

**Section 8--Carbocation Stability and the Occurrence  
of Molecular Rearrangements**

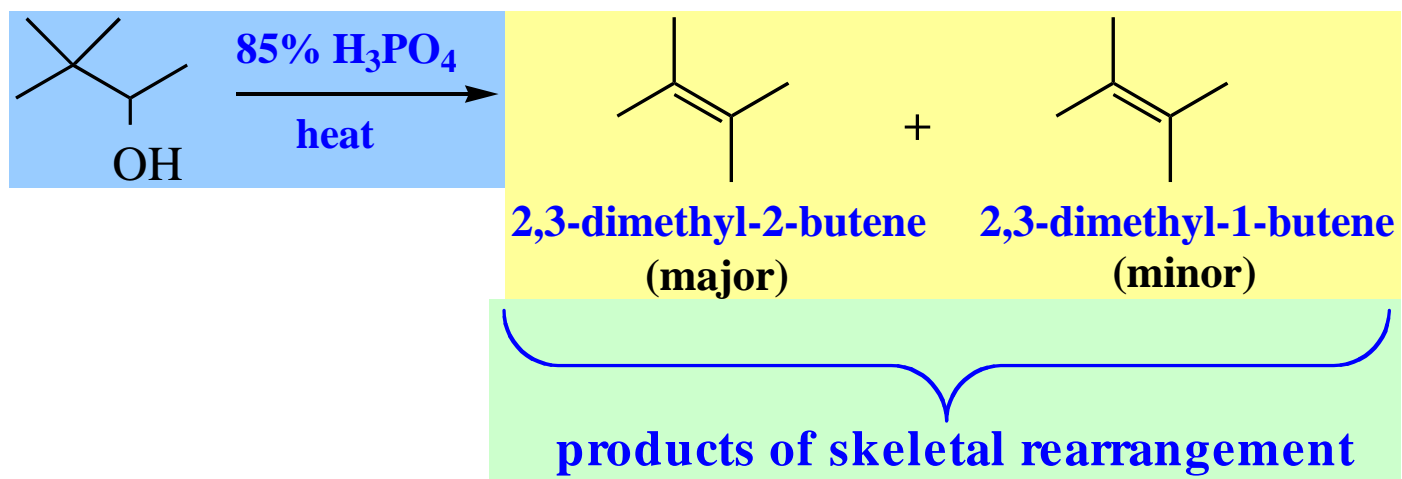
# Carbocation Stability and Molecular Rearrangements

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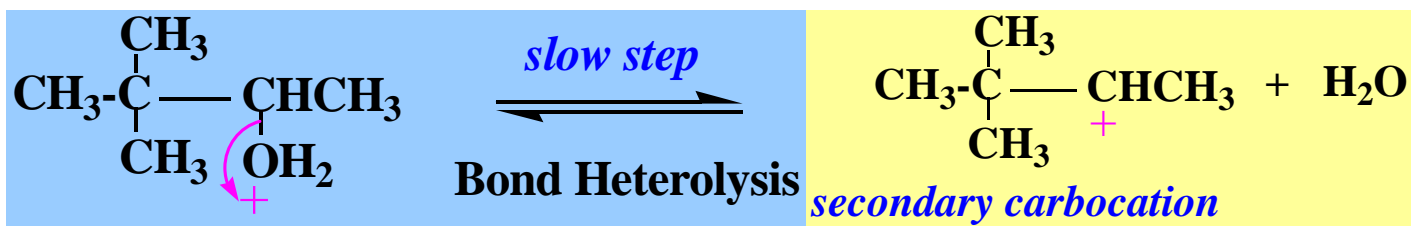
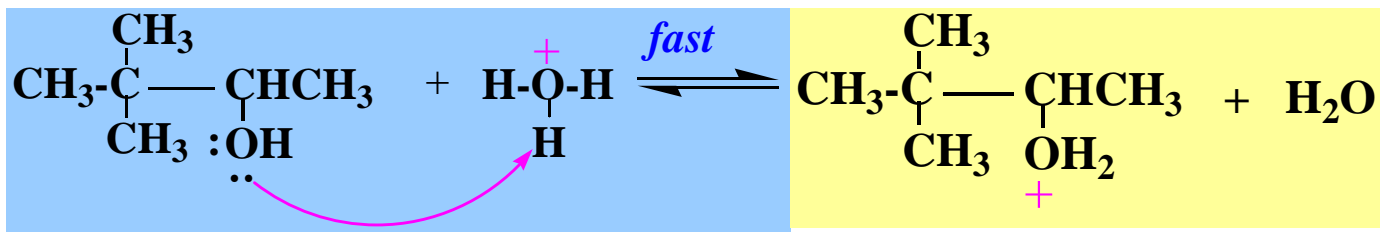
Carbon skeletal rearrangements are commonly observed with carbocation intermediates. The guiding principle is that a **less stable carbocation transforms into a more stable carbocation**.

## Example: The Dehydration of 3,3-Dimethyl-2-butanol

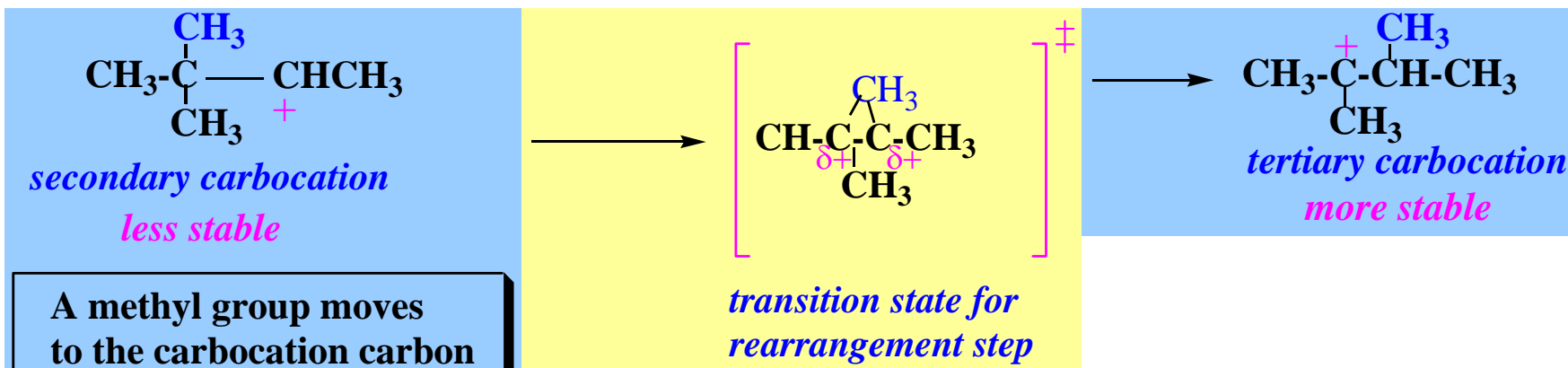
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# A Proposed Mechanism



