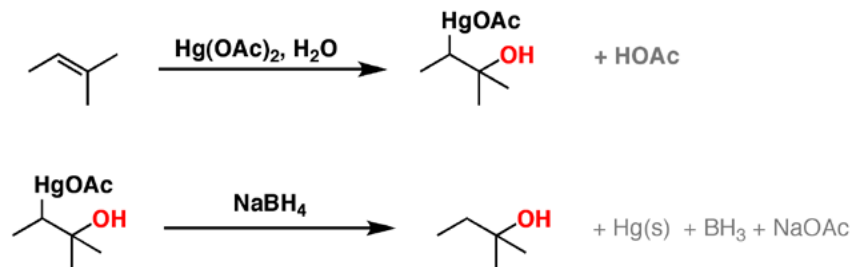


NaBH₄ (continued)

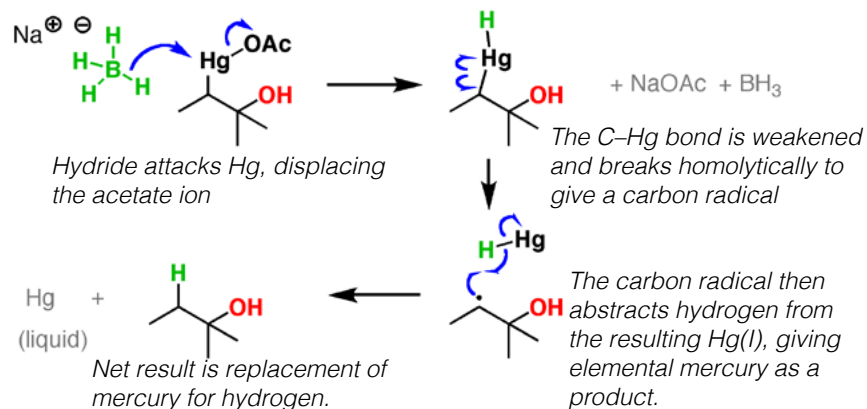
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How it works: *In the oxymercuration reaction*

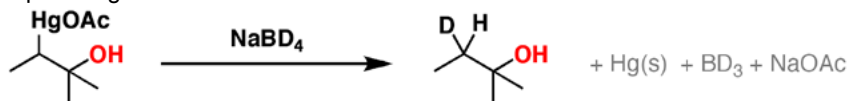
In the oxymercuration reaction, NaBH₄ is used to break the carbon-mercury bond and replace it with hydrogen (second step)



The mechanism for this process is **rarely covered in textbooks** but is covered here for the sake of completeness.

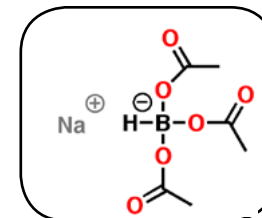


The deuterated version of NaBH₄, sodium borodeuteride (NaBD₄) will replace Hg with D.



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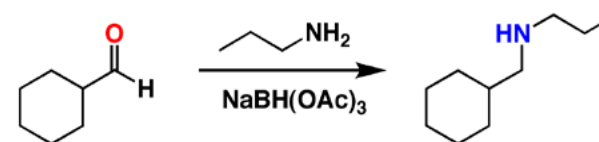
NaBH(OAc)₃ Sodium triacetoxy borohydride



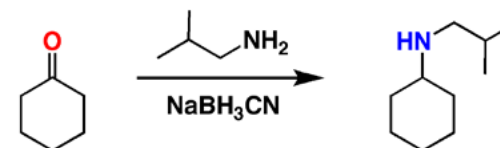
What it's used for: Sodium triacetoxy borohydride is a reducing agent. It is most often used for the reductive amination of ketones (and aldehydes) to amines. In this respect it is identical to sodium cyanoborohydride (NaCNBH₃). Reduction is often performed under mildly acidic conditions.

Similar to: NaCNBH₃, NaBH₄

Example 1: Reductive amination - conversion of aldehydes to amines



Example 2: Reductive amination - conversion of ketones to amines

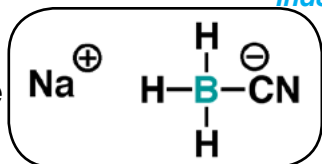


How it works: *Reductive amination*

Reductive amination with NaBH(OAc)₃ works essentially the same way as it does for sodium cyanoborohydride (NaBH₃CN)

NaCNBH₃

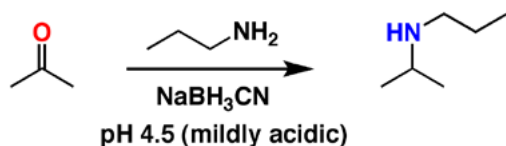
Sodium cyanoborohydride



What it's used for: Sodium cyanoborohydride is a reducing agent. It is generally used for reductive amination - the reduction of imines (or "iminiums") to amines. It's common to perform this reaction under slightly acidic conditions (pH 4-5)

Similar to: NaBH₄, NaBH(OAc)₃

Example 1: Reductive amination - conversion of ketones to amines



Example 2: Reductive amination - conversion of aldehydes to amines

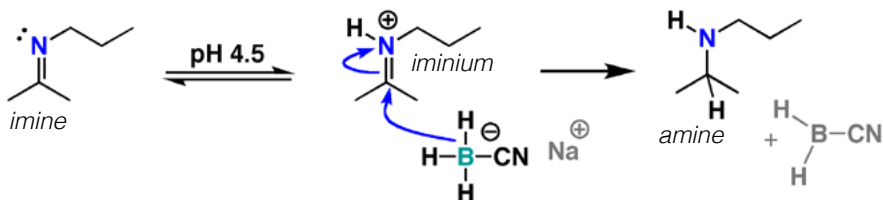


How it works: *Reductive amination*

The first step is formation of an imine from the aldehyde/ketone and the amine:



At pH 4-5 a significant proportion of the imine is present as its conjugate acid ("iminium") which is a more reactive electrophile than the imine.

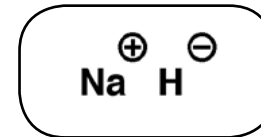


Interestingly, NaCNBH₃ is a poorer reducing agent than NaBH₄. It is used because at slightly acidic pH (~4-5) it is selective for reducing iminium ions (the conjugate acids of imines) over aldehydes and ketones.

The process of converting a ketone or aldehyde to an amine in the presence of a reducing agent such as NaBH₃CN is called "reductive amination".

NaH

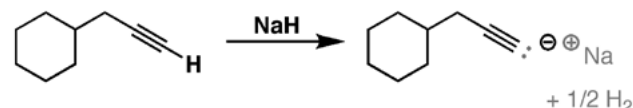
Sodium Hydride



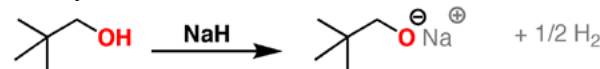
What it's used for: Sodium hydride is a strong base and a poor nucleophile. It is useful for deprotonating alcohols and alkynes, among others. One advantage of using NaH is that the byproduct is H₂, a gas which does not further interfere with the reaction.

Similar to: Potassium hydride (KH), lithium hydride (LiH)

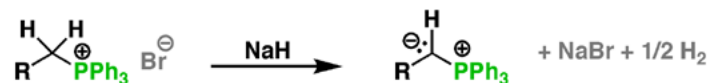
Example 1: Acid-base reaction - conversion of alkynes to acetylides



Example 2: Acid-base reaction - conversion of alcohols to alkoxides



Example 3: Deprotonation of phosphonium salts to form ylides



How it works: *Deprotonation*

H⁻ is a strong base, the conjugate base of hydrogen (pK_a = 42)

It will readily deprotonate alcohols (pK_a 16-18), alkynes (pK_a 25), and other species that are more acidic than hydrogen.

One advantage of using NaH (and KH) is that the conjugate acid is a gas (H₂) and will bubble out of the reaction vessel, not interfering with the reaction further. This also means that the deprotonation is irreversible.

For most purposes it can be used interchangeably with NaNH₂ and other strong bases.

NaIO₄ Sodium periodate

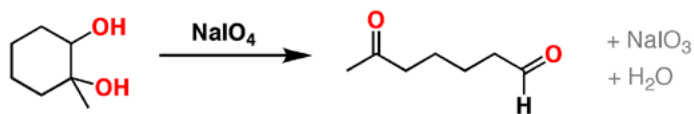
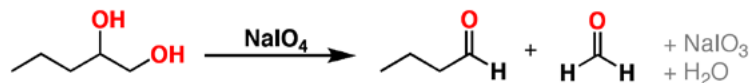


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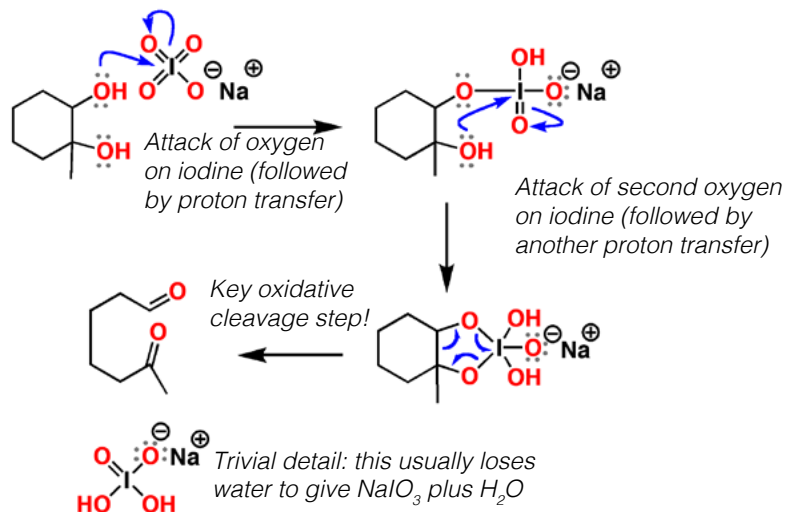
What it's used for: Sodium periodate is a strong oxidant. It will cleave 1,2 diols (vicinal diols) to give aldehydes and ketones.

Similar to: Periodic acid (HIO₄), Lead (IV) acetate [Pb(OAc)₄]

Example 1: Oxidative cleavage - conversion of diols to aldehydes/ketones



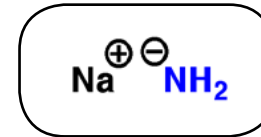
How it works: *Oxidative cleavage of diols to give aldehydes/ketones*



Note that in this process iodine (VII) has been reduced to iodine (V)

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NaNH₂ Sodium amide

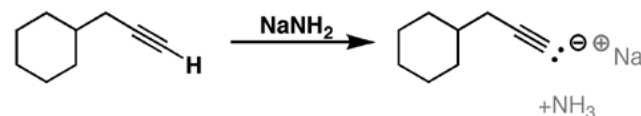


Also known as: Sodamide

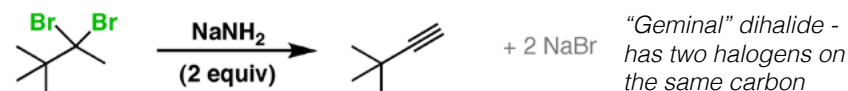
What it's used for: Sodium amide is a very strong base, useful for the deprotonation of alkynes and also in elimination reactions toward the formation of alkynes from dihalides. It can also be used to generate arynes ("benzynes") which can undergo nucleophilic attack.

Similar to: LiNH₂, KNH₂. Essentially the same base strength as LDA, although less sterically hindered.

Example 1: Acid-base reaction - conversion of alkynes to acetylides



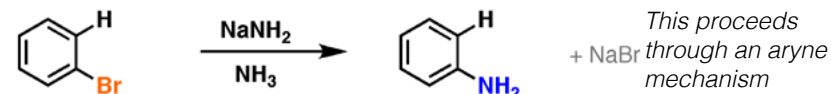
Example 2 - Elimination - conversion of geminal dihalides to alkynes



Example 3: Acid-base reaction - conversion of vicinal dihalides to alkynes



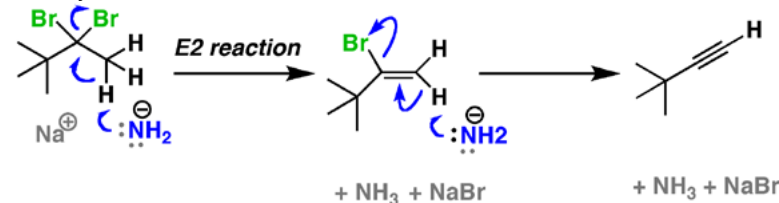
Example 4: Conversion of aryl halides to aryl amines (via arynes)



How it works: *As a strong base*

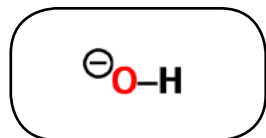
NaNH₂ is the conjugate base of ammonia (pK_a 38). It is sufficiently strong to deprotonate alkynes, which cannot be done reliably with NaOH.

NaNH₂ is also a useful reagent for performing the elimination of geminal dihalides to alkynes.



NaOH

Sodium hydroxide

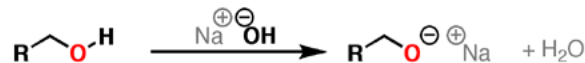


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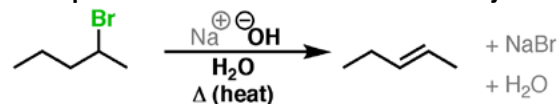
What it's used for: Hydroxide ion (often encountered as NaOH or KOH) is a strong base and good nucleophile. It is impossible to mention all of its applications here but a few of its crucial reactions are highlighted.

Similar to: Similar in action to other strong bases.

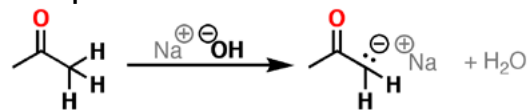
Example 1: Acid-base reaction - conversion of alcohols to alkoxides



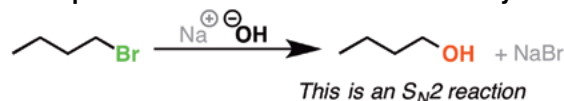
Example 2: Elimination - conversion of alkyl halides to alkenes



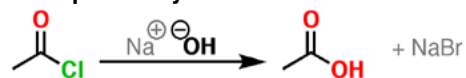
Example 3: Acid-base reaction - conversion of ketones/aldehydes to enolates



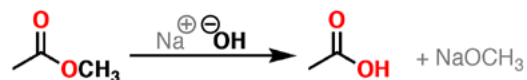
Example 4: Substitution - conversion of alkyl halides to alcohols



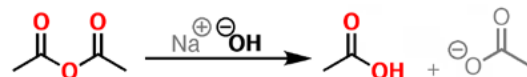
Example 5: Acyl substitution - conversion of acyl halides to carboxylic acids



Example 6: Acyl substitution (saponification) - conversion of esters to carboxylic acids



Example 7: Acyl substitution - conversion of anhydrides to carboxylic acids

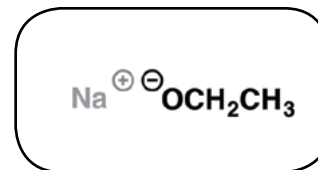


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NaOEt

Sodium Ethoxide

Base



Also known as: NaOCH₂CH₃

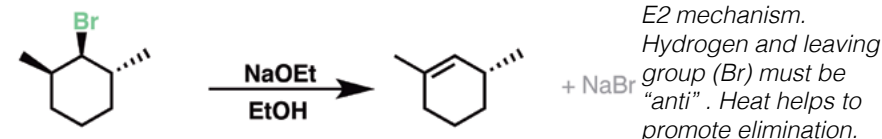
What it's used for: Strong base and good nucleophile. Most often seen as a base for promoting elimination reactions (E2). Can also be used as a nucleophile in S_N2 reactions, particularly if the alkyl halide is primary.

The conjugate base of ethanol. Not really a "reagent", per se, but gets so much use that it deserves its own entry.

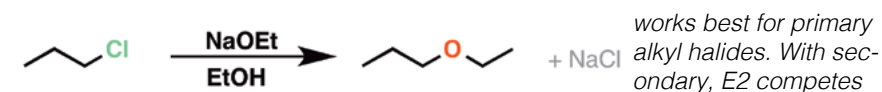
Equivalent to: KOEt, LiOEt, ⁻OEt. Similar to NaOMe (NaOCH₃)

Note that NaOEt is not really a "reagent", it's an organic molecule. The examples shown below are illustrative, but far from comprehensive.

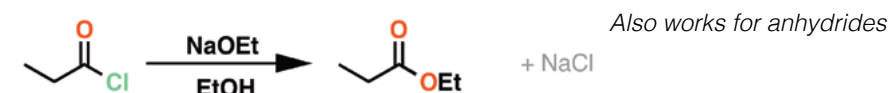
Example 1: Elimination of alkyl halides (E2)



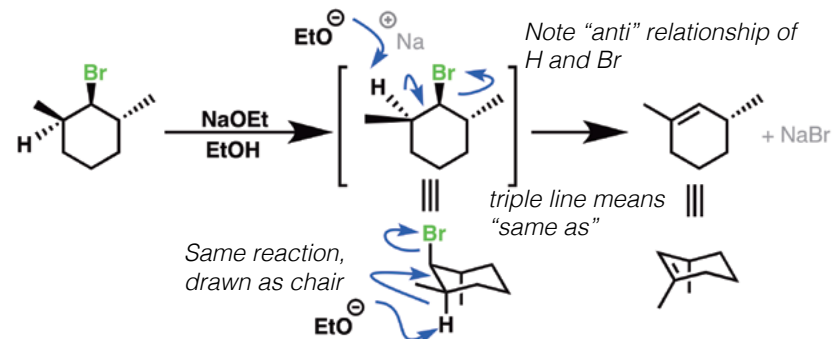
Example 2: Substitution (S_N2) of alkyl halides



Example 3: Reaction with acyl halides to form esters

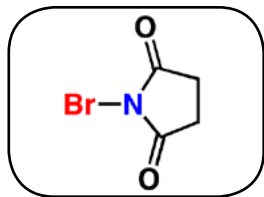


How it works: E2 Reaction



NBS

N-Bromosuccinimide

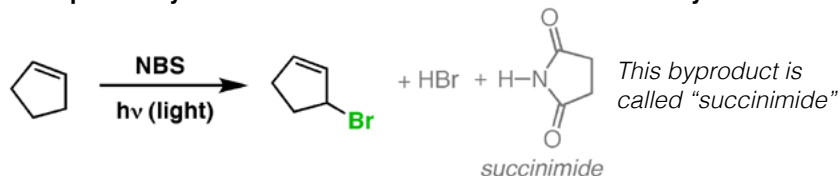


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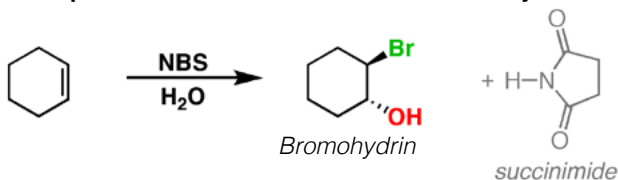
What it's used for: NBS is a source of reactive, electrophilic bromine. It is often used for allylic bromination and in formation of halohydrins from alkenes. Since it is a crystalline solid it is more convenient to use than liquid elemental Br_2 .

