الكلية	**العلوم**
القسم	**علوم الكيمياء**
المادة باللغة الانجليزية	Organic chemistry
المادة باللغة العربية	**الكيمياء العضوية**
المرحلة الدراسية	**الثانية**
اسم التدريسي	**وهج رائد عباس**
عنوان المحاضرة باللغة الانجليزية	Aliphatic Hydrocarbons
عنوان المحاضرة باللغة العربية	**الهايدروكاربونات الاليفاتية**
رقم المحاضرة	**2**
المصادر والمراجع	Fundamental of organic chemistry, T. W. Craham Solomon
	Organic chemistry, 10th Ed, T. W. Craham Solomon & Craig B. fryhle
	Organic chemistry, 8th Ed, L. G. WADE JR

ALIPHATIC HYDROCARBONE

By Wahaj Raed

Hydrocarbons: are compounds made up of only the elements carbon and hydrogen. They may be aliphatic or aromatic.

Aliphatic hydrocarbons:

Aliphatic hydrocarbons can be divided into three subgroups.

Alkanes: have only C–C σ bonds and no functional group. Ethane, CH_3 -CH_3, is a simple alkane.

Alkenes: have a C – C double bond as a functional group. Ethylene, $CH_2=CH_2$, is a simple alkene.

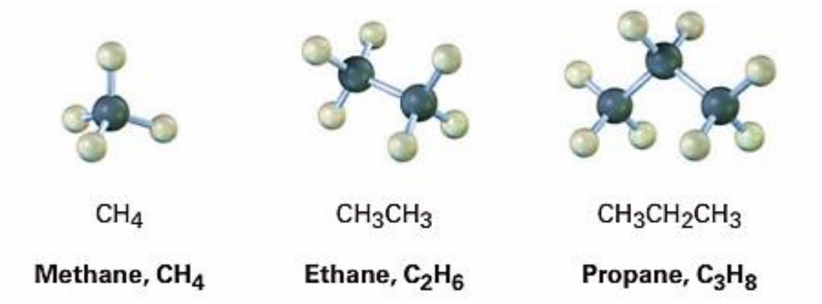
Alkynes: have a C – C triple bond as a functional group. Acetylene, C_2H_2, is a simple alkyne.

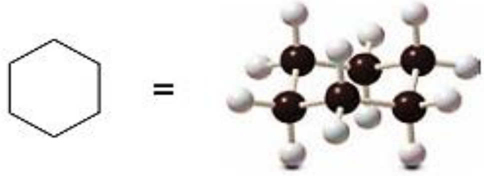
Alkanes

Alkanes are aliphatic hydrocarbons having only C – C and C – H bonds. Because their carbon atoms can be joined together in chains or rings, they can be categorized as acyclic or cyclic. Alkanes are often described as saturated hydrocarbons: hydrocarbons because they contain only carbon and hydrogen; saturated because they have only C-C and C- H single bonds and thus contain the maximum possible number of hydrogens per carbon.

Acyclic alkanes: have the molecular formula C_nH_{2n+2} (where n = an integer) and contain only linear and branched chains of carbon atoms. They are also called saturated hydrocarbons because they have the maximum number of hydrogen atoms per carbon.

Cycloalkanes contain carbons joined in one or more rings. Because their general formula is C_nH_{2n}, they have two fewer H atoms than an acyclic alkane with the same number of carbons. The primary sources of alkanes are natural gas and petroleum. These fossil fuels account for approximately 85% of the total energy consumed in the United States. Nuclear electric power, hydroelectric power, and renewable energy sources such as solar and wind power, make up most of the remaining 15%. In addition, these fossil fuels provide the bulk of the raw materials for the organic chemicals used worldwide.

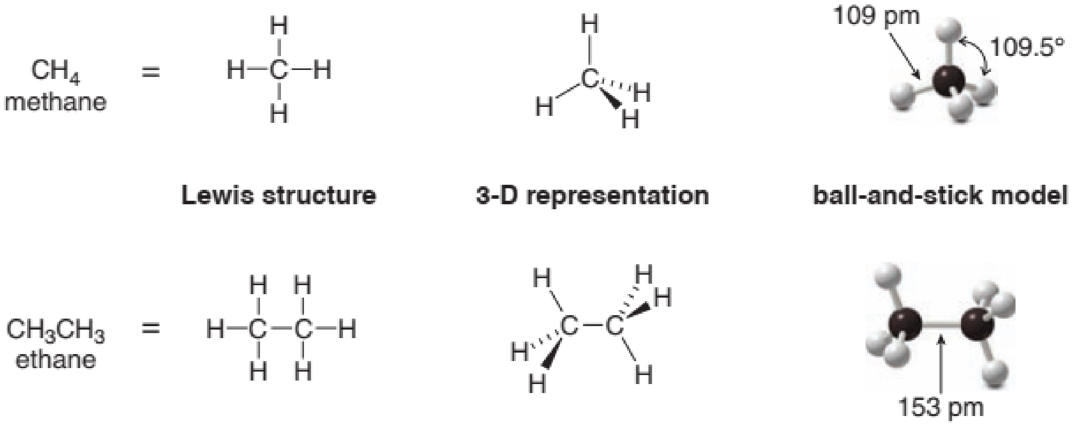




cyclohexane
C_6H_{12}

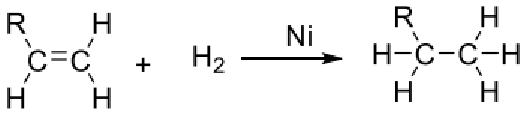
Shape of alkanes

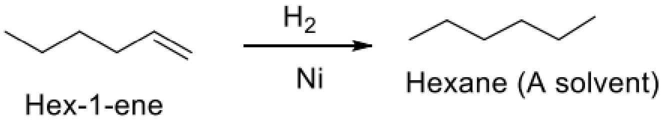
All C atoms in an alkane are surrounded by four groups, making them sp3 hybridized and tetrahedral, and all bond angles are 109.5°.



Synthesis of alkanes

Catalytic hydrogenation of alkenes or alkynes. a common strategy to alkanes. Catalytic hydrogenation is the common method for converting unsaturated oils to saturated fats in a process commonly referred to as “hardening of oils”.



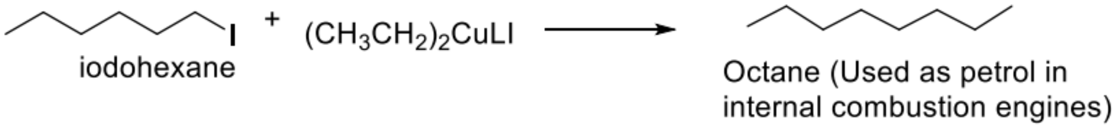


$$CH_3-C\equiv CH \xrightarrow[Ni]{H_2} CH_3CH_2CH_3$$

Propyne — Propane (A gas)

Organocuprates (Gilman reagents) couple with alkyl halides.

provide alkanes. The reaction of organocuprates with alkyl halides is a substitution reaction made possible by the polarization of the C-I as a result of the differences in electronegativities between carbon and iodine. Note that the C-Cu bond is less polarized and therefore more covalent compared with the C-Li or C-Mg bonds.



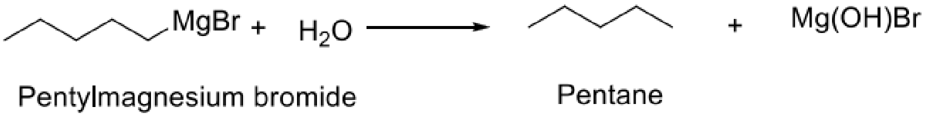
Reactions of ionic organometallic reagents with water.

The most common organometallic reagents used are organolithium and organo-magnesium reagents.

$$R-M + H_2O \longrightarrow R-H + MOH$$

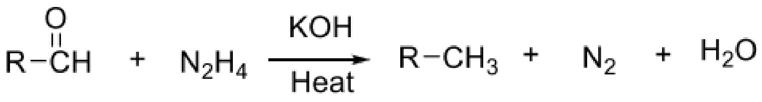
$$CH_3Li + H_2O \longrightarrow CH_4 + LiOH$$

Methyllithium — Methane (A Fuel)

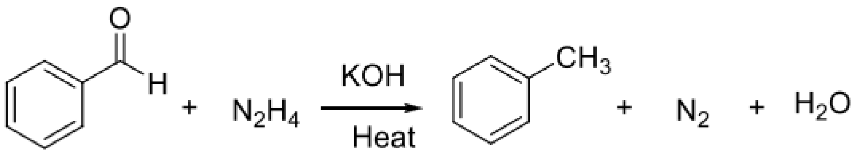


Reduction (deoxygenation) of aldehydes and ketones.

provides access to hydrocarbons. One of the most common methods for deoxygenation of aldehydes and ketones is the Wolff Kishner reduction. It involves heating an aldehyde or ketone with hydrazine in the presence of a base (KOH).



$$R-\overset{O}{\overset{\|}{C}}H + N_2H_4 \xrightarrow[Heat]{KOH} R-CH_3 + N_2 + H_2O$$



Benzaldehyde

Toluene

Reaction of alkanes

Oxidation and Reduction Reactions:

Oxidation and reduction are opposite processes. As in acid–base reactions, there are always two components in these reactions. One component is oxidized and one is reduced. To determine if an organic compound undergoes oxidation or reduction, we concentrate on the carbon atoms of the starting material and product, and compare the relative number of C – H and C – Z bonds, where Z = an element more electronegative than carbon (usually O, N, or X). Oxidation and reduction are then defined in two complementary ways.

Oxidation results in an increase in the number of C – Z bonds, or in a decrease in the number of C – H bonds.

Reduction results in a decrease in the number of C – Z bonds, or in an increase in the number of C – H bond.

The oxidation of alkanes by O_2 to give carbon dioxide and water is by far their most economically important reaction. Oxidation of saturated hydrocarbons is the basis for their use as energy sources for heat (natural gas, liquefied petroleum gas (LPG), and fuel oil) and power (gasoline, diesel fuel, and aviation fuel). Following are balanced equations for the complete oxidation of methane (the major component of natural gas) and propane (the major component of LPG).

$$\underset{\textbf{Methane}}{CH_4} + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H° = -890.4\ kJ\ (-212.8\ kcal)/mol$$

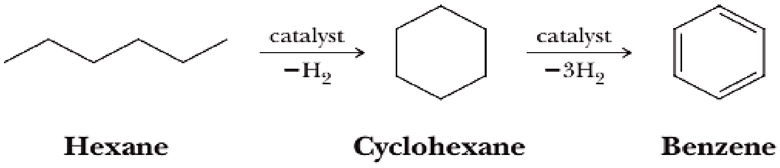
$$\underset{\textbf{Propane}}{CH_3CH_2CH_3} + 5O_2 \longrightarrow 3CO_2 + 4H_2O \qquad \Delta H° = -2220\ kJ\ (-530.6\ kcal)/mol$$

Cracking:

is a process whereby a saturated hydrocarbon is converted into an unsaturated hydrocarbon plus H_2. Ethane is cracked by heating it in a furnace at 800 - 900°Cfor a fraction of a second.

$$\underset{\textbf{Ethane}}{CH_3CH_3} \xrightarrow{800\text{–}900°C} \underset{\substack{\textbf{Ethene}\\ \textbf{(Ethylene)}}}{CH_2{=}CH_2} + H_2$$

The two most common reforming processes are cracking, as illustrated by the thermal conversion of ethane to ethylene, and catalytic reforming. Catalytic reforming is illustrated by the conversion of hexane first to cyclohexane and then to benzene.