## Rearrangement Step

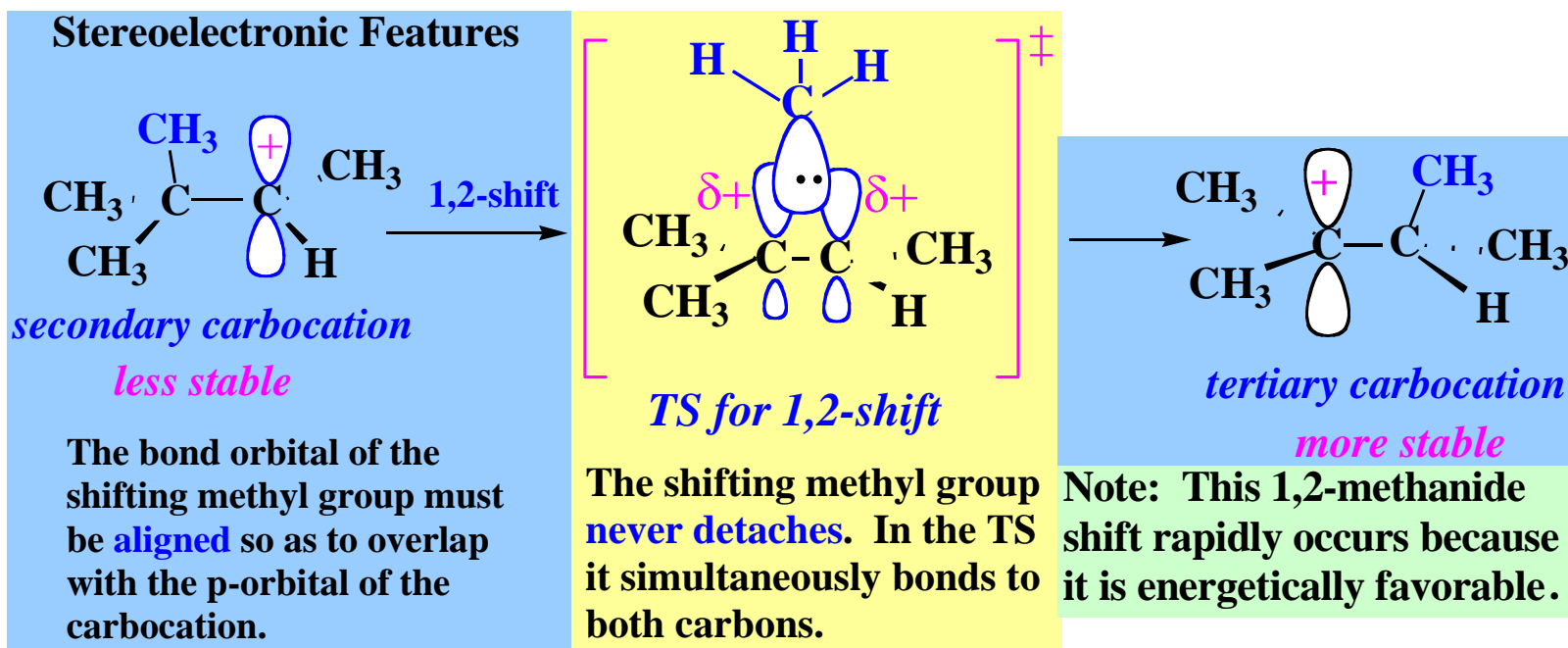


A methyl group moves to the carbocation carbon with its pair of electrons a **1,2-shift of H<sub>3</sub>C:**

The observed alkene products are produced from deprotonations of the tertiary carbocation.

# 1,2-Methanide Shifts: A Closer Look

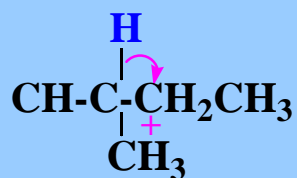
A 1,2 shift of an alkyl group with its pair of bonding electrons is called an **alkanide shift**. The 1,2 shift of a methyl group is called a **methanide shift**.



## 1,2-Hydride Shifts

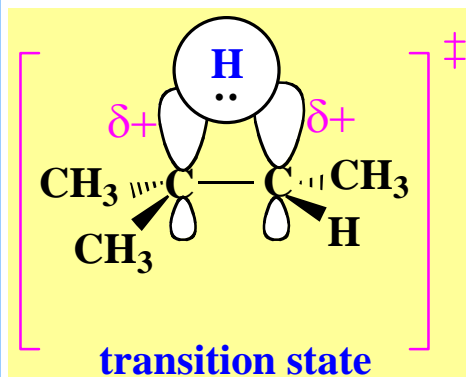
The shift of a **hydride (H<sup>-</sup>)** to an adjacent carbocation center to form a new, more stable, carbocation is common in carbocation intermediates.

### 1,2-hydride shift

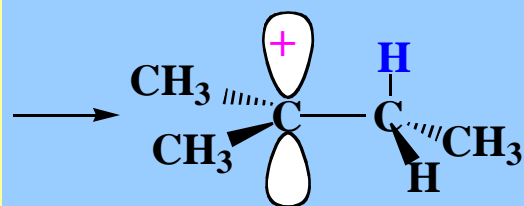


*secondary carbocation*  
*less stable*

Hydrogen shifts with its pair of bonding electrons.



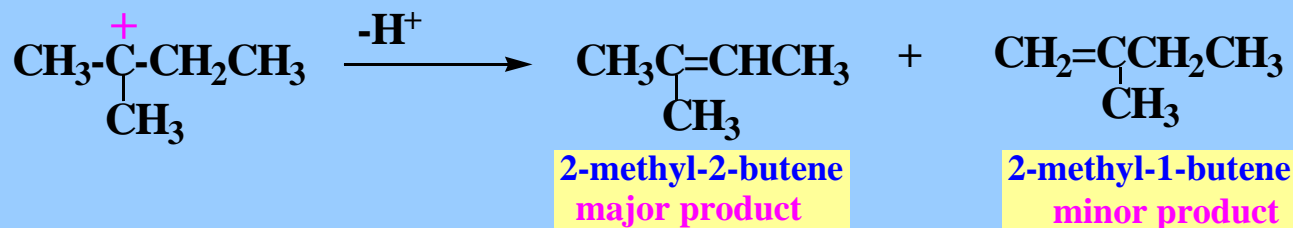
*transition state*



*tertiary carbocation*  
*more stable*

The shifting hydride never becomes detached.

The alkene products are formed by deprotonation of the 3<sup>o</sup> carbocation.