Similar to: Br_2 , NCS (N-chlorosuccinimide), NIS (N-iodosuccinimide)

Example 1: Allylic bromination - conversion of alkenes to allylic bromides

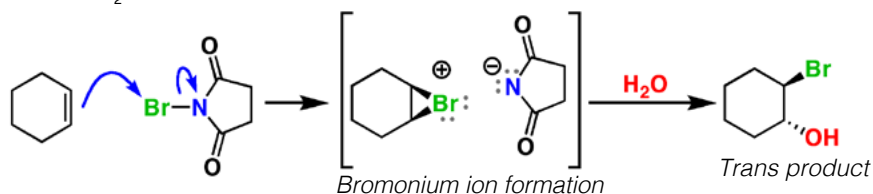


Example 2: Conversion of alkenes to bromohydrins

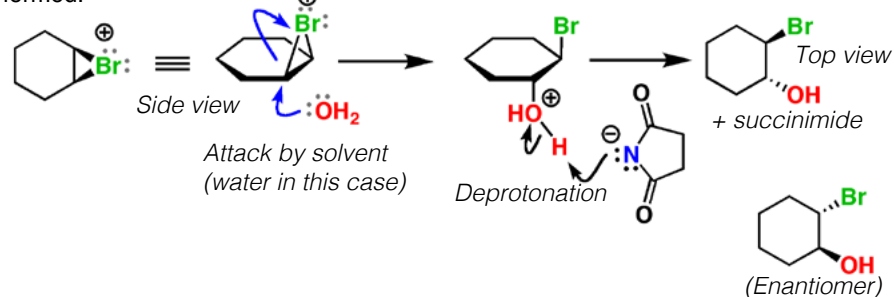


How it works: Halohydrin formation

As with Br_2 , alkenes treated with NBS will form bromonium ions:



The trans product is formed exclusively due to attack of nucleophile on the face opposite the bromonium ion. Note - in this case a 1:1 mixture of enantiomers is formed.



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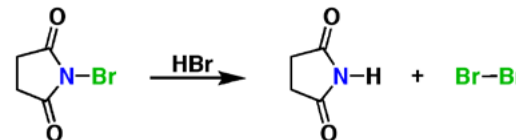
NBS

(continued)

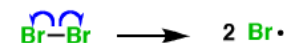
How it works: Allylic bromination

NBS provides a constant, low concentration of Br_2 , which is formed when HBr (from propagation step 1) reacts with NBS. This is useful because the low concentration of Br_2 prevents dibromination of the double bond from occurring.

Generation of Br_2



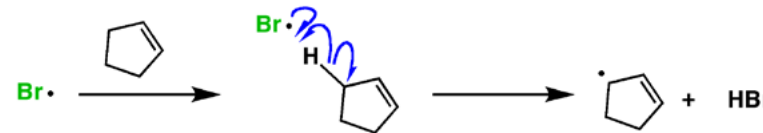
Initiation step



When bromine is heated or treated with light, homolytic cleavage of the $\text{Br}-\text{Br}$ bond results in the formation of two bromine radicals.

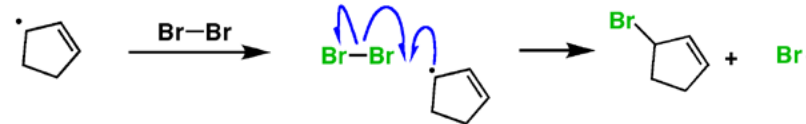
Propagation step 1

In the first propagation step, the bromine radical removes a hydrogen from the allylic carbon, giving a resonance-stabilized free radical.



Propagation step 2

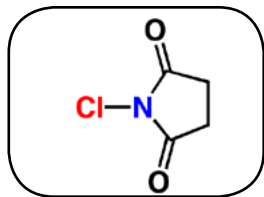
In the second propagation step, the allylic radical reacts with Br_2 , giving the allylic bromide and regenerating a new Br radical. This continues the catalytic cycle.



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NCS

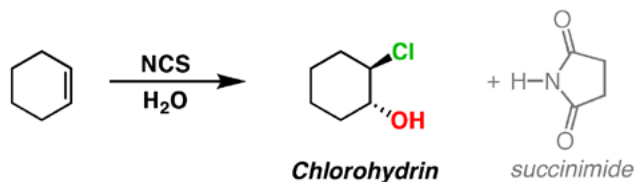
N-Chloro Succinimide


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What it's used for: N-chlorosuccinimide is a source of reactive (electrophilic) chlorine. It is used for the formation of chlorohydrins from alkenes. A crystalline solid, it is more easily handled than dangerous chlorine gas.

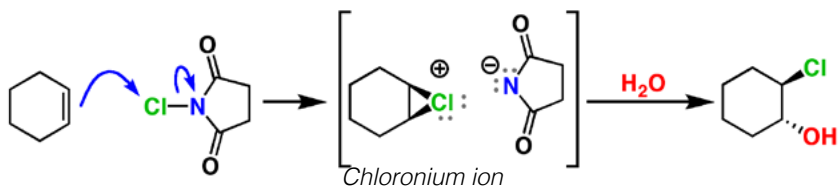
Similar to: Cl_2 , N-bromosuccinimide (NBS), N-iodosuccinimide (NIS)

Example 1: Conversion of alkenes to chlorohydrins

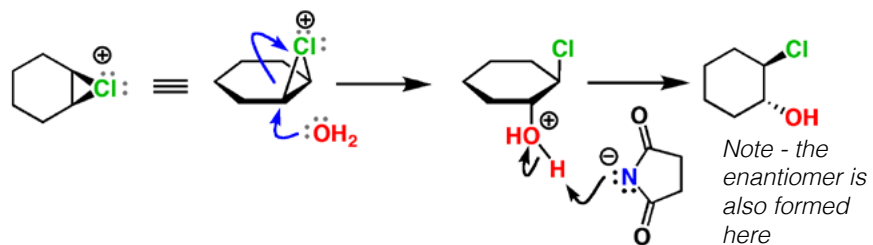


How it works: Formation of chlorohydrins

The first step in chlorohydrin formation is attack of the nucleophilic alkene upon the electrophilic chlorine. This forms an intermediate chloronium ion. In the presence of a nucleophilic solvent such as H_2O , this chloronium ion is attacked to give the chlorohydrin.

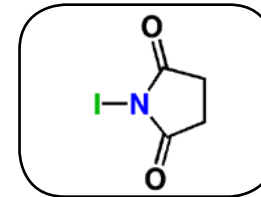


Since attack on the chloronium ion occurs exclusively from the back side, the trans product is formed exclusively.


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NIS

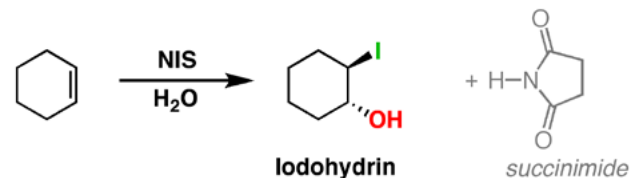
N-Iodo Succinimide



What it's used for: N-iodosuccinimide is a source of electrophilic iodine, similar to NBS and NCS. When added to an alkene in the presence of water, it will form iodohydrins.

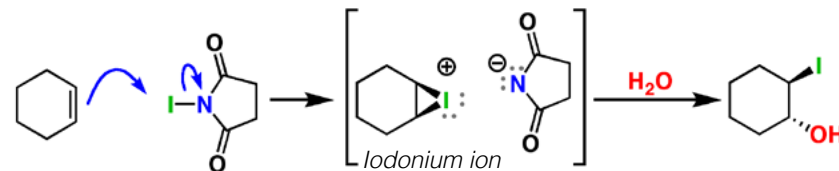
Similar to: I_2 , NBS, NCS.

Example 1: Conversion of alkenes to iodohydrins

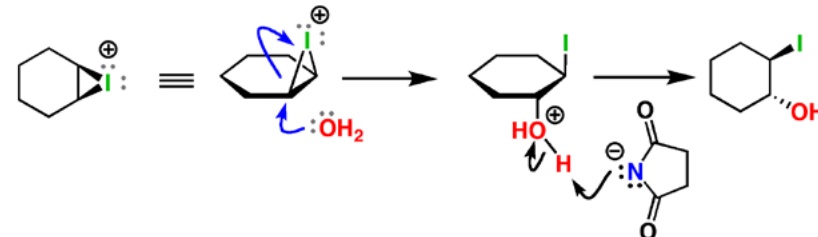


How it works: Iodohydrin formation

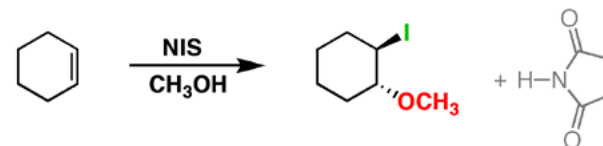
The reaction proceeds via attack of the alkene upon the iodine, followed by attack of nucleophilic solvent upon the iodonium ion.



Since attack on the iodonium ion occurs exclusively from the back side, the trans product is formed exclusively.

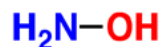


If other nucleophilic solvents are used (e.g. alcohols), ethers will be formed. This is an example of *iodoetherification*.


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NH₂OH

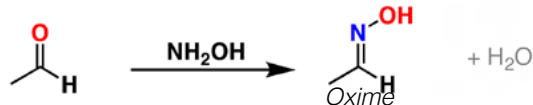
Hydroxylamine



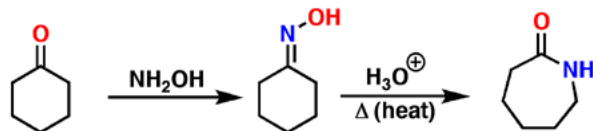
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What it's used for: Hydroxylamine is a good nucleophile. It is most commonly used for the formation of oximes, a precursor to the Beckmann rearrangement.

Example 1: Conversion of ketones/aldehydes to oximes

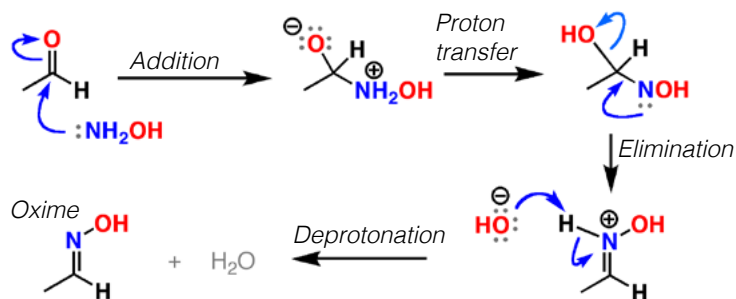


Example 2: Beckmann rearrangement - conversion of oximes to amides



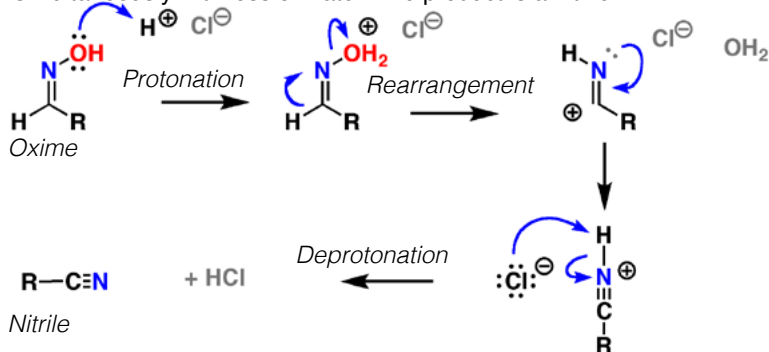
How it works: Conversion of ketones/aldehydes to oximes

Treatment of an aldehyde or ketone with NH_2OH leads to formation of an oxime. Mild acid (although not shown) can accelerate this reaction.



How it works: Beckmann rearrangement

Treatment of the oxime with acid and heat leads to a rearrangement occurring simultaneously with loss of water. The product is a nitrile.



NH₃

Ammonia

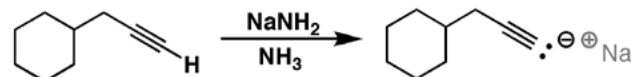


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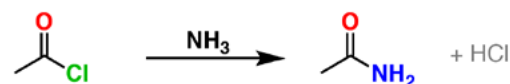
Also known as: NH_3 (l) (signifies it is a liquid)

What it's used for: Ammonia is a base and a nucleophile. It is often used as a solvent in reactions involving lithium (Li), sodium (Na), and potassium (K). It has quite a low boiling point (-33°C)

Example 1: As a solvent - conversion of alkynes to acetylides



Example 2: As a nucleophile - conversion of acyl chlorides to amides

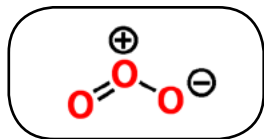


How it works:

NH_3 is the simplest amine and is a Lewis base due to its unshared lone pair of electrons.

Being the conjugate acid of NaNH_2 , it is the perfect solvent for this base, much like MeOH is used as a solvent for NaOMe .

O₃ Ozone

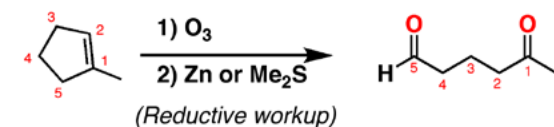


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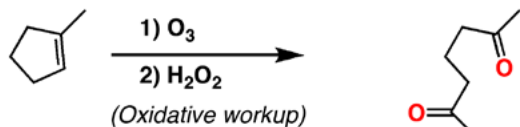
What it's used for: Ozone is an oxidizing agent. It will cleave alkenes and alkynes to give carbonyl compounds, in a reaction called "oxidative cleavage". The products formed can be dependent on the type of workup used. Reductive workup preserves aldehydes, whereas oxidative workup will oxidize any aldehydes to carboxylic acids.

Similar to: KMnO_4

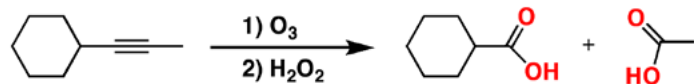
Example 1: Oxidative cleavage (reductive workup) - conversion of alkenes to aldehydes/ketones



Example 2: Oxidative cleavage (oxidative workup) - conversion of alkenes to carboxylic acids/ketones

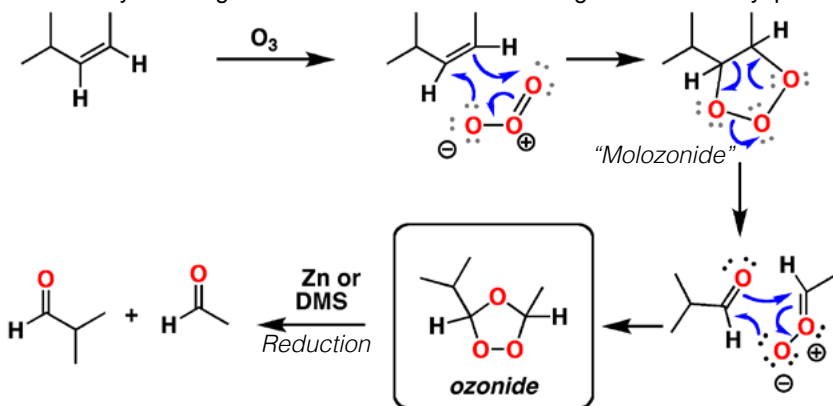


Example 3: Oxidative cleavage - conversion of alkynes to carboxylic acids



How it works: Oxidative cleavage of alkenes

Treatment of an alkene with ozone leads to initial formation of a molozonide, followed by rearrangement to an ozonide. Reduction gives the carbonyl products.



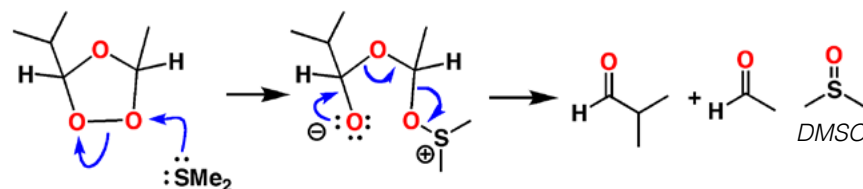
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O₃ (continued)

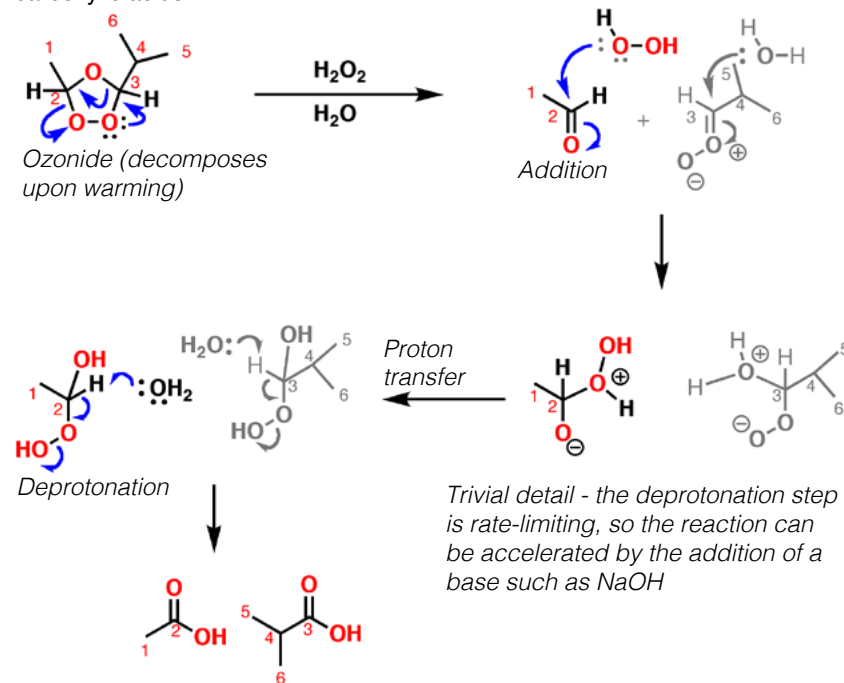
How it works: Reductive workup

Dimethyl sulfide is a reducing agent. It breaks the weak O-O bond, and expels dimethyl sulfoxide (DMSO)



How it works: Oxidative workup

Hydrogen peroxide oxidizes aldehydes to carboxylic acids. Upon warming, the ozonide opens up to an aldehyde and carbonyl oxide, which are converted to carboxylic acids.