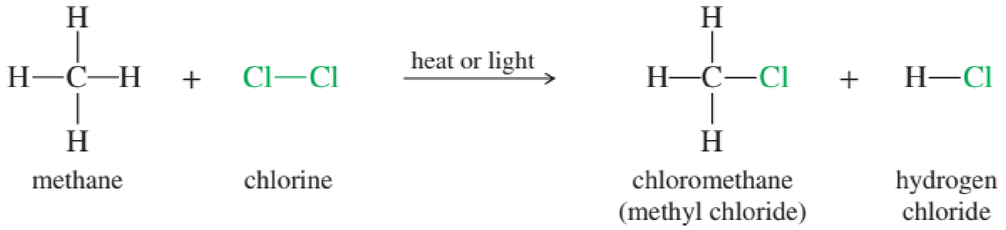


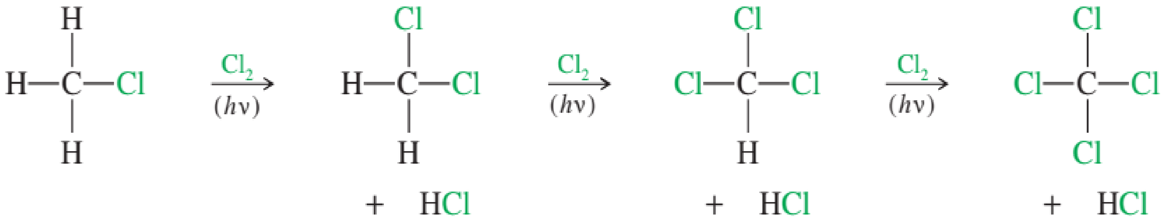
Synthesis gas is prepared by passing steam over hot coal; it is also prepared by partial oxidation of methane with oxygen.

$$\underset{\textbf{Methane}}{CH_4} + \frac{1}{2}O_2 \xrightarrow{\text{catalyst}} CO + 2H_2$$

Halogenation of alkanes:

The chlorination of methane is an important industrial reaction, with a relatively simple mechanism that illustrates many of the important principles of a reaction. The reaction of methane with chlorine produces a mixture of chlorinated products, whose composition depends on the amount of chlorine added and also on the reaction conditions. Either light or heat is needed for the reaction to take place at a useful rate. When chlorine is added to methane, the first reaction is

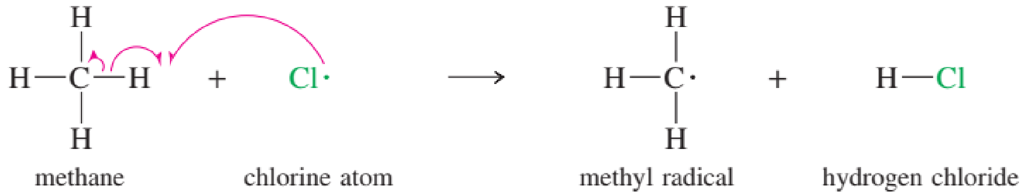


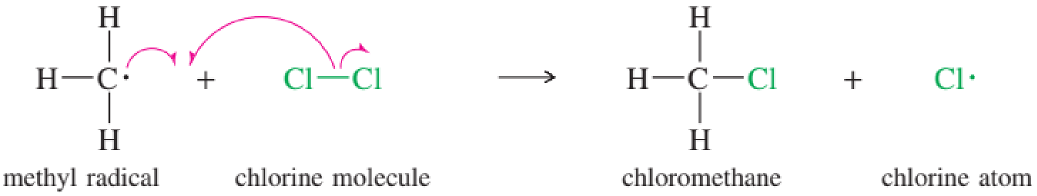


A chain reaction mechanism has been proposed to explain the chlorination of methane. A chain reaction consists of three kinds of steps:

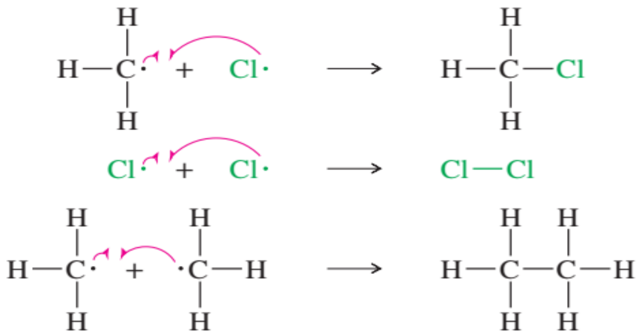
1. The initiation step, which generates a reactive intermediate.

2 .Propagation steps, in which the reactive intermediate reacts with a stable molecule to form a product and another reactive intermediate, allowing the chain to continue until the supply of reactants is exhausted or the reactive intermediate is destroyed.



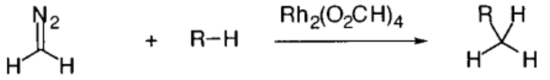


3 .Termination steps, side reactions that destroy reactive intermediates and tend to slow or stop the reaction.



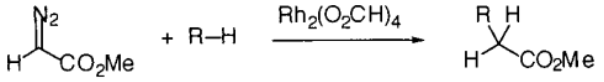
The reaction of alkane with diazonium compounds (C-H insertion reaction)

We employed dirhodium tetraformate (I) as a model of a common catalyst, the dirhodium tetracarboxylate-catalyzed C-H bond activation /C-C bond formation reaction of a diazo compound with an alkane revealed the energetics and the geometry of important intermediates and transition states in the catalytic cycle. dirhodium tetraacetate, in the interest of computational facility. With this model catalyst, two model catalytic reactions were studied. The reaction is initiated by complexation between the rhodium catalyst and the diazo compound. One was the reaction of diazomethane with methane or propane (CH_2 insertion, eq 1). This reaction has not been reported in the literature. Nonetheless, this simple model was investigated to understand the fundamental characters of the dirhodium-carbene complex and the mechanism of its C-H insertion reaction. The central mechanistic principle established with this model was found to hold also in a more realistic reaction model. The reaction of methyl diazoacetate with methane or propane (CH_3 and CH_2 insertion) was also studied (eq 2). This system is much more relevant to the actual synthetic reactions. Unlike the relatively unreactive substrates such as methane and propane, SiH_4 and dimethyl ether reacted with the rhodium carbene complex without any activation energy. A 1:1 stoichiometry of the rhodium catalyst and the diazo compound. The reaction is initiated by complexation between the rhodium catalyst and the diazo compound The carbene carbon of the complex is strongly electrophilic because of its vacant 2p orbital. The C-H activation/C-C formation proceeds in a single step through a three-centered hydride transfer-like transition state with a small activation energy. Only one of the two rhodium atoms works as a carbene binding site throughout the reaction, and the other rhodium atom assists the C-H insertion reaction. The second Rh atom acts as a mobile ligand for the first one to enhance the electrophilicity of the carbene moiety and to facilitate the cleavage of the rhodium-carbon bond. The calculations reproduce experimental data including the activation enthalpy of the nitrogen extrusion, the kinetic isotope effect of the C-H insertion, and the reactivity order of the C-H bond.



(1)

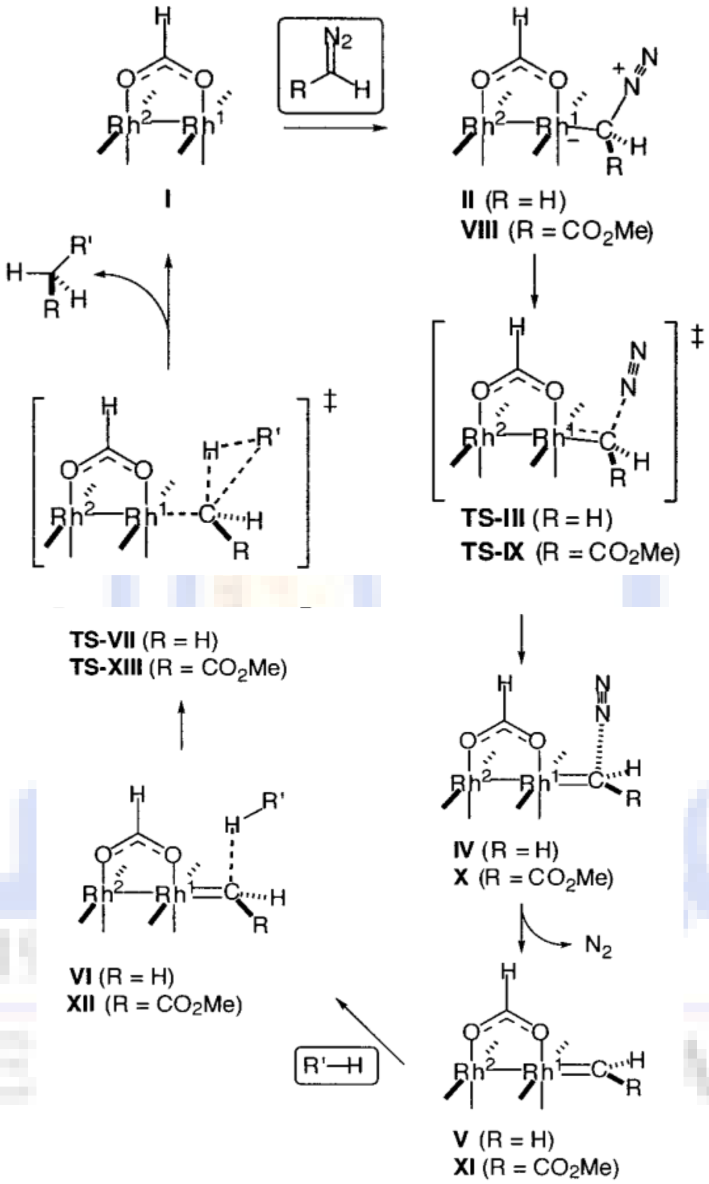
R = CH_3, $(CH_3)_2CH$



(2)

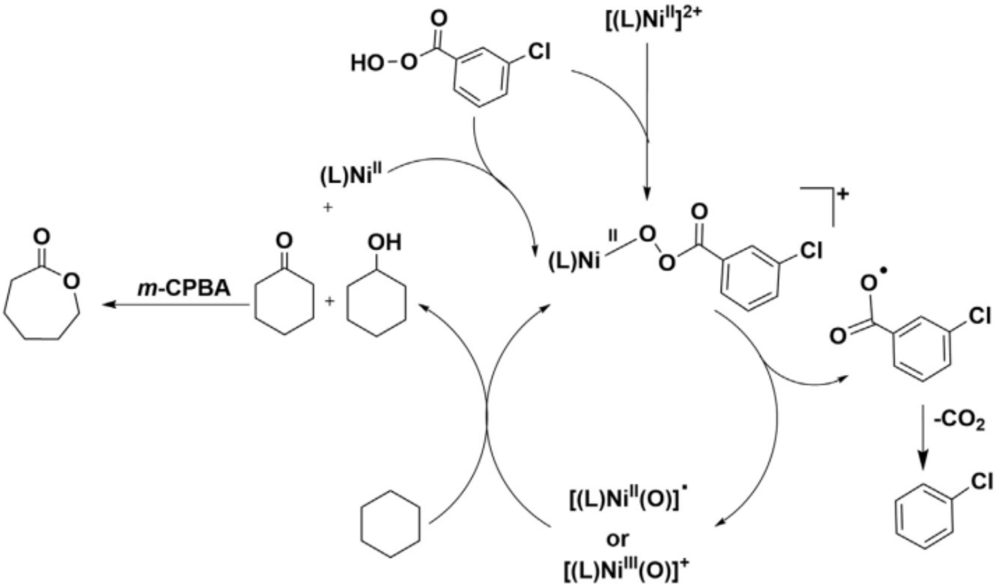
R = CH_3 , $CH_3CH_2CH_2$, $(CH_3)_2CH$

Mechanism:



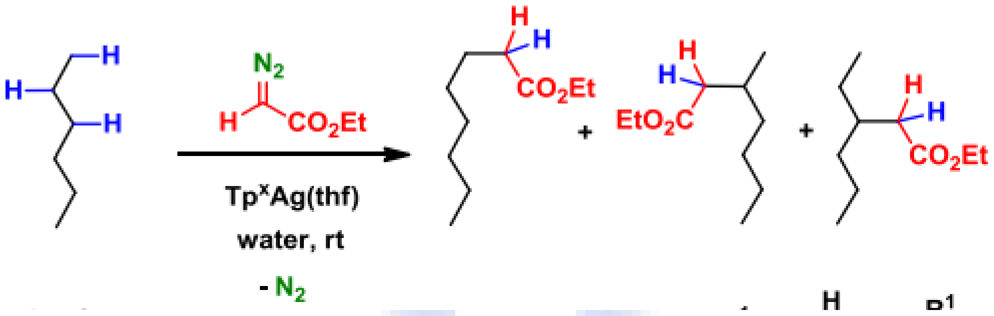
Alkane Hydroxylation:

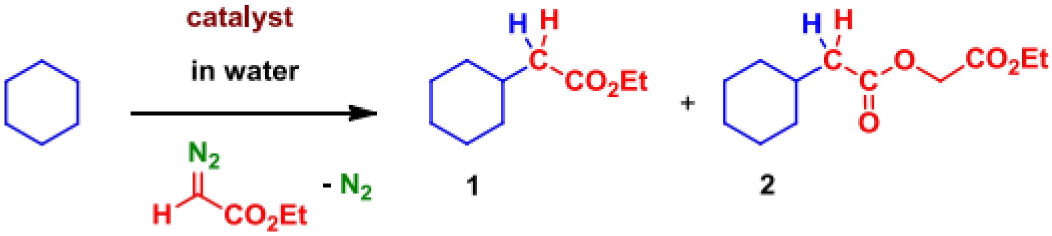
In most of the alkane oxidation reactions catalysed by nickel(II) complexes. In the first step, the nickel(II) complexes react with m-CPBA (m-chloroperoxybenzoic acid) to give the adduct [(L)Ni^{II}(OOC(O)PhCl(X] which undergoes homolytic cleavage of O-O bond to give a transient [(L)Ni^{II}($\dot{O}$)(X)] species and chlorobenzoate radical. The [(L)NiII($\dot{O}$)X)] species reacts with alkanes to give the alcohol and the chlorobenzoate radical decomposes to form chlorobenzene and CO_2. The formation of chlorobenzene from chlorobenzoate radical indirectly supports the formation of [(L(Ni^{II}($\dot{O}$)X)] species responsible for the catalytic activity. Palaniandavar and coworkers quantified the formation of chlorobenzene up to 60%, which supports the involvement of the Ni^{II}-O radical intermediate in the catalytic cycle. both the Ni^{II}-alkylperoxo and Ni^{II}-acylperoxo species and confirmed the interaction of oxidant with the nickel(II) complexes without changing the oxidation state of nickel. Also, can utilized these species for oxygen atom transfer and proposed that Ni^{II}-$\dot{O}$ or Ni^{III}-O intermediates are involved in oxygen atom transfer reactions.



Intramolecular Functionalization

Alkanes have been functionalized in water as the reaction medium, using a silver-based catalyst, upon insertion of carbene ($CHCO_2Et$ from N_2CHCO_2Et) groups into their carbon-hydrogen bonds of hexane, cyclohexane or 2-methylbutane, among others. This methodology involve the functionalization of carbon-hydrogen bonds by metal-mediated carbene insertion, use of Rh- or Ru-based catalysts for the intramolecular insertion of a carbene group into a carbon-hydrogen bond, that in addition is somewhat activated by the presence of a neighboring heteroatom. So, its the functionalization of alkanes with diazo compounds. in water as reaction medium only a few examples of the intramolecular functionalization have been described.





Tp= Trispyrazolylborate ligands, Tp^x with substituted

Spectroscopy Of Alkane:

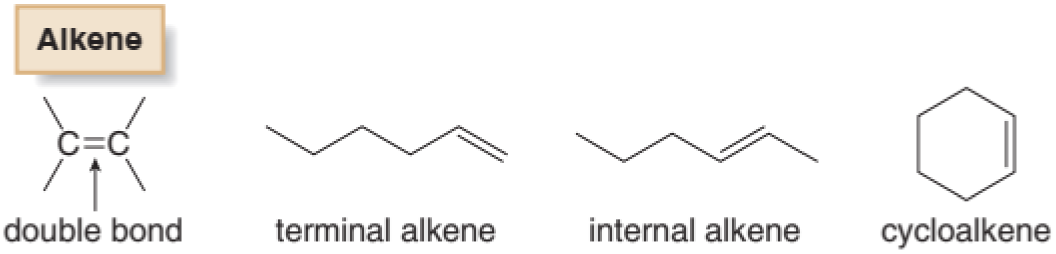
IR: C-H bond stretching at frequency 3000-2850 cm^{-1}, -CH_3 bend at 1450 & 1375 cm^{-1} , and -CH_2 bend at 1465cm^{-1}

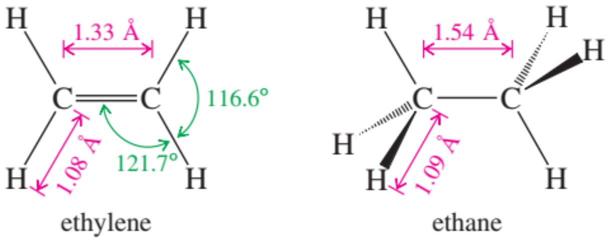
^{1}H-NMR: methyl group (CH_3) will produce a signal near 0.9 ppm, a methylene group (CH_2) will produce a signal near 1.2 ppm, and a methine group (CH) will produce a signal near 1.7 ppm. When alkane undergo in the reaction, the chemical shift of C-H change. For example halogenation reaction signal of C-H proton appear in the range 2.5–4.0 ppm.

13C-NMR: methyl group (CH_3) will produce a signal near (8-25) ppm, a methylene group (CH_2) will produce a signal near (20-45) ppm, and a methine group (CH) will produce a signal near (40-60) ppm. And R_4C will produce a signal near (36-70). When alkane undergo in the reaction, the chemical shift of C-H change. For example halogenation reaction signal of C-H carbon appear in the range (15-80) ppm.

Alkene

Alkenes are hydrocarbons with carbon–carbon double bonds. Alkenes are sometimes called olefins. Terminal alkenes have the double bond at the end of the carbon chain, whereas internal alkenes have at least one carbon atom bonded to each end of the double bond. Cycloalkenes contain a double bond in a ring. The double bond of an alkene consists of one σ bond and one π bond. Each of the carbon–hydrogen sigma bonds is formed by overlap of an sp2 hybrid orbital on carbon with the 1s orbital of a hydrogen atom. The bond length in ethylene (1.08 Å) is slightly shorter than the bond in ethane (1.09 Å) because the orbital in ethylene has more s character (one-third s) than an orbital (onefourth s). The s orbital is closer to the nucleus than the p orbital, contributing to shorter bonds.

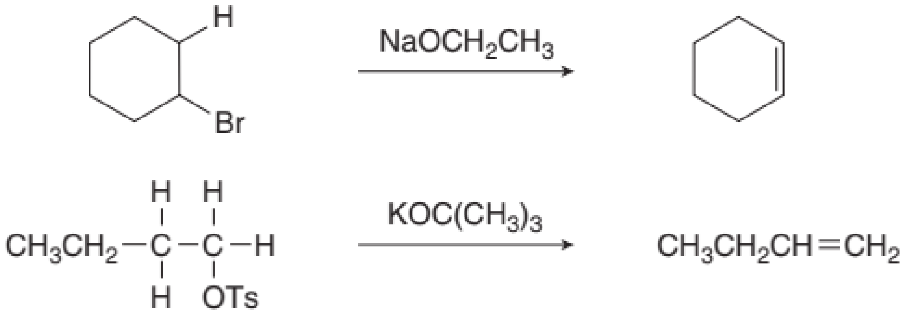




The π bond is much weaker than the σ bond of a C – C double bond, making it much more easily broken. As a result, alkenes undergo many reactions that alkanes do not, Because a carbon–carbon double bond is relatively reactive, it is considered to be a functional group, and alkenes are characterized by the reactions of their double bonds.

Preparation Of Alkenes

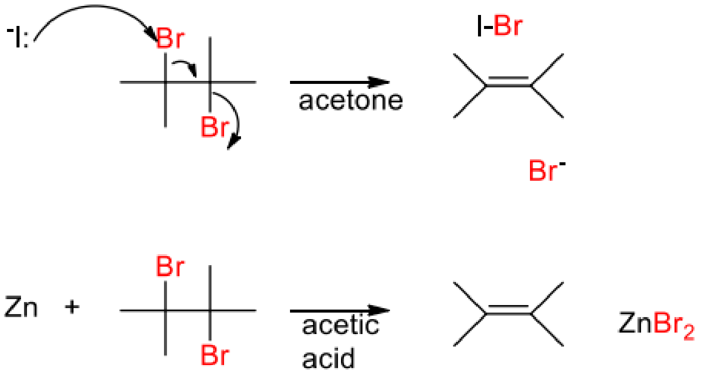
Alkenes can be prepared from alkyl halides and alcohols via elimination reactions. For example, dehydrohalogenation of alkyl halides with strong base yields alkenes via an E2 mechanism.



Typical bases include –OH and –OR [especially –OC(CH3)3], and nonnucleophilic bases such as DBU and DBN. Alkyl tosylates can also be used as starting materials under similar reaction conditions.

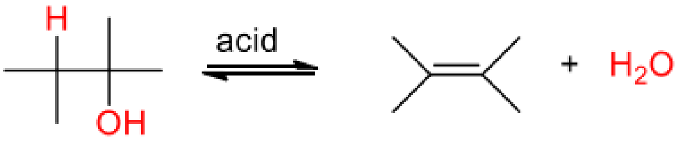
Reduction of Vicinal Dibromides

The action of iodide ion on vicinal dibromides to produce alkenes is an elimination, a reduction and a dehalogenation reaction. (The same reaction can be achieved through the action of zinc metal in acetic acid). The reaction prefers to go through the anti-coplanar T.S.

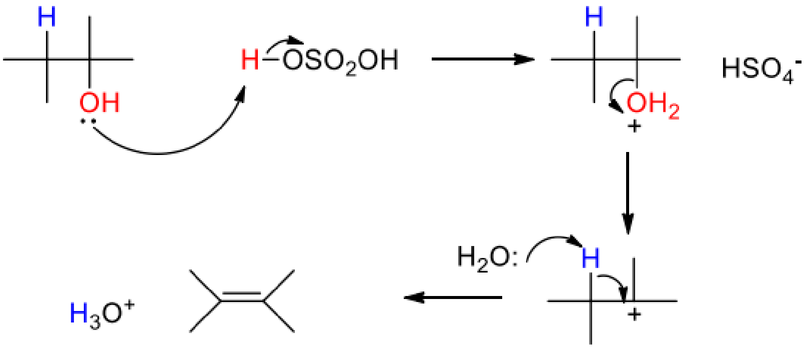


Alcohol Dehydration

The dehydration (removal of water) of alcohols is a good synthetic route to alkenes. The acid-catalyzed dehydration of alcohols with H_2SO_4 or TsOH yields alkenes, too. The reaction occurs via an E1 mechanism for 2° and 3° alcohols, and an E2 mechanism for 1° alcohols. E1 reactions involve carbocation intermediates, so rearrangements are possible. Dehydration can also be carried out with $POCl_3$ and pyridine by an E2 mechanism.