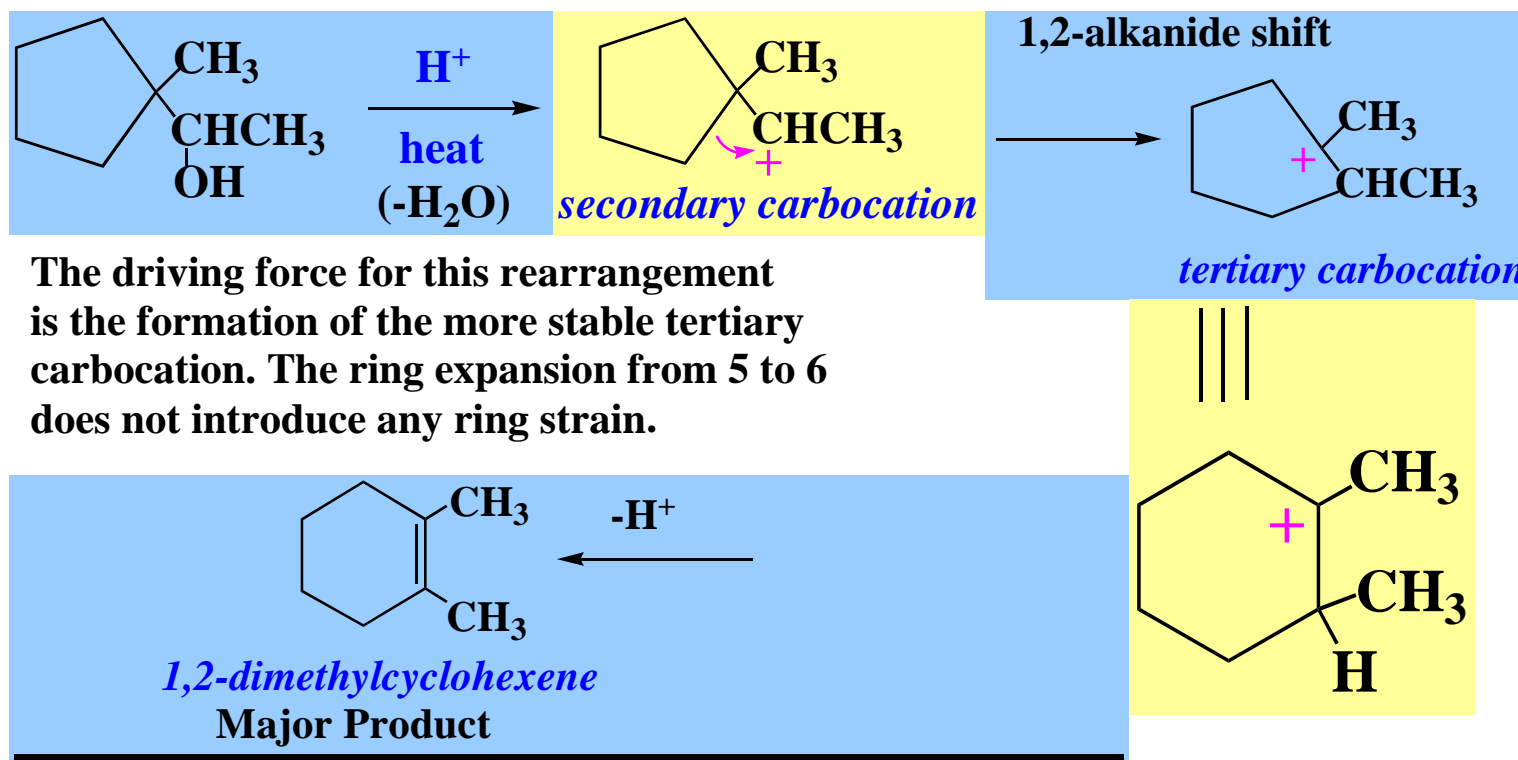


*2-methyl-2-butene*  
*major product*

*2-methyl-1-butene*  
*minor product*

## Ring Expansion by 1,2-Alkanide Shift

1,2-Alkanide shifts also occur in cyclic carbocations leading to a change in size of the ring. Such shifts take place when ring strain is not introduced.





## **Section 9--Synthesis of Alkynes by Elimination Reactions**

# Alkynes by Elimination Reactions

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Alkynes may be prepared from alkenes in a two-step synthetic sequence of bromination-debromination.

## General Scheme

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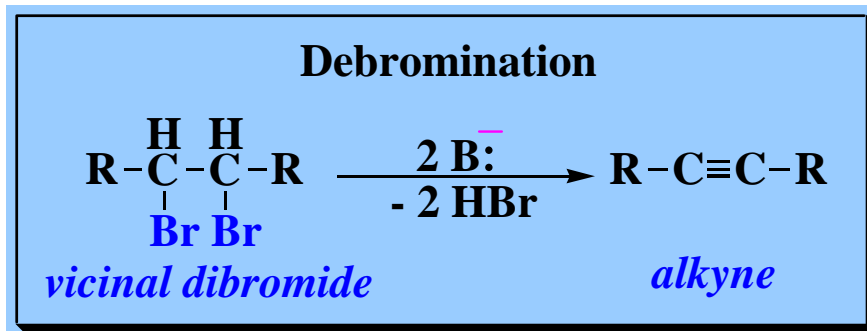


The base must be **sufficiently strong** to affect two successive dehydrobromination reactions.

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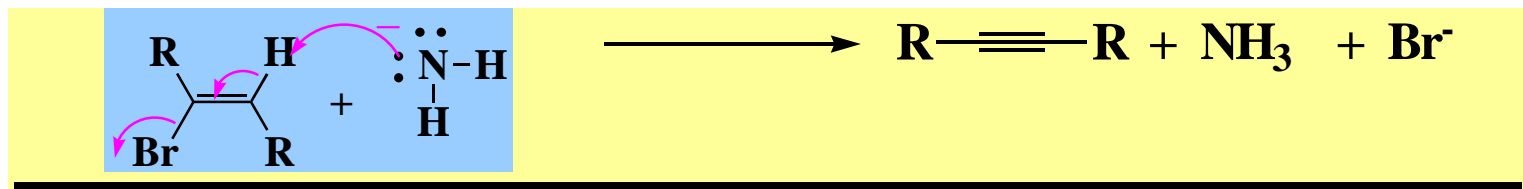
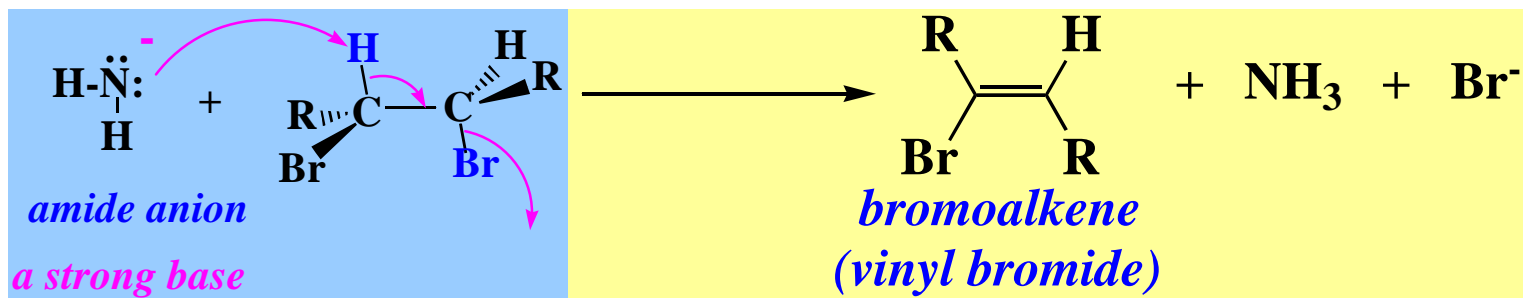
The details of the bromination reaction of alkenes will be discussed later.

# Alkynes from Vicinal Dibromides



A base sufficiently strong for the two successive dehydrobromination reactions is **sodium amide** ( $\text{Na}^+\text{NH}_2^-$ ) in liquid ammonia ( $-33^\circ \text{C}$ ) or in a hydrocarbon solvent at elevated temperature.

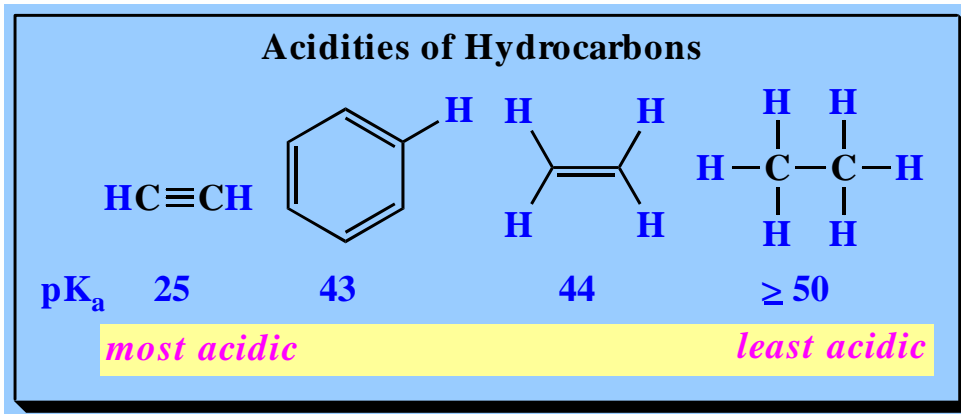
## Two Successive Dehydrobrominations



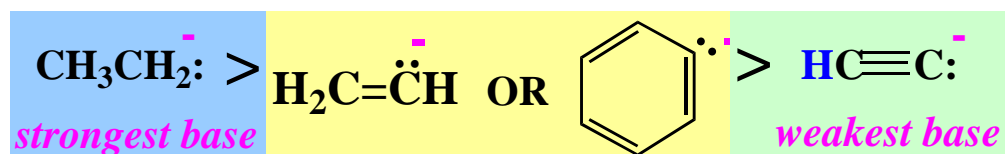
**Section 10--The Acidity of the Terminal Alkynes**