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R₂CuLi

Organocuprates

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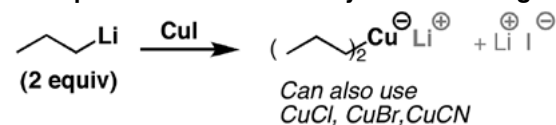


Also known as: Gilman reagents

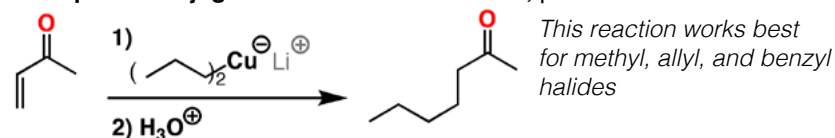
What it's used for: Organocuprate reagents (Gilman reagents) are carbon nucleophiles. They will perform [1,4] additions ("conjugate additions") to α,β unsaturated ketones, as well as S_N2 reactions with certain types of alkyl halides. They can also add to acyl halides to give ketones.

Similar to: Grignard reagents, organolithium reagents

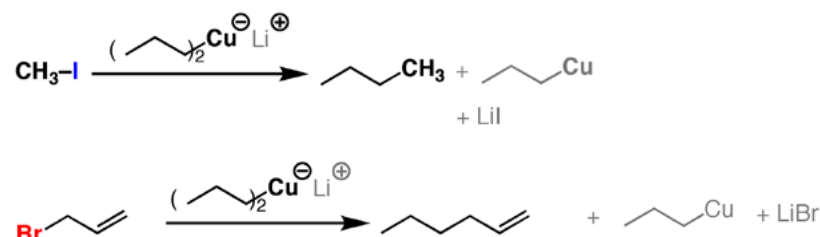
Example 1: Conversion of alkylolithiums to organocuprates



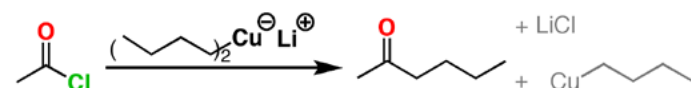
Example 2: Conjugate addition - addition to α, β unsaturated ketones



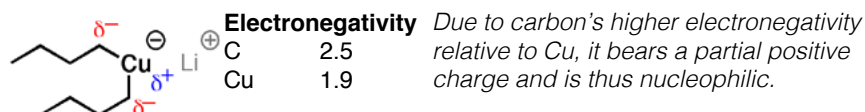
Example 3: Substitution - conversion of alkyl halides to alkanes (S_N2)



Example 4: Acyl substitution - conversion of acyl halides to ketones



How it works: As a nucleophile



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RLi

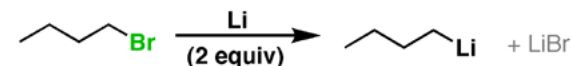
Organolithium reagents



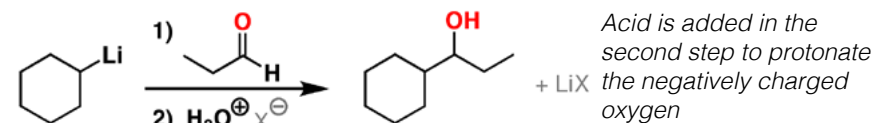
What it's used for: Organolithium reagents are extremely strong bases and good nucleophiles. They react with carbonyl compounds (aldehydes, ketones, esters, etc.) and epoxides. Being strong bases, they will also react with groups containing acidic hydrogens.

Similar to: Grignard reagents

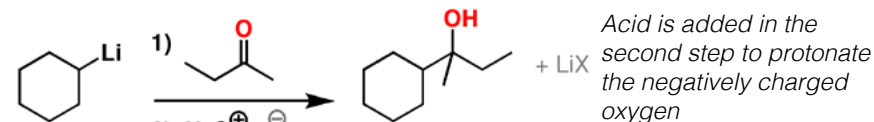
Example 1: Conversion of alkyl halides to organolithiums



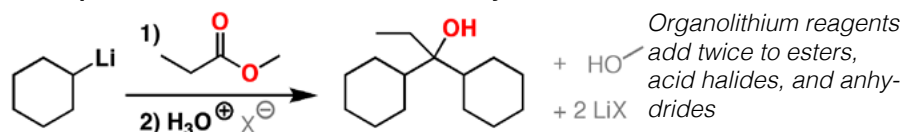
Example 2: Conversion of aldehydes to secondary alcohols



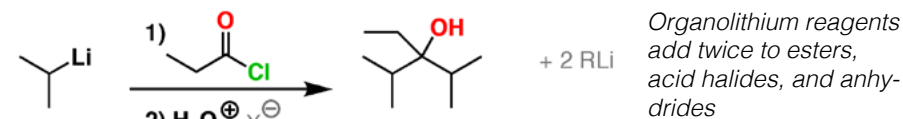
Example 3: Conversion of ketones to tertiary alcohols



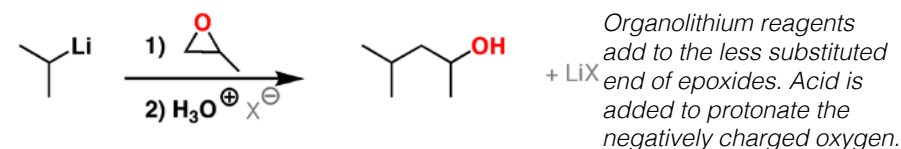
Example 4: Conversion of esters to tertiary alcohols



Example 5: Conversion of acyl halides to tertiary alcohols



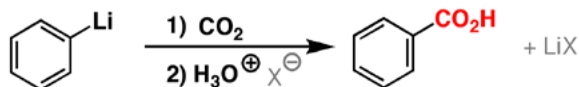
Example 6: Epoxide opening - conversion of epoxides to alcohols



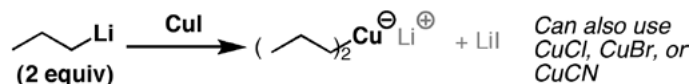
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R-Li (continued)

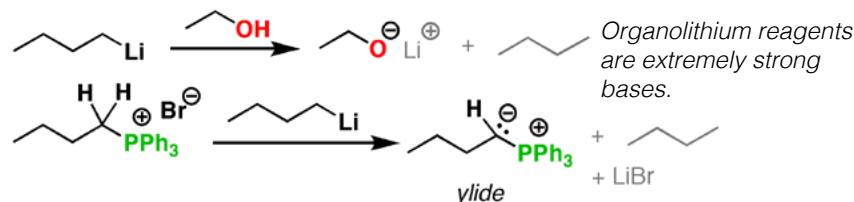
Example 7: Reaction with carbon dioxide



Example 8: Formation of organocuprates



Example 9: As a base

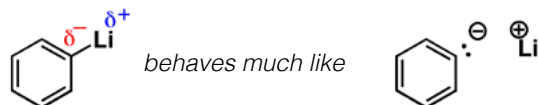


Example 10: Addition to carboxylic acids

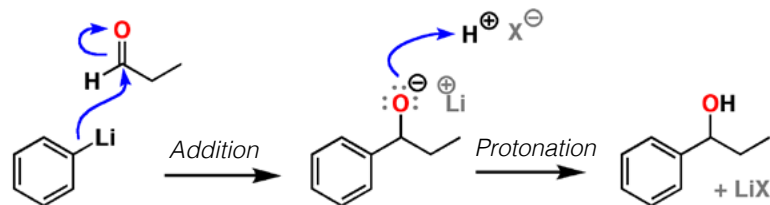


How it works: Addition to aldehydes/ketones

Organolithium reagents are extremely strong nucleophiles. The electrons in the C-Li bond are highly polarized toward carbon:



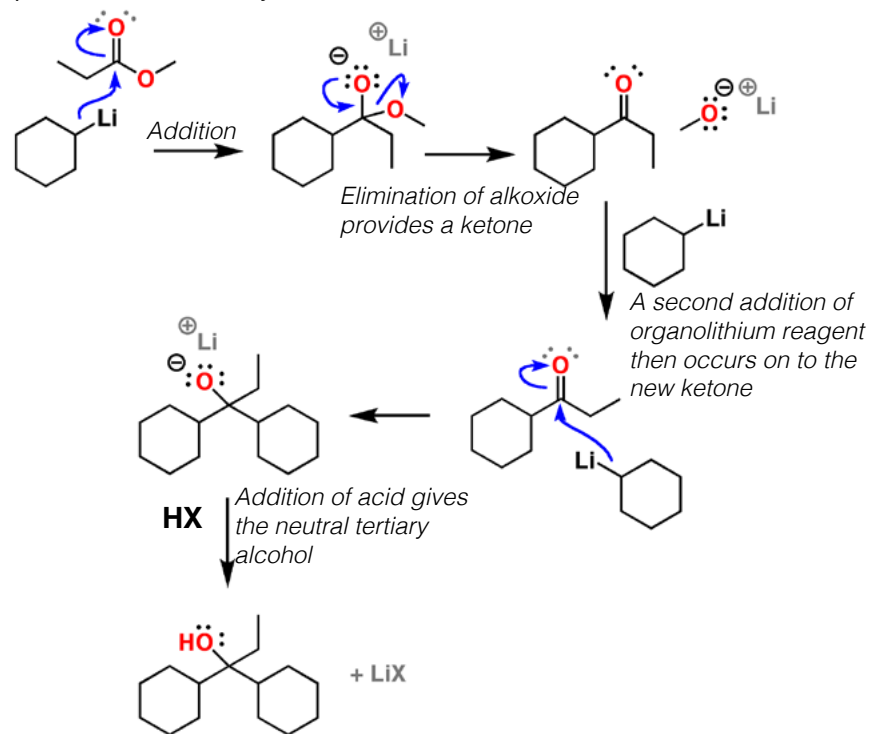
Organolithium reagents readily add to the electrophilic carbonyl atom in aldehydes and ketones. Subsequent addition of acid gives the neutral alcohol.



R-Li (continued)

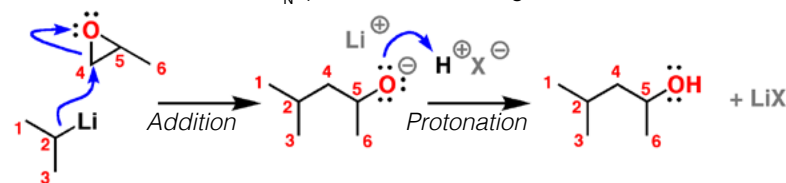
How it works: Addition to esters / acid halides / anhydrides

Organolithium reagents add twice to these groups. The reaction proceeds through addition, elimination, and a second addition. Addition of acid at the end provides a neutral tertiary alcohol.

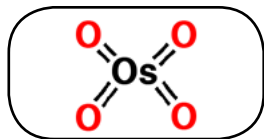


How it works: Addition to epoxides

Organolithium reagents add to the least hindered end of epoxides (you can think of this like an $\text{S}_{\text{N}}2$). Protonation then gives the neutral alcohol.



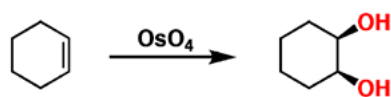
OsO₄ Osmium tetroxide


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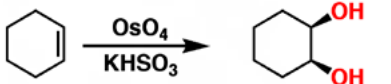
What it's used for: Osmium tetroxide is a reagent for the formation of 1,2-diols (vicinal diols) from alkenes. The selectivity for this reaction is always *syn*.

Similar to: [KMnO₄](#) (cold, dilute)

Example 1: Dihydroxylation - conversion of alkenes to give vicinal diols



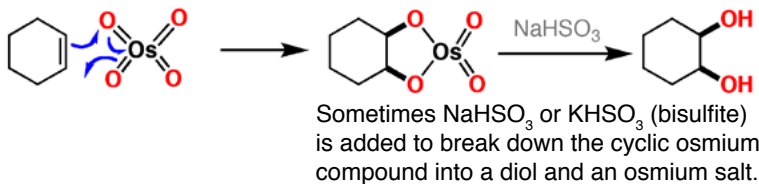
The stereochemistry of a "vicinal diol" this reaction is always "syn"



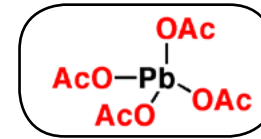
In the lab, [KHSO₃](#) helps to remove the osmium from this reaction. Its presence has no effect on the final product (as shown here)

How it works: Dihydroxylation of alkenes

Oxygens both approach the alkene from the same face.


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Pb(OAc)₄ Lead tetraacetate

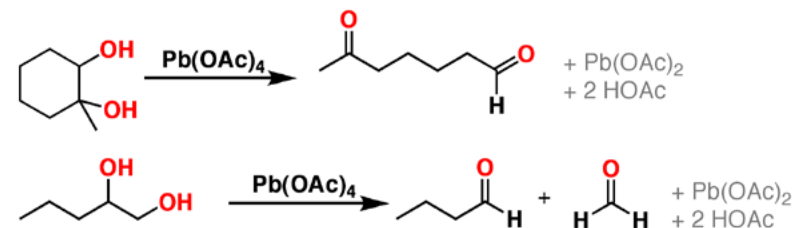


Also known as: Lead (IV) acetate

What it's used for: Lead tetraacetate will cleave 1,2-diols (vicinal diols) into aldehydes/ketones, similar to [NaIO₄](#) and [HIO₄](#).

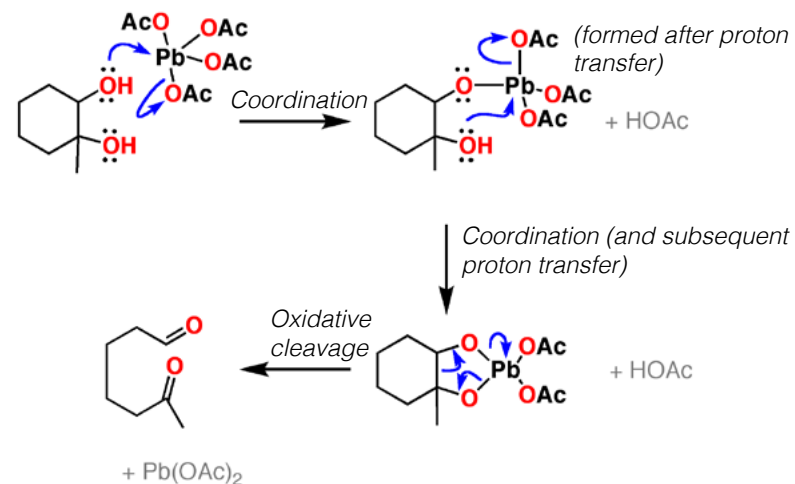
Similar to: Sodium periodate ([NaIO₄](#)), periodic acid ([HIO₄](#)).

Example 1: Oxidative cleavage - conversion of diols to aldehydes / ketones.



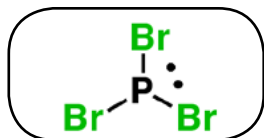
How it works: Cleavage of diols to aldehydes/ketones

Lead (IV) acetate is an oxidizing agent. It works by coordinating to the 1,2-diol and then breaking the carbon-carbon bond in a cyclic mechanism:



Note that Pb(IV) has been reduced to Pb(II). The acetate groups are liberated as acetic acid.

PBr_3 Phosphorus tribromide

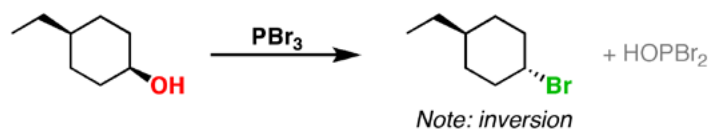


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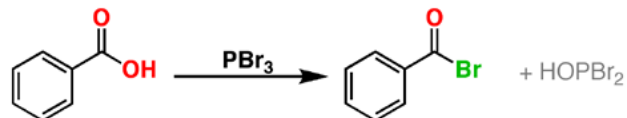
What it's used for: Phosphorus tribromide is a reagent for converting alcohols to alkyl bromides. It will also convert carboxylic acids to acid bromides (acyl bromides)

Similar to: Thionyl bromide (SOBr_2)

Example 1: Substitution - conversion of alcohols to alkyl bromides

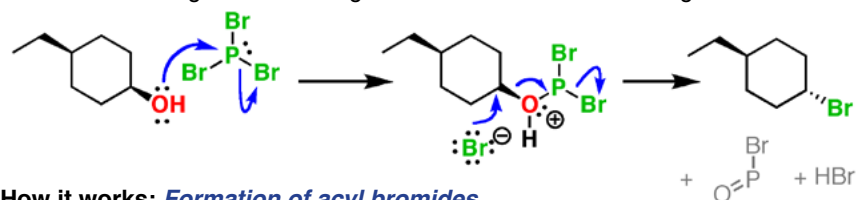


Example 2: Acyl substitution - conversion of carboxylic acids to acyl bromides

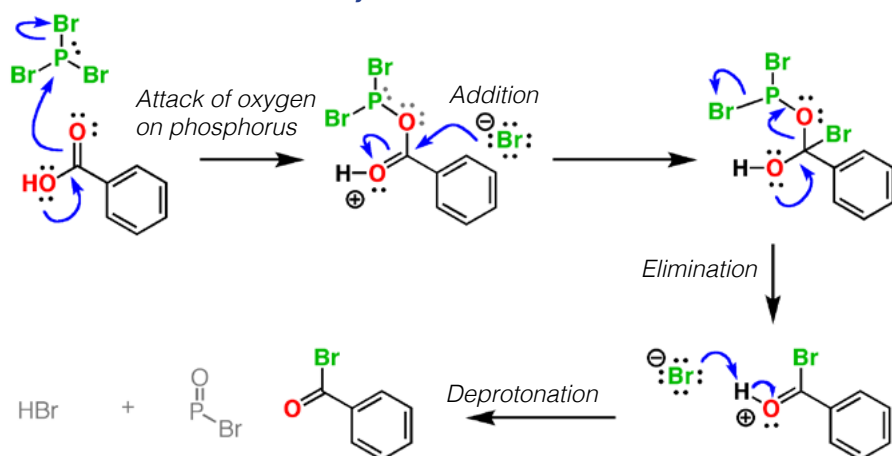


How it works: Formation of alkyl bromides from alcohols

Phosphorus tribromide is useful for converting alcohols into alkyl bromides with inversion of configuration. Driving force is formation of the strong P=O bond



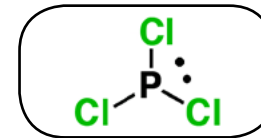
How it works: Formation of acyl bromides



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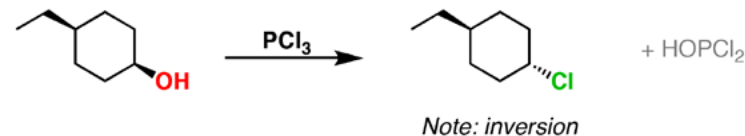
PCl_3 Phosphorus trichloride



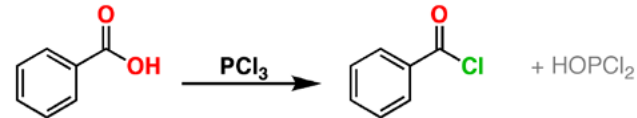
What it's used for: Phosphorus trichloride is a reagent for the conversion of alcohols to alkyl chlorides. It will also convert carboxylic acids to acid chlorides (acyl chlorides)

Similar to: SOCl_2 , PCl_5 . Mechanisms exactly the same as for PBr_3 .