Mechanism:

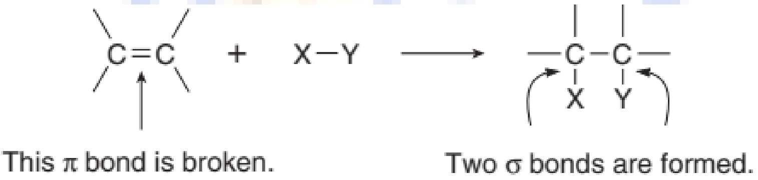


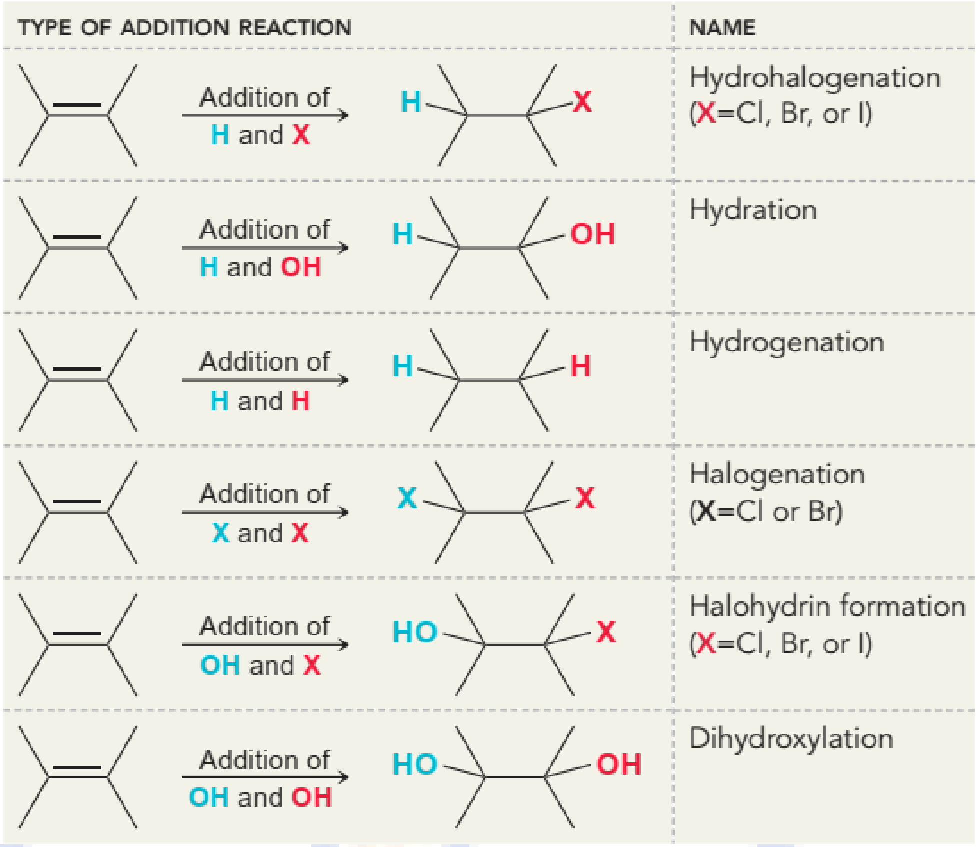
**Also, alkenes can preparation from cracking of alkanes.

Alkene Reaction

Addition Reactions

Because the C – C π bond of an alkene is much weaker than a C – C σ bond, the characteristic reaction of alkenes is addition: the o bond is broken and two new r bonds are formed. Every reaction of alkenes involves addition: the o bond is always broken. Because alkenes are electron rich, simple alkenes do not react with nucleophiles or bases, reagents that are themselves electron rich. Alkenes react with electrophiles.

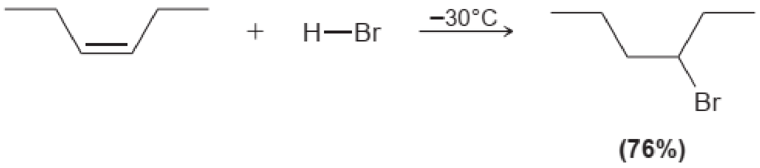




TYPE OF ADDITION REACTION	NAME
Addition of H and X	Hydrohalogenation (X=Cl, Br, or I)
Addition of H and OH	Hydration
Addition of H and H	Hydrogenation
Addition of X and X	Halogenation (X=Cl or Br)
Addition of OH and X	Halohydrin formation (X=Cl, Br, or I)
Addition of OH and OH	Dihydroxylation

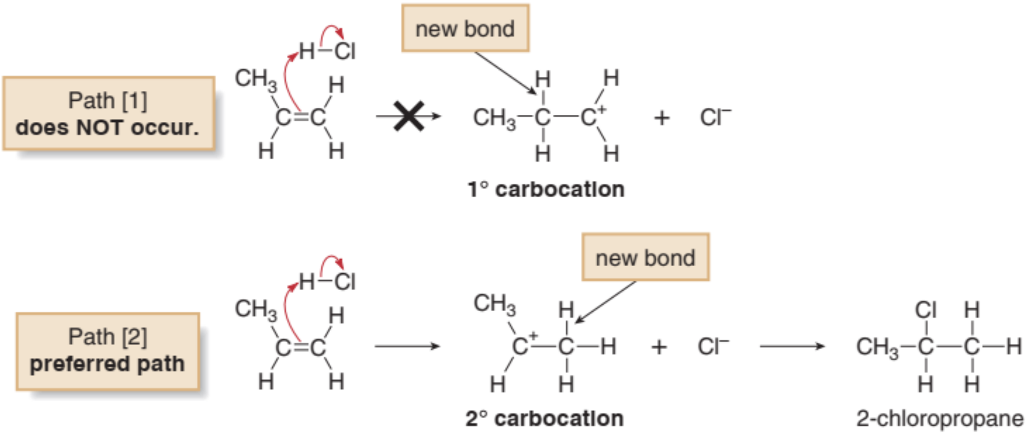
Hydrohalogenation

The treatment of alkenes with HX (where X = Cl, Br, or I) results in an addition reaction called hydrohalogenation, in which H and X are added across the π bond:

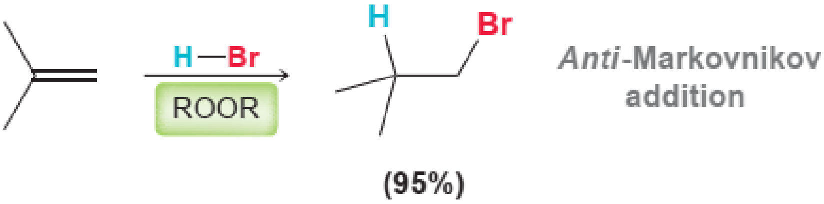


In cases where the alkene is unsymmetrical, the ultimate placement of H and X must be considered. In the following example, there are two possible vinylic positions where X can be placed.

Markovnikov rule: In the addition of HX to an unsymmetrical alkene, the H atom bonds to the less substituted carbon atom—that is, the carbon that has more H atoms to begin with. The regioselectivity of electrophilic addition depend on this rule.

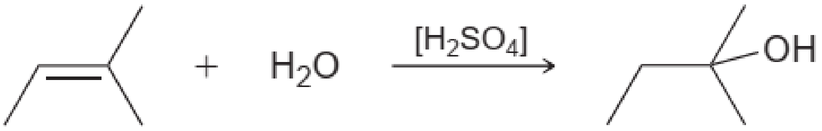


The addition in the above reaction depends on the stability of carbocation that formed as intermediate compound in the reaction mechanism. The more stable, more substituted carbocation is formed by addition of the electrophile to the less substituted carbon. Specifically, Markovnikov addition was observed whenever purified reagents were used, while the use of impure reagents sometimes led to anti-Markovnikov addition. Further investigation revealed the identity of the impurity that most greatly affected the regioselectivity of the reaction. It was found that peroxides (ROOR), even in trace amounts, would cause HBr to add across an alkene in an anti-Markovnikov fashion.

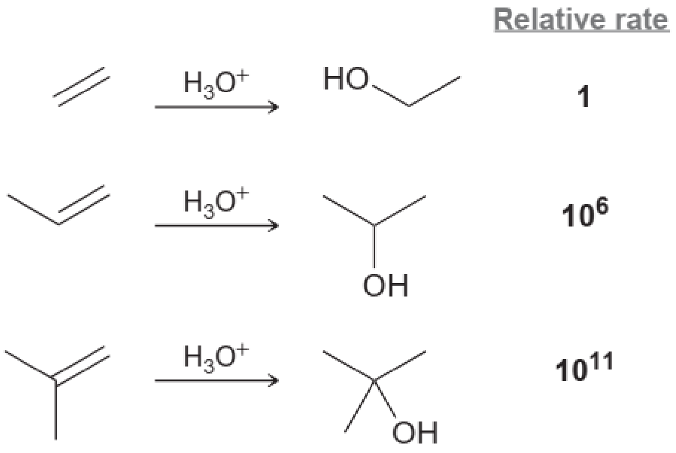


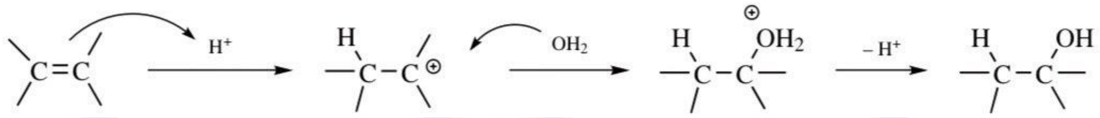
Hydration

Adding water (H and OH) across a double bond to yield alcohols, a process called hydration. The reaction takes place on treatment of the alkene with water and a strong acid catalyst, such as H_2SO_4. protonation of an alkene double bond yields a carbocation intermediate, which reacts with water to yield a protonated alcohol product, ROH_2+. Loss of H+ from this protonated alcohol gives the neutral alcohol and regenerates the acid catalyst.

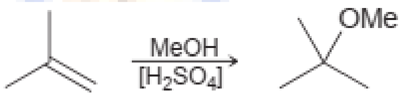


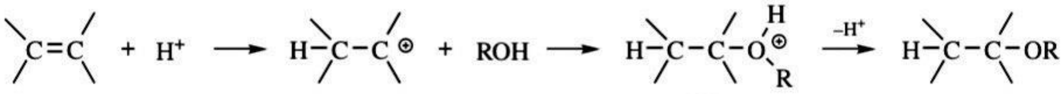
The rate of an acid-catalyzed hydration is very much dependent on the structure of the starting alkene. Compare the relative rates of the following three reactions, and analyze the effects of an alkyl substituent on the relative rate of each reaction. With each additional alkyl group, the reaction rate increases by many orders of magnitude.



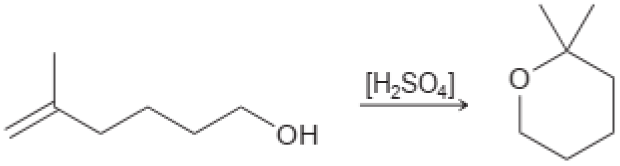


If an alkene is protonated and the solvent is an alcohol rather than water, a reaction takes place that is very similar to acid-catalyzed hydration, but in the second step of the mechanism the alcohol functions as a nucleophile instead of water. Draw a plausible mechanism for the following process:

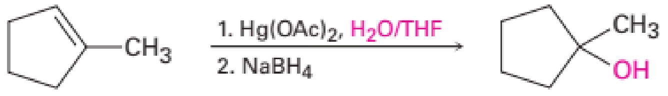




Using the reaction in the previous problem as a reference, propose a plausible mechanism for the following intramolecular reaction:



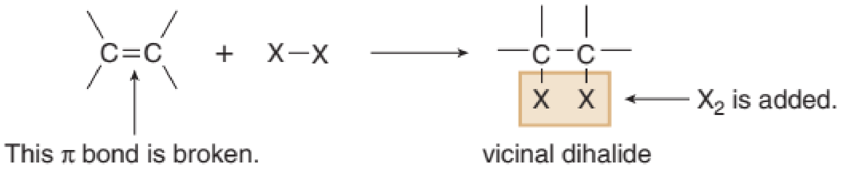
Alkenes are often hydrated by the oxymercuration–demercuration procedure. Oxymercuration involves electrophilic addition of Hg^{2+} to the alkene on reaction with mercury(II) acetate [$(CH_3CO_2)_2Hg$, often abbreviated Hg(OAc)2] in aqueous tetrahydrofuran (THF) solvent. When the intermediate organomercury compound is then treated with sodium borohydride, $NaBH_4$, demercuration occurs to produce an alcohol. For example:

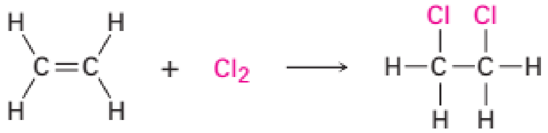


1-Methylcyclopentene **1-Methylcyclopentanol (92%)**

Halogenation of Alkenes: Addition of X_2

Bromine and chlorine add rapidly to alkenes to yield 1,2-dihalides, a process called halogenation. For example, more than 18 million tons 1,2-dichloroethane (ethylene dichloride) is synthesized worldwide each year, much of it by addition of Cl_2 to ethylene. The product is used both as a solvent and as starting material for the manufacture of poly(vinyl chloride), PVC. Fluorine is too reactive and difficult to control for most laboratory applications, and iodine does not react with most alkenes.