**Section 11--Replacement of the Acetylenic Hydrogen Atom  
of Terminal Alkynes**

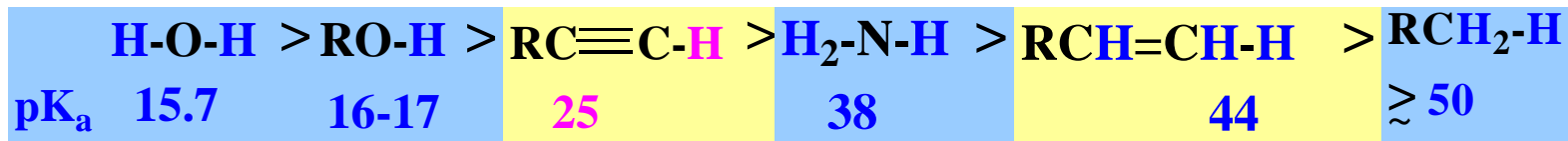
# The Acidity of Terminal Alkynes



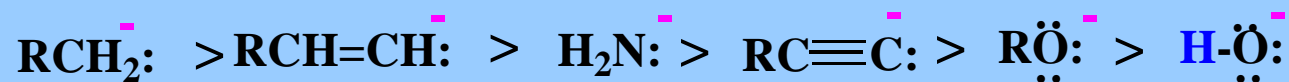
The order of base strength of the conjugate bases is:



Among a broader range of compounds, the relative acidity of terminal alkynes is:



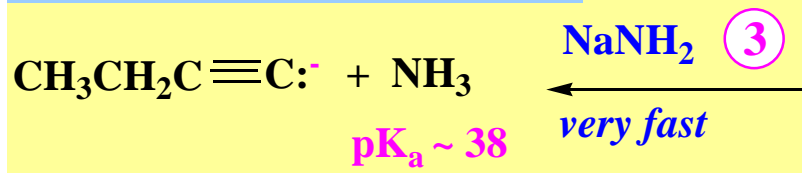
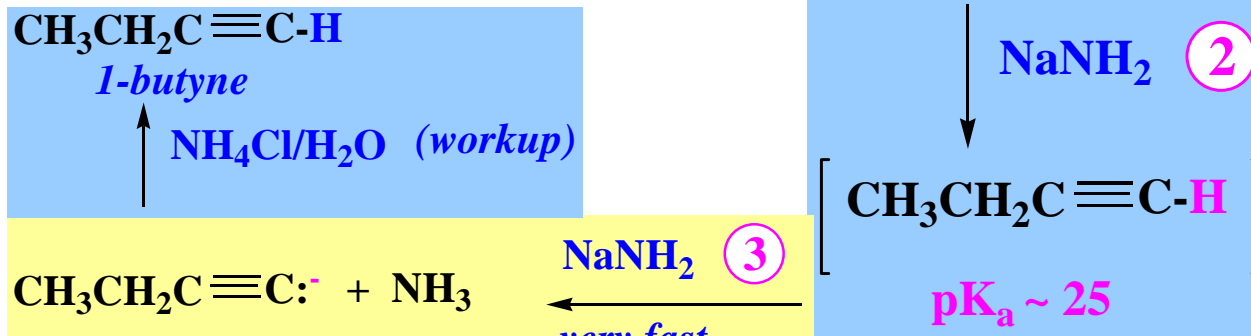
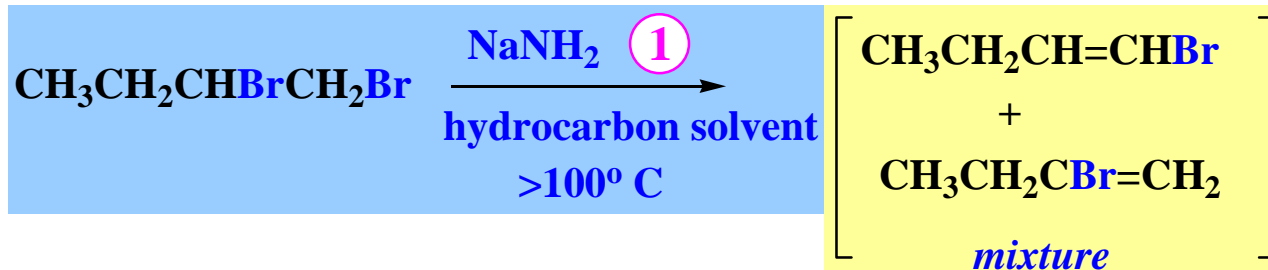
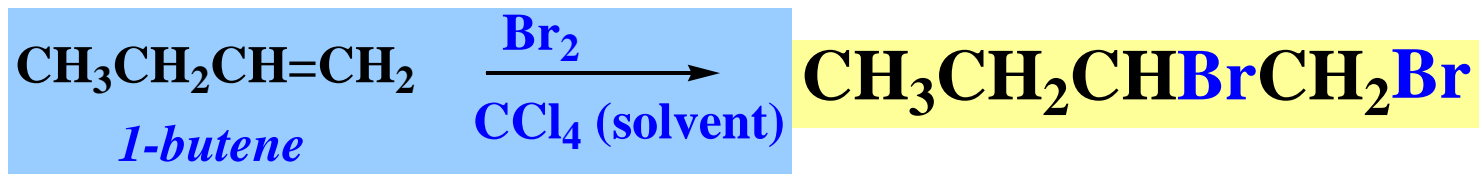
and the relative base strengths of the conjugate bases are:



# Synthesis of Terminal Alkynes

Three equivalents of base must be used in the synthesis of terminal alkynes because of the acidity of the alkynyl-H ( $pK_a \sim 25$ ).

## Example



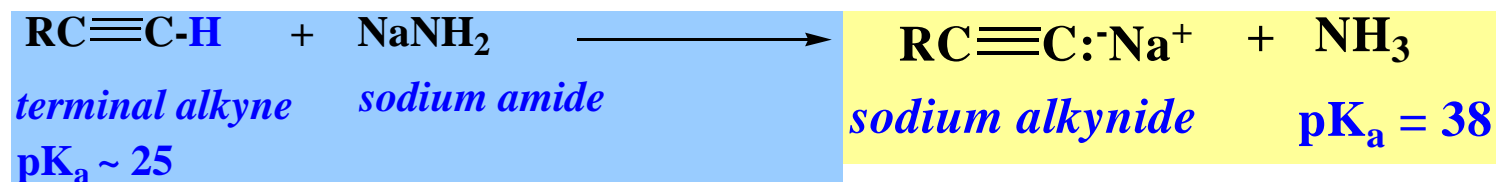
## Replacement of the Alkynyl Hydrogen: Alkylation

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The acidity of the alkynyl hydrogen is the basis of an alkylation reaction wherein an alkyl group is introduced.

