INTERNATIONAL COLLEGE OF PHARMACEUTICAL INNOVATION
国际创新药学院

Fundamentals of Medicinal and Pharmaceutical Chemistry

FUNCHEM.17 Alkenes: Structures, properties and geometric structural isomers

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Learning outcomes

At the end of this lecture, the learner will be able to

- Interpret and apply the correct use of curved arrows in representing electron movement in reaction mechanisms.
- Recall and explain the reaction profile, products, and mechanism of reactions of symmetrical and unsymmetrical alkenes with acids.
- Identify and explain geometric isomerism in alkenes.
- Describe examples of alkene geometric isomerism in biological systems.
- Recall the synthesis of alkenes from halides and from alcohols.

Recommended reading

- Organic chemistry with biological application (John McMurry)
- Chapter 7

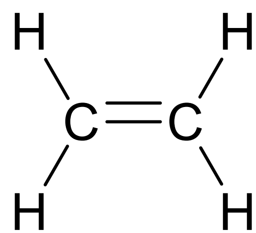
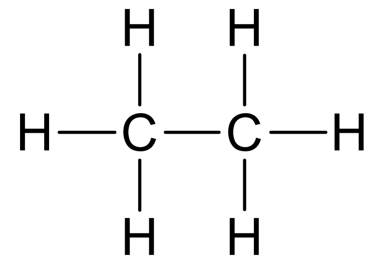
7.4 Alkene Stereochemistry and the E,Z Designation

7.5 Stability of Alkenes

7.6 Electrophilic Addition Reactions of Alkenes

7.7 Orientation of Electrophilic Addition

Ethene and Ethane - Comparison

		
C to C bond energy	724 kJ/mol 452(σ bond) + 272 (π bond)	377 kJ/mol
C to C bond length	1.33 Å	1.54 Å
Reactions	Adds Br_2 fast in dark at room temperature.	Do <u>not</u> react with Br_2 *in dark* at room temperature.

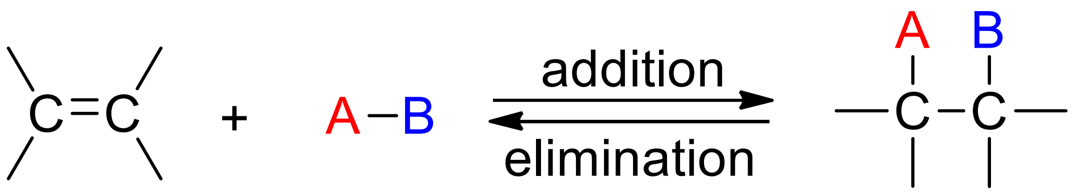
Note: 1 Å = 10^{-10} m

Addition Reactions of Alkenes

Alkenes undergo addition reactions with a variety of reagents of the general type A-B.

This reaction can often be reversed in what is called an elimination reaction

to produce an alkene (we will see this at the end of the next lecture).



In general chemical reactions are discussed in terms or breaking and making bonds.

In this addition reaction

the carbon to carbon π bond and the A–B σ bond have been broken

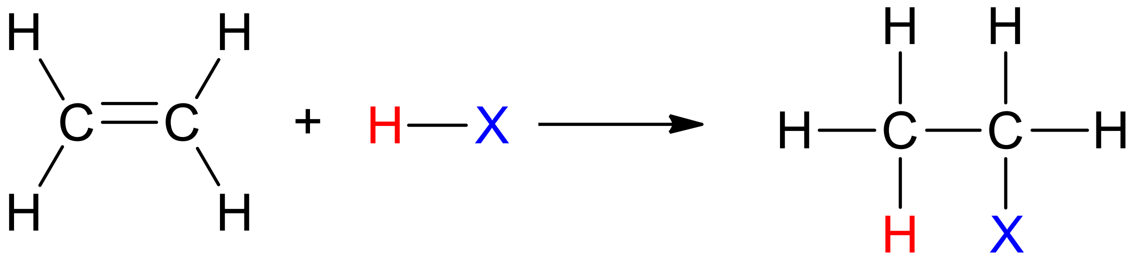
and

two new σ bonds C–A and C–B have been formed.

Addition Reactions of Alkenes

Addition of acids, HX

These reactions are fast at 25 ℃.



$$H{-}X \;=\; H{-}F,\; H{-}Cl,\; H{-}Br,\; H{-}I$$

$$H{-}OSO_3H,\; H{-}O{-}\underset{\overset{\|}{O}}{C}{-}R$$

These are examples of electrophilic addition reactions since the rate determining step (the slowest step of a reaction, *i.e.* the one that determines the rate) involves addition of an electrophile.

Electrophiles are electron seeking species *e.g.* $H^{\oplus}$, $Br^{\oplus}$, $Cl^{\oplus}$.

Lewis Acids (electron pair acceptors) may be regarded as electrophiles *e.g.* BF_3.

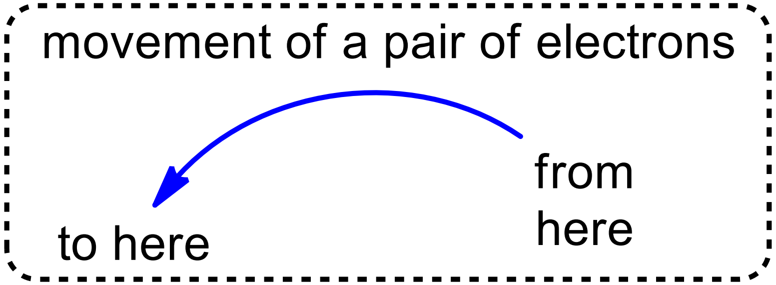
Electrophilic Addition Reaction Mechanisms

A mechanism is a step-by-step account of what happens during a reaction.

It shows all of the chemical species that are formed during the course of the reaction (reagents, intermediates, products).