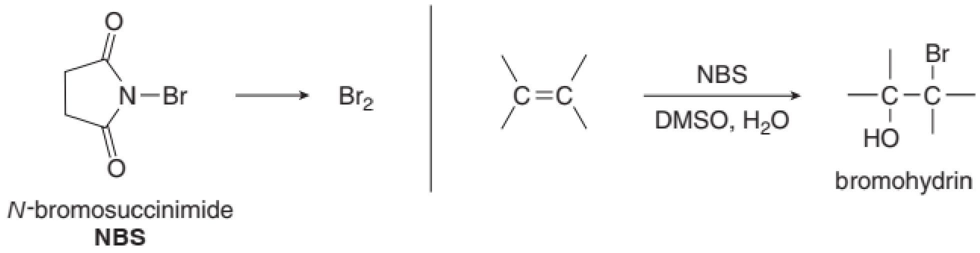
Ethylene **1,2-Dichloroethane (ethylene dichloride)**

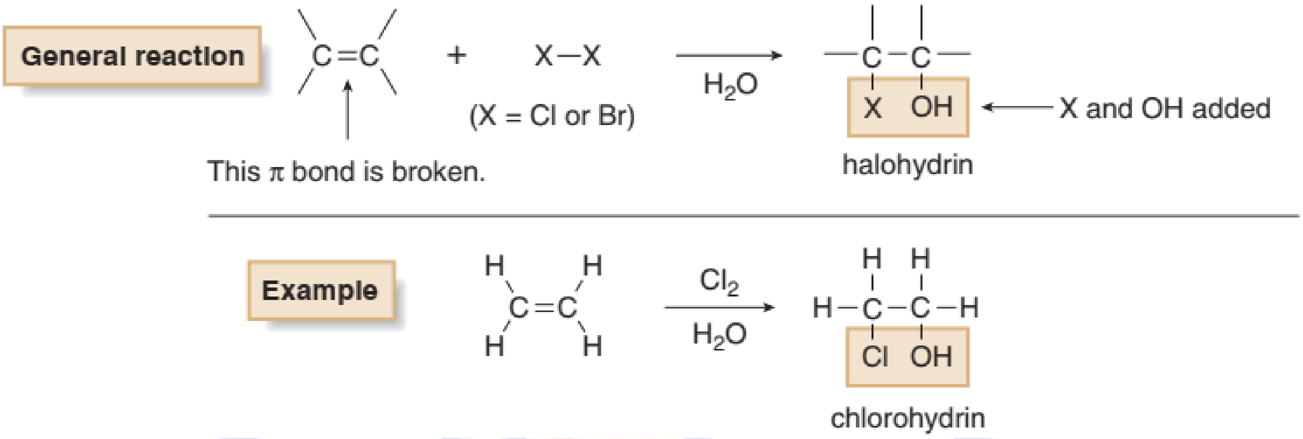
The electron-rich double bond induces a dipole in an approaching halogen molecule, making one halogen atom electron deficient and the other electron rich ($X^{\delta+} – X^{\delta-}$). The electrophilic halogen atom is then attracted to the nucleophilic double bond, making addition possible. Is these reaction of alkenes, no rearrange-ments occur, and second, only anti addition of X_2 is observed.

Halohydrin Formation

Treatment of an alkene with a halogen X_2 and H_2O forms a halohydrin by addition of the elements of X and OH to the double bond. Although the combination of Br2 and

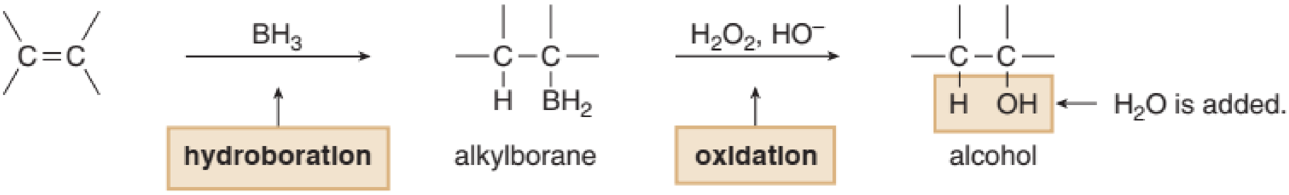
H_2O effectively forms bromohydrins from alkenes, other reagents can also be used. Bromohydrins are also formed with N-bromosuccinimide (abbreviated as NBS) in aqueous DMSO [$(CH_3)_2S = O$]. NBS serves as a source of Br_2, which then goes on to form a bromohydrin.





Hydroboration–Oxidation

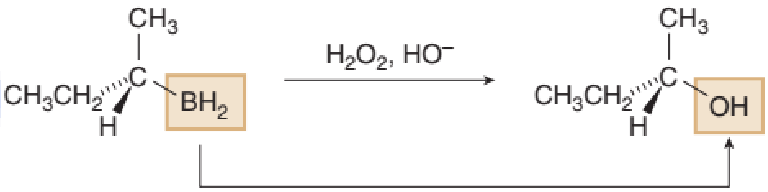
Hydroboration–oxidation is a two-step reaction sequence that converts an alkene to an alcohol.



Hydroboration is the addition of borane (BH_3) to an alkene, forming an alkylborane Oxidation converts the C – B bond of the alkylborane to a C – O bond. The term organoborane is used for any compound with a carbon–boron bond.

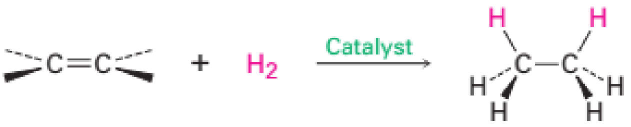
Oxidation of the Alkylborane

Because alkylboranes react rapidly with water and spontaneously burn when exposed to the air, they are oxidized, without isolation, with basic hydrogen peroxide (H_2O_2, HO–). Oxidation replaces the C – B bond with a C – O bond, forming a new OH group with retention of configuration; that is, the OH group replaces the BH2 group in the same position relative to the other three groups on carbon.

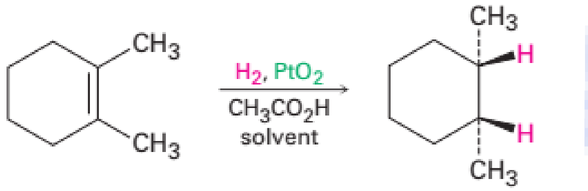


Hydrogenation

Alkenes react with H_2 in the presence of a metal catalyst such as palladium or platinum to yield the corresponding saturated alkane addition products. We describe the result by saying that the double bond has been hydrogenated, or reduced. Platinum and palladium are the most common laboratory catalysts for alkene hydrogenations. Palladium is normally used as a very fine powder “supported” on an inert material such as charcoal (Pd/C) to maximize surface area. Platinum is normally used as PtO_2, a reagent known as Adams’ catalyst after its discoverer, Roger Adams.

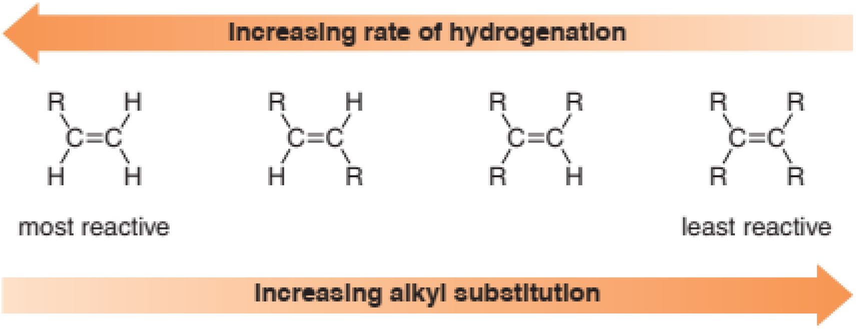


An alkene **An alkane**



1,2-Dimethyl-cyclohexene ***cis*-1,2-Dimethyl-cyclohexane (82%)**

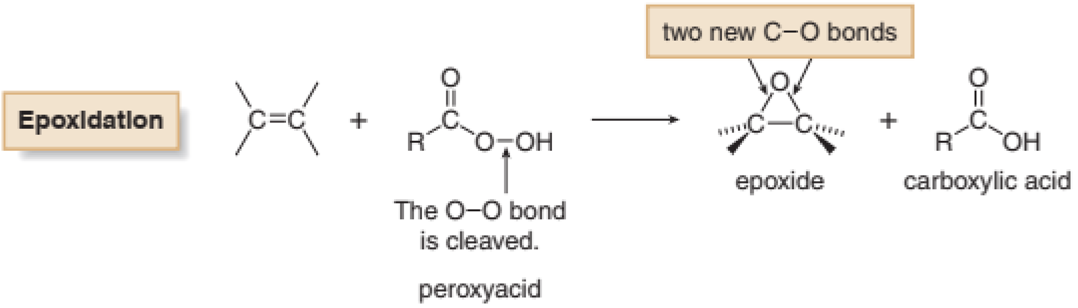
Rapid, sequential addition of H2 occurs from the side of the alkene complexed to the metal surface, resulting in syn addition. Less crowded double bonds complex more readily to the catalyst surface, resulting in faster reaction.



Oxidation of alkenes

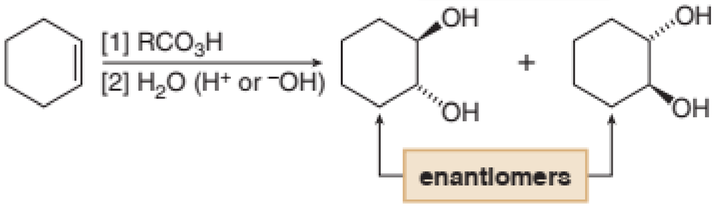
Epoxidation:

Epoxidation is the addition of a single oxygen atom to an alkene to form an epoxide. The weak π bond of the alkene is broken and two new C – O σ bonds are formed. Epoxidation is typically carried out with a peroxyacid, resulting in cleavage of the weak O – O bond of the reagent.



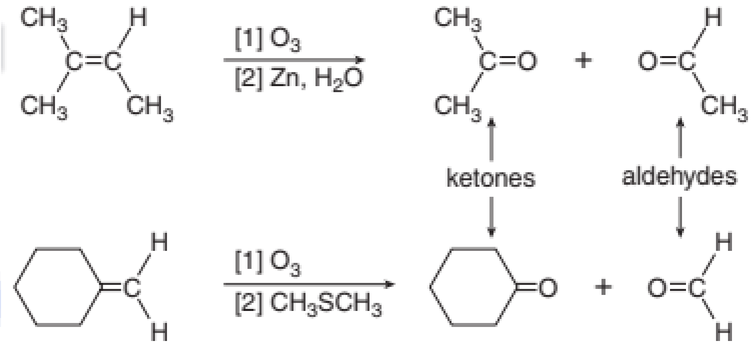
Dihydroxylation

Dihydroxylation is the addition of two hydroxy groups to a double bond, forming a 1,2-diol or glycol. Depending on the reagent, the two new OH groups can be added to the opposite sides (anti addition) or the same side (syn addition) of the double bond.



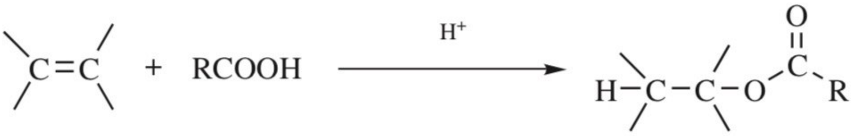
Oxidative Cleavage of Alkenes

Oxidative cleavage of an alkene breaks both the r and o bonds of the double bond to form two carbonyl groups. Depending on the number of R groups bonded to the double bond, oxidative cleavage yields either ketones or aldehydes.



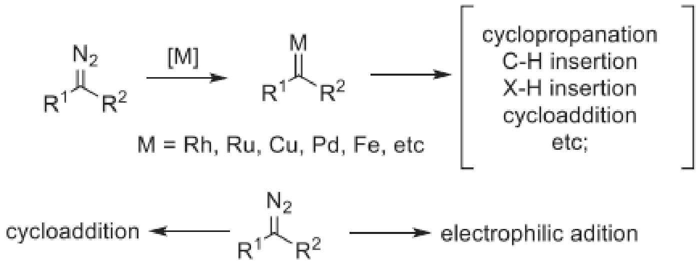
Ester formation (hydro- acyloxy addition)

Carboxylic esters are produce by the addition of carboxylic acid to alkenes, a reaction that is usually acid catalyzed and similar in mechanism to H_2O addition. The addition follow the Markovnikov's rule.