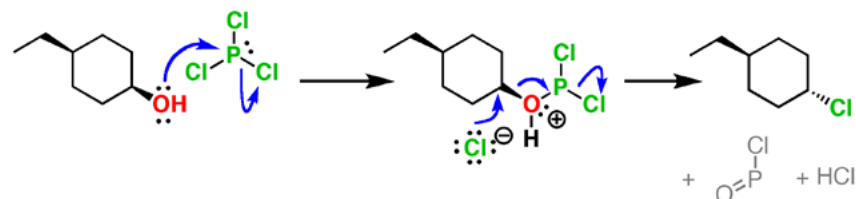
Example 1: Substitution - conversion of alcohols to alkyl chlorides



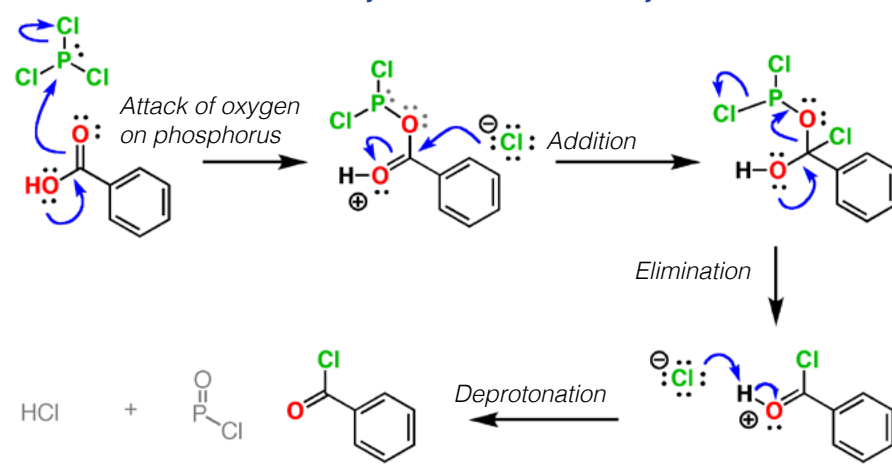
Example 2: Acyl substitution - conversion of carboxylic acids to acyl chlorides



How it works: Formation of alkyl chlorides from alcohols

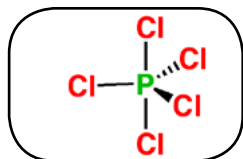


How it works: Formation of acyl chlorides from carboxylic acids



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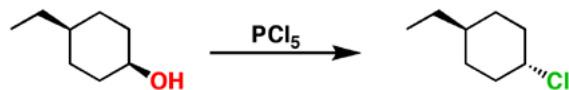
PCl_5 Phosphorus Pentachloride


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What it's used for: Phosphorus pentachloride will convert alcohols to alkyl chlorides, and carboxylic acids to acid chlorides (acyl chlorides)

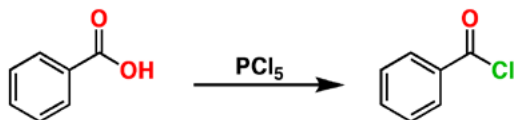
Similar to: SOCl_2 , PCl_3

Example 1: Formation of alkyl bromides from alcohols



Note: inversion

Example 2: Formation of acid bromides from carboxylic acids

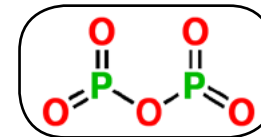


How it works: *Formation of alkyl chlorides and acyl chlorides*

PCl_5 operates by a mechanism essentially identical to that of PCl_3 and PBr_3 .

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P_2O_5 Phosphorus pentoxide

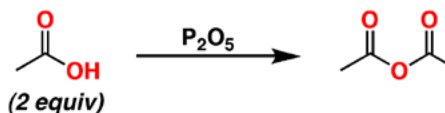


Also known as: Phosphoric anhydride; phosphorus (V) oxide; P_4H_{10}

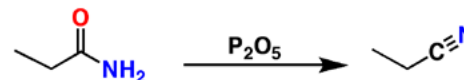
What it's used for: P_2O_5 is a reagent used for dehydration. It is used for conversion of carboxylic acids to anhydrides, and also the formation of nitriles from amides.

Similar to: P_4O_{10} (this behaves exactly the same as P_2O_5)

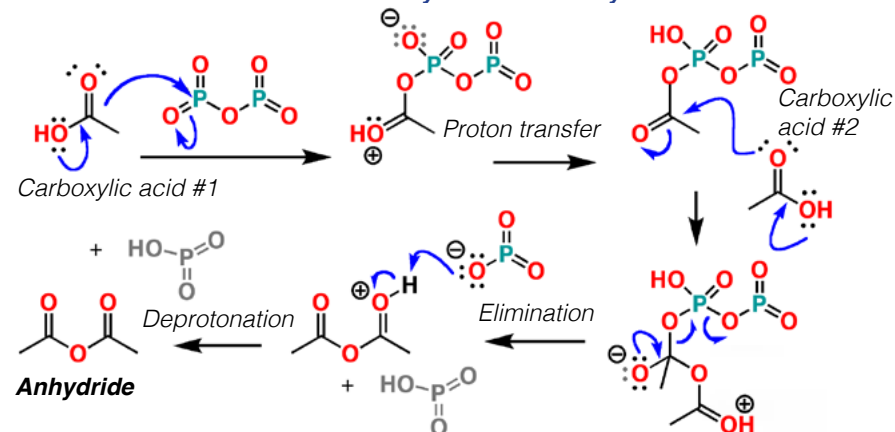
Example 1: Conversion of carboxylic acids to anhydrides



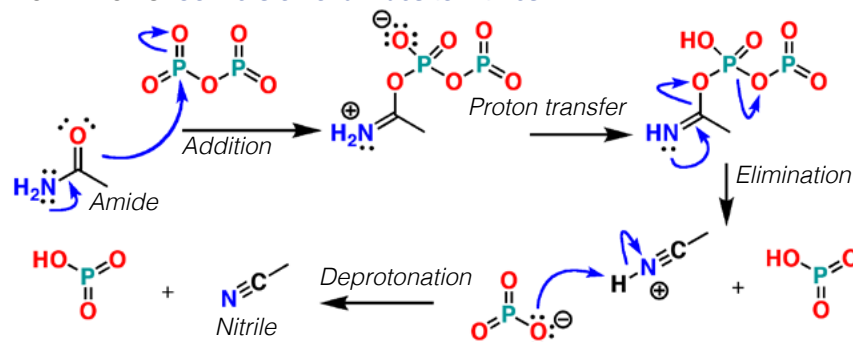
Example 2: Conversion of amides to nitriles



How it works: *Conversion of carboxylic acids to anhydrides*



How it works: *Conversion of amides to nitriles*


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Pd/C

Palladium on carbon

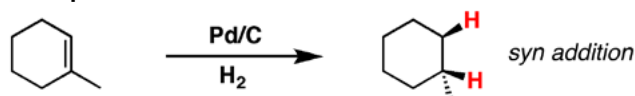
Pd / C

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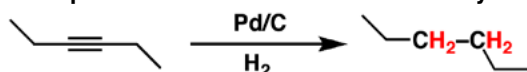
What it's used for: Palladium adsorbed on charcoal (carbon) [Pd/C] is a heterogeneous catalyst. In the presence of hydrogen gas (H_2) it will convert alkenes and alkynes to alkanes, with *syn* addition of hydrogen.

Similar to: [Lindlar's catalyst](#), "palladium" (Pd), platinum (Pt), platinum on carbon (Pt/C), nickel (Ni), ruthenium on carbon (Ru/C), rhodium on carbon (Rh)

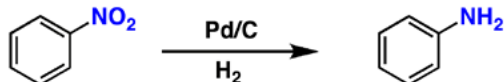
Example 1: Reduction - conversion of alkenes to alkanes



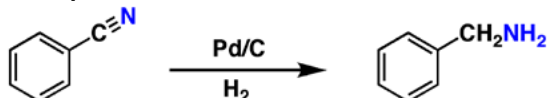
Example 2: Reduction - conversion of alkynes to alkanes



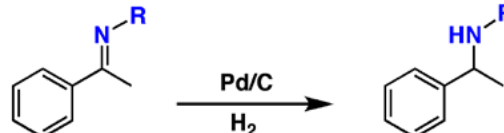
Example 3: Reduction - conversion of nitro groups to primary amines



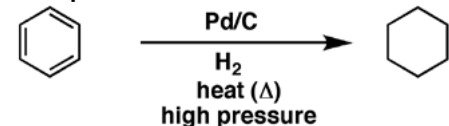
Example 4: Reduction - conversion of nitriles to primary amines



Example 5: Reduction - conversion of imines to amines

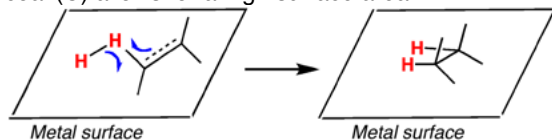


Example 6: Reduction - conversion of arenes to cyclic alkanes



How it works: [Hydrogenation](#)

Both hydrogen gas and the alkene are adsorbed onto the surface of the catalyst. The hydrogens are then delivered in *syn* fashion. Adsorbing palladium onto a material like charcoal (C) allows for a high surface area.

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Pt

Platinum

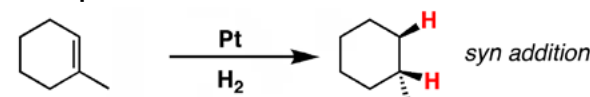
Pt

Also known as: Pt/C

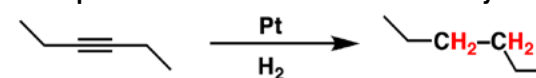
What it's used for: Platinum, a "noble metal", is used for the reduction of carbon-carbon multiple bonds in the presence of hydrogen gas.

Similar to: Palladium on carbon ([Pd/C](#)), Nickel (Ni), Ruthenium on carbon (Ru/C)

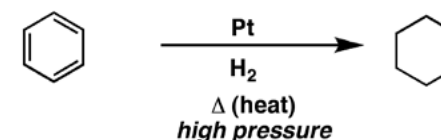
Example 1: Reduction - conversion of alkenes to alkanes



Example 2: Reduction - conversion of alkynes to alkanes

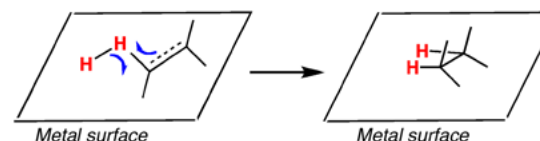


Example 3: Reduction - conversion of arenes to cyclic alkanes



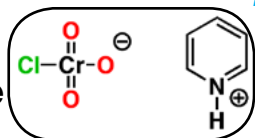
How it works: [Hydrogenation](#)

Like palladium on carbon (Pd/C), platinum is a heterogeneous catalyst. Both hydrogen gas and the alkene are adsorbed on to the surface of the catalyst. The hydrogens are then delivered in *syn* fashion.

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PCC

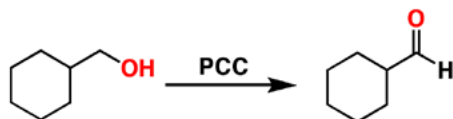
Pyridinium chlorochromate

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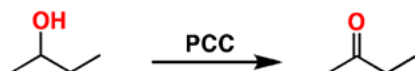
What it's used for: Pyridinium chlorochromate (PCC) is a reagent for the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. It is much milder than reactants such as H_2CrO_4 and KMnO_4 (which will oxidize primary alcohols to carboxylic acids).

Similar to: CrO_3 /pyridine, Dess-Martin periodinane (DMP)

Example 1: Oxidation - conversion of primary alcohols to aldehydes

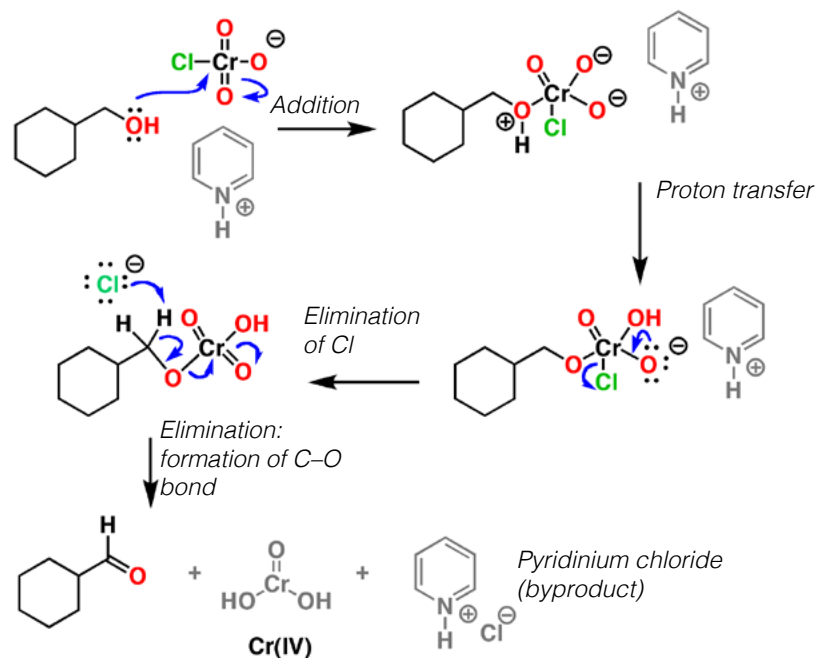


Example 2: Oxidation - conversion of secondary alcohols to ketones

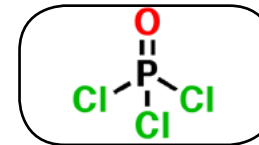


How it works: *Oxidation of primary alcohols to aldehydes*

The alcohol coordinates to the chromium (VI) atom, displacing chlorine, which then acts as a base, resulting in formation of a new C–O bond and reduction of Cr(VI) to Cr(IV).

[Index](#)[Index](#) POCl_3

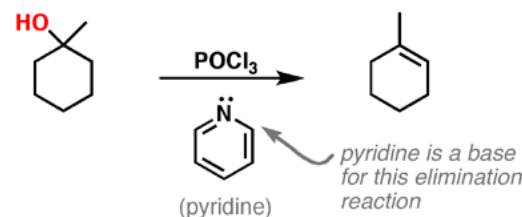
Phosphorus oxychloride



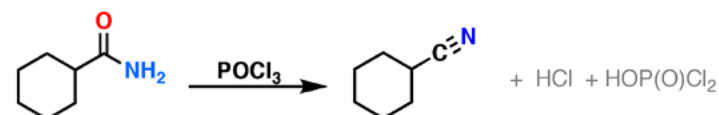
What it's used for: Phosphorus oxychloride (POCl_3) is used for the dehydration of alcohols to alkenes. Essentially it converts alcohols to a good leaving group, which is then removed by added base (often pyridine). It can also be used to convert amides to nitriles.

Similar to: LiAlH_4 (LAH), $\text{LiAlH}(\text{O}t\text{-Bu})_3$

Example 1: Elimination - conversion of alcohols to alkenes

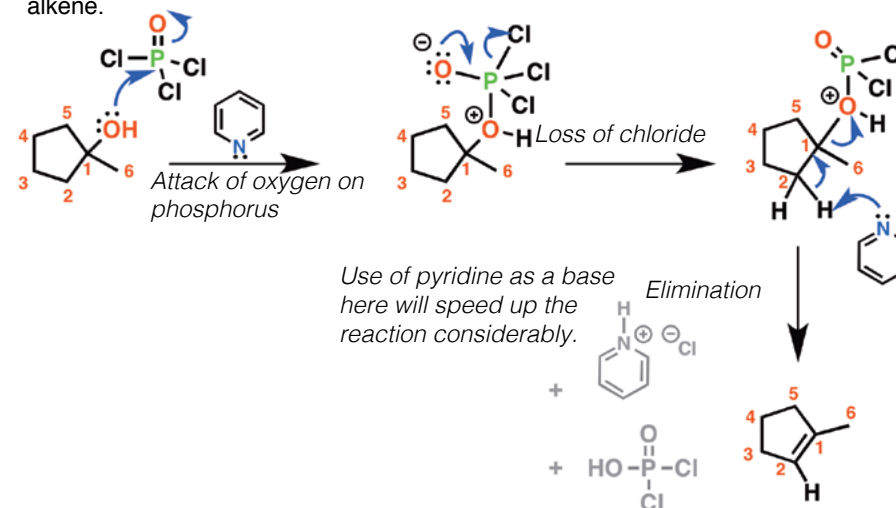


Example 2: Conversion of amides to nitriles

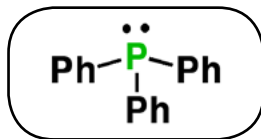


How it works: *Elimination of alcohols to alkenes*

In this reaction, the alcohol oxygen attacks phosphorus, displacing chloride ion. Then, elimination of the newly formed leaving group leads to formation of the alkene.