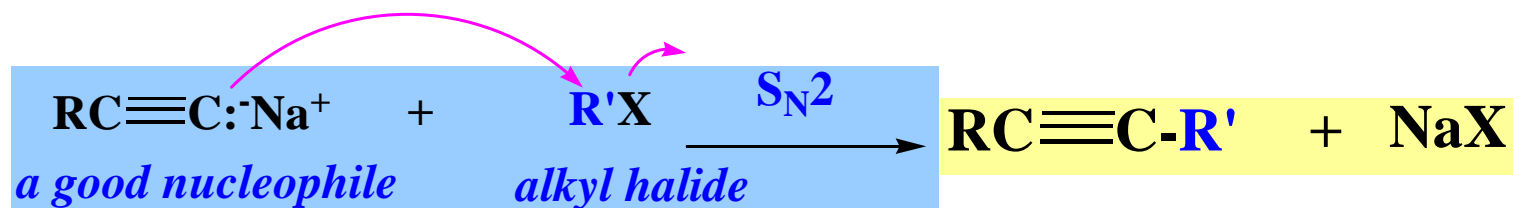
### A Two-Step Synthesis

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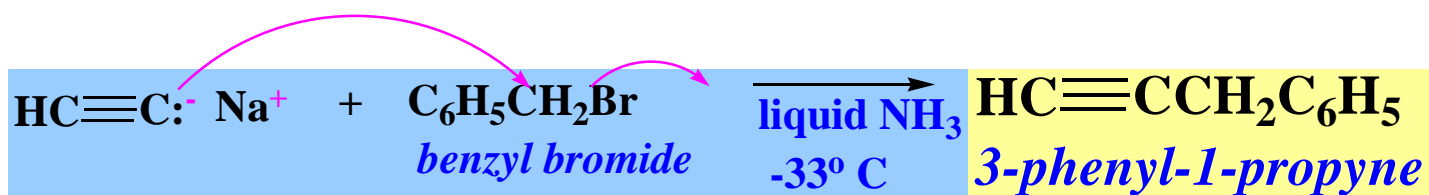
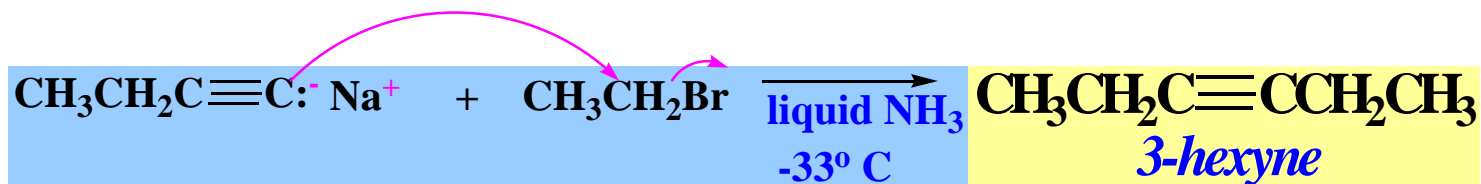
### Alkylation

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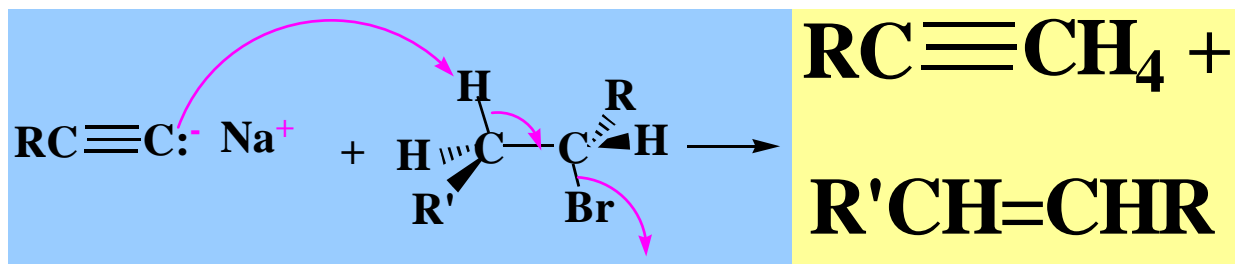
## Examples of Alkylation Reactions

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**A Limitation: With 2° and 3° alkyl halides, the E2 dominates.**



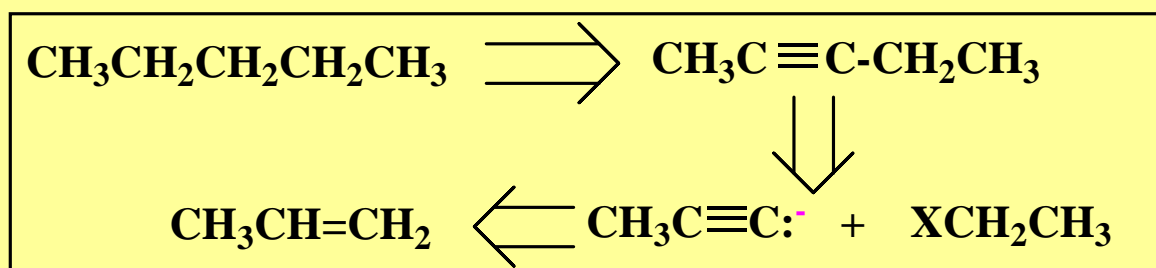
## Quiz Chapter 7 Section 11

Provide a synthesis of pentane from propene using any needed reagents and alkyl halides.

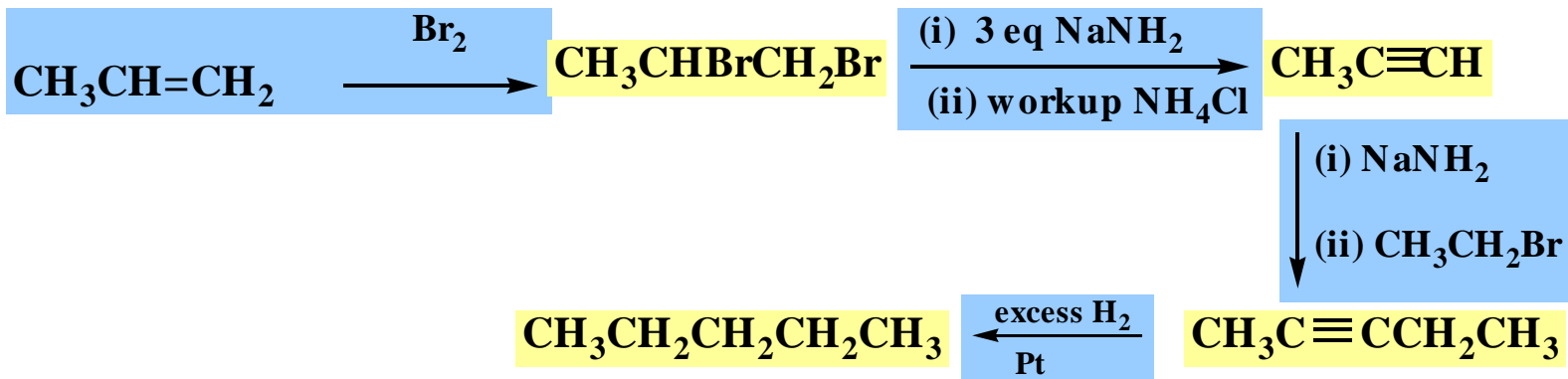
*solution*



*Retrosynthetic analysis suggests the following steps to couple the two hydrocarbon units:*