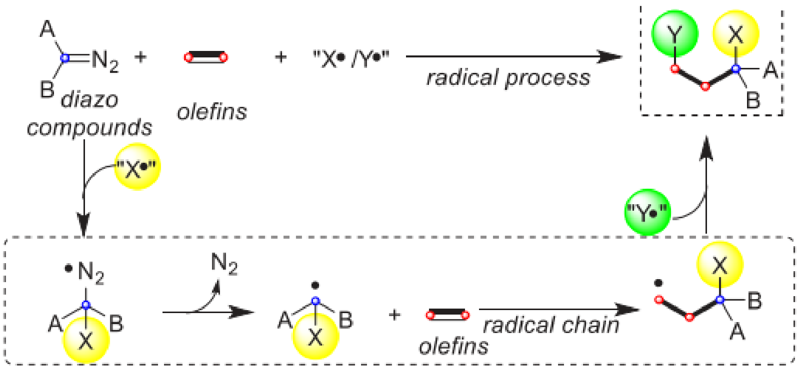


Reaction of alkene with diazonium compounds

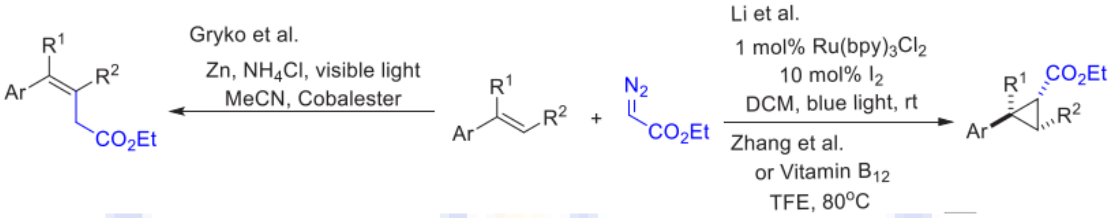
Diazo compounds are used extensively as synthetic building blocks in numerous reactions due to their high reactivity and diverse applications. They form metal carbene intermediates with many transition metal catalysts and undergo cyclo-propanation, C−H insertion, X−H insertion, cycloaddition, and other transformations



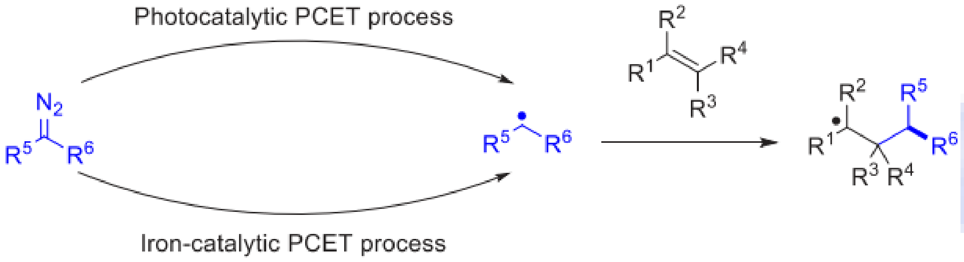
Their able to effect cycloaddition or electrophilic addition to form diazonium ions. Also, its posses ability to undergo free radical reactions, particularly addition reactions with alkenes. The general methodologies effectively involving selective radical addition to the diazo compound by X, which produces a diazinyl radical that, upon loss of dinitrogen, forms a carbon radical capable of addition to a C=C bond.

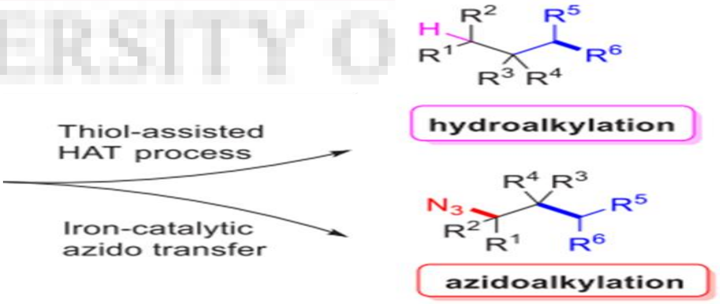


Effective trapping of the resulting carbon radical by Y is an additional challenge to the overall transformation. The formation of carbon-centered radicals from diazo compounds with release of dinitrogen have been reported.



There are two complementary protocols with diazo compounds as the precursors of carbon radicals achieving functionalization of diverse alkenes. Hydroalkylation is achieved using the combination of photocatalyst Ru(bpy)$_3$Cl$_2$·6H2O and organo-catalyst 4-methylbenzenethiol. Alternatively, azidoalkylation is catalyzed by iron acetate with tert-butyl hydroperoxide (TBHP). Mechanistic studies showed both of these processes involve free radical intermediates, and the traditional cyclopropane products.





Spectroscopy Of Alkenes:

IR: =C-H Stretch for sp2 C-H occurs at values greater than 3000 cm^{-1} (3095–3010 cm−1). =C-H Out-of-plane (oop) bending occurs in the range 1000–650 cm^{-1}.These bands can be used to determine the degree of substitution on the double bond. C=C Stretch occurs at 1660–1600 cm^{-1}.

^{1}H-NMR: =C-H (allylic) produce a signal near 2ppm, while vinylic appear at the range (4.5-6.5) ppm. The chemical shift change when alkene undergo the reaction. For example, addition H_2O to alkene change the chemical shift to 2-5 ppm as broad peak.

^{13}C-NMR: C=C give a signal at the range of chemical shift (110-150) ppm.

Alkynes

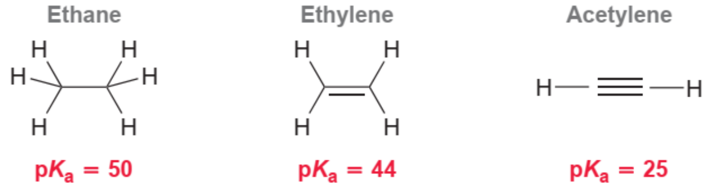
Alkynes are hydrocarbons that contain carbon–carbon triple bonds. Alkynes are also called acetylenes because they are derivatives of acetylene, the simplest alkyne. was once widely used in industry as the starting material for the preparation of acetaldehyde, acetic acid, vinyl chloride, and other high-volume chemicals, but more efficient routes to these substances using ethylene as starting material are now available. Acetylene is still used in the preparation of acrylic polymers, but is probably best known as the gas burned in high-temperature oxy–acetylene welding torches.

$H-C\equiv C-H$	$CH_3CH_2-C\equiv C-H$	$CH_3-C\equiv C-CH_3$
acetylene	ethylacetylene	dimethylacetylene
ethyne	but-1-yne	but-2-yne

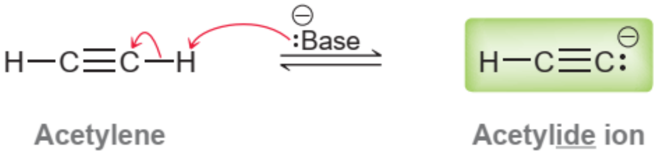
The chemistry of the carbon–carbon triple bond is similar to that of the double bond. Alkynes undergo most of the same reactions as alkenes, especially the additions and the oxidations.

Acidity of Acetylene and Terminal Alkynes

Terminal alkynes are much more acidic than other hydrocarbons. Removal of an acetylenic proton forms an acetylide ion, which plays a central role in alkyne chemistry. The acidity of an acetylenic hydrogen stems from the nature of the sp hybrid. The acidity of a bond varies with its hybridization, increasing with the increasing s character of the orbitals.



Recall that a lower pKa corresponds to a greater acidity. Therefore, acetylene (pKa = 25) is significantly more acidic than ethane or ethylene. To be precise, acetylene is 19 orders of magnitude (10^9 times) more acidic than ethylene. The relative acidity of acetylene can be explained by exploring the stability of its conjugate base, called an acetylide ion (the suffix “ide” indicates the presence of a negative charge):



Preparation of alkynes

Manufacture preparation of Acetylene

Acetylene, one of the cheapest organic chemicals, is made from coal or from natural gas. The synthesis from coal involves heating lime and coke (roasted coal) in an electric furnace to produce calcium carbide. Addition of water to calcium carbide produces acetylene and hydrated lime.

$$\underset{\text{coke}}{3\,C} + \underset{\text{lime}}{CaO} \xrightarrow{\text{electric furnace, 2500 °C}} \underset{\text{calcium carbide}}{CaC_2} + CO$$

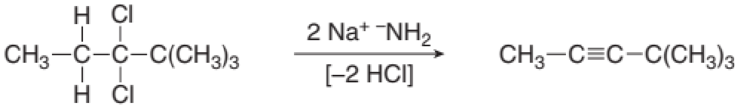
$$CaC_2 + 2\,H_2O \longrightarrow \underset{\text{acetylene}}{H-C\equiv C-H} + \underset{\text{hydrated lime}}{Ca(OH)_2}$$

The synthesis of acetylene from natural gas is a simple process. Natural gas consists mostly of methane, which forms acetylene when it is heated for a very short period of time.

$$2\,CH_4 \xrightarrow[\text{0.01 sec}]{\text{1500 °C}} H-C\equiv C-H + 3\,H_2$$

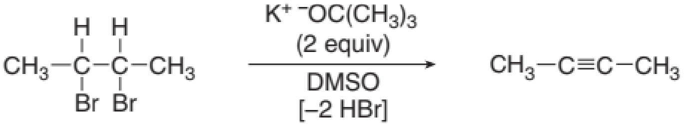
Elimination reaction

Alkynes can be prepared from alkyl dihalides. An alkyl dihalide has two leaving groups. A strong base removes two equivalents of HX from a vicinal or geminal dihalide to yield an alkyne by two successive E2 eliminations.



$$CH_3-CH_2-CCl_2-C(CH_3)_3 \xrightarrow[\text{[–2 HCl]}]{2\,Na^+\,{}^-NH_2} CH_3-C\equiv C-C(CH_3)_3$$

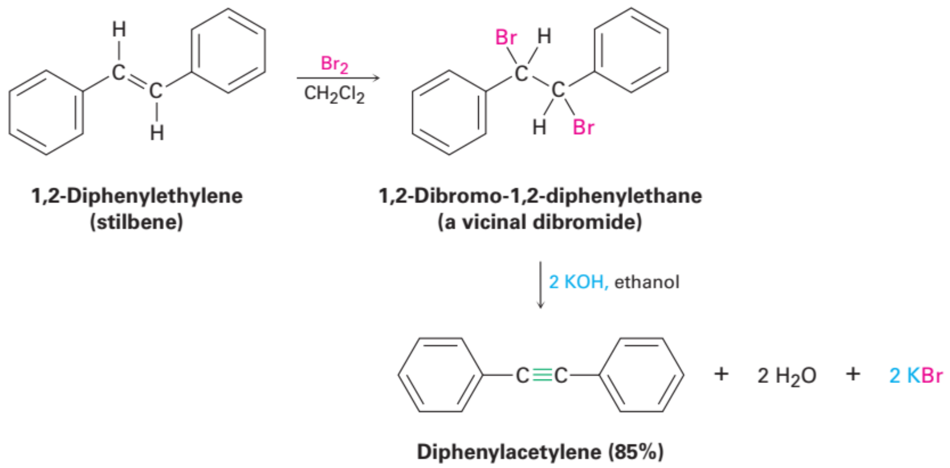
geminal dichloride



$$CH_3-CHBr-CHBr-CH_3 \xrightarrow[\substack{\text{DMSO}\\ \text{[–2 HBr]}}]{\substack{K^+\,{}^-OC(CH_3)_3\\ \text{(2 equiv)}}} CH_3-C\equiv C-CH_3$$

vicinal dibromide

The starting vicinal dihalides are themselves readily available by addition of Br_2 or Cl_2 to alkenes. Thus, the overall halogenation/dehydrohalogenation sequence makes it possible to go from an alkene to an alkyne.