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PPh₃ Triphenylphosphine



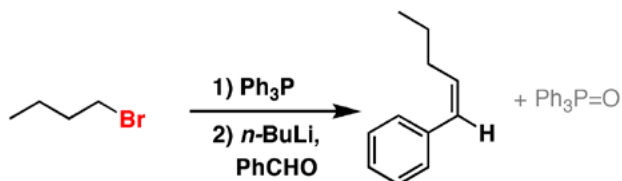
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Also known as: Triphenylphosphane

What it's used for: PPh₃ is commonly used for formation of ylides in the Wittig reaction. It can also be used for reductive workup in the ozonolysis of alkenes.

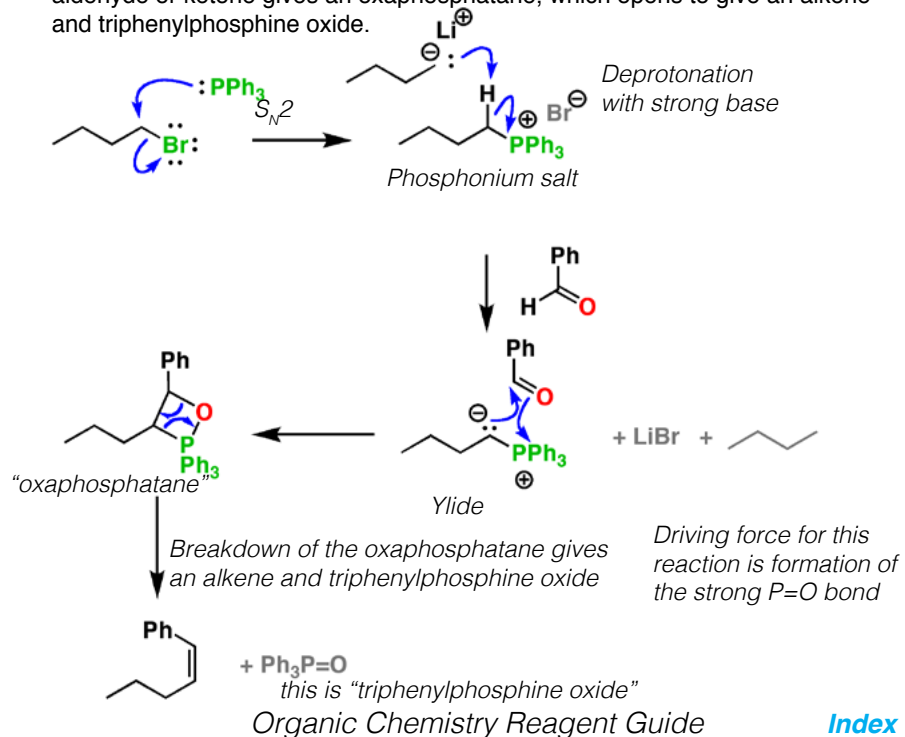
Similar to: Dimethyl sulfide (in the reductive workup of ozonolysis)

Example 1: Wittig reaction - conversion of aldehydes/ketones to alkenes



How it works: The Wittig reaction

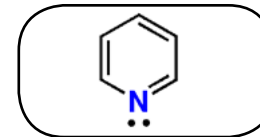
Triphenylphosphine is a good nucleophile, and will react with alkyl halides to form phosphonium salts. Treatment of the phosphonium salt with a strong base such as *n*-BuLi results in the formation of an ylide. Reaction of the ylide with an aldehyde or ketone gives an oxaphosphetane, which opens to give an alkene and triphenylphosphine oxide.



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Pyridine

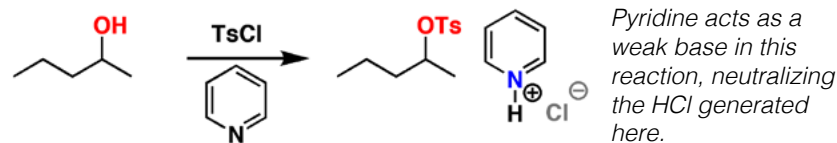


Also known as: Often abbreviated "pyr" or "py"

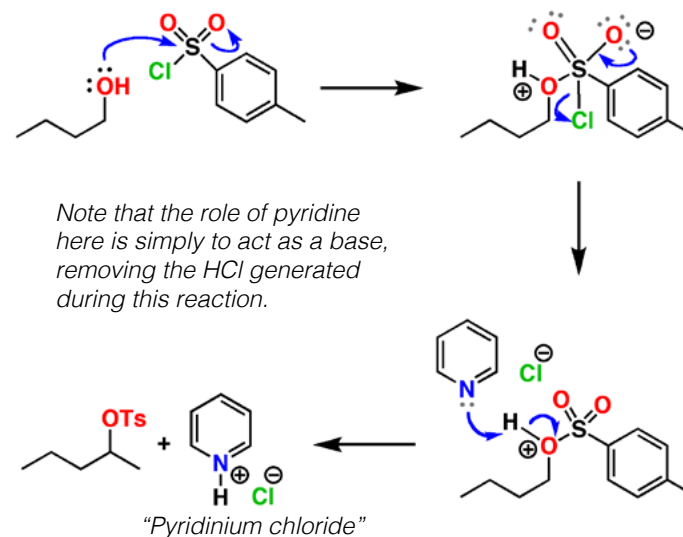
What it's used for: Pyridine is a mild base. Since it bears no charge it is especially soluble in organic solvents. It is often used in reactions that generate HCl and other strong acids - it acts much like a "sponge" for strong acid.

Similar to: Triethylamine (NEt₃), NaOH, other bases

Example 1: Conversion of alcohols to tosylates or mesylates



How it works: Formation of tosylates/mesylates



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Ra-Ni Raney Nickel

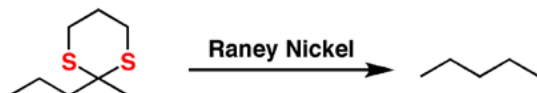
Ra-Ni

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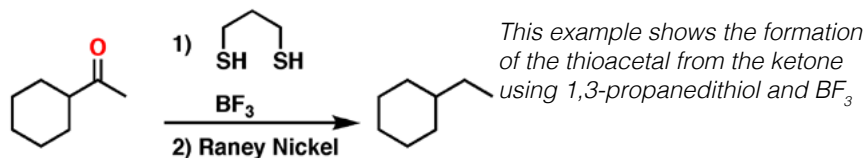
What it's used for: Raney nickel is a reagent for the reduction (hydrogenation) of double bonds. It is also used for the direct replacement of sulfur by hydrogen.

Similar to: [Pd/C](#), [Pt](#), Ni, and other heterogeneous catalysts.

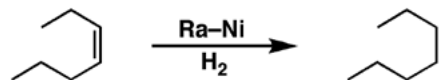
Example 1: Reduction - conversion of thioacetals to alkanes



Example 2: Reduction - conversion of thioacetals to alkanes



Example 3: Hydrogenation - conversion of alkenes to alkanes



How it works: *Reduction of thioacetals*

Raney Nickel is an alloy of nickel and aluminum which contains adsorbed hydrogen on its surface (hence, H_2 gas is not necessary in many cases!). Its exact mode of action for the reduction of C–S bonds is somewhat obscure.

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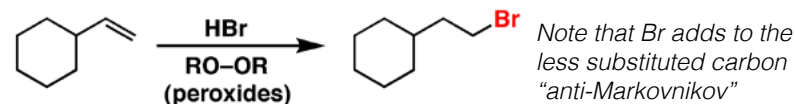
RO-OR Peroxides

RO-OR

What it's used for: Peroxides are used to initiate free-radical reactions. The oxygen-oxygen bond is very weak, and will fragment homolytically to generate free radicals.

Similar to: [AIBN](#), benzoyl peroxide

Example 1: Free-radical addition - conversion of alkenes to alkyl bromides

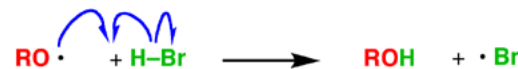


How it works: *Free radical bromination*

Peroxides, which have the general formula RO–OR, will fragment homolytically upon heating to provide alkoxy radicals RO•.



These radicals are very reactive and will readily remove hydrogen from various groups, leading to free radical chain processes.

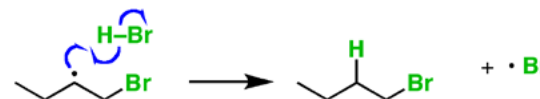


Addition occurs to the less substituted carbon (i.e. “anti-Markovnikov” because this results in the more stable (i.e. most substituted) secondary radical.

Propagation step 1

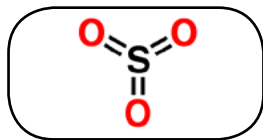


Propagation step 2



The bromine radical generated here can re-enter the reaction at propagation step 1 (addition to the alkene)

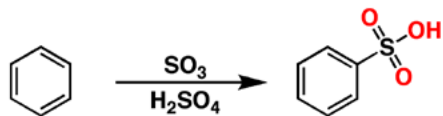
SO₃ Sulfur trioxide



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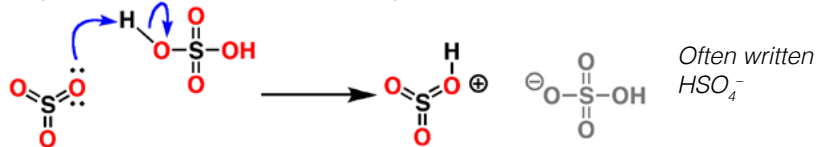
What it's used for: Sulfur trioxide is a reagent for the sulfonylation of aromatic groups. In the presence of acid, it will lead to the formation of sulfonic acids.

Example 1: Sulfonylation - conversion of arenes to aryl sulfonic acids

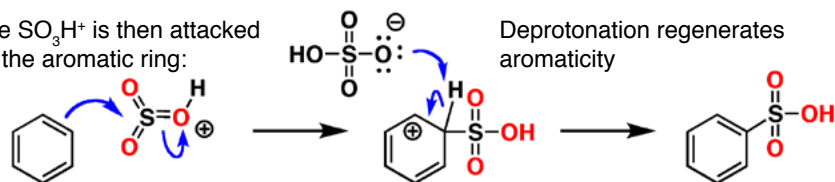


How it works: Formation of sulfonic acids

SO₃ is often used in the presence of sulfuric acid. Protonation of SO₃ gives SO₃H⁺, a better electrophile than SO₃.

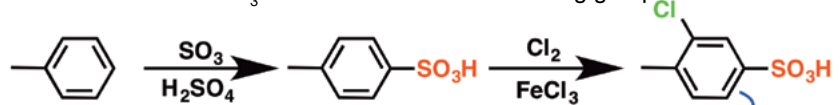


The SO₃H⁺ is then attacked by the aromatic ring:

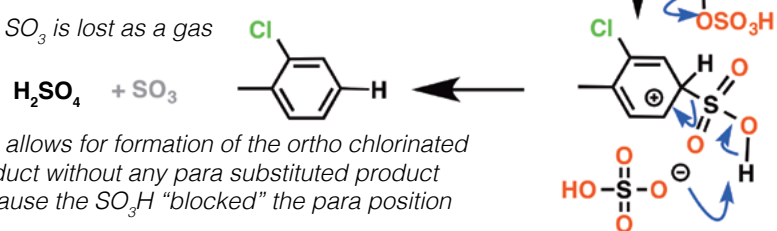


Note that H₂SO₄ is regenerated in this step; it is a catalyst here.

If treated with strong acid in the absence of SO₃, the SO₃H can be removed. This makes the SO₃H a useful removable "blocking group"



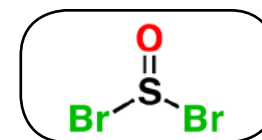
SO₃ is lost as a gas



This allows for formation of the ortho chlorinated product without any para substituted product because the SO₃H "blocked" the para position

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SOBr₂ Thionyl bromide



What it's used for: Thionyl bromide is a useful reagent for the formation of alkyl bromides from alcohols, as well as acid bromides (acyl bromides) from carboxylic acids.

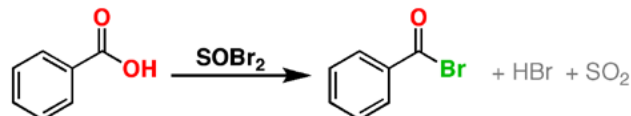
Similar to: PBr₃, SOCl₂ (operates by the same mechanism)

Example 1: Conversion of alcohols to alkyl bromides



note: inversion

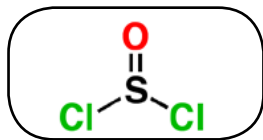
Example 2: Conversion of carboxylic acids to acyl bromides



How it works: Formation of alkyl bromides

Identical in all respects to SOCl₂ (see section)

SOCl₂ Thionyl chloride

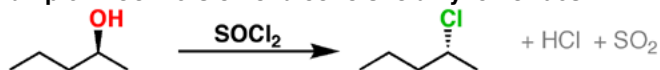


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What it's used for: Thionyl chloride is used for the formation of alkyl chlorides from alcohols, and acid chlorides (acyl chlorides) from carboxylic acids.

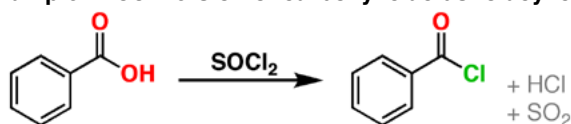
Similar to: PCl₃, PCl₅, SOBr₂

Example 1: Conversion of alcohols to alkyl chlorides



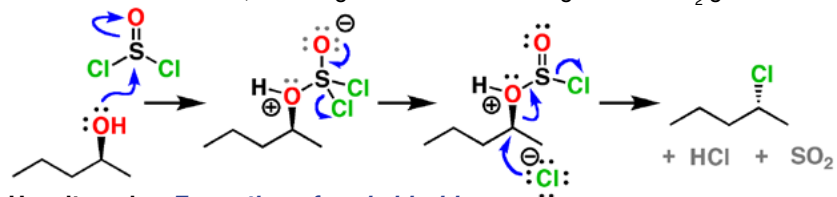
note: inversion

Example 2: Conversion of carboxylic acids to acyl chlorides



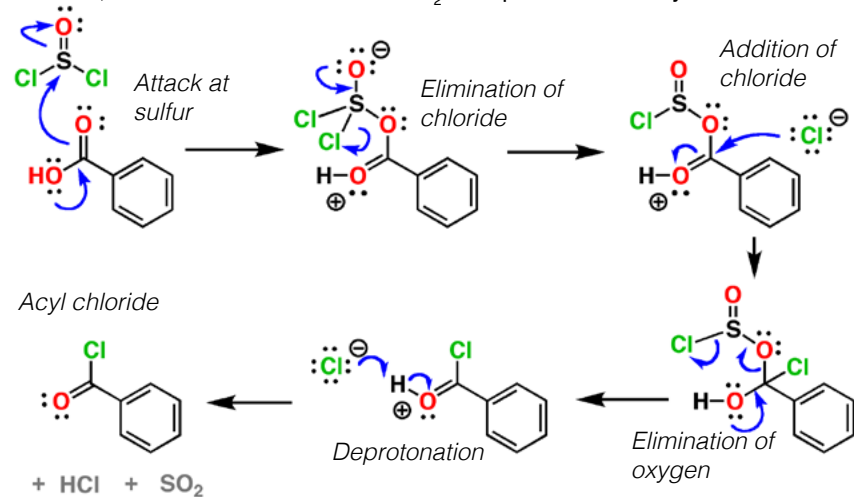
How it works: Formation of alkyl chlorides

This reaction proceeds through attack of oxygen on sulfur and then S_N2 attack of chloride ion on carbon, resulting in inversion of configuration. SO₂ gas is liberated.



How it works: Formation of acyl chlorides

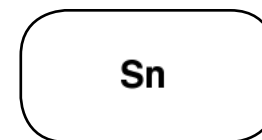
Attack of oxygen at sulfur is followed by addition of chloride ion and elimination of O-SOCl, which loses Cl⁻ to become SO₂. The product is an acyl chloride.



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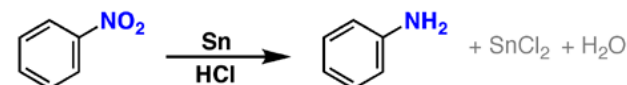
Sn Tin



What it's used for: Tin is a reducing agent. In the presence of strong acids, it will reduce nitro groups to amines.