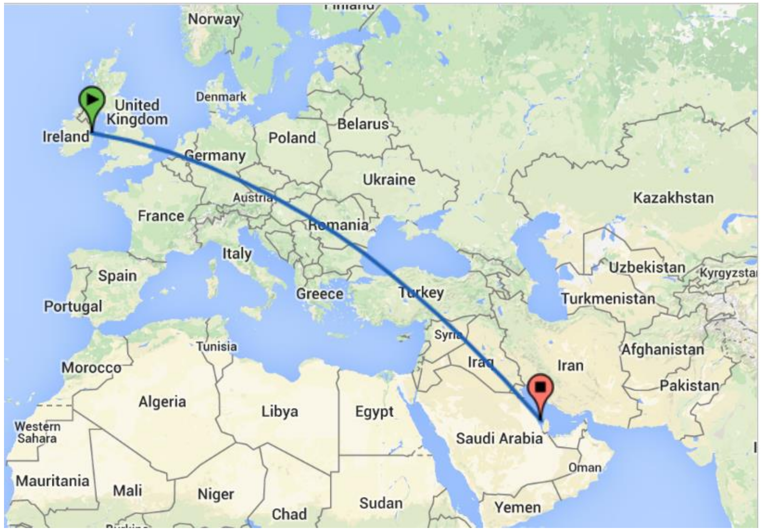
It also shows which bonds are broken and which are formed, usually by using curved (curly) arrows which show where electrons move to.

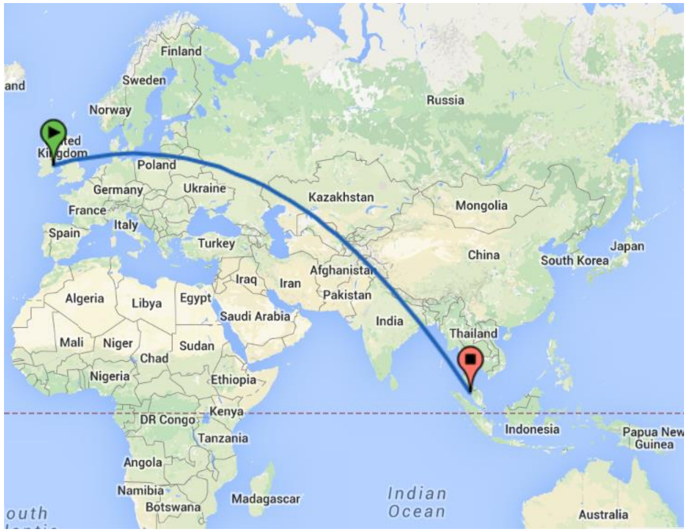
How to describe making and breaking of covalent bonds?



Writing a Reaction Mechanism… is Like Planning a Trip

You need to know:





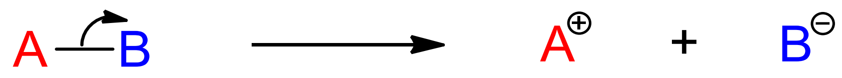
1 - Where you leave from (reagents) and where you arrive (products)

2 - Where you will stop on the way (intermediates)

3 - Which route you will use (movement of electrons)

Curly Arrows

Bond breaking



The arrow indicates that the pair of electrons that form the A-B bond are leaving A and becoming the exclusive property of B.

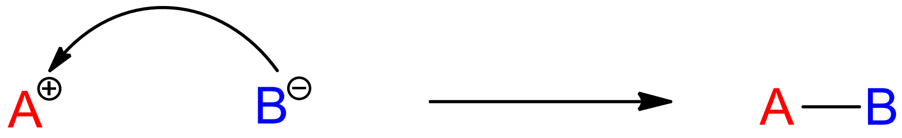
A becomes positively charged because it is losing an electron.

B becomes negatively charged because it gains an electron.

The curly arrow starts in the center of the bond and the head should lie on the B atom, because both the electrons will end up in an orbital on the $B^{\ominus}$ ion.

Curly Arrows

Bond Forming



The arrow indicates that an electron pair that was the exclusive property of B is now shared in the bond formed between A and B.

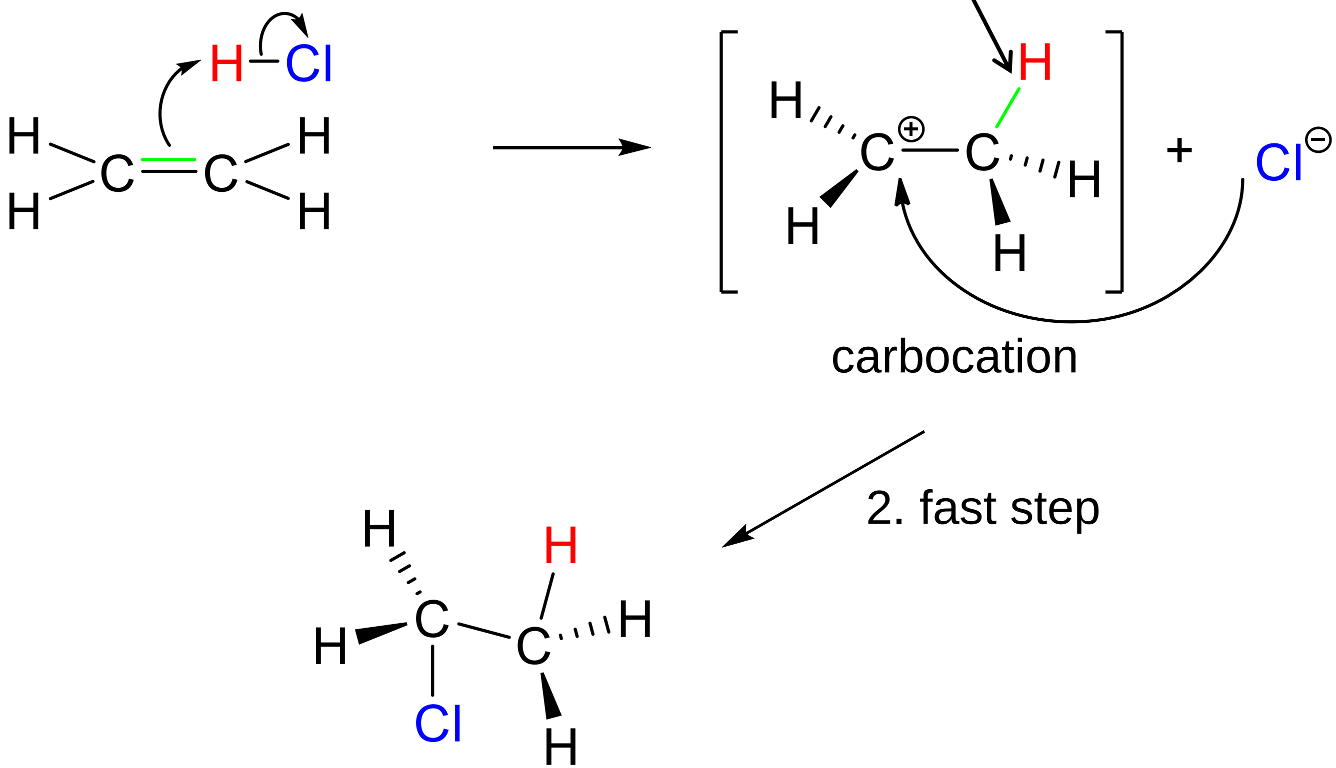
The arrows starts at the source of the moving electrons and the head is drawn in the place where the new bond will be formed.