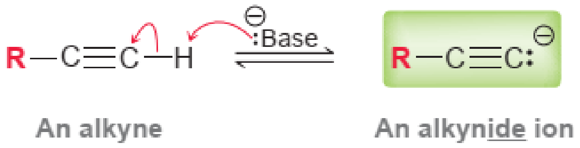
1,2-Diphenylethylene (stilbene)

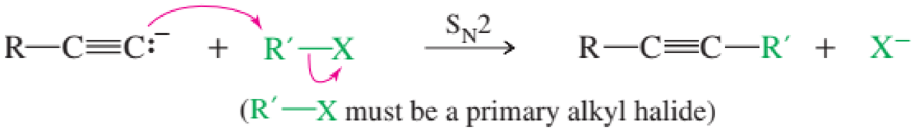
1,2-Dibromo-1,2-diphenylethane (a vicinal dibromide)

Diphenylacetylene (85%)

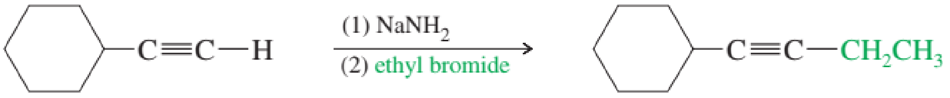
Alkylation of Acetylide Ions

An acetylide ion is a strong base and a powerful nucleophile. It can displace a halide ion from a suitable substrate, giving a substituted acetylene.





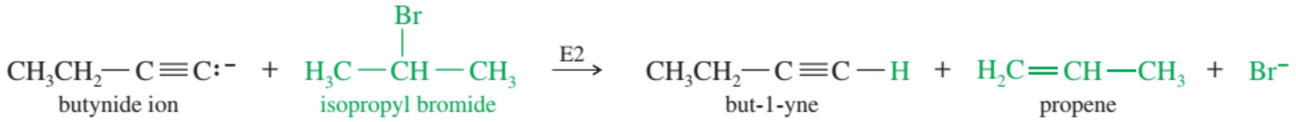
If this reaction is to produce a good yield, the alkyl halide must be an excellent substrate: It must be methyl or primary, with no bulky substituents or branches close to the reaction center. In the following examples, acetylide ions displace primary halides to form elongated alkynes.



ethynylcyclohexane (cyclohexylacetylene)

1-cyclohexylbut-1-yne (ethylcyclohexylacetylene) (70%)

If the back-side approach is hindered, the acetylide ion may abstract a proton, giving elimination by the E2 mechanism.

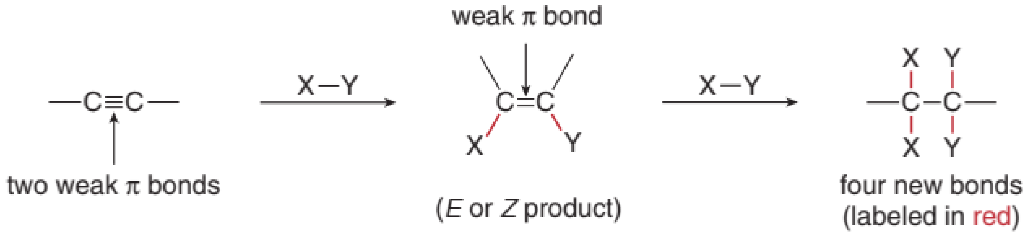


$$CH_3CH_2-C\equiv C:^- + H_3C-\overset{\displaystyle Br}{\overset{|}{C}H}-CH_3 \xrightarrow{E2} CH_3CH_2-C\equiv C-H + H_2C=CH-CH_3 + Br^-$$

butynide ion isopropyl bromide but-1-yne propene

Reaction of alkynes

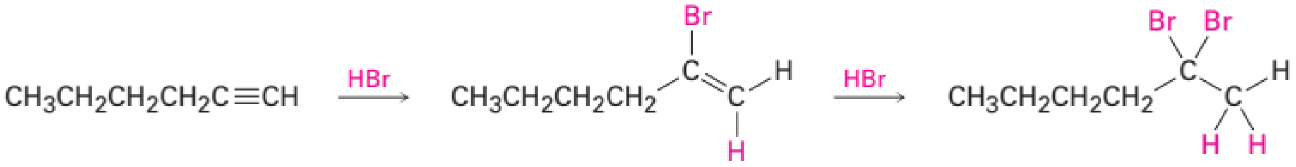
Like alkenes, alkynes undergo addition reactions because they contain weak π bonds. Two sequential reactions take place: addition of one equivalent of reagent forms an alkene, which then adds a second equivalent of reagent to yield a product having four new bonds.



Alkynes are electron rich, The two π bonds form a cylinder of electron density between the two sp hybridized carbon atoms, and this exposed electron density makes a triple bond nucleophilic. As a result, alkynes react with electrophiles.

Addition of HX

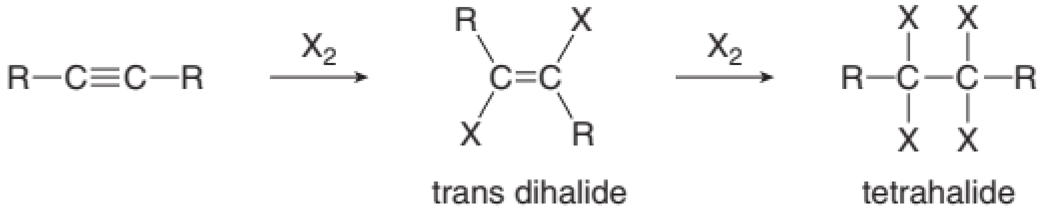
Alkynes undergo hydrohalogenation, the addition of hydrogen halides, HX (X = Cl, Br, I). Two equivalents of HX are usually used: addition of one mole forms a vinyl halide, which then reacts with a second mole of HX to form a geminal dihalide. Addition of HX to an alkyne is example of electrophilic addition, because the electrophilic (H) end of the reagent is attracted to the electron-rich triple bond. The reaction often can be stopped after addition of 1 equivalent of HX, but reaction with an excess of HX leads to a dihalide product. the regiochemistry of addition follows Markovnikov’s rule, with halogen adding to the more highly substituted side of the alkyne bond and hydrogen adding to the less highly substituted side.



1-Hexyne **2-Bromo-1-hexene** **2,2-Dibromohexane**

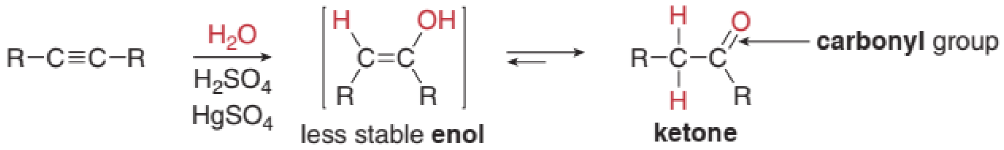
Addition of X_2

Halogens, X_2 (X = Cl or Br), add to alkynes in much the same way they add to alkenes. Addition of one mole of X_2 forms a trans dihalide, which can then react with a second mole of X_2 to yield a tetrahalide.



Addition of Water

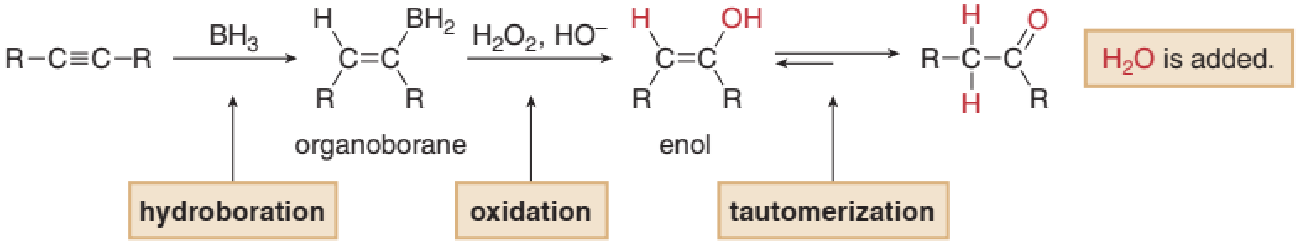
Although the addition of H_2O to an alkyne resembles the acid-catalyzed addition of H_2O to an alkene in some ways, an important difference exists. In the presence of strong acid or Hg^{2+} catalyst, the elements of H_2O add to the triple bond, but the initial addition product, an enol, is unstable and rearranges to a product containing a carbonyl group—that is, a C = O. A carbonyl compound having two alkyl groups bonded to the C = O carbon is called a ketone.



Internal alkynes undergo hydration with concentrated acid, whereas terminal alkynes require the presence of an additional Hg^{2+} catalyst usually $HgSO_4$ to yield methyl ketones by Markovnikov addition of H_2O.

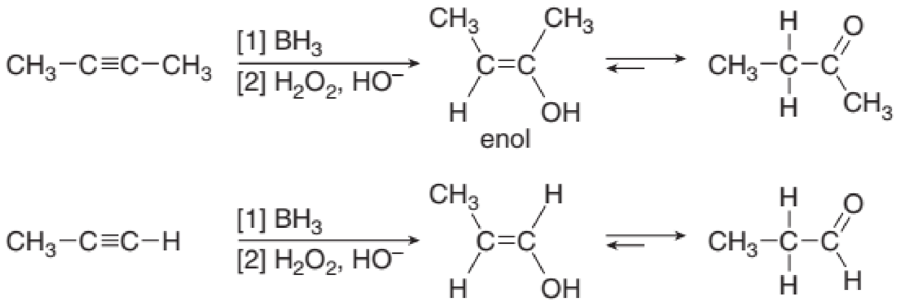
Hydroboration–Oxidation

Hydroboration–oxidation is a two-step reaction sequence that converts an alkyne to a carbonyl compound.



Addition of borane forms an organoborane. Oxidation with basic H_2O_2 forms an enol. Tautomerization of the enol forms a carbonyl compound. The overall result is addition of H_2O to a triple bond.

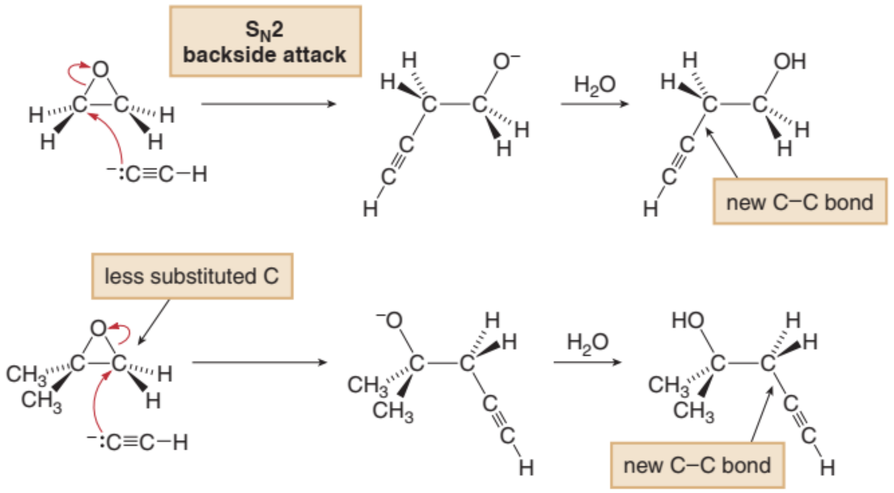
Hydroboration–oxidation of an internal alkyne forms a ketone. Hydroboration of a terminal alkyne adds BH_2 to the less substituted, terminal carbon. After oxidation to the enol, tautomerization yields an aldehyde, a carbonyl compound having a hydrogen atom bonded to the carbonyl carbon.



Addition of H_2O using H_2O, H2SO4, and $HgSO_4$ forms methyl ketones from terminal alkynes. Addition of H_2O using BH3, then H_2O_2, HO– forms aldehydes from terminal alkynes.

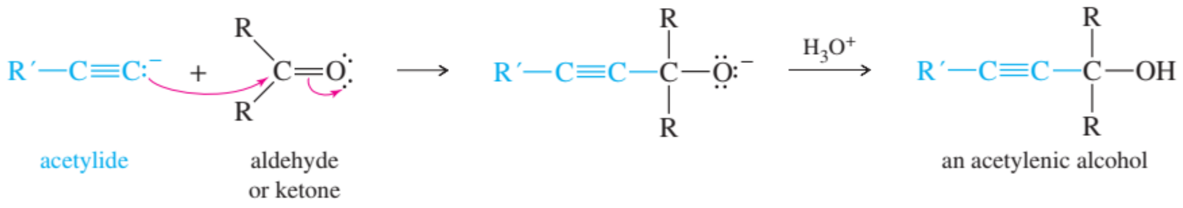
Reaction of Acetylide Anions with Epoxides

Acetylide anions are strong nucleophiles that open epoxide rings by an SN2 mechanism. This reaction also results in the formation of a new carbon–carbon bond. Backside attack occurs at the less substituted end of the epoxide.



Addition of Acetylide Ions to Carbonyl Groups

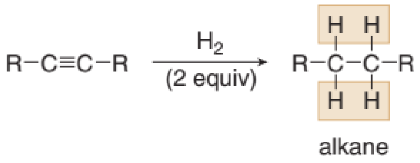
Acetylide ions are strong nucleophiles and strong bases. In addition to displacing halide ions in reactions, they can add to carbonyl groups. Because oxygen is more electronegative than carbon, the double bond is polarized. The oxygen atom has a partial negative charge balanced by an equal amount of positive charge on the carbon atom. An acetylide ion can serve as the nucleophile in this addition to a carbonyl group. The acetylide ion adds to the carbonyl group to form an alkoxide ion. Addition of dilute acid (in a separate step) protonates the alkoxide to give the alcohol.

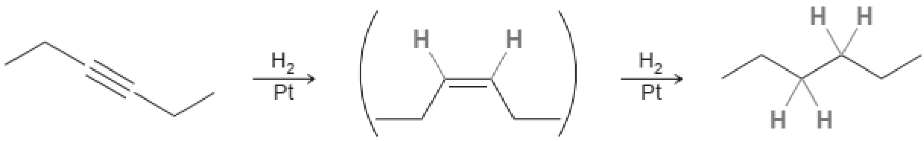


Addition to formaldehyde gives primary alcohol, addition to higher aldehyde gives secondary alcohol, addition to ketone gives secondary alcohol

Reduction of Alkynes

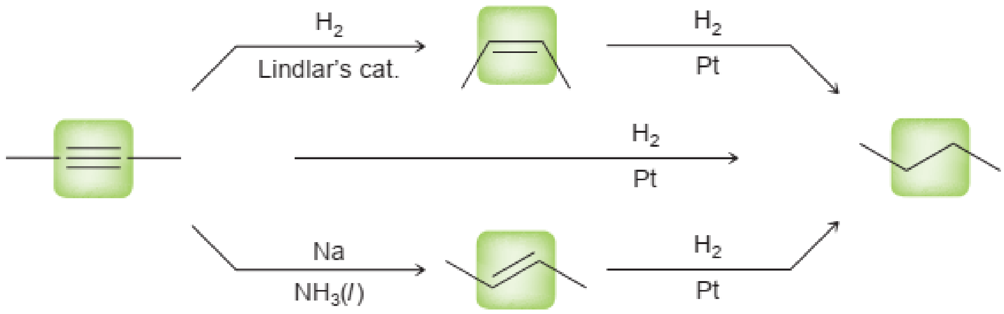
Reduction of an alkyne adds H_2 to one or both of the π bonds. There are three different ways by which the elements of H_2 can be added to a triple bond. Adding two equivalents of H_2 forms an alkane. Adding one equivalent of H_2 in an anti fashion forms a trans alkene.





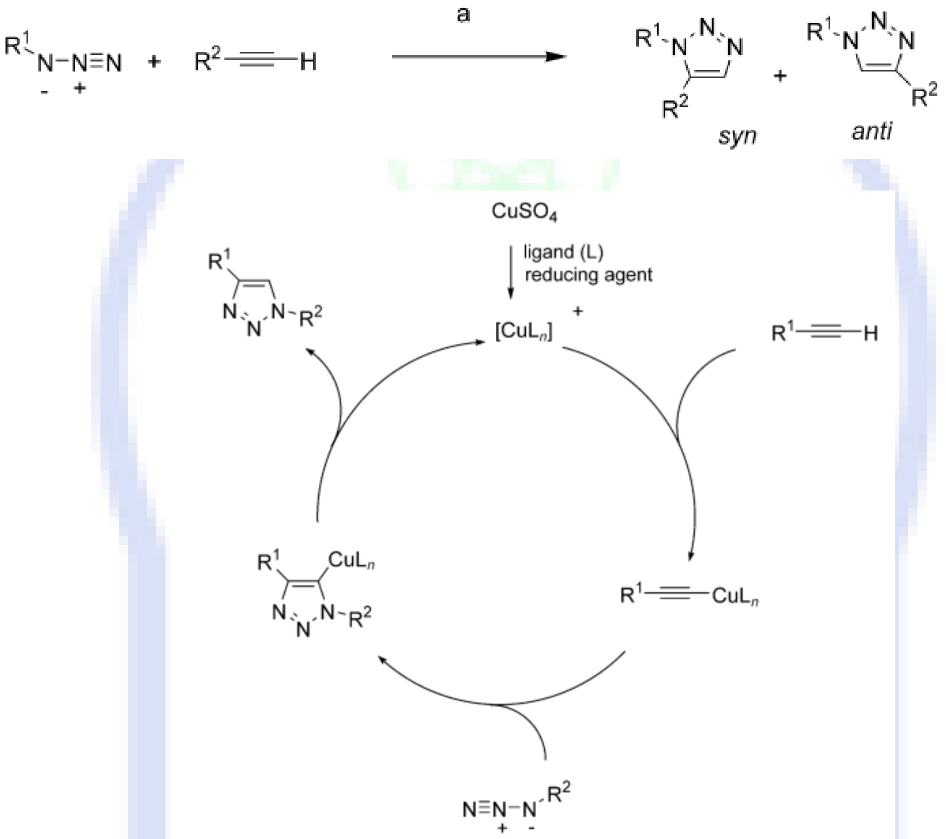
Alkynes can also be reduced to trans alkenes via an entirely different reaction called dissolving metal reduction.

To produce an alkane, an alkyne can be treated with H_2 in the presence of a metal catalyst, such as Pt, Pd, or Ni. To produce a cis alkene, an alkyne can be treated with H_2 in the presence of a poisoned catalyst, such as Lindlar's catalyst or Ni_2B. To produce a trans alkene, an alkyne can be treated with sodium in liquid ammonia



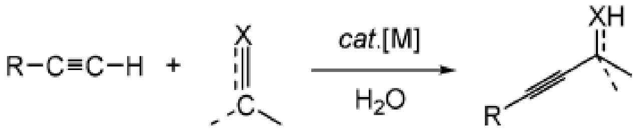
Reaction with azide compounds (azide - alkyne coupling)

Introduced that use the azide moiety as a functional group and offer two advantages: 1) the azide moiety is absent in almost all natural existing compounds and 2) despite a high intrinsic reactivity, azides allow selective ligation with a very limitedset of reaction partners. Alkene react with azide compound used metal catalyst. The catalytic amounts of Cu(I) salts not only dramatically increase the reaction rate, but also improve the regioselectivity to deliver exclusively the 1,4- disubstituted product.

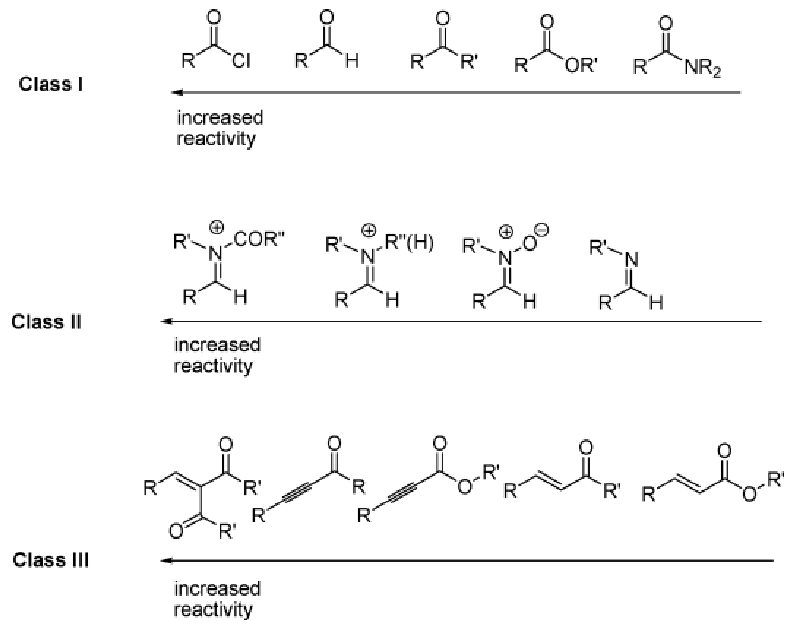


Catalytic Nucleophilic Additions of Terminal Alkynes

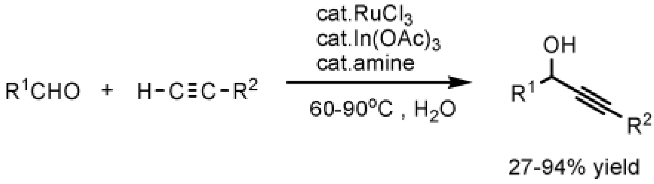
The nucleophilic addition of terminal alkynes to various unsaturated electrophiles is a classical reaction in organic chemistry, allowing the formation of a C-C bond while simultaneously introducing the alkyne functionality. Various terminal alkynes can react efficiently with a wide range of such electrophiles in water (or organic solvent) in the presence of simple and readily available catalysts, such as copper, silver, gold, iron, palladium, and others. Most importantly, these reactions can tolerate various functional groups and, in many cases, perform better in water than in organic solvents, clearly defying classical reactivities predicated on the relative acidities of water, alcohols, and terminal alkynes. The method s include the following: (i) catalytic reaction of terminal alkynes with acid chloride, (ii) catalytic addition of terminal alkynes to aldehydes and ketones, (iii) catalytic addition of alkynes to C=N bonds, and (iv) catalytic conjugate additions.

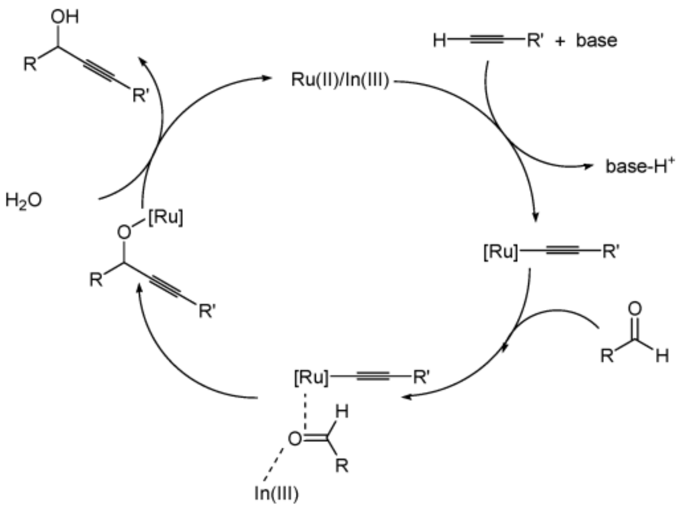


Relative Reactivity of Three Classes of Electrophiles toward Alkynes



Example





Spectroscopy Of Alkynes

IR: C-H Stretch for sp C-H usually occurs near 3300 cm^{-1}.C-C triple bond Stretch occurs near 2150 cm^{-1}; conjugation moves stretch to lower frequency. Disubstituted or symmetrically substituted triple bonds give either no absorption or weak absorption.

^{1}H-NMR: Terminal alkyne give signal in the chemical shift near to 2.5 ppm. Reaction of alkyne such as, reduction was change the chemical shift to (4.5-6.5) ppm indicate that the alkene was formed, and change the chemical shift to (0.9-1.2) ppm indicate the alkane was formed.

^{13}C-NMR: Internal carbon-carbon triple bond produce a signal at the chemical shift (75-95) ppm, while terminal alkyne produce a signal at (65-90) ppm.

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