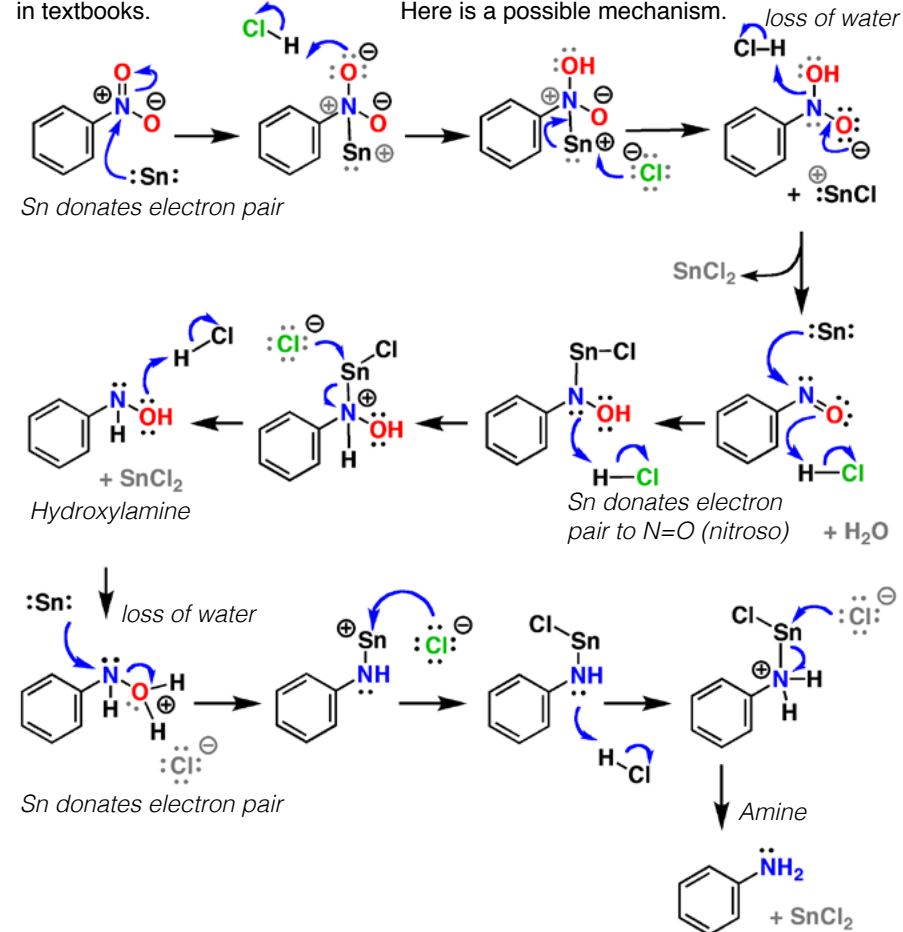
Similar to: Tin (II) chloride (SnCl₂), Iron metal (Fe), Zinc (Zn).

Example 1: Reduction - conversion of nitro groups to amines



How it works: **Reduction of nitro groups**

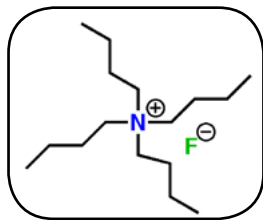
The mechanism has not been determined with 100% certainty. Often not depicted in textbooks. Here is a possible mechanism.



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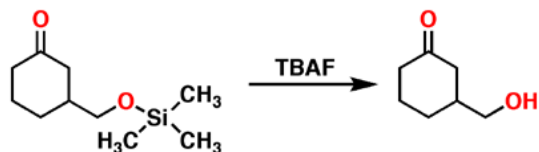
TBAF

Tetrabutyl ammonium fluoride


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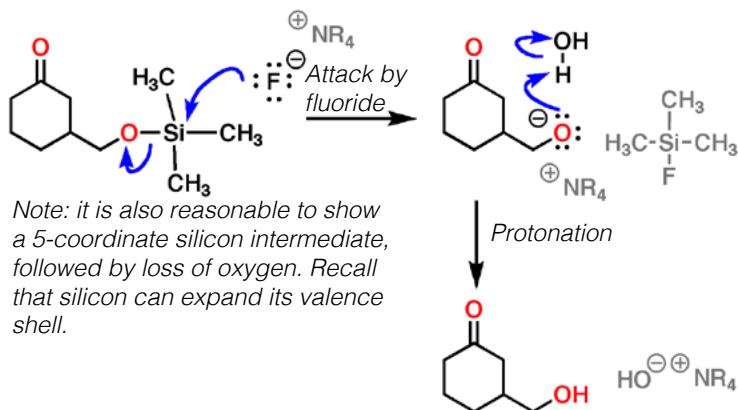
What it's used for: Tetrabutyl ammonium fluoride (TBAF) is a source of fluoride ion. It is used to cleave silyl ethers, which are common protecting groups for alcohols (fluorine forms very strong bonds with silicon)

Example 1: Alcohol deprotection - conversion of silyl ethers to alcohols



How it works: *Deprotection of silyl ethers*

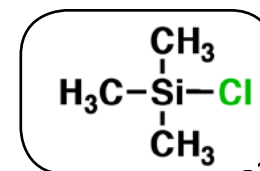
Fluorine forms very strong bonds to silicon. It is on this principle that fluoride ion acts to break O-Si bonds and form Si-F bonds. Since TBAF is generally used as a solution in water, the resulting alkoxide is protonated by the aqueous solvent.



Note that the tetrabutylammonium cation here is abbreviated NR_4^+

TMSCl

Trimethylsilyl chloride

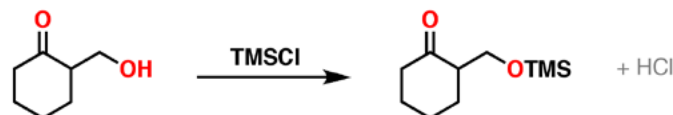
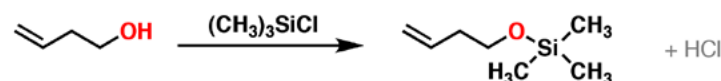

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Also known as: Chlorotrimethylsilane, $(\text{CH}_3)_3\text{SiCl}$

What it's used for: TMSCl is a protecting group for alcohols. When added to alcohols it is inert to most reagents except for fluoride ion (F^-) and acid. The addition of a weak base such as pyridine can serve to remove the HCl byproduct that is formed during this reaction.

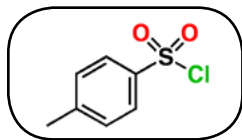
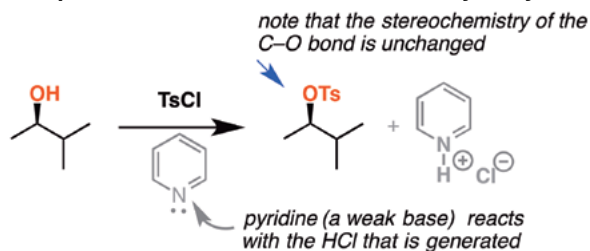
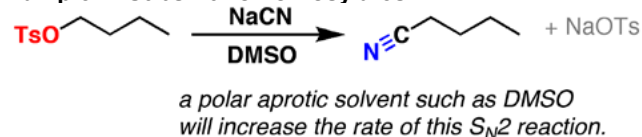
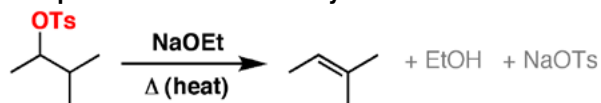
Similar to: TBSCl

Example 1: Alcohol protection - conversion of alcohols to silyl ethers

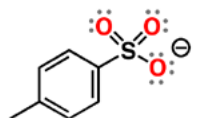


How it works: *Protection of alcohols*

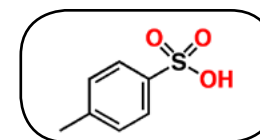
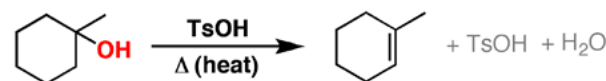
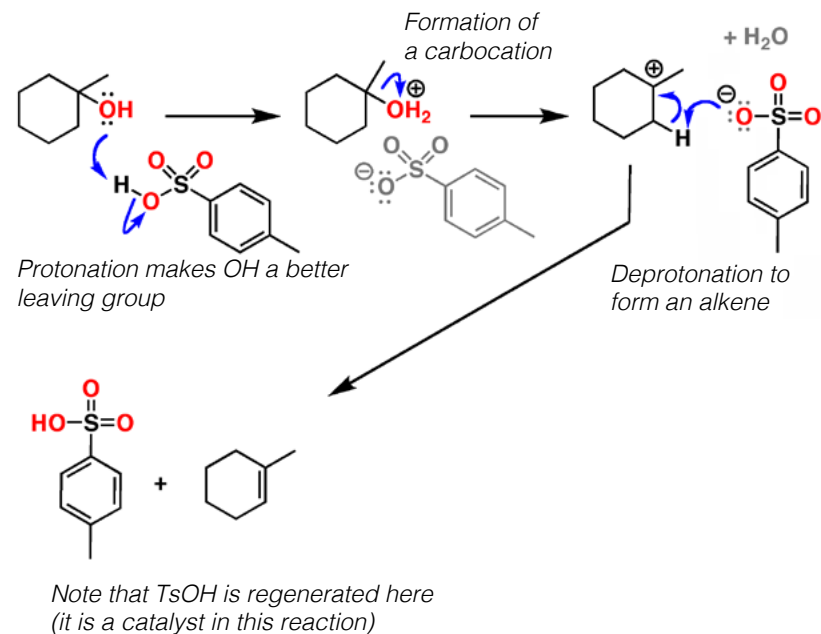
The reaction for protection of alcohols is quite straightforward - attack of the alcohol on silicon accompanied by loss of the chloride leaving group. Addition of a base such as pyridine will neutralize the HCl that is formed during the reaction.

TsCl**p-Toluenesulfonyl chloride**[Index](#)**Also known as:** TosCl, p-TsCl, Tosyl chloride**What it's used for:** Tosyl chloride (TsCl) will convert alcohols to sulfonates, which are excellent leaving groups in elimination and substitution reactions. TsO^- is the conjugate base of the strong acid TsOH.**Similar to:** Mesityl chloride ([MsCl](#)), p-bromobenzenesulfonyl chloride ([BsCl](#))**Example 1: Conversion of alcohols to alkyl tosylates****Example 2: Substitution of tosylates****Example 3: Elimination of tosylates****How it works: Tosylates as leaving groups**

Weak bases are excellent leaving groups. By converting OH (a strong base and poor leaving group) to OTs (a much weaker base and leaving group) it becomes many orders of magnitude easier to do substitution and elimination reactions.



Note how the negative charge on oxygen can be delocalized on to the other oxygen atoms through resonance.

TsOH**p-Toluenesulfonic acid**[Index](#)**Also known as:** Tonic acid, TosOH,**What it's used for:** Tonic acid is a strong acid, similar in strength to sulfuric acid (pKa of -2.8). One feature is that the conjugate base is a poor nucleophile, which makes it useful for the dehydration of alcohols to form alkenes. Also it is a white crystalline solid, which makes it slightly more convenient to use than H_2SO_4 in some cases.**Similar to:** Sulfuric acid (H_2SO_4)**Example 1: Elimination - conversion of alcohols to alkenes****How it works: Acid-catalyzed elimination of alcohols to give alkenes**

Zn Zinc

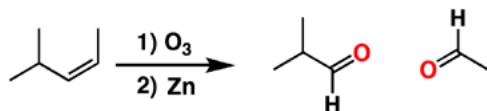
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Zn

What it's used for: Zinc is a metal reducing agent. It is useful for the reduction of ozonides, and also in the reduction of nitro groups to amines (in the presence of acid)

Similar to: [Dimethyl sulfide](#) (in workup of ozonolysis), [Sn](#) (in reduction of nitro groups)

Example 1: Ozonolysis (reductive workup) - conversion of alkenes to aldehydes/ketones

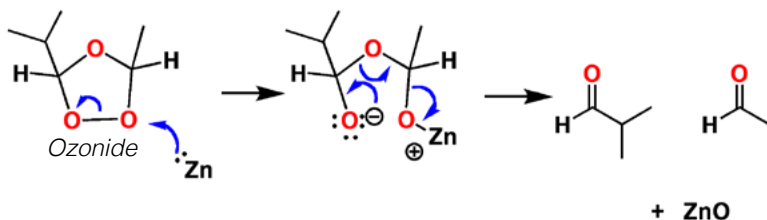


Example 2: Reduction - conversion of nitro groups to primary amines



How it works: [Reduction of ozonides](#)

Zinc is easily oxidized and can donate electrons to various groups. One application is in the reduction of ozonides.



For a suggestion on how metals such as Zn, Sn, and Fe reduce nitro groups in the presence of acids such as HCl, see the section on tin (Sn)

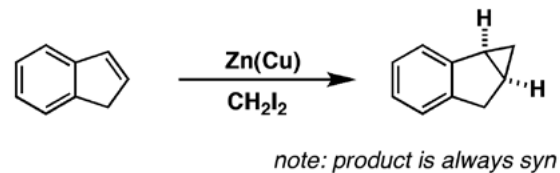
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Zn/Cu Zinc-Copper Couple

Zn(Cu)

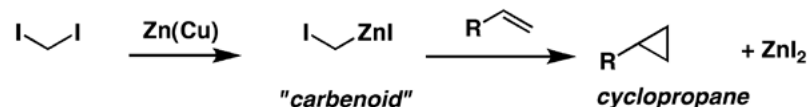
What it's used for: Zinc-copper couple is a reducing agent, used to form carbenes (actually "carbenoids") from alkyl dihalides. When these are added to alkenes, they form cyclopropanes.

Example 1: Simmons-Smith reaction - formation of cyclopropanes from alkenes



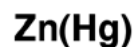
How it works: [Cyclopropanation of alkenes](#)

Zinc-copper couple is an alloy of zinc and copper that can reduce dihalides to metal carbenoids. The carbenoid performs the cyclopropanation reaction.



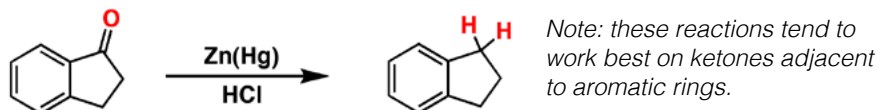
Zinc-copper couple itself is a metal cluster (not a molecule). The mechanism of action for formation of the Zn-carbon bond is probably similar to that of organolithium and Grignard reagents.

Zinc amalgam



What it's used for: In the presence of acid, zinc amalgam will reduce ketones to alkanes, in a process called the Clemmensen reaction (or Clemmensen reduction)

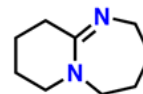
Example 1: The Clemmensen Reduction

How it works: *The Clemmensen Reduction*

Metals that are fused with mercury are called *amalgams*, and their precise mode of action is somewhat obscure. The strong acid (HCl) serves to activate the carbonyl toward reduction, as well as assist in the eventual removal of the carbonyl oxygen as H₂O

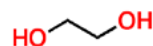
Odds And Ends

DBU (1,8-Diazabicycloundec-7-ene)



Base; used in elimination reactions. Bulky, non-nucleophilic base.

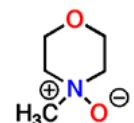
Ethylene glycol



Used as solvent in Wolff Kishner and as a [protecting group](#) (acetal) for ketones. High boiling solvent.

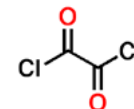
KHSO₃ (Potassium bisulfate) Used in [dihydroxylation](#) reaction workup; breaks up "osmate ester".

NMO (N-methylmorpholine N-oxide)



Used as oxidant in [dihydroxylation](#) reaction of alkenes. Allows for catalytic use of (expensive) OsO₄

Oxalyl chloride

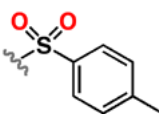
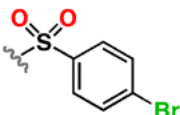
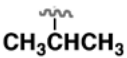
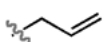
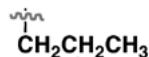
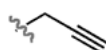
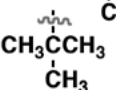
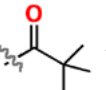
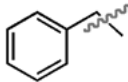


Similar to thionyl chloride; used in Swern oxidation of alcohols to give aldehydes and ketones. Converts DMSO to active electrophile.

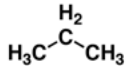
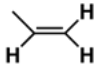
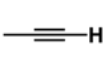
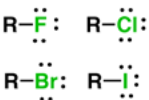
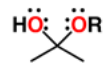
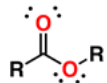
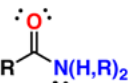
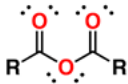
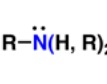
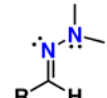
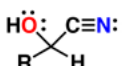
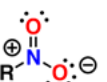
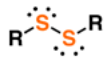
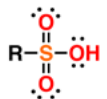
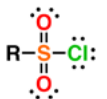
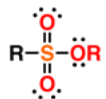
See a reagent in your introductory course or textbook that isn't depicted anywhere in the Guide?

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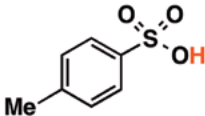
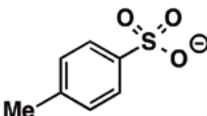
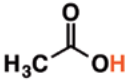
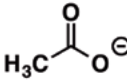
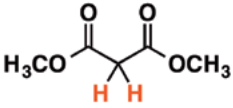
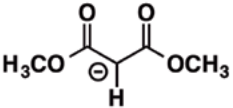
Common Abbreviations and Terms

Me	$-\text{CH}_3$	Methyl	Ac		acetyl
Et	$-\text{CH}_2\text{CH}_3$	Ethyl	Ts		p-toluenesulfonyl (tosyl)
Pr	$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl	Ms		methanesulfonyl (mesyl)
Bu	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl	Bs		p-bromobenzenesulfonyl (brosyl)
i-Pr		isopropyl	Allyl		
s-Bu		sec-butyl	Vinyl		
i-Bu		isobutyl	Propargyl		
t-Bu		tert-butyl	Piv		Pivaoyl
Ph (C_6H_5-)		phenyl			
Bn ($\text{C}_6\text{H}_5\text{CH}_2-$)		benzyl			
1°	primary	3°	tertiary		
2°	secondary	4°	quaternary		
LG	leaving group	N-	denotes a substituent directly bound to nitrogen		
Nu:	nucleophile	EDG	electron donating group		
B:	base	EWG	electron withdrawing group		
R	any carbon substituent	Acyl			
Ar	an aromatic substituent	Carbonyl			

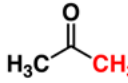
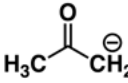
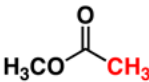
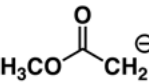
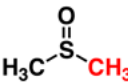
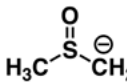
Functional Groups

				
alkane	alkene	alkyne	benzene ring (phenyl)	alkyl halide
				
alcohol	ether	hemiacetal	acetal	epoxide
				
aldehyde	ketone	ester	carboxylic acid	amide
				
acid chloride	anhydride	enol	amine	imine
				
enamine	oxime	hydrazone	nitrile	cyanohydrin
				
nitro	sulfide (thioether)	thiol	disulfide	sulfoxide
				
sulfone	sulfonic acid	sulfonyl chloride	sulfonate ester	

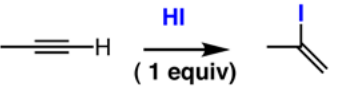
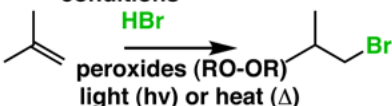
pKas of Common Functional Groups

Functional group	Example	pKa	Conjugate Base
Hydroiodic acid	HI	-10	$I^{\ominus}$
Hydrobromic acid	HBr	-9	$Br^{\ominus}$
Hydrochloric acid	HCl	-8	$Cl^{\ominus}$
Sulfuric acid	H ₂ SO ₄	-3	HSO ₄ [⊖]
Sulfonic acids	 (tosic acid)	-3	
Hydronium ion	H ₃ O [⊕]	-1.7	H ₂ O
Hydrofluoric acid	H-F	3.2	F [⊖]
Carboxylic acids		~4	
Protonated amines	NH ₄ [⊕] Cl [⊖]	9-11	NH ₃
Thiols	CH ₃ S-H	13	CH ₃ S [⊖]
Malonates		13	
Water	HO-H	16	HO [⊖]

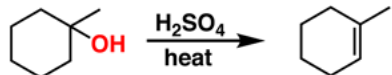
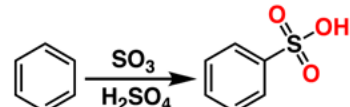
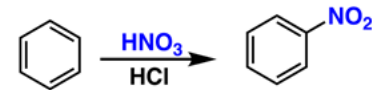
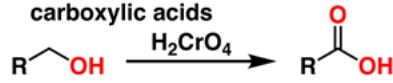
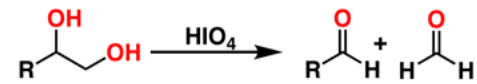
pKas of Common Functional Groups

Functional group	Example	pKa	Conjugate Base
Alcohol	H ₃ C-OH	17	H ₃ C-O [⊖]
Ketone/ aldehyde		20-24	
Ester		25	
Nitrile	H ₃ C-C≡N	25	H ₂ C [⊖] -C≡N
Alkyne	R-C≡C-H	25	R-C≡C [⊖]
Sulfoxide		31	
Amine	NH ₃	~35-38	NH ₂ [⊖]
Hydrogen	H-H	42	H [⊖]
Alkene		~43	
Alkane	H ₃ C-CH ₂ -CH ₃	~50	H ₃ C-CH ₂ -CH ₂ [⊖]

Notes on Acids

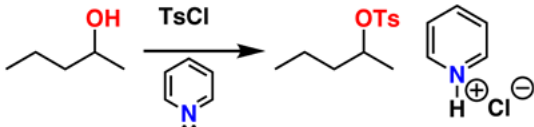
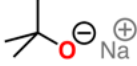
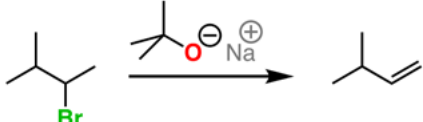
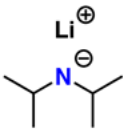
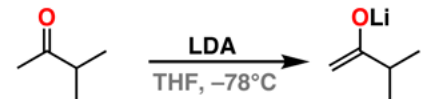
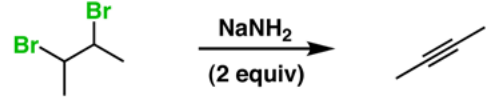
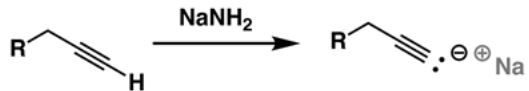
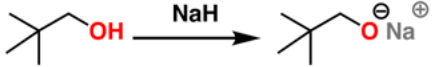
Acids	pKa	Special Uses
Hydroiodic acid H-I	-10	• Addition to alkenes/alkynes  <i>Addition of I occurs at the most substituted carbon</i>  • Formation of alkyl halides from alcohols  • Best reagent for cleavage of ethers to alcohols and alkyl halides 
Hydrobromic acid H-Br	-9	• Addition to alkenes/alkynes (similar to HI, above) • Formation of alkyl halides from alcohols (similar to HI, above) • Addition to alkenes under radical conditions 
Hydrochloric acid H-Cl	-8	• Addition to alkenes/alkynes (similar to HI/HBr, above) • Formation of alkyl halides from alcohols (similar to HI/HBr, above)

Notes on Acids

Sulfuric acid H ₂ SO ₄	-2.5	• Non-nucleophilic acid, good for E1 reactions  • Acid for sulfonylation of aromatics 
Nitric acid H-NO ₃	-1.3	• Nitration of aromatics  <i>HCl is used as a catalyst in this reaction.</i>
Chromic acid H ₂ CrO ₄	-0.8	• Oxidation of alcohols to carboxylic acids  • Will also oxidize aldehydes to carboxylic acids • Will oxidize secondary alcohols to ketones
Periodic acid H-IO ₄		• Cleavage of diols to aldehydes/ketones 
Nitrous acid H-O-N=O	3.3	• Formation of diazonium salts  <i>diazonium salt</i>

Notes on Bases

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Base	pKa (of conjugate acid)	Use
Pyridine 	5	• Soluble in organic solvents, useful for reactions that generate HCl and HBr, such as: 
Sodium tert-butoxide 	19	• Strong, bulky base for elimination reactions, tends to give less-substituted alkene 
LDA 	36	• Formation of less-substituted enolates 
Sodium amide 	38	• Elimination of dihalides to give alkynes  • Deprotonation of alkynes 
Sodium hydride NaH	42	• Strong, non-nucleophilic base 

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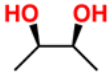
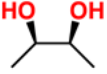
Oxidizing Agents

Transformation	Reagent
Primary Alcohol $\rightarrow$ Aldehyde 	• PCC • CrO_3 / pyridine • Dess-Martin periodinane
Secondary Alcohol $\rightarrow$ Ketone 	• PCC • CrO_3 / pyridine • H_2CrO_4 (note: same as $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ or $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, or CrO_3/H^+) • KMnO_4 • Dess-Martin Periodinane
Aldehyde $\rightarrow$ Carboxylic acid 	• H_2CrO_4 (see note above) • KMnO_4 • H_2O_2
Alcohol $\rightarrow$ Carboxylic acid 	• KMnO_4 • H_2CrO_4 (see note above)
Alkane $\rightarrow$ Carboxylic acid 	• KMnO_4
Alkene $\rightarrow$ Aldehyde / Ketone 	• O_3 , then Zn • O_3 , then CH_3SCH_3 (DMS)
Alkene $\rightarrow$ Carboxylic acids/ Ketones 	• O_3 , then H_2O_2 • KMnO_4 , heat, H_3O^+
Alkyne $\rightarrow$ Carboxylic acids 	• O_3 , then H_2SO_4 • KMnO_4 , heat, H_3O^+

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Oxidizing Agents

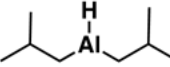
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Transformation		Reagent
Alkene	Diol (vicinal diol)	
	 <i>always syn</i>	• OsO₄ • KMnO₄, HO[⊖]
Alkene	Epoxide	
		• mCPBA
Diol	Aldehyde	
		• NaIO₄ • Pb(OAc)₄ • HIO₄
Ketone	Ester	
		• mCPBA

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Reducing Agents

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Transformation		Reagent
Carboxylic acid	Alcohol	
		• LiAlH₄
Ester	Alcohol	
		• LiAlH₄
Ester	Aldehyde	
		• DIBAL 
Acyl halide	Aldehyde	
		• LiAlH[OC(CH₃)₃]
Amide	Amine	
		• LiAlH₄
Aldehyde	Alcohol	
		• LiAlH₄ • DIBAL • NaBH₄
Aldehyde/ketone	Alkane	
		• NH₂NH₂ / HO[⊖] (Wolff-Kishner) • Zn/Hg + HCl (Clemmensen)
Nitrile	Aldehyde	
		• DIBAL, then H₂O
Nitrile	Amine	
		• LiAlH₄

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Reducing Agents

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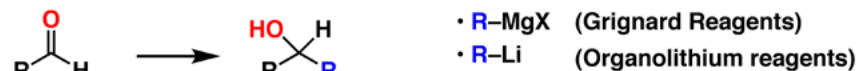
Transformation	Reagent
Alkene → Alkane	Pt/C Pd/C Ni Ru + H ₂
Alkyne → Alkane	
Alkyne → Alkene (cis)	• Lindlar's catalyst + H ₂ • Ni ₂ B
Alkyne → Alkene (trans)	• Na/NH ₃
Nitro group → Amine	• Zn/HCl • Sn/HCl • Fe/HCl • Pd/H ₂
Sulfonate ester → Alkane	• LiAlH ₄
Alkyl halide → Alkane	• LiAlH ₄ • Mg, then H ⁺ • Li, then H ⁺

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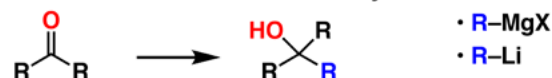
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Organometallic Reagents

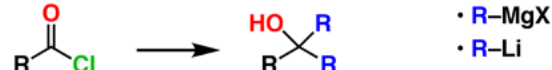
Conversion of aldehydes to secondary alcohols



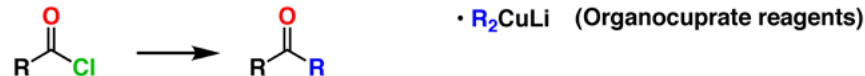
Conversion of ketones to tertiary alcohols



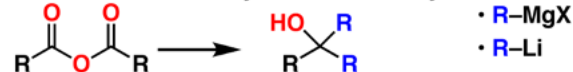
Conversion of acyl halides to tertiary alcohols



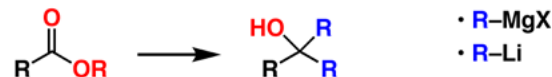
Conversion of acyl halides to ketones



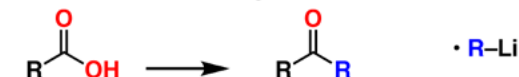
Conversion of anhydrides to tertiary alcohols



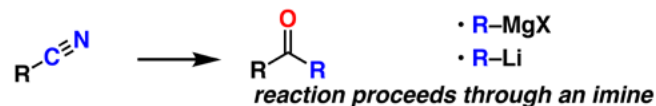
Conversion of esters to tertiary alcohols



Conversion of carboxylic acids to ketones



Conversion of nitriles to ketones

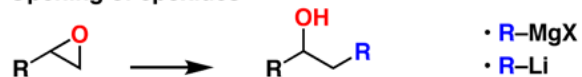


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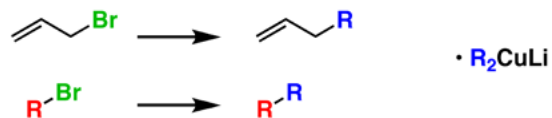
Organometallic Reagents

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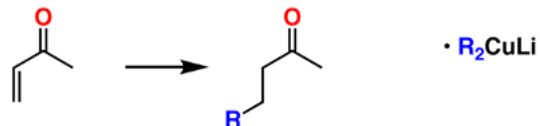
Opening of epoxides



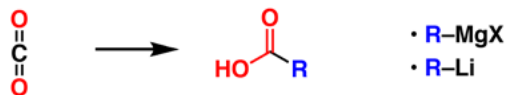
Reaction with alkyl halides or tosylates



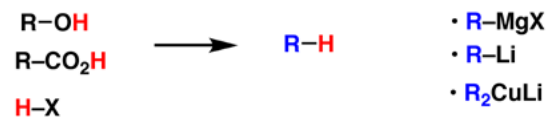
Conjugate addition (1,4 addition)



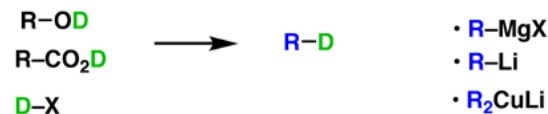
Addition to carbon dioxide to form carboxylic acids



Reaction with acidic hydrogen to form R-H



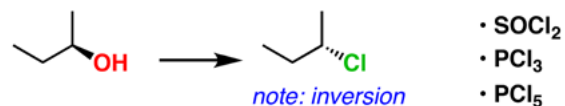
Reaction with acidic deuterium to form R-D



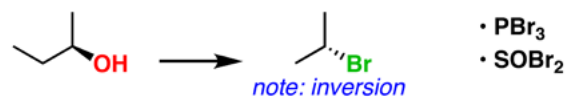
Reagents for Making Alkyl/ Acyl Halides

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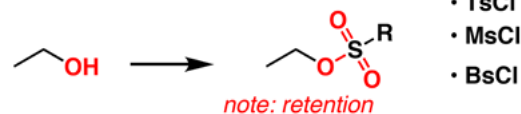
Alcohol to alkyl chloride



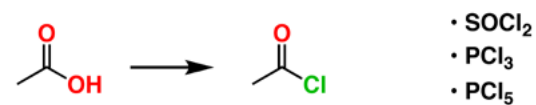
Alcohol to alkyl bromide



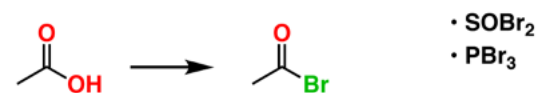
Alcohol to alkyl sulfonate



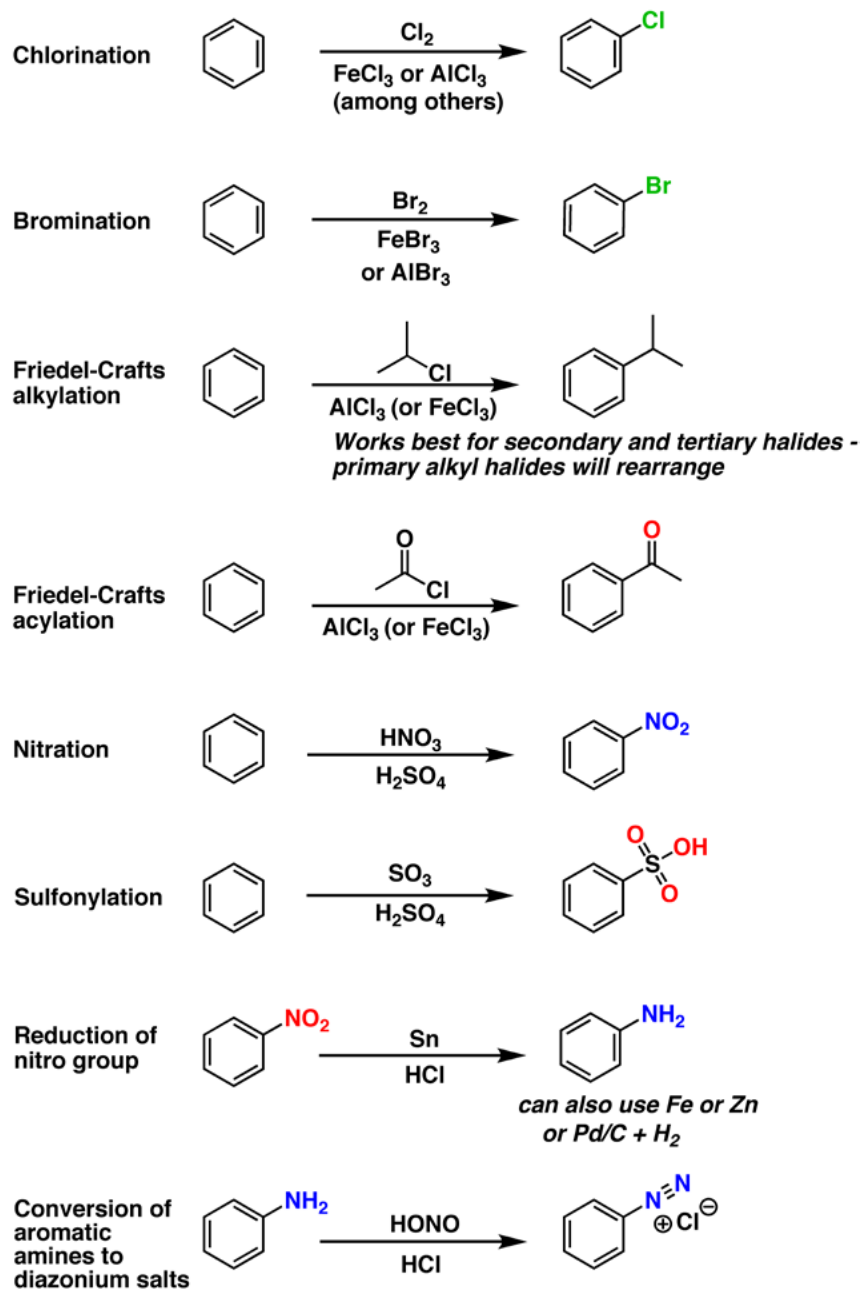
Carboxylic acid to acyl chloride



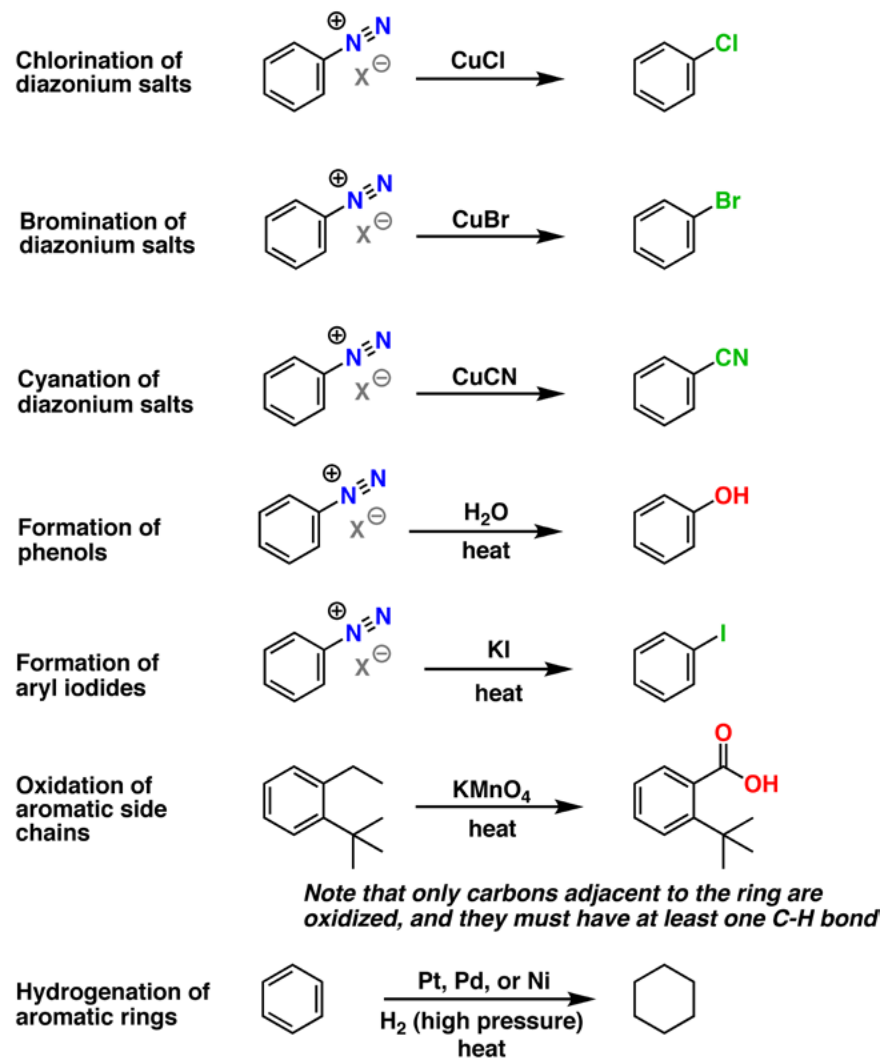
Carboxylic acid to acyl bromide

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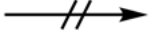
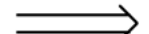
Reagents Involving Aromatic Rings