Mechanism for Addition of HCl to Ethene

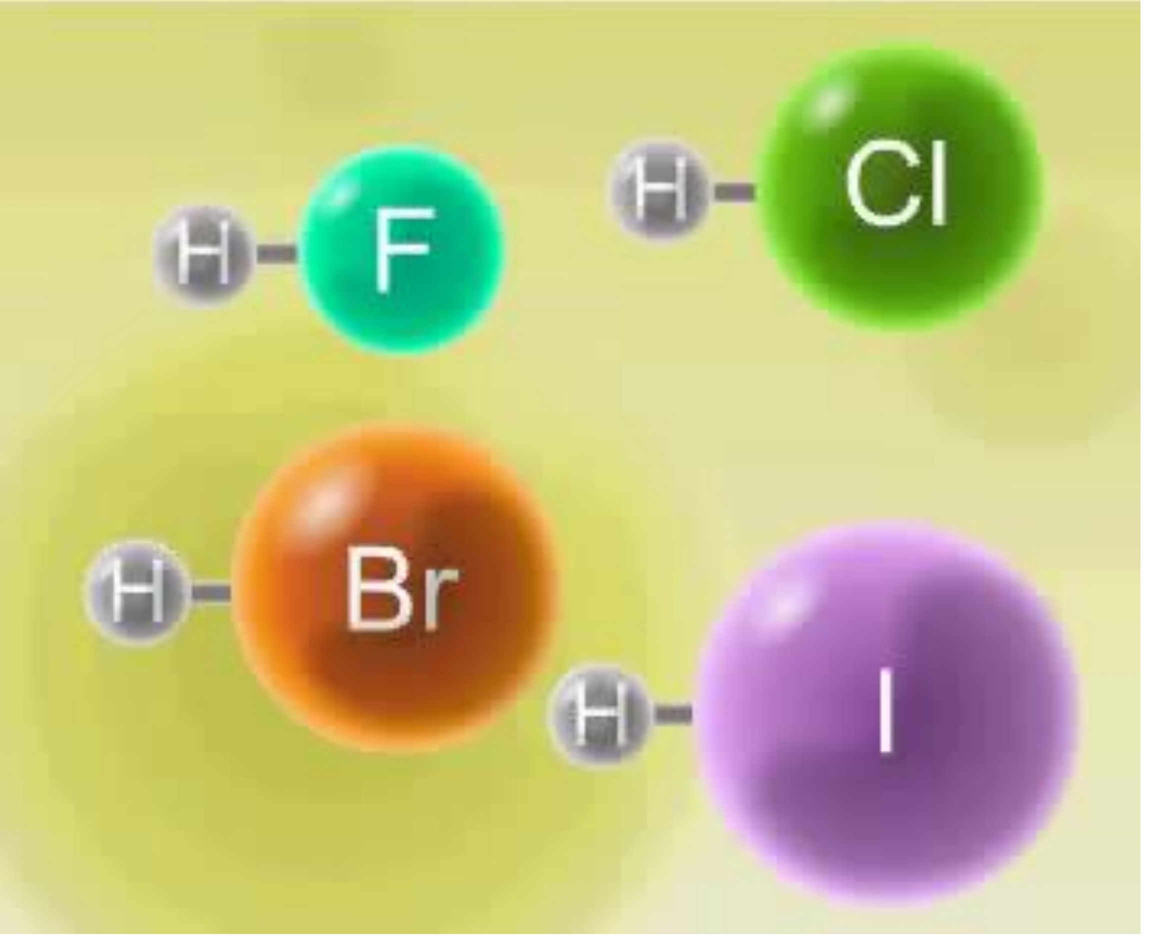
The reaction involves 2 steps:

1. The rate determining (slowest) step

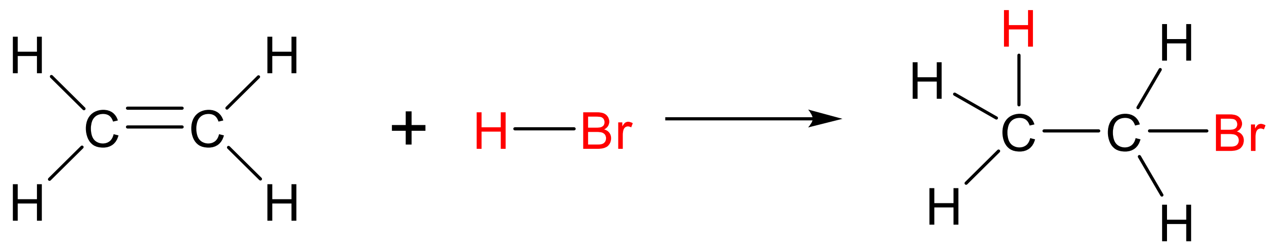
$H^{\oplus}$ (the electrophile) forms a σ bond with one of the carbons using (what were) the 2π electrons.

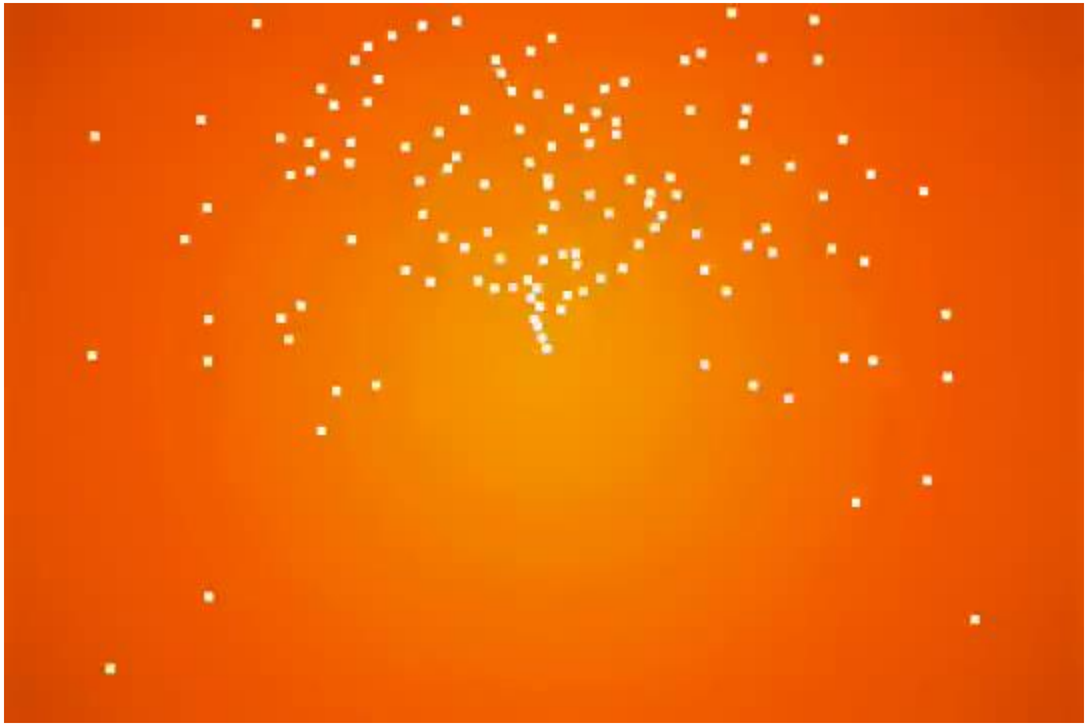


Addition of HCl to Ethene



Mechanism is the Same for Addition of HBr to Ethene





Note: Practice writing this mechanism out yourself on paper

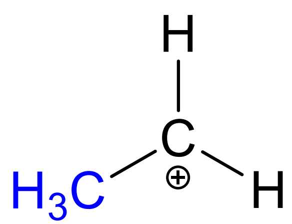
Carbocations

A carbocation contains a positively charged carbon atom.

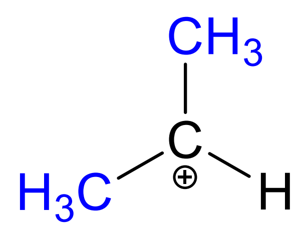
Carbocations are highly reactive.

The geometry around the $C^{\oplus}$ is trigonal planar.

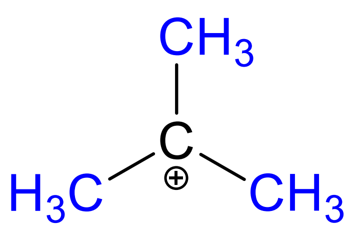
Primary, Secondary and Tertiary Carbocations



Primary carbocation
$C^{\oplus}$ attached to one other carbon.



Secondary carbocation
$C^{\oplus}$ attached to two other carbons.

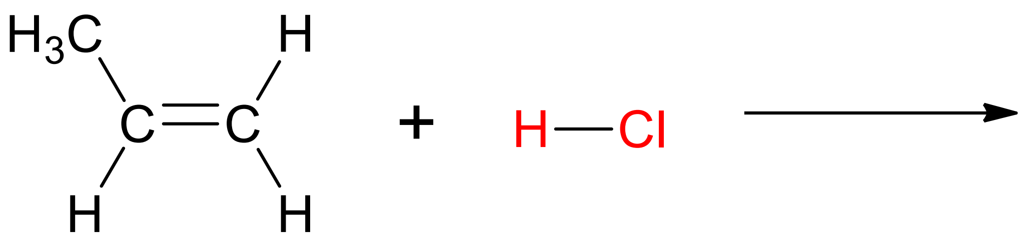


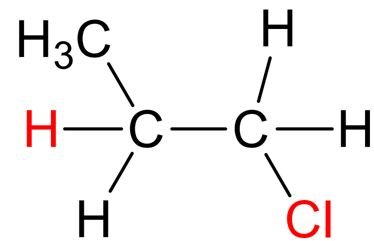
Tertiary carbocation
$C^{\oplus}$ attached to three other carbons.