*proposed synthesis*

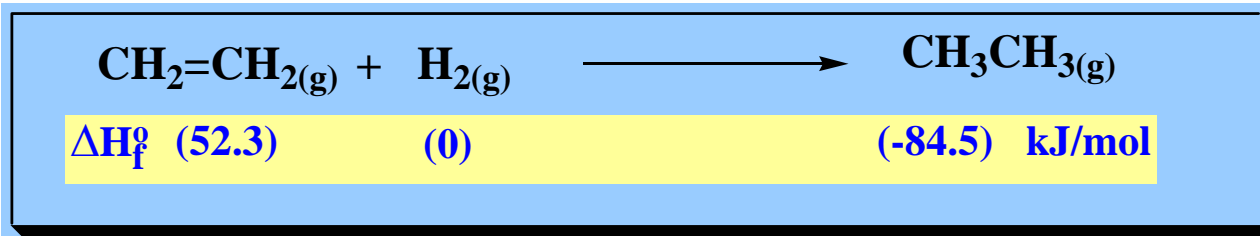


**Section 13--Hydrogenation of Alkenes**

**Section 14--Hydrogenation: The Function of the Catalyst**

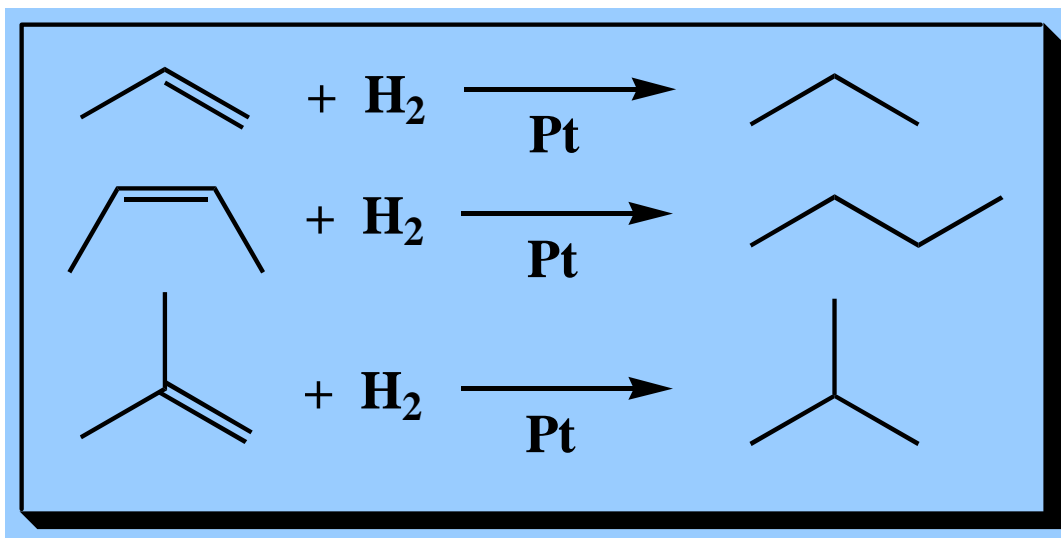
## Hydrogenation of Alkenes: An Addition Reaction

The addition of H<sub>2</sub> to an alkene to produce an alkane is **exothermic** ( $\Delta H^\circ \sim -126$  kJ/mol), but very slow in the absence of a metal catalyst (Pt, Pd, Ni).



$$\Delta H^\circ = \sum \Delta H_{\text{prod}}^\circ - \sum \Delta H_{\text{react}}^\circ = -136.8 \text{ kJ/mol}$$

In the presence of a **metal catalyst**, these hydrogenations proceed rapidly at room temperature in common solvents.

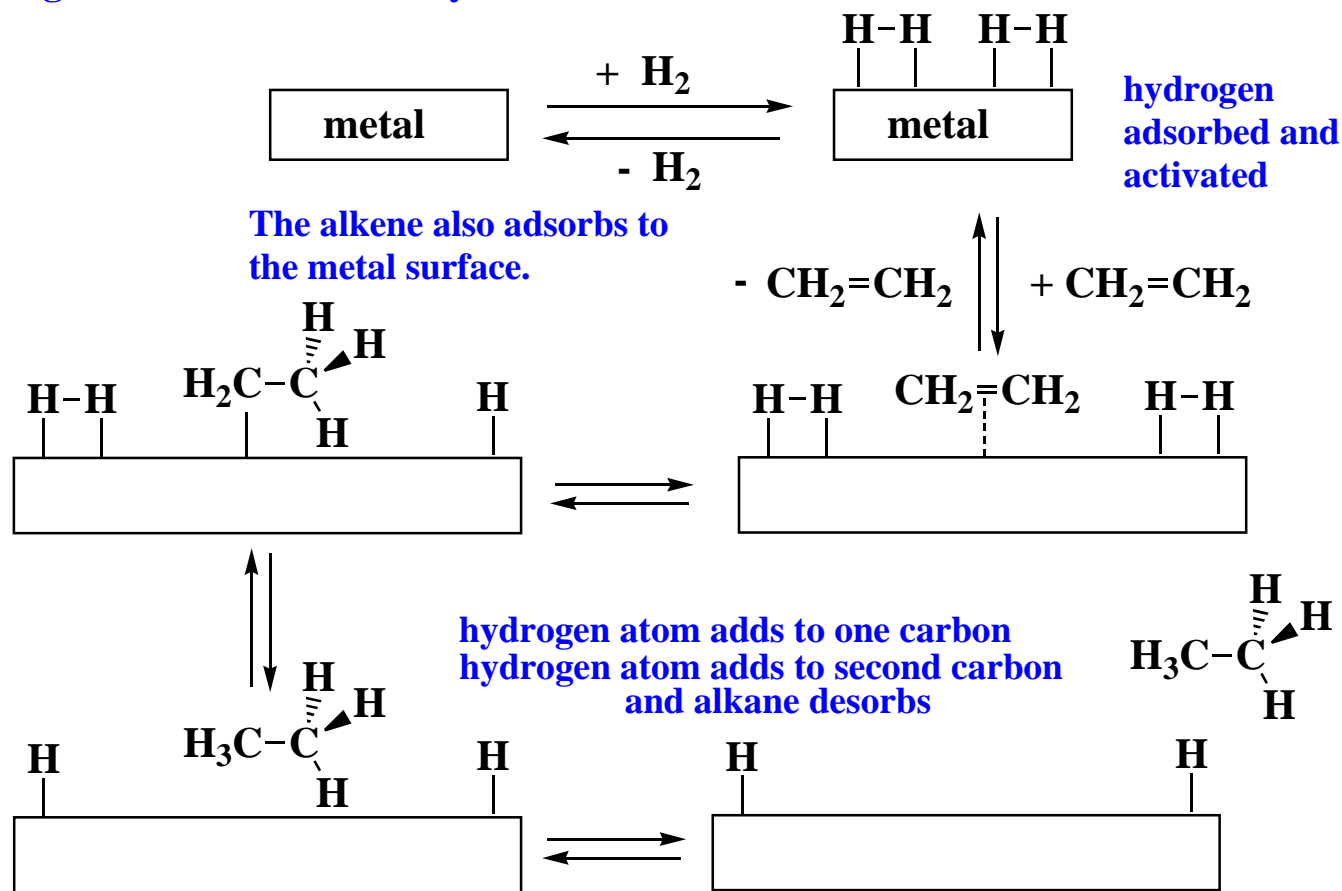


# Catalytic Hydrogenation

In the absence of a metal catalyst, hydrogenation is slow because of a **large energy of activation** (energy barrier). The metal catalyst provides a low energy reaction pathway between the reactant and product states.