Reagents Involving Aromatic Rings

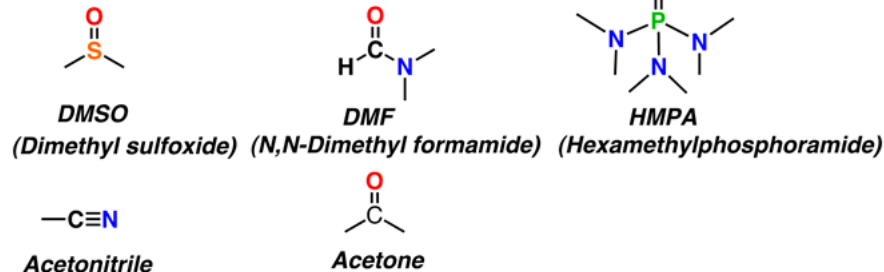


Types of Arrows

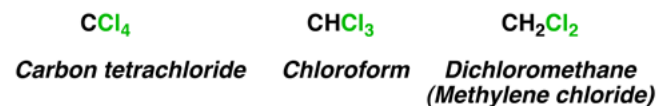
- 1. Reaction Arrow**  "this goes to this"
- 2. Equilibrium Arrows**
 -  "reaction goes reversibly between products and reactants"
 -  "reaction goes reversibly, but favors products"
 -  "reaction goes reversibly, but favors reactants".
- 3. Resonance Arrow**  "these two molecules are resonance structures"
- 4. Curved arrow (double)**  "take a pair of electrons from here, and move them to there".
- 5. Curved arrow (single)**  "take a single electron from here, and move it there".
- 6. Dashed arrow**  "we'd like to do this, but haven't done it"
- 7. Broken arrows**
 -  "this doesn't work"
 - 
- 8. Retrosynthesis arrow**  "Make this from this"

Types of Solvents

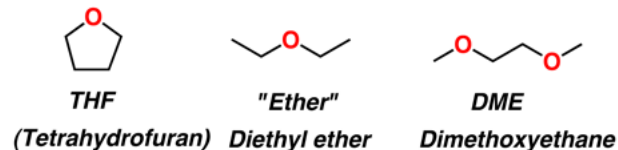
Polar Aprotic Solvents common uses: for S_N2 reactions



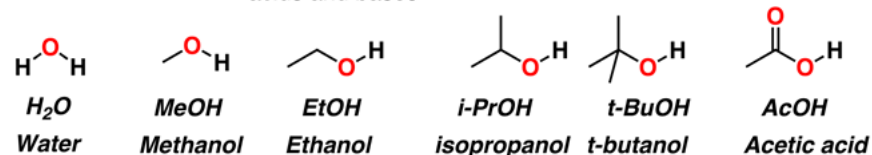
Chlorinated Solvents common uses: free radical reactions, halogenation reactions



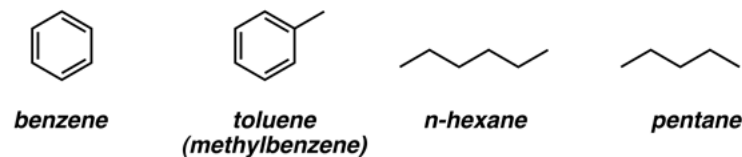
Ethers common uses: Grignard reactions, reactions of organolithiums



Polar protic solvents common uses: S_N1 and E_1 reactions, reactions involving acids and bases



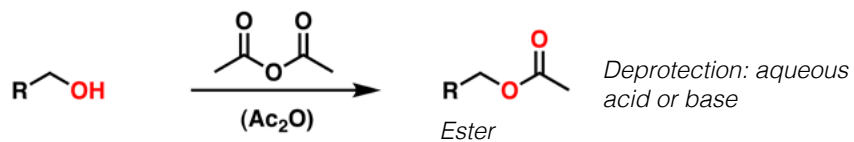
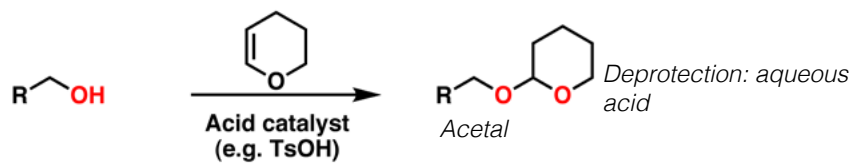
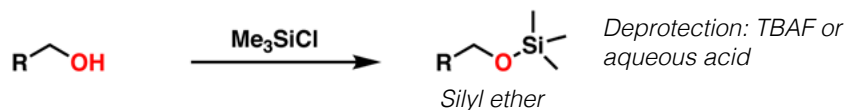
Hydrocarbon solvents



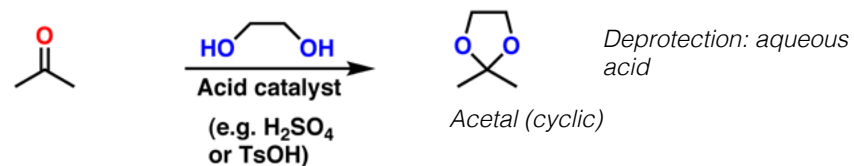
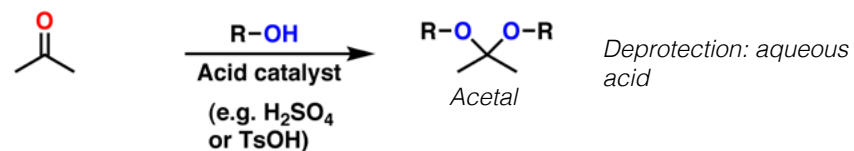
Protecting Groups

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Protection of alcohols



Protection of aldehydes and ketones

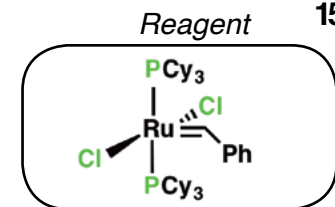


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Grubbs' Catalyst

Note: Cy = cyclohexane, so PCy₃ is tri-cyclohexyl phosphine

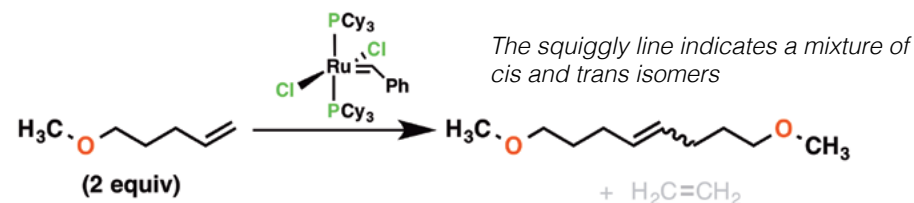


What it's used for: Reagent used for olefin metathesis. Three main reactions are encountered, which all follow the same type of mechanism: ring-closing metathesis, cross metathesis, and ring-opening metathesis polymerization.

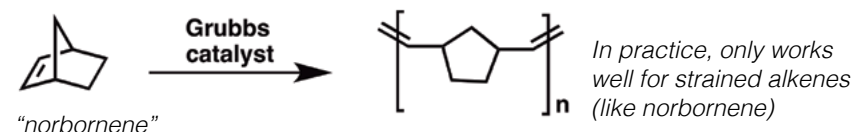
Example 1: Ring closing metathesis



Example 2: Cross metathesis



Example 3: Ring opening metathesis polymerization

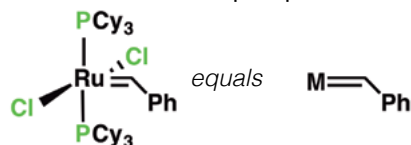


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How it works: *Olefin metathesis*

Editorial: This reagent really doesn't belong in 99% of introductory organic chemistry courses because the key reactions of transition metals (ligand exchange, coordination, oxidative addition, reductive elimination) have not been properly introduced. Introducing transition metal reactions just causes more confusion.

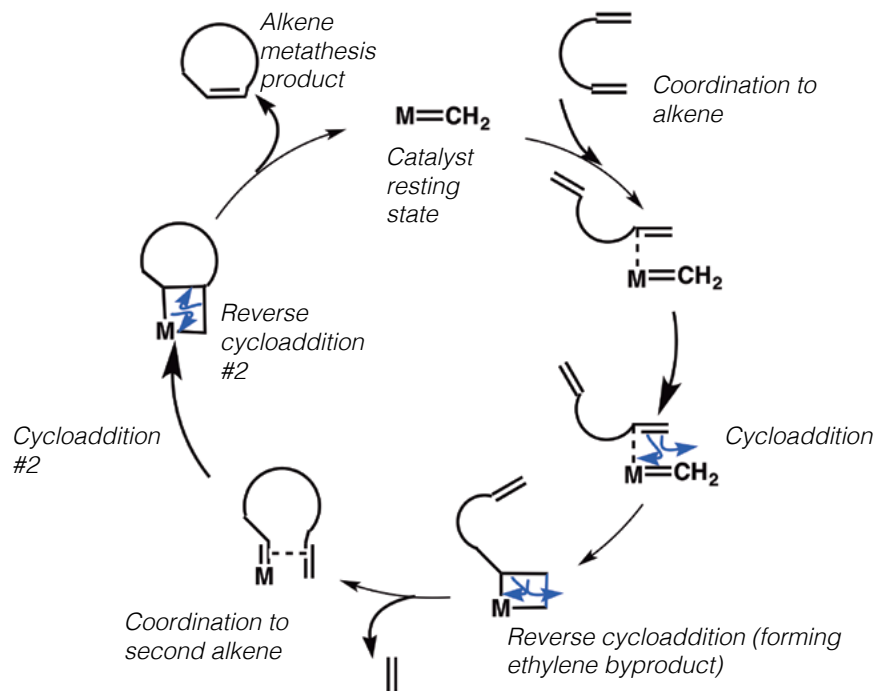
For our mechanism, we'll simplify drawing by representing ruthenium and the attached chlorines and phosphines as "M".



The Grubbs catalyst comes attached to phenyl, but the active catalyst is generally ruthenium methylidene ($=\text{CH}_2$). Reaction with one equivalent of alkene (through the general mechanism below) results in the active catalyst.

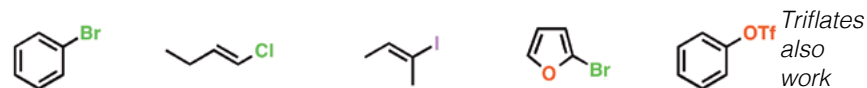


Here's the catalytic cycle for a typical ring-closing metathesis. The curved line represents a carbon chain of indeterminate length.

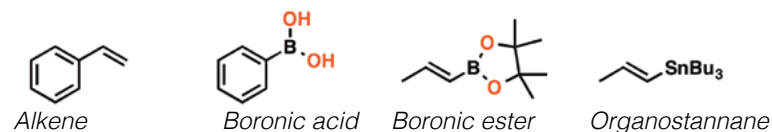


Cross Coupling Reagents

Alkenyl halide: All palladium-catalyzed reactions covered in introductory courses have an alkenyl (or aryl) halide coupling partner. The first step of cross-coupling reactions (including the Heck) is oxidative addition of $\text{Pd}(0)$ into the C-X bond.

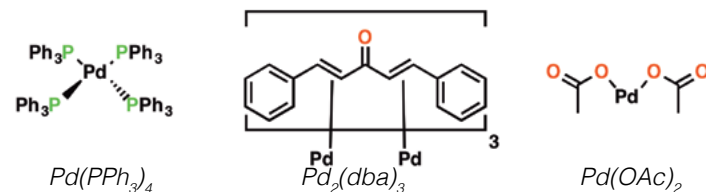


Coupling partner: The differences in "names" among the different palladium-catalyzed C-C bond forming reactions boils down to the choice of coupling partner. In the Heck reaction, the coupling partner is an alkene. In the Suzuki reaction, the coupling partner is a boronic acid or boronic ester. In the Stille reaction the coupling partner is an organostannane.

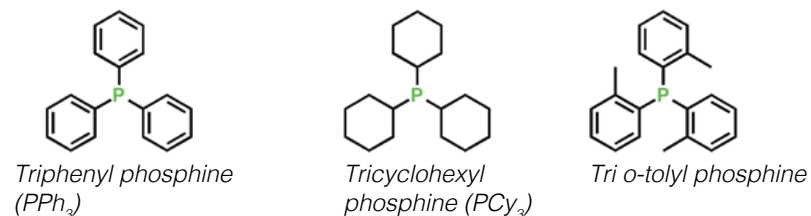


Palladium sources: The most commonly observed source of palladium is $\text{Pd}(\text{PPh}_3)_4$ "tetrakis" because it is a source of Pd in the (0) oxidation state. Another source of $\text{Pd}(0)$ is $\text{Pd}_2(\text{dba})_3$ where "dba" is dibenzylidene acetone. A final source of Pd is $\text{Pd}(\text{OAc})_2$. This is generally converted to $\text{Pd}(0)$ under the reaction conditions.

For our purposes there is no practical difference between these reagents.



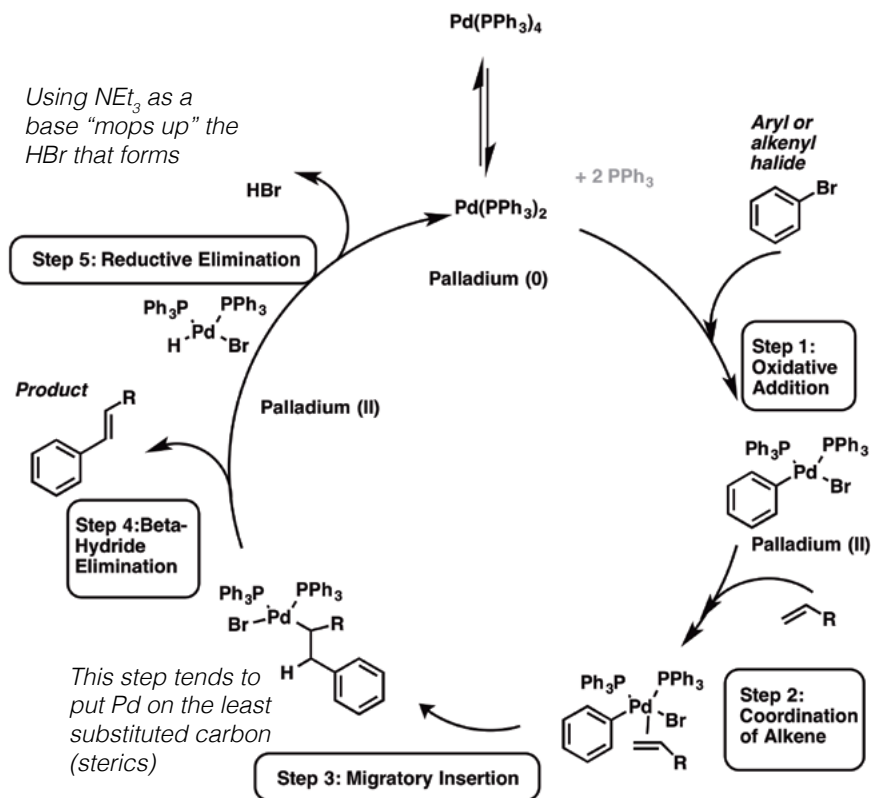
Ligands: "Ligands" are Lewis bases that coordinate to metals, for example triphenylphosphine, PPh_3 . Some variants on triphenylphosphine are sometimes seen, for example tricyclohexylphosphine (PCy_3) or tri *o*-tolyl phosphine. For our purposes there is no practical difference between these reagents.



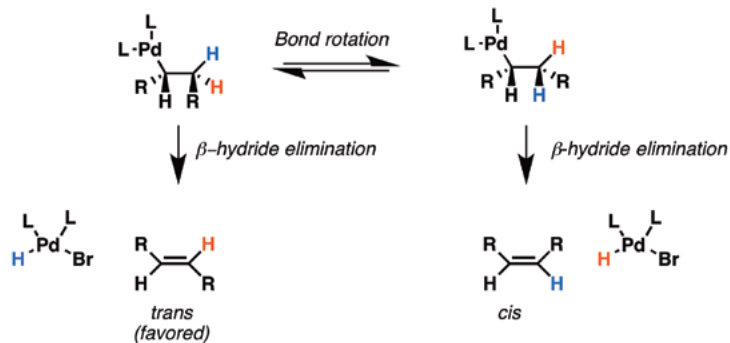
Additives: Used to help the reaction proceed in some way. These are usually bases, such as NEt_3 in the Heck reaction, or NaOH in the Suzuki reaction.

Cross Coupling

How it works: *Heck reaction*



The beta-hydride elimination step requires the Pd to be "syn" with the hydrogen. Formation of trans alkenes is preferred.



Cross Coupling

How it works: *Suzuki reaction*