Order of carbocation stability:

tertiary > secondary > primary

Addition of HX to <u>Unsymmetrical</u> Alkenes
(works for X = Cl, Br, I)

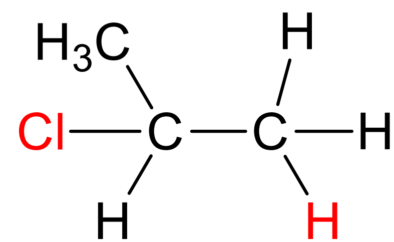




1-chloropropane

0%

or / and



2-chloropropane

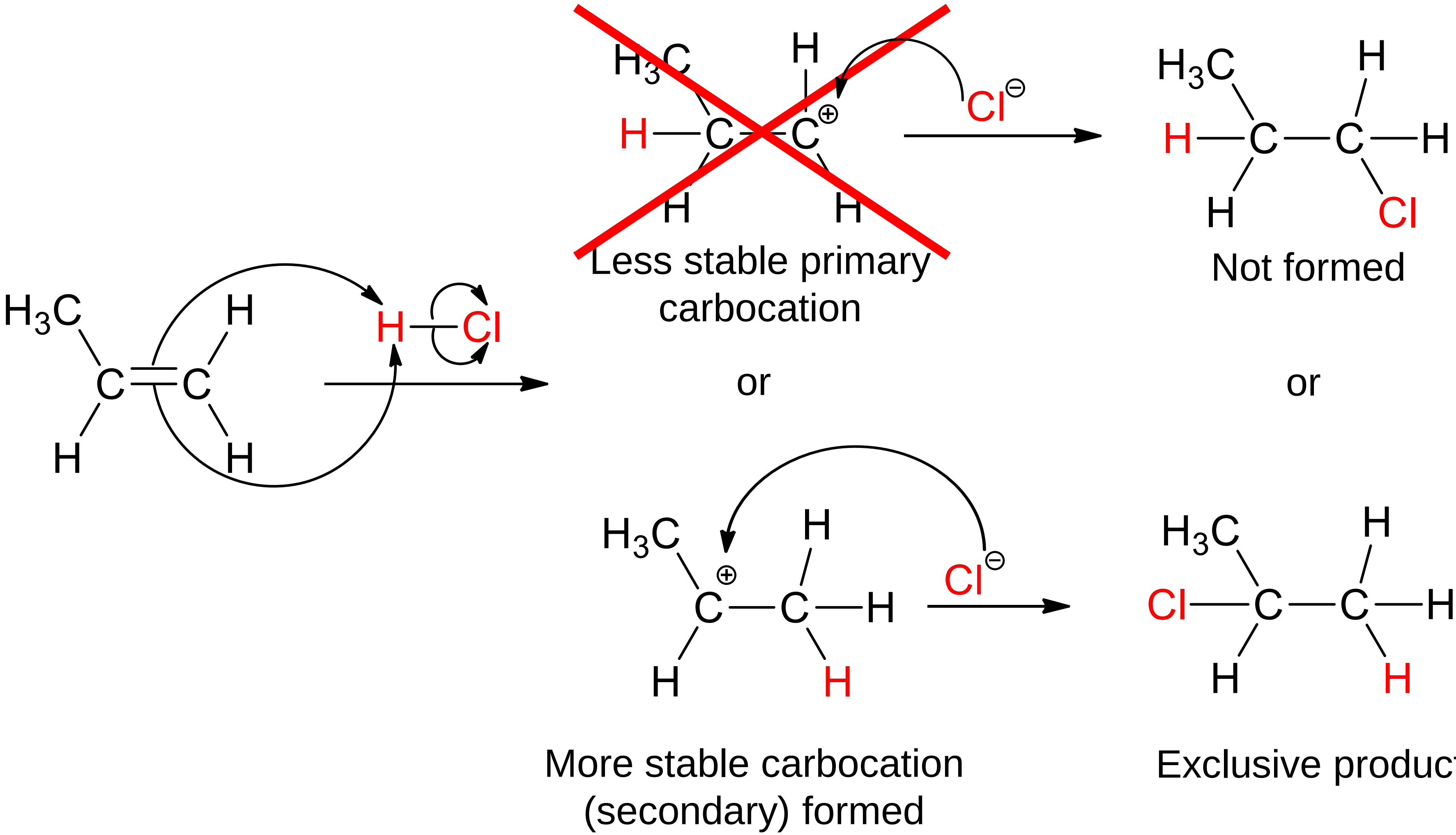
100%

Unsymmetrical because
left side of double bond
differs from right side.

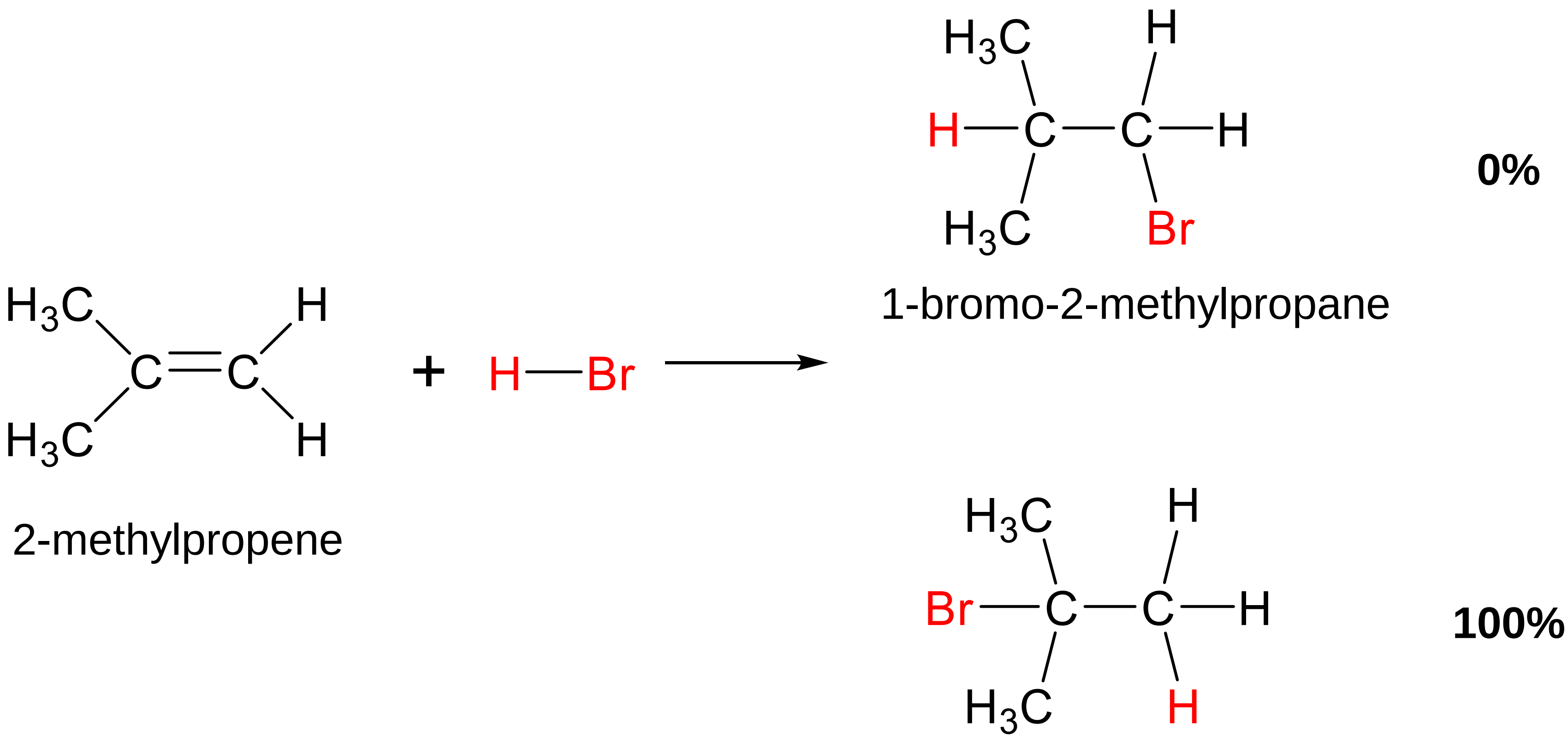
Why?

The answer lies somewhere on the journey from reagents to product

Addition of HX to Propene – Why Only 1 Product?



Addition of HX to Unsymmetrical Alkenes

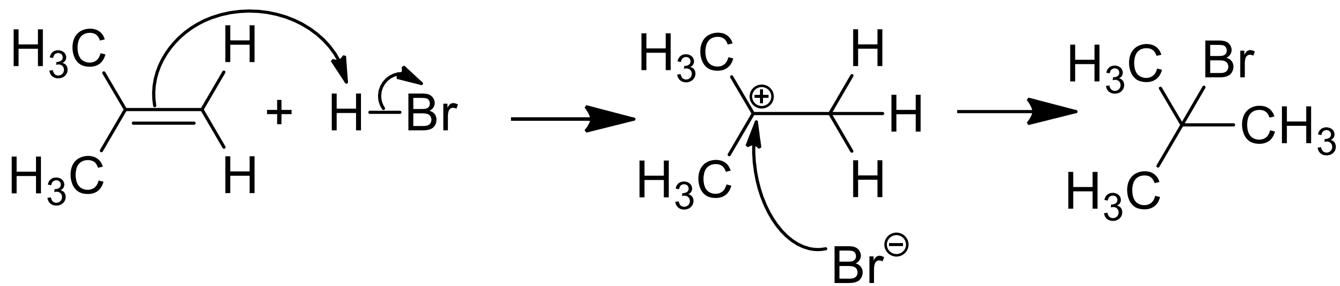


2-methylpropene

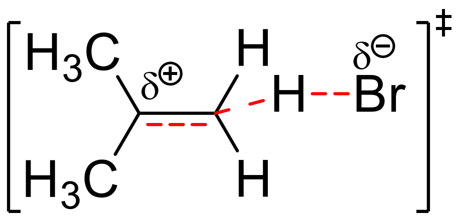
1-bromo-2-methylpropane 0%

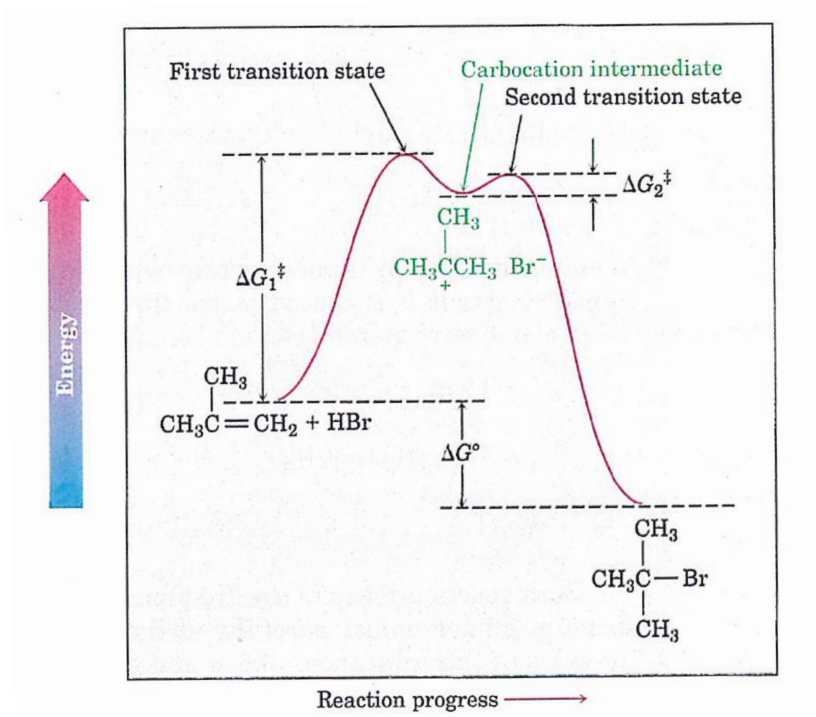
2-bromo-2-methylpropane 100%

Reaction Energy Diagram for HBr Addition to 2-Methylpropene

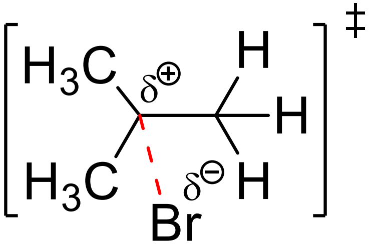


1st transition state





2nd transition state



Energy diagram has two peaks (transition states) separated by a valley (carbocation).

The energy level of the intermediates are higher than the starting alkene but the reaction as a whole is exergonic.

Markovnikov's Rule

Markovnikov's Rule -- is a formal statement of the previous observations

This rule states that --

In the addition of HX to an unsymmetrical alkene,

the $H^{\oplus}$ adds to the C which already has the

greater number of hydrogens attached to it:

the $X^{\ominus}$ adds to the other carbon.

Vladimir Markovnikov
(1838-1904)

Hydration of Alkenes: Electrophilic Addition

Water adds to alkenes in the presence of acid ($H^{\oplus}$) catalyst and heat to give alcohols.

$$H_2C{=}CH_2 \;+\; H_2O \xrightarrow[\text{heat}]{H^{\oplus}} H_3C{-}CH_2OH$$

ethanol

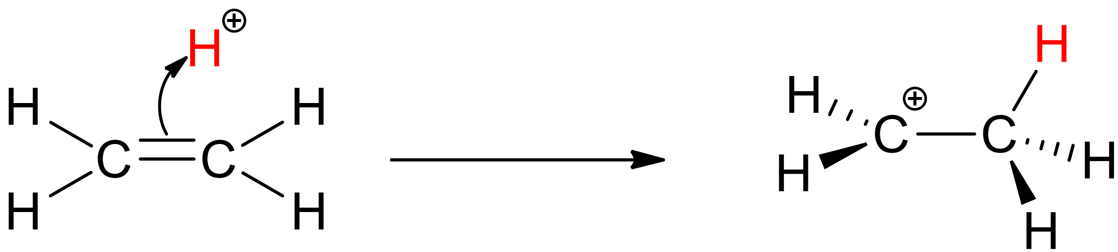
$$(CH_3)_2C{=}CH_2 \;+\; H_2O \xrightarrow[\text{heat}]{H^{\oplus}} (CH_3)_2\underset{\displaystyle |\atop \displaystyle OH}{C}{-}CH_3$$

2-methylpropene

2-methylpropan-2-ol

Mechanism for Hydration of Alkenes

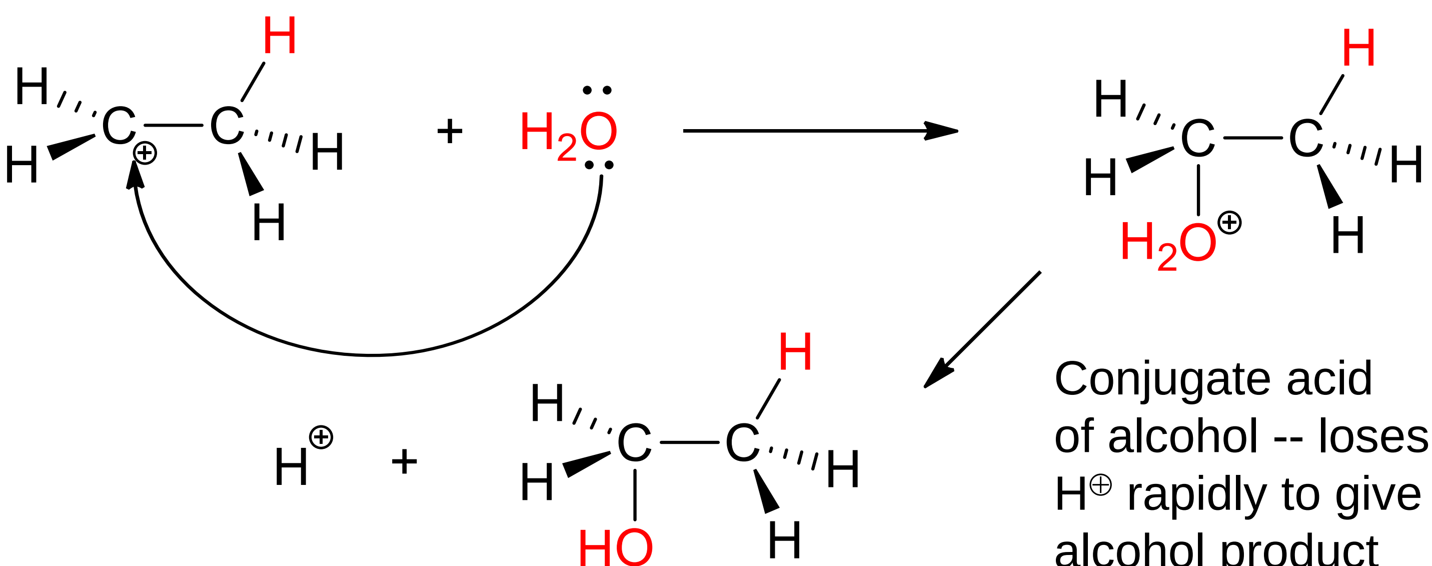
1. Rate determining step



ethene

$H^{\oplus}$ is a catalyst -- small amounts required but not used up overall during the reaction. Used up in step 1 but regenerated in step 2.

2. Fast step

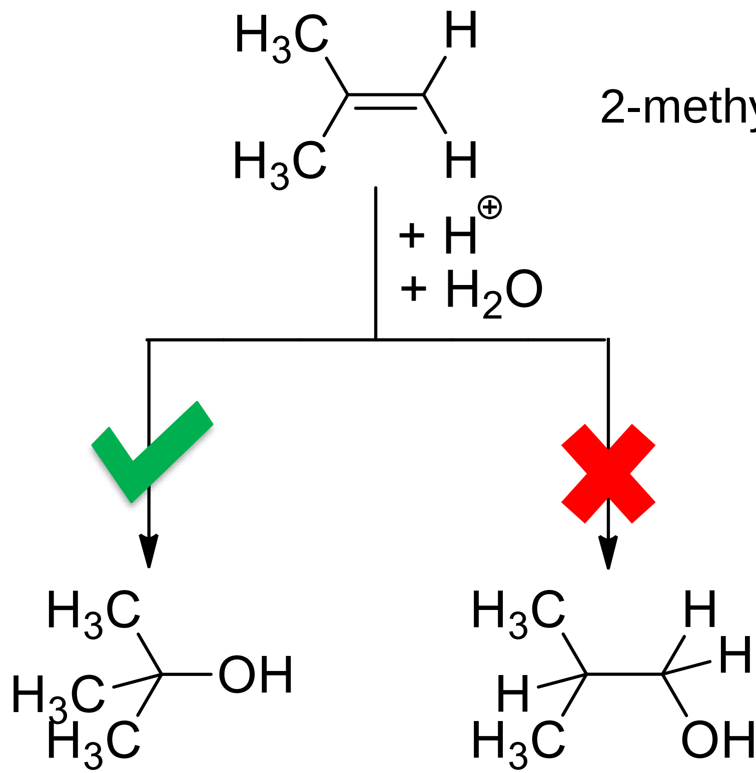


ethanol

Conjugate acid of alcohol -- loses $H^{\oplus}$ rapidly to give alcohol product

Hydration of 2-Methylpropene

(two possible products)



2-methylprop-1-ene

2-methylpropan-2-ol

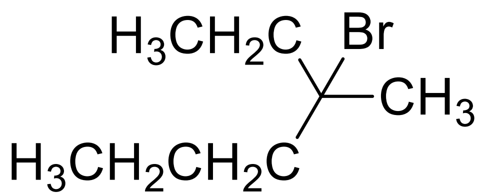
2-methylpropan-1-ol

2-Methylpropan-2-ol is the sole product as the reaction corresponds to the Markovnikov addition of water.

Note: Draw out the full reaction mechanism to see why 2-methylpropan-1-ol is not formed.

Practice Example

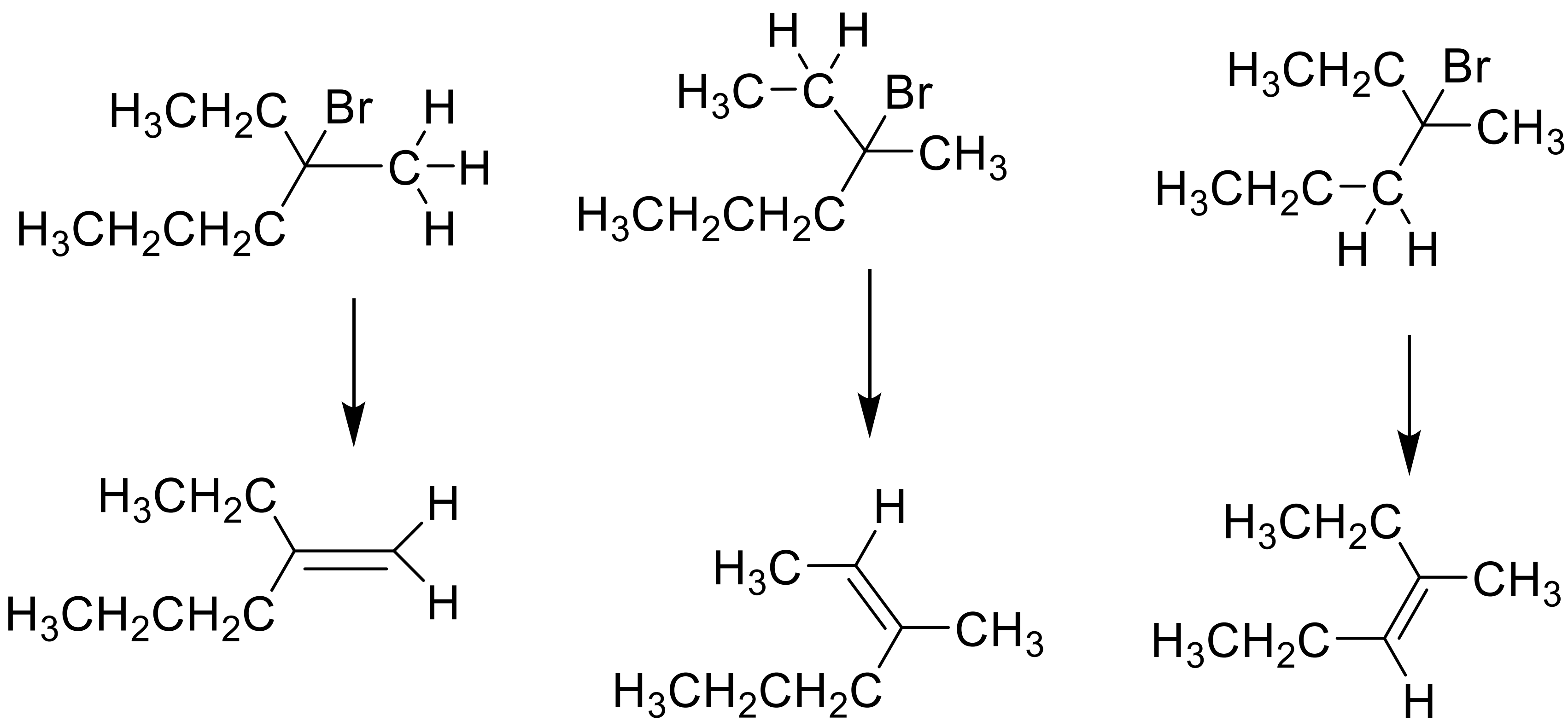
Give the structure of a starting alkene A which upon reaction with HBr produces 3-bromo-3-methylhexane.



3-bromo-3-methylhexane

Answer

Draw out all three possibilities for alkene starting materials



Carry out the forward reaction with HBr for each to answer the question

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Keep Up With Your Chemistry Studies !