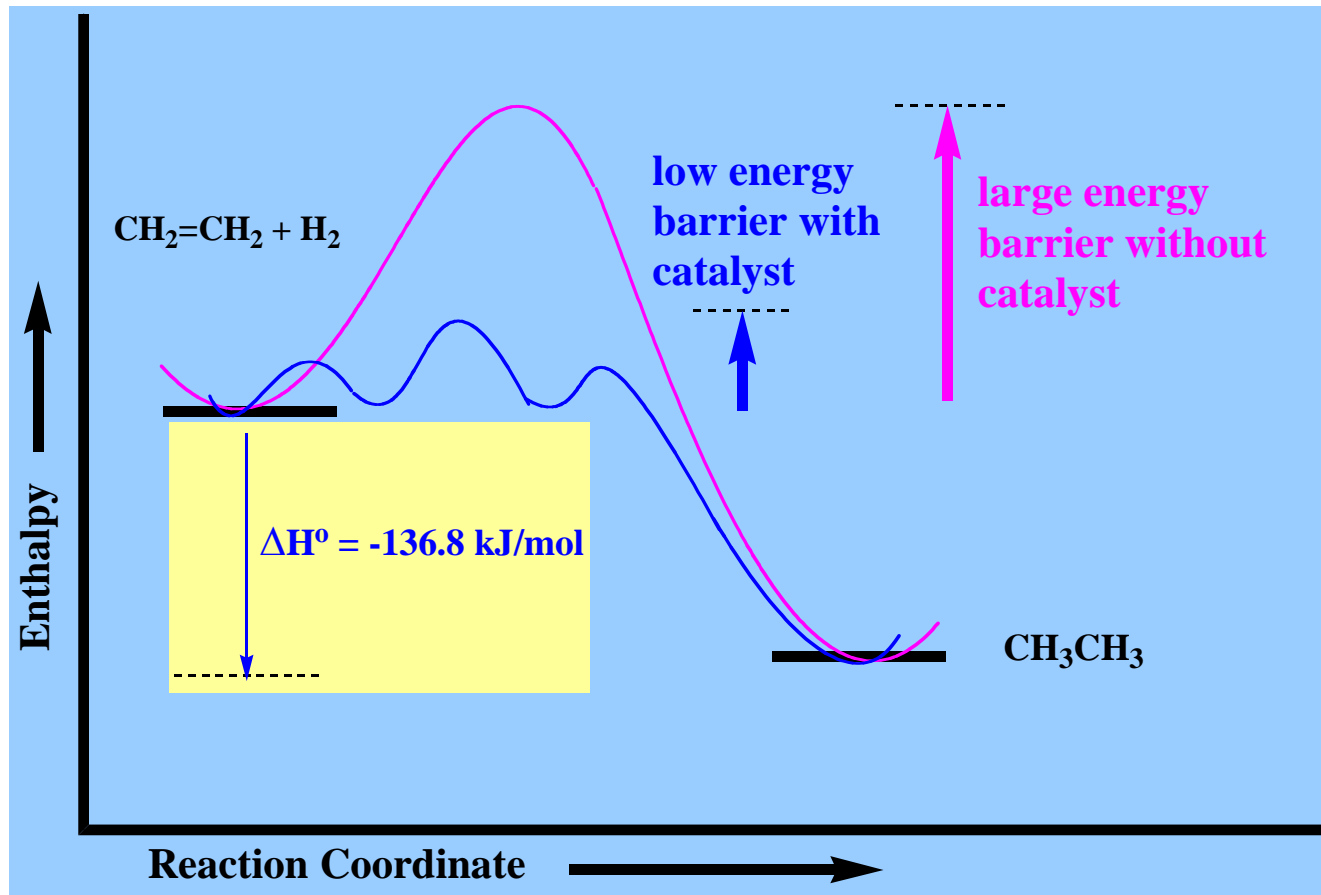
## Proposed Mechanism for Catalytic Hydrogenation

Hydrogen molecules reversibly adsorb on the surface of the metal.



# Energetics of Catalytic Hydrogenation

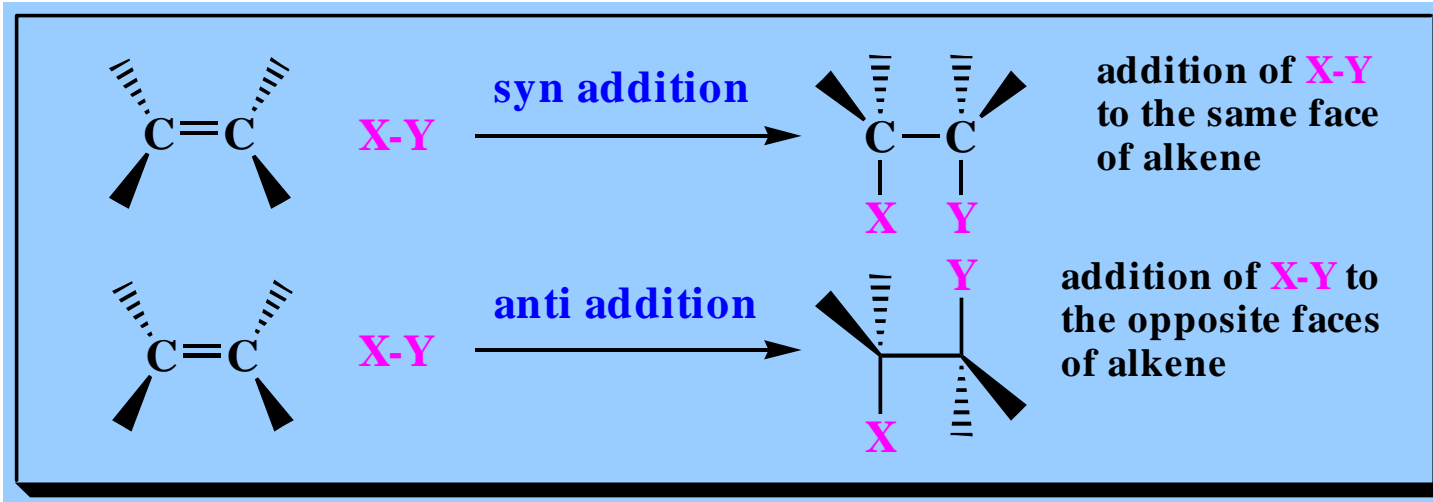
Catalysts change the rates of chemical reactions but do not change the overall thermodynamics.



# Stereochemistry of Additions to Alkenes

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There are two modes of addition to an alkene:



Catalytic hydrogenation is a **syn** addition.

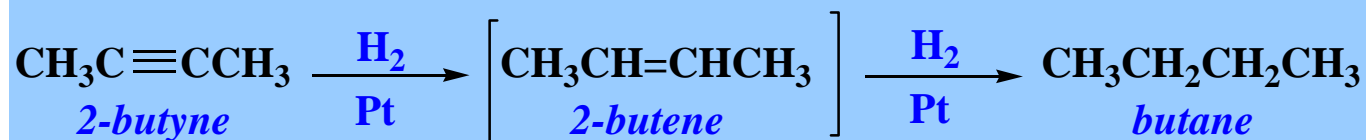
However, this outcome is only noticed in hydrogenation reactions that yield two stereocenters.

## **Section 15--Hydrogenation of Alkynes**

## Hydrogenation of Alkynes

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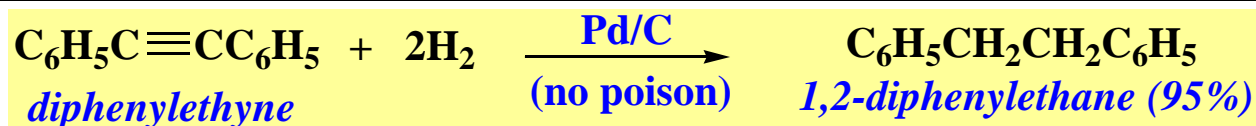
Catalytic hydrogenation of the triple bond occurs stepwise and may be controlled to yield alkenes:



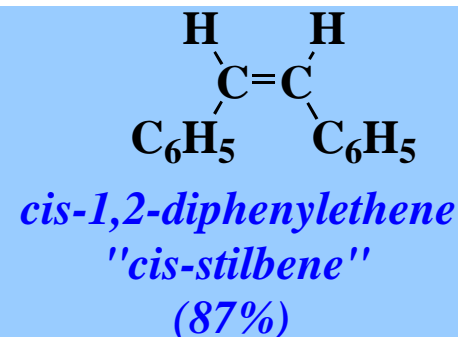
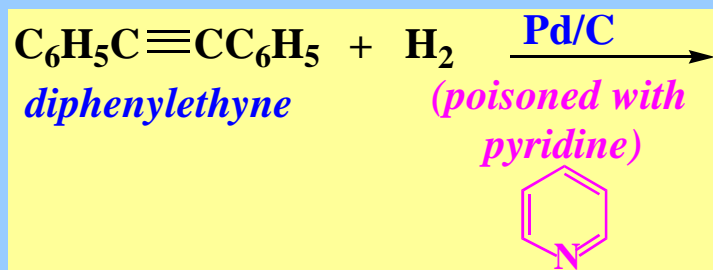
If the catalyst is "**poisoned**" with a compound that selectively interferes with the hydrogenation of the alkene, the alkene product may be isolated. "Catalyst poisons" are salts of  $\text{Pb}^{2+}$  and some nitrogen compounds such as pyridine and other amines.

### Example: Hydrogenation of Diphenylethyne

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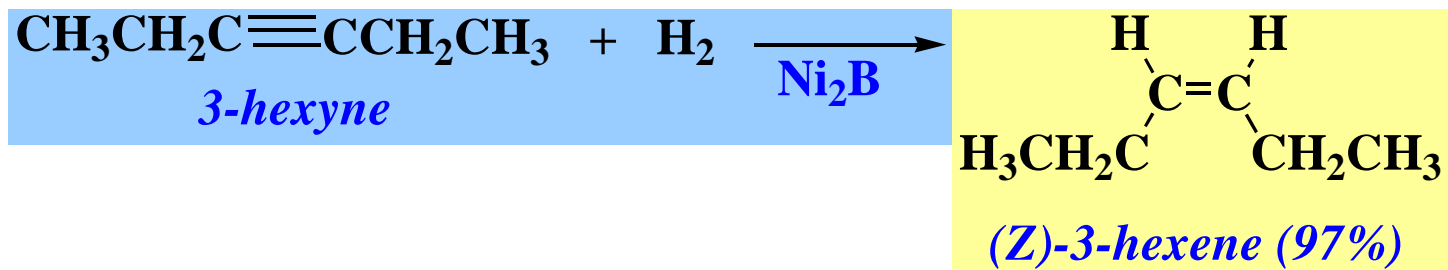
Pd/C is palladium metal finely dispersed on powdered charcoal.



## Syn-Hydrogenation of Alkynes: *cis*-Alkenes

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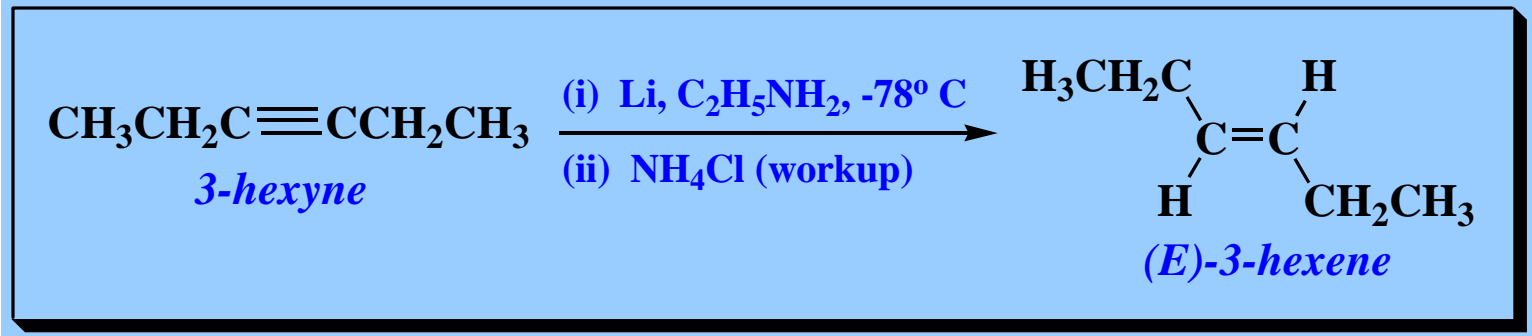
The selective catalytic hydrogenation of alkynes with a "poisoned" catalyst is a **syn-addition** that yields **cis-alkenes**. A second way to carry out this transformation is with a **nickel boride catalyst** ( $\text{Ni}_2\text{B}$ ) sold commercially as P-2.



## Anti-Hydrogenation of Alkynes: *trans*-Alkenes

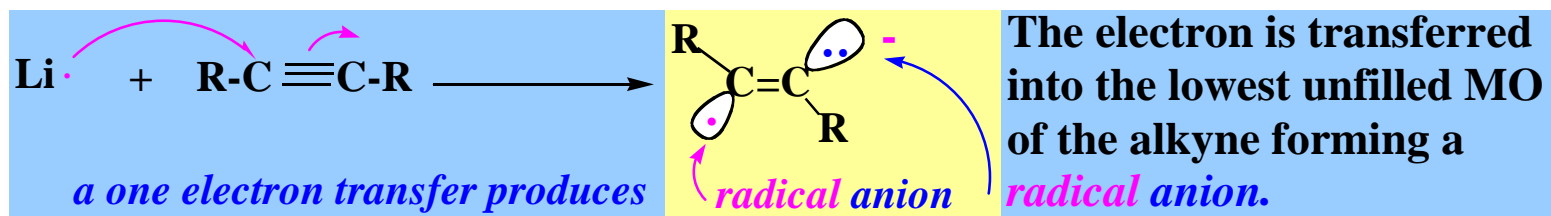
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Alkynes are reduced to *trans*-alkenes by **alkali metals** (Li or Na) in liquid ammonia (-33° C) or ethylamine (BP 16.6° C) at low temperatures. Because these metals dissolve as they react, these and other similar reductions are called **dissolving metal reductions**.

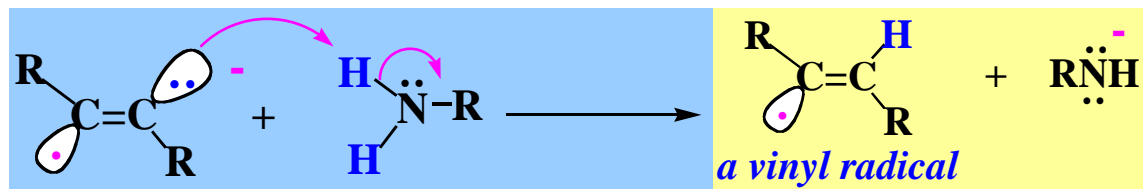


# A Mechanism for the Dissolving Metal Reduction of Alkynes

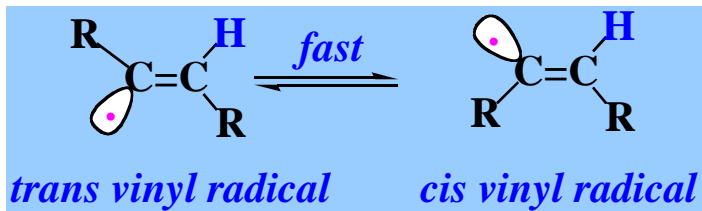
The reduction of an alkyne by an alkali metal in liquid ammonia or an amine solvent begins with an electron transfer (redox step):



The radical anion is a strong base and is protonated by the solvent:



The vinyl radical can exist in two stereoisomeric forms that rapidly interchange:



The *trans*-radical dominates in the equilibrium. Electron transfer produces a vinyl carbanion (a strong base) that is protonated to give the alkene:

