5.8

Preparation of Alkenes:
Elimination Reactions

b-Elimination Reactions Overview

dehydrogenation of alkanes:

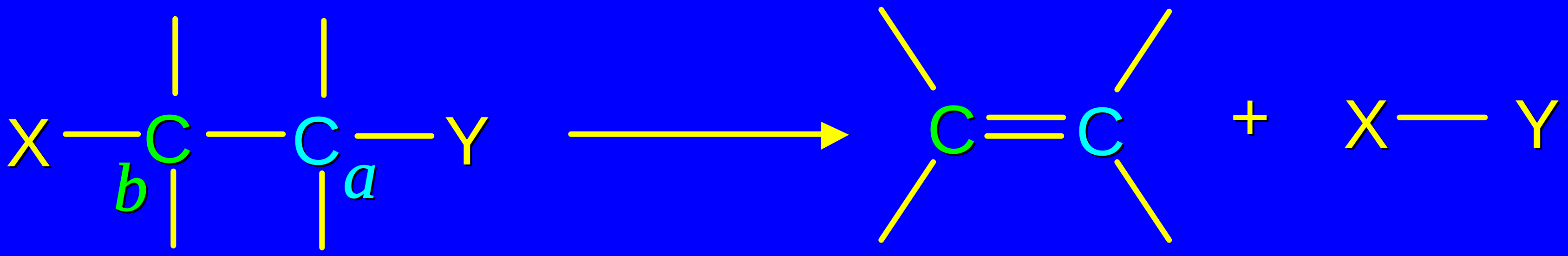
X = Y = H

dehydration of alcohols:

X = H; Y = OH

dehydrohalogenation of alkyl halides:

X = H; Y = Br, etc.



Dehydrogenation

limited to industrial syntheses of ethylene, propene, 1,3-butadiene, and styrene

important economically, but rarely used in laboratory-scale syntheses

$$CH_3CH_3 \xrightarrow{750^\circ C} H_2C{=}CH_2 + H_2$$

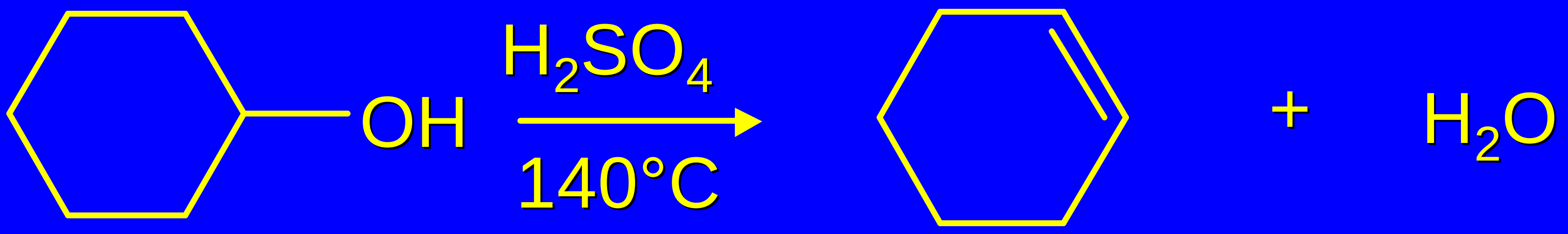
$$CH_3CH_2CH_3 \xrightarrow{750^\circ C} H_2C{=}CHCH_3 + H_2$$

5.9

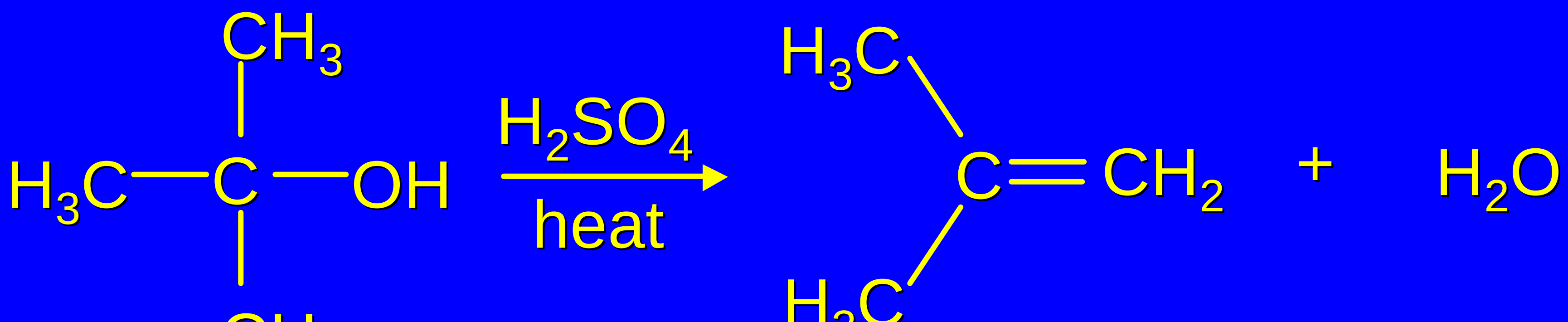
Dehydration of Alcohols

Dehydration of Alcohols

$$CH_3CH_2OH \xrightarrow[160°C]{H_2SO_4} H_2C{=}CH_2 + H_2O$$



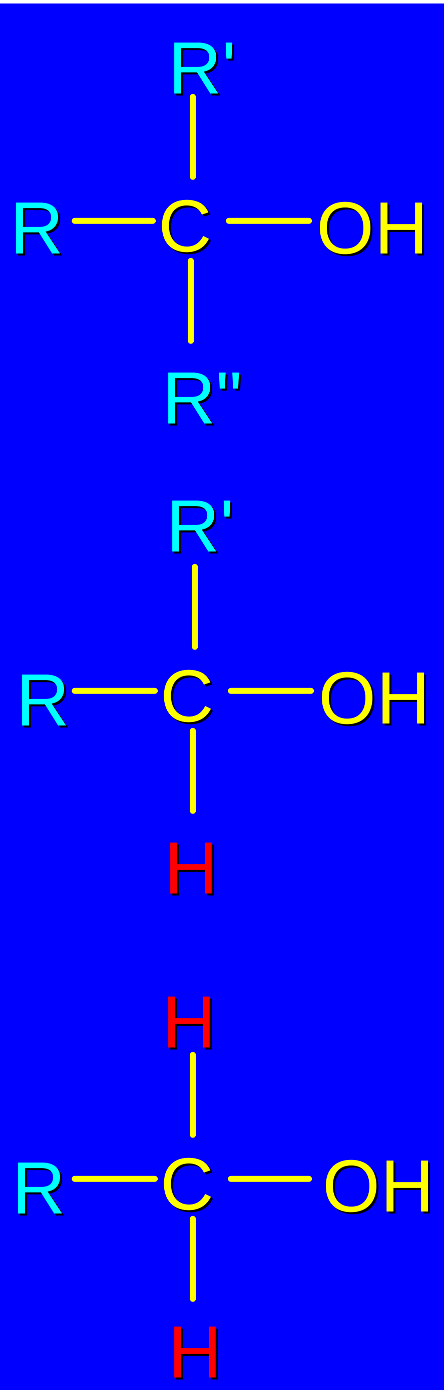
(79-87%)



$$(CH_3)_3COH \xrightarrow[heat]{H_2SO_4} (CH_3)_2C{=}CH_2 + H_2O$$

(82%)

Relative Reactivity



$$\mathrm{R-\overset{\displaystyle R'}{\underset{\displaystyle R''}{C}}-OH}$$

tertiary:
most reactive

$$\mathrm{R-\overset{\displaystyle R'}{\underset{\displaystyle H}{C}}-OH}$$

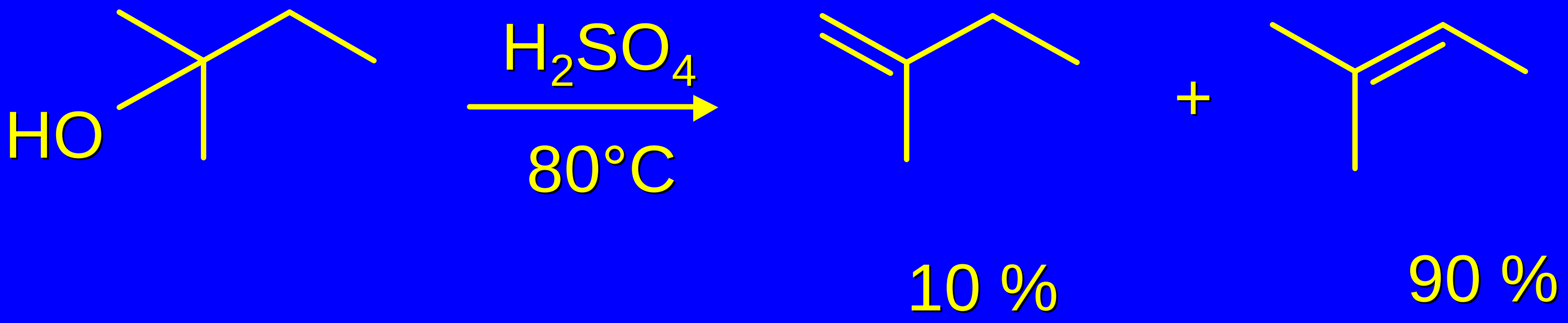
$$\mathrm{R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

primary:
least reactive

5.10

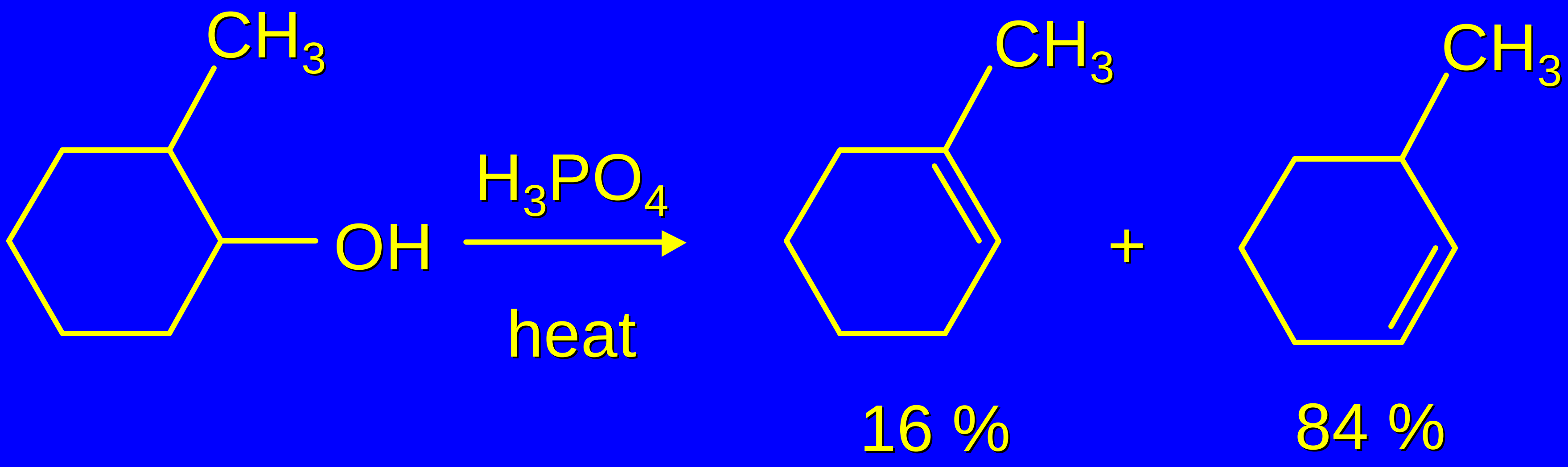
Regioselectivity in Alcohol Dehydration: The Zaitsev Rule

Regioselectivity



A reaction that can proceed in more than one direction, but in which one direction predominates, is said to be regioselective.

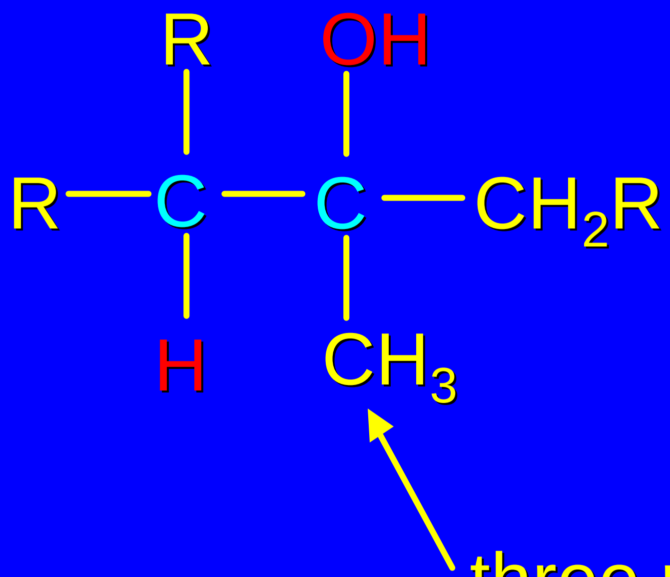
Regioselectivity



A reaction that can proceed in more than one direction, but in which one direction predominates, is said to be regioselective.

The Zaitsev Rule

When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.

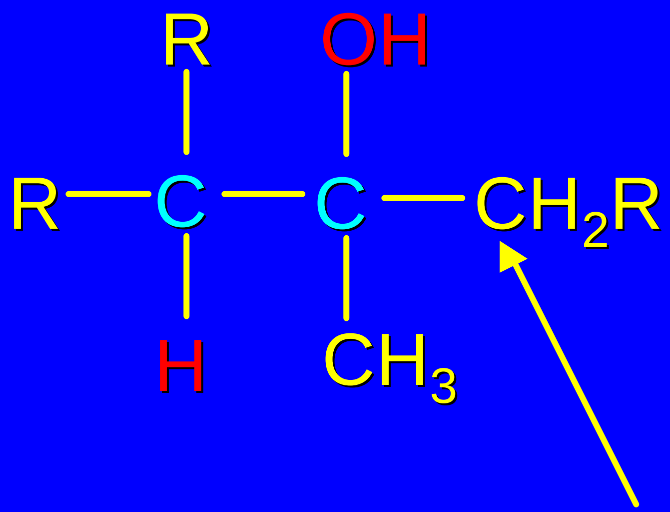


$R-C(R)(H)-C(OH)(CH_3)-CH_2R$

three protons on this β carbon

The Zaitsev Rule

When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.

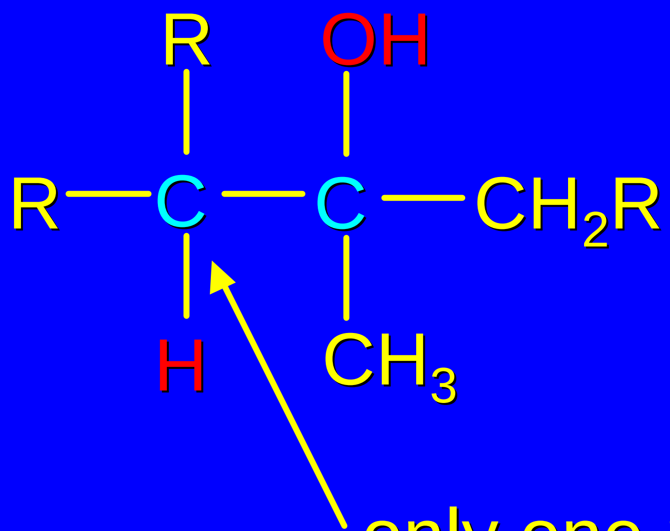


$$R-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_2R$$

two protons on this β carbon

The Zaitsev Rule

When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.

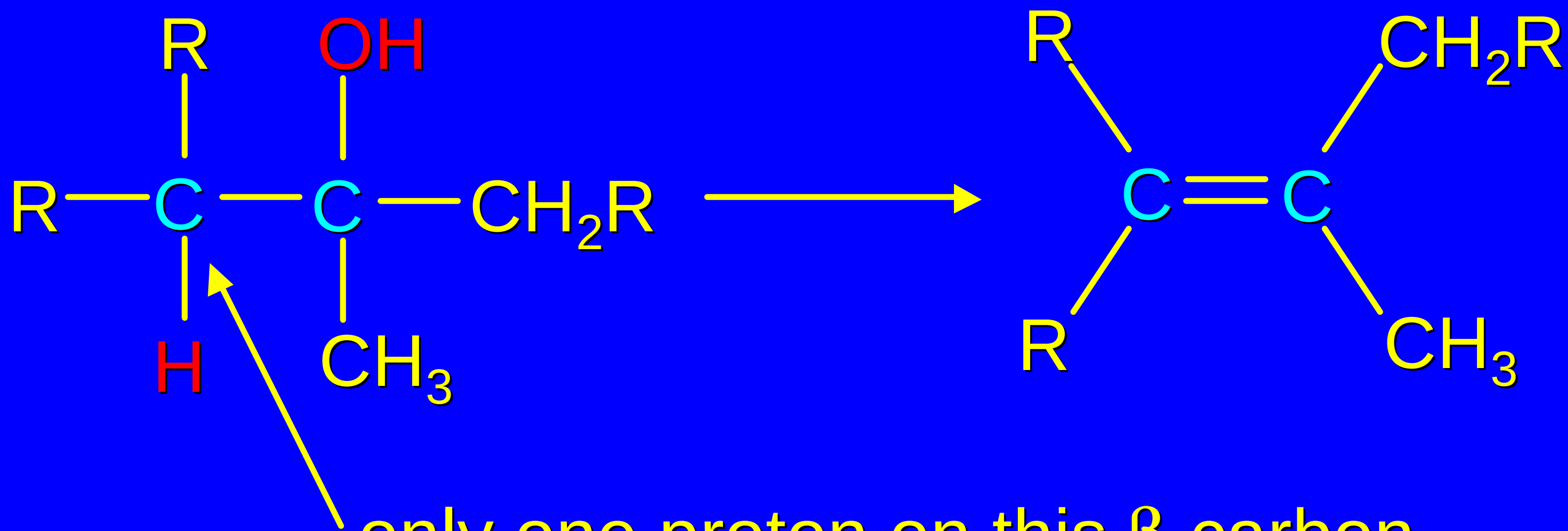


$$R-\overset{R}{\underset{H}{C}}-\overset{OH}{\underset{CH_3}{C}}-CH_2R$$

only one proton on this β carbon

The Zaitsev Rule

When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.

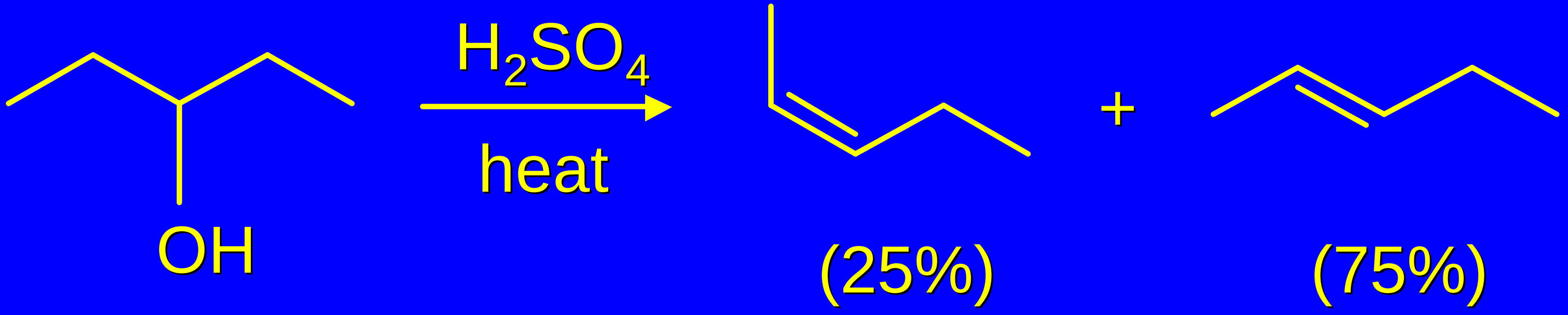


only one proton on this β carbon

5.11

Stereoselectivity in Alcohol Dehydration

Stereoselectivity



A stereoselective reaction is one in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amounts than any other.

5.12

The Mechanism of Acid-Catalyzed Dehydration of Alcohols

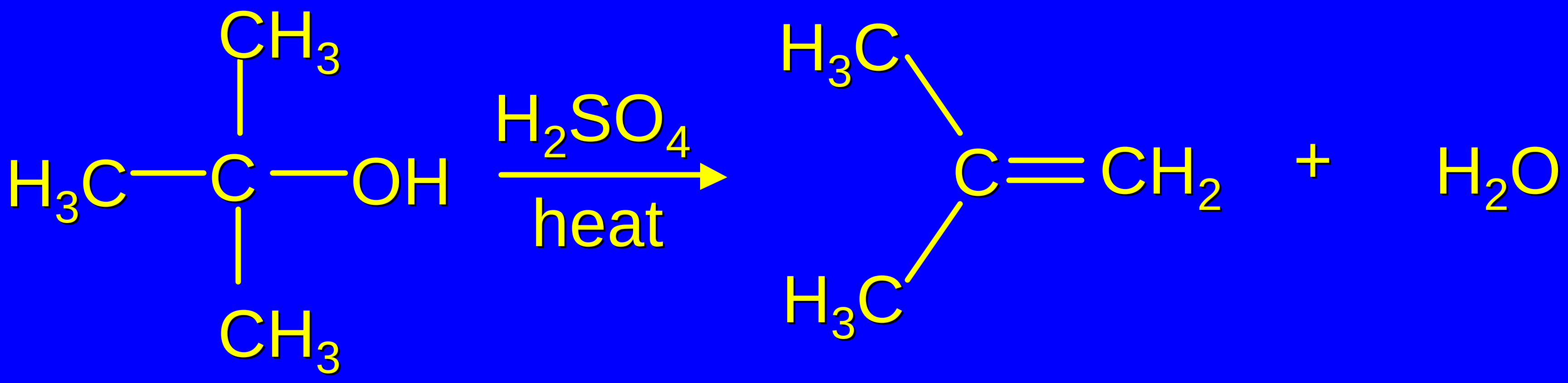
A connecting point...

The dehydration of alcohols and the reaction of alcohols with hydrogen halides share the following common features:

1) Both reactions are promoted by acids
2) The relative reactivity decreases in the order tertiary > secondary > primary

These similarities suggest that carbocations are intermediates in the acid-catalyzed dehydration of alcohols, just as they are in the reaction of alcohols with hydrogen halides.

Dehydration of tert-Butyl Alcohol

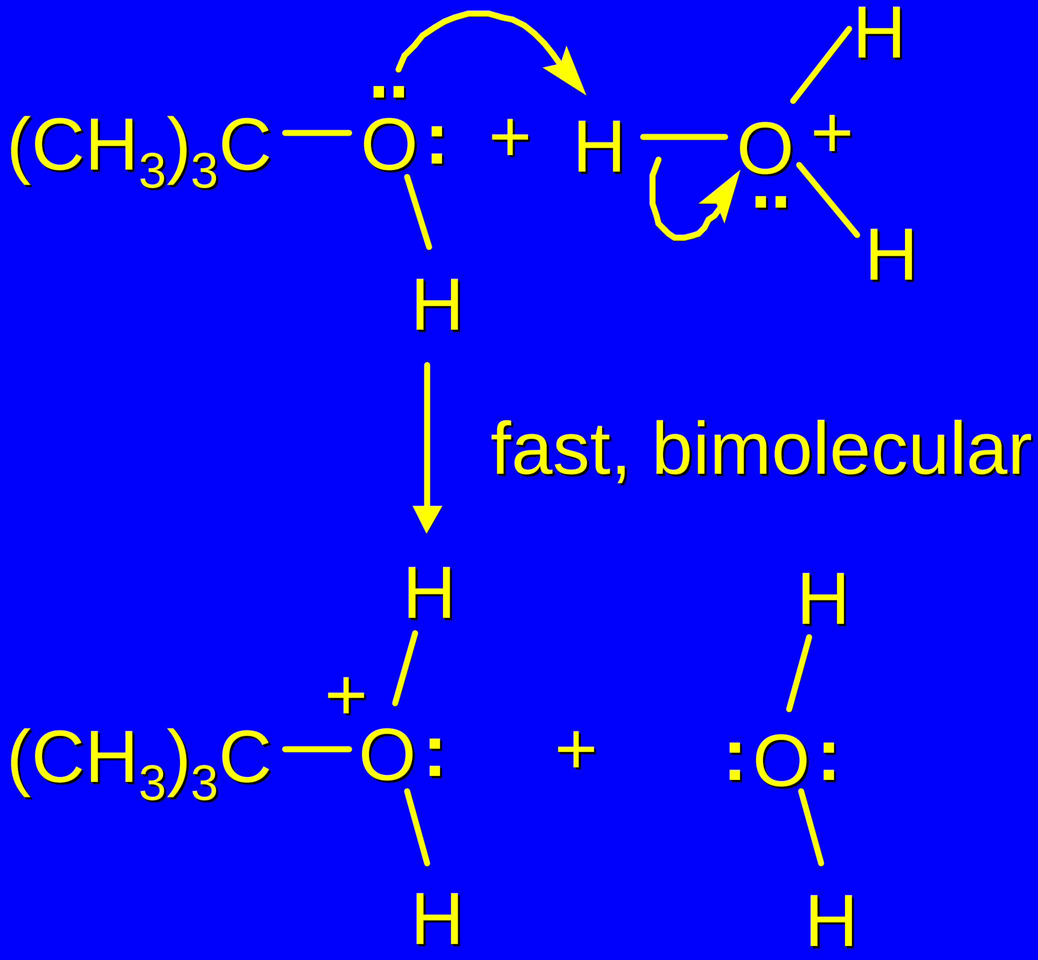


$$(CH_3)_3COH \xrightarrow[\text{heat}]{H_2SO_4} (CH_3)_2C{=}CH_2 + H_2O$$

first two steps of mechanism are identical to those for the reaction of *tert*-butyl alcohol with hydrogen halides

Mechanism

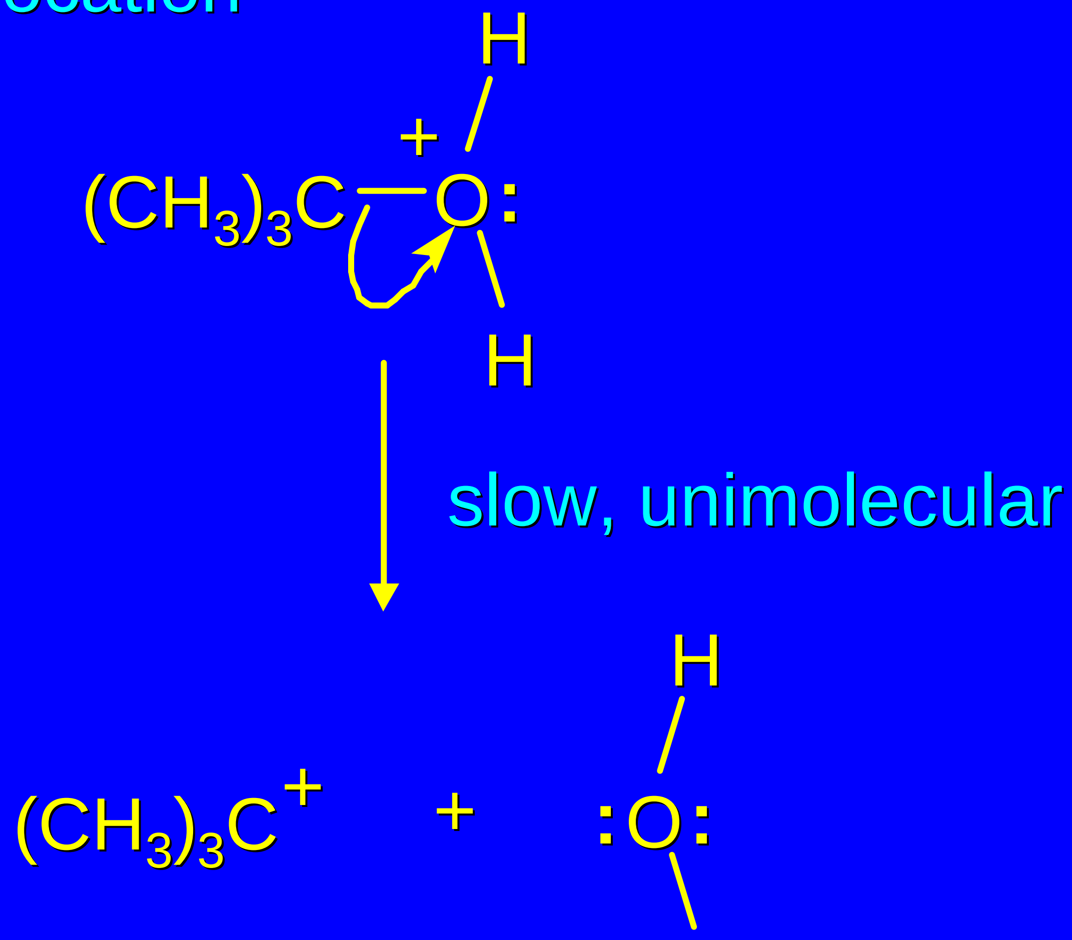
Step 1: Proton transfer to *tert*-butyl alcohol



tert-Butyloxonium ion

Mechanism

Step 2: Dissociation of *tert*-butyloxonium ion to carbocation

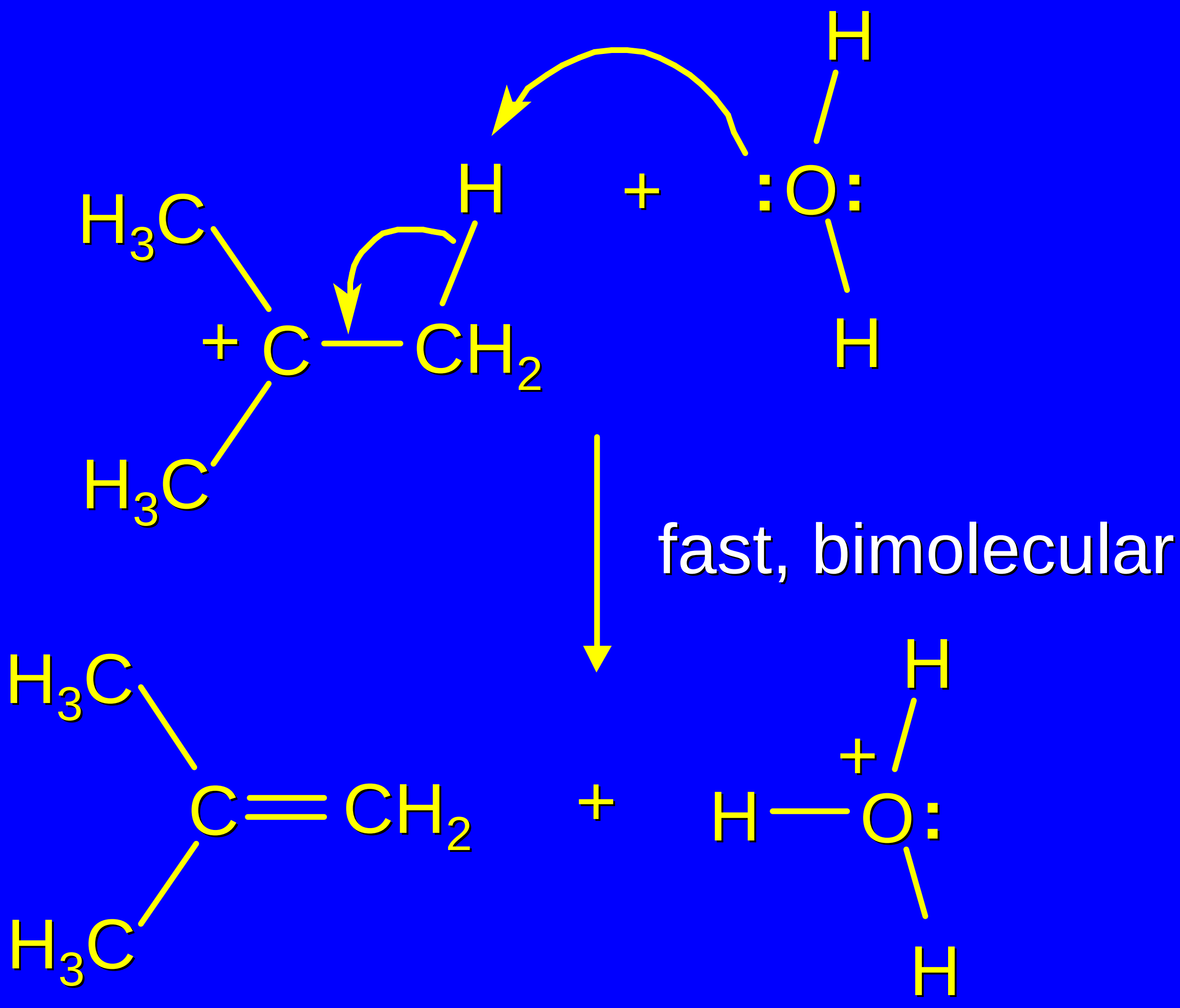


slow, unimolecular

tert-Butyl cation

Mechanism

Step 3: Deprotonation of *tert*-butyl cation.



Carbocations

are intermediates in the acid-catalyzed dehydration of tertiary and secondary alcohols

carbocations can:

- react with nucleophiles
- lose a β-proton to form an alkene

Dehydration of Primary Alcohols

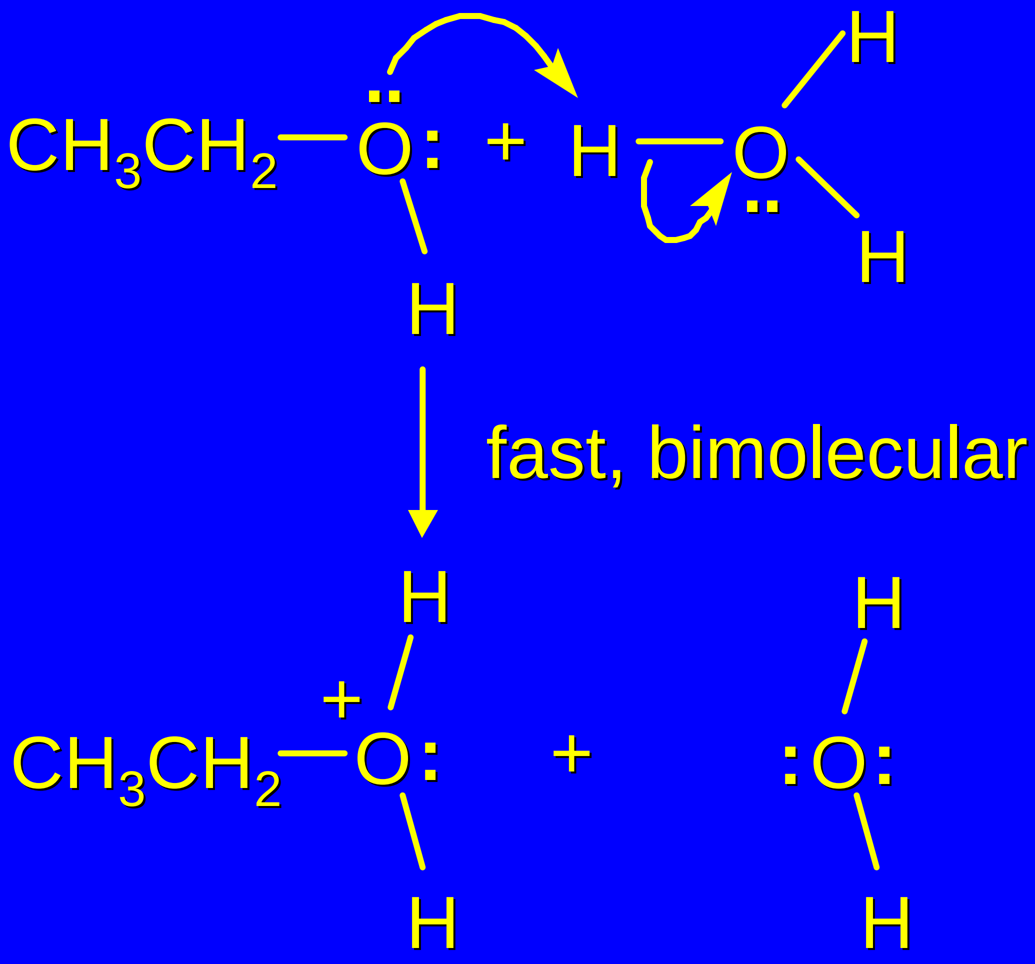
$$CH_3CH_2OH \xrightarrow[160^\circ C]{H_2SO_4} H_2C{=}CH_2 \quad + \quad H_2O$$

avoids carbocation because primary carbocations are too unstable

oxonium ion loses water and a proton in a bimolecular step

Mechanism

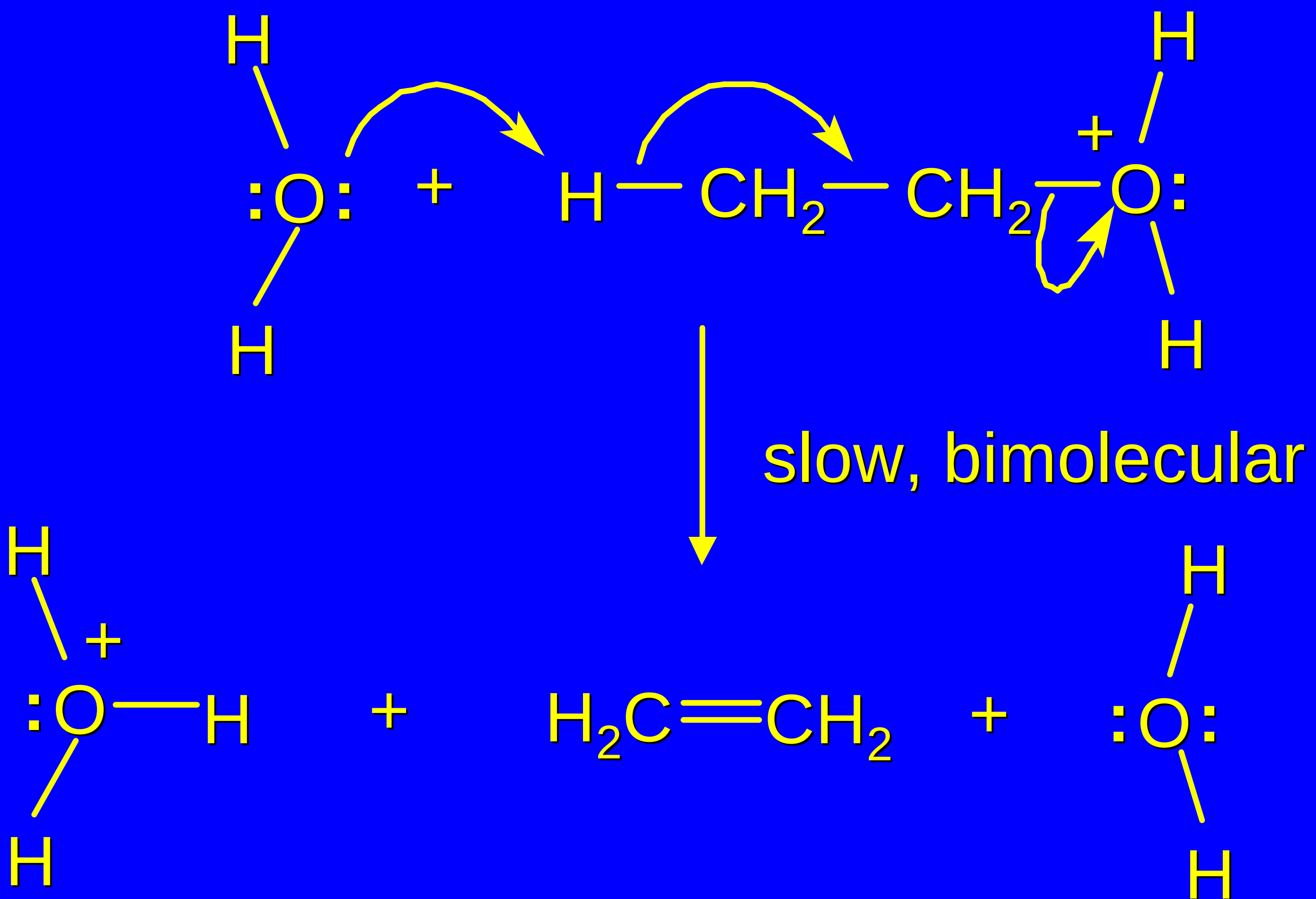
Step 1: Proton transfer from acid to ethanol



Ethyloxonium ion

Mechanism

Step 2: Oxonium ion loses both a proton and a water molecule in the same step.

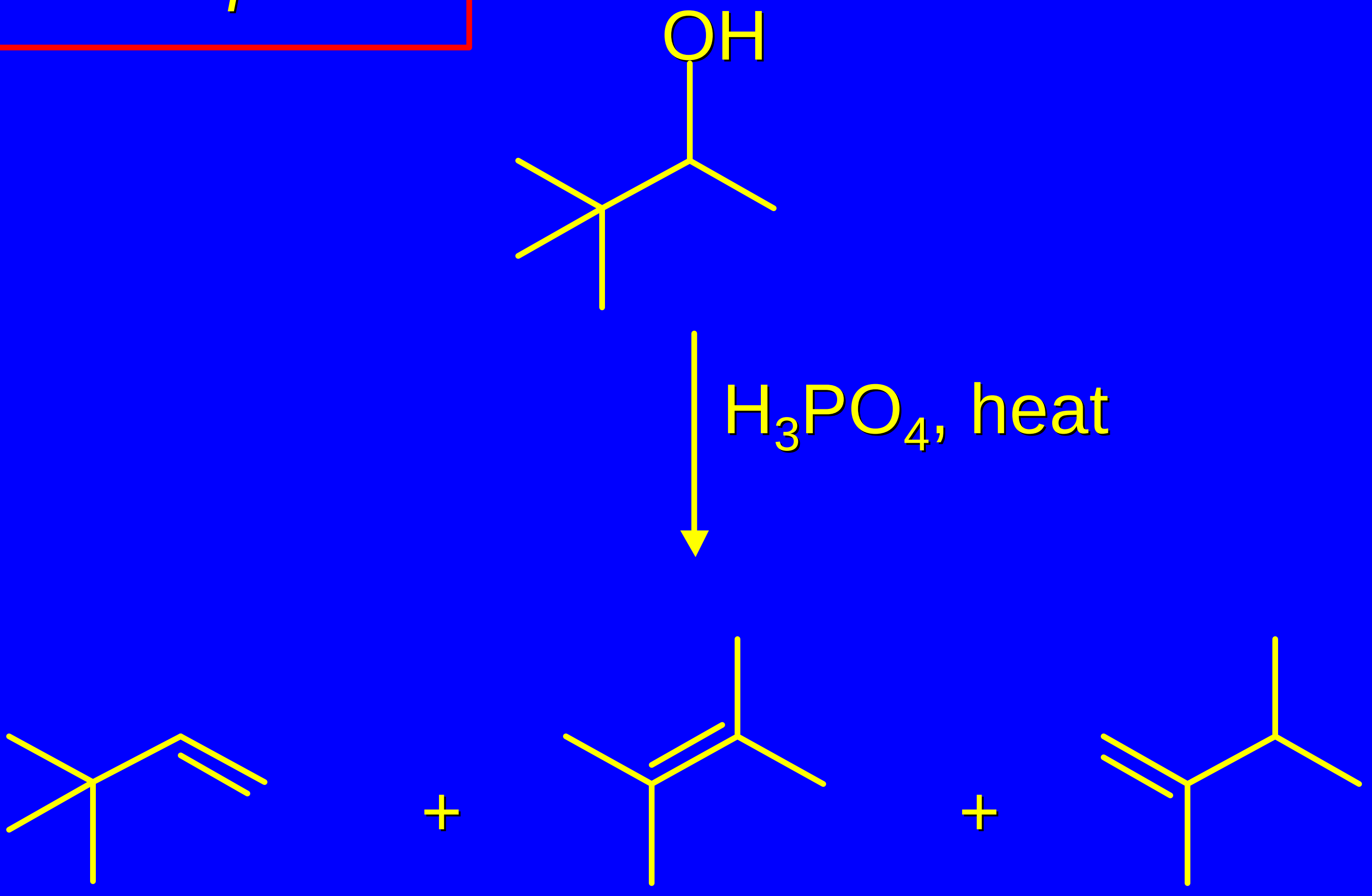


5.13

Rearrangements in Alcohol Dehydration

Sometimes the alkene product does not have the same carbon skeleton as the starting alcohol.

Example



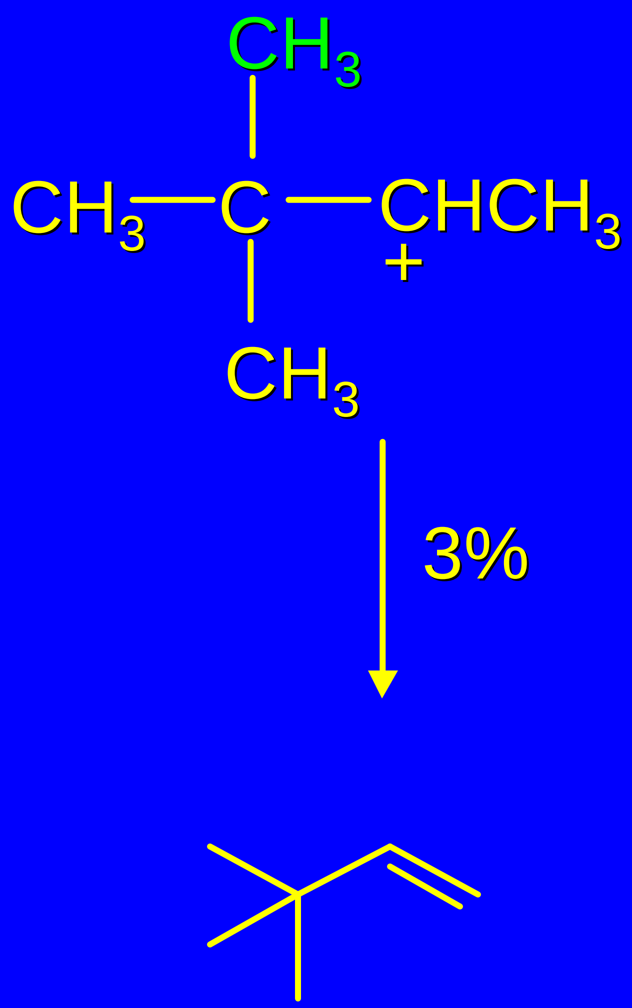
H_3PO_4, heat

3%

64%

33%

Rearrangement involves alkyl group migration

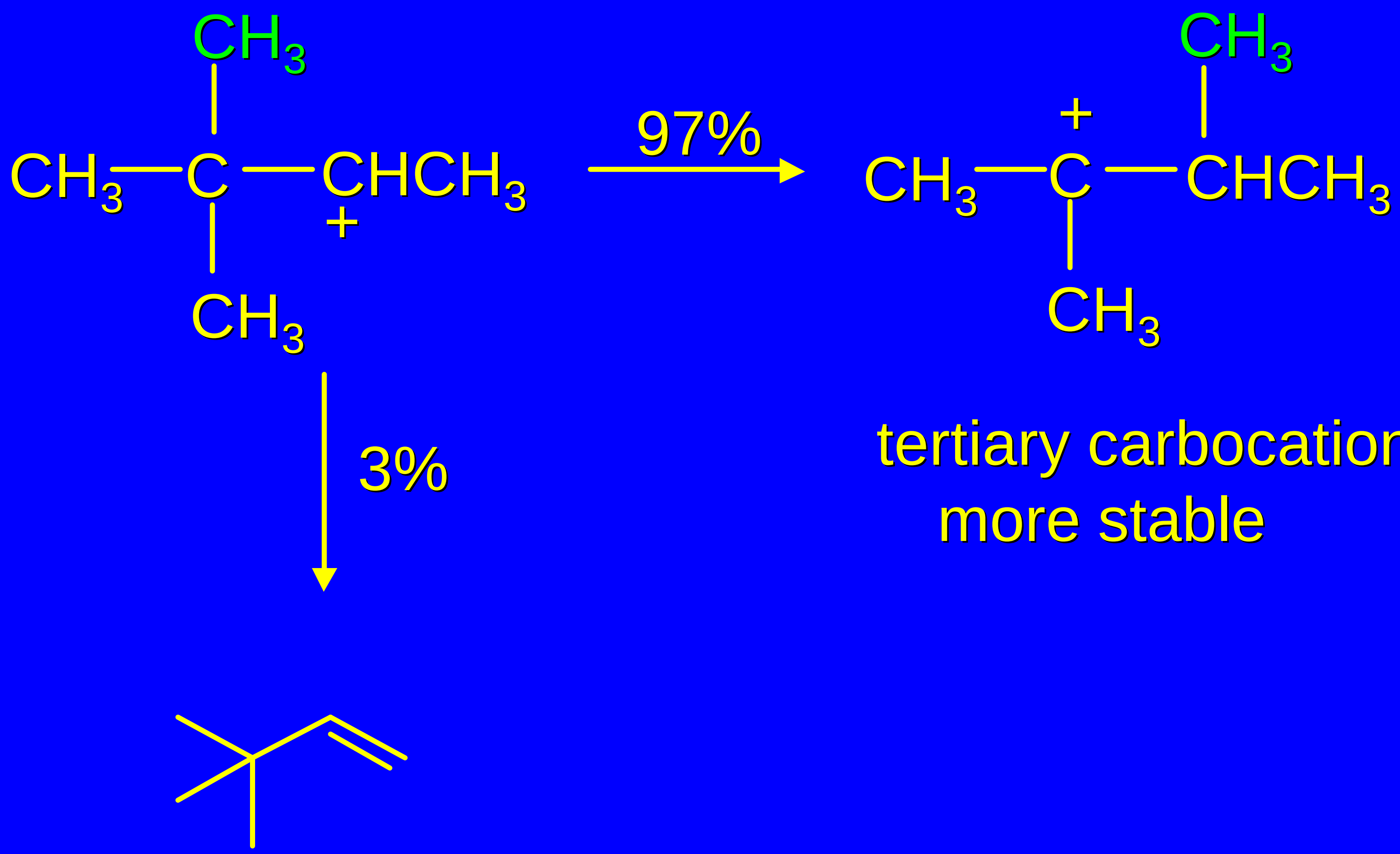


carbocation can lose a proton as shown

or it can undergo a methyl migration

CH_3 group migrates with its pair of electrons to adjacent positively charged carbon

Rearrangement involves alkyl group migration

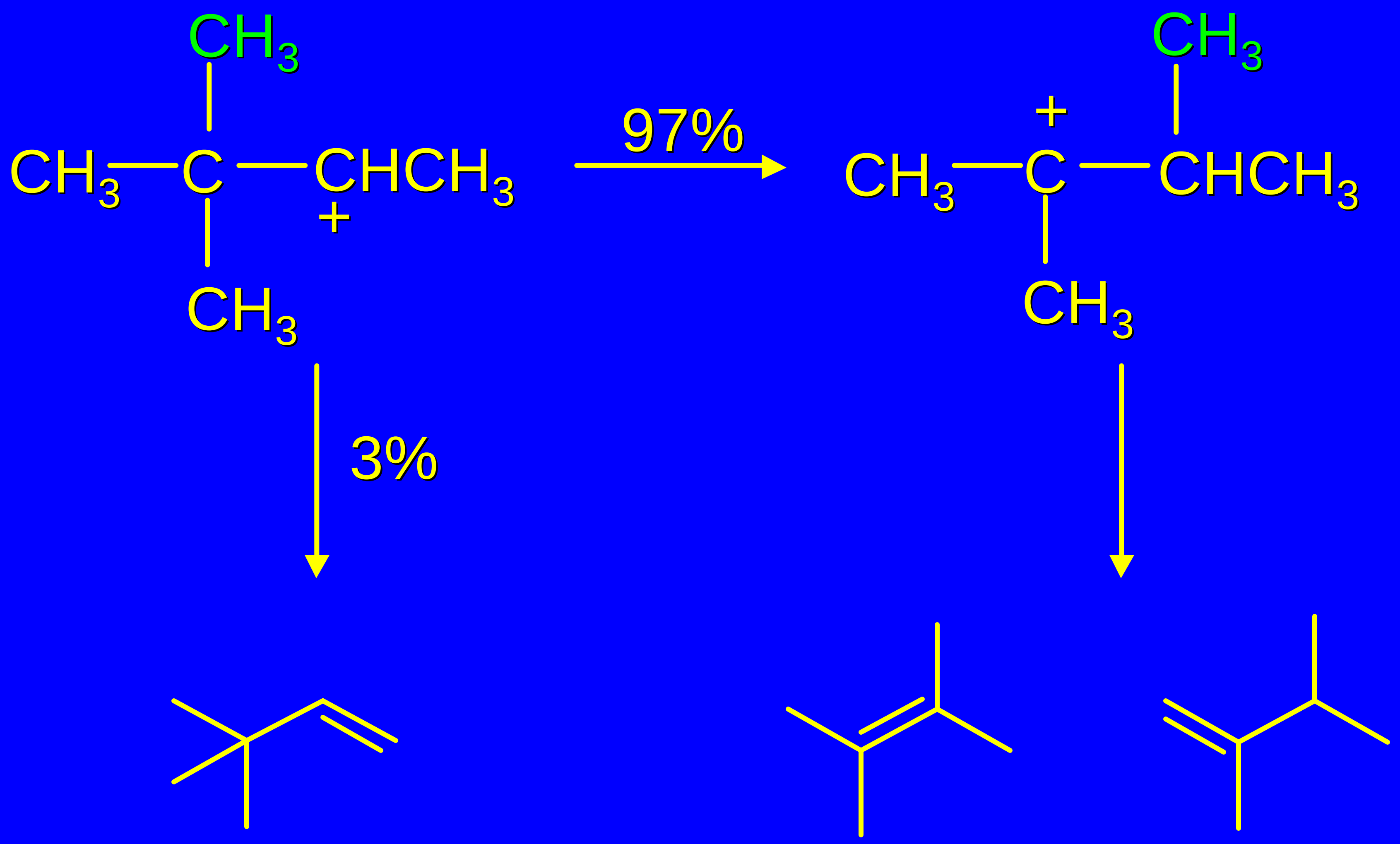


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{+}{C}HCH_3 \xrightarrow{97\%} CH_3-\underset{CH_3}{\overset{+}{C}}-\overset{CH_3}{C}HCH_3$$

3%

tertiary carbocation;
more stable

Rearrangement involves alkyl group migration



Another rearrangement

$CH_3CH_2CH_2CH_2OH$

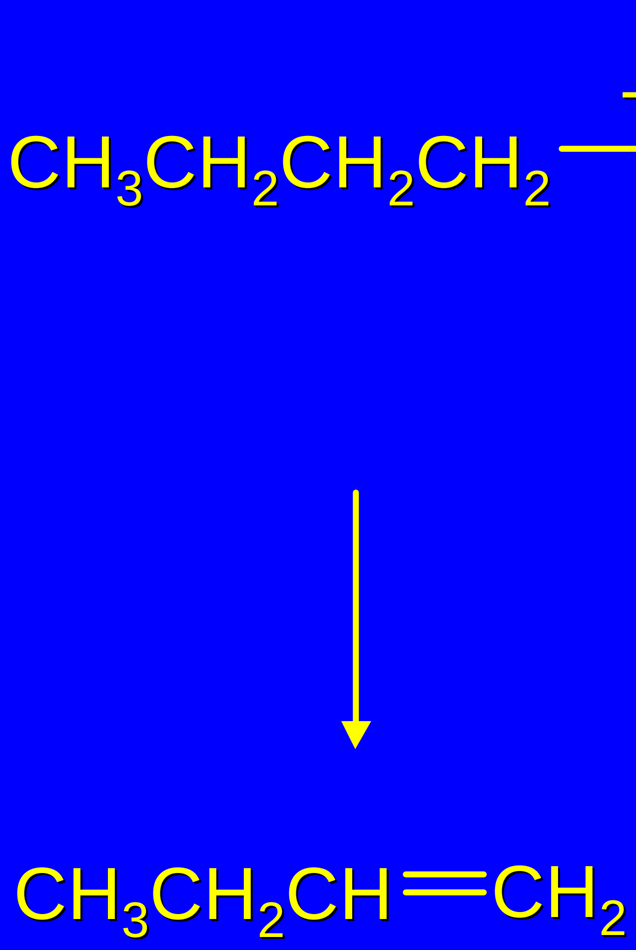
$$\Big\downarrow \; H_3PO_4\text{, heat}$$

$CH_3CH_2CH{=}CH_2$ + $CH_3CH{=}CHCH_3$

12%

mixture of *cis* (32%)
and *trans*-2-butene (56%)

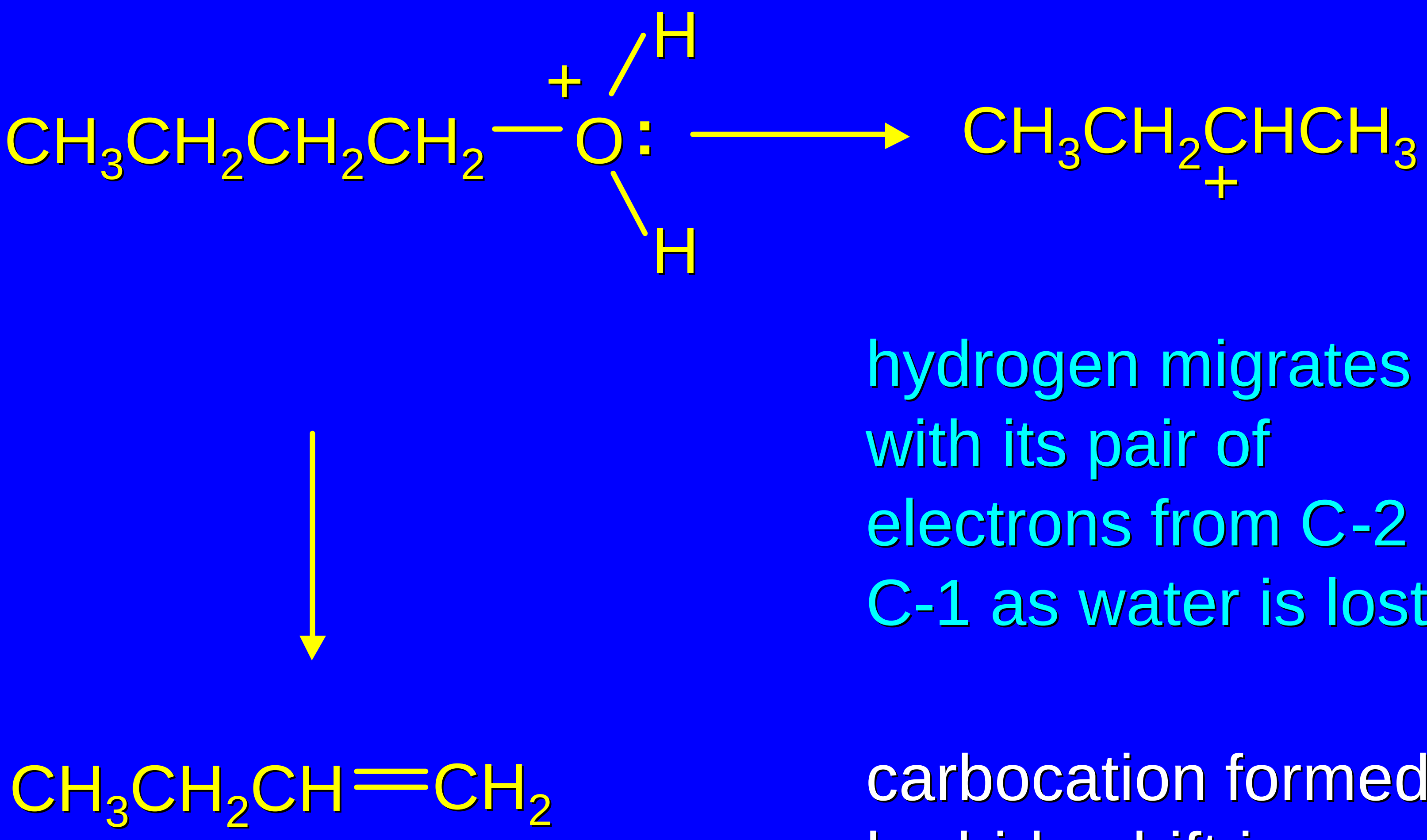
Rearrangement involves hydride shift



oxonium ion can lose water and a proton (from C-2) to give 1-butene

doesn't give a carbocation directly because primary carbocations are too unstable

Rearrangement involves hydride shift



$$CH_3CH_2CH_2CH_2-\overset{+}{O}H_2 \longrightarrow CH_3CH_2\overset{+}{C}HCH_3$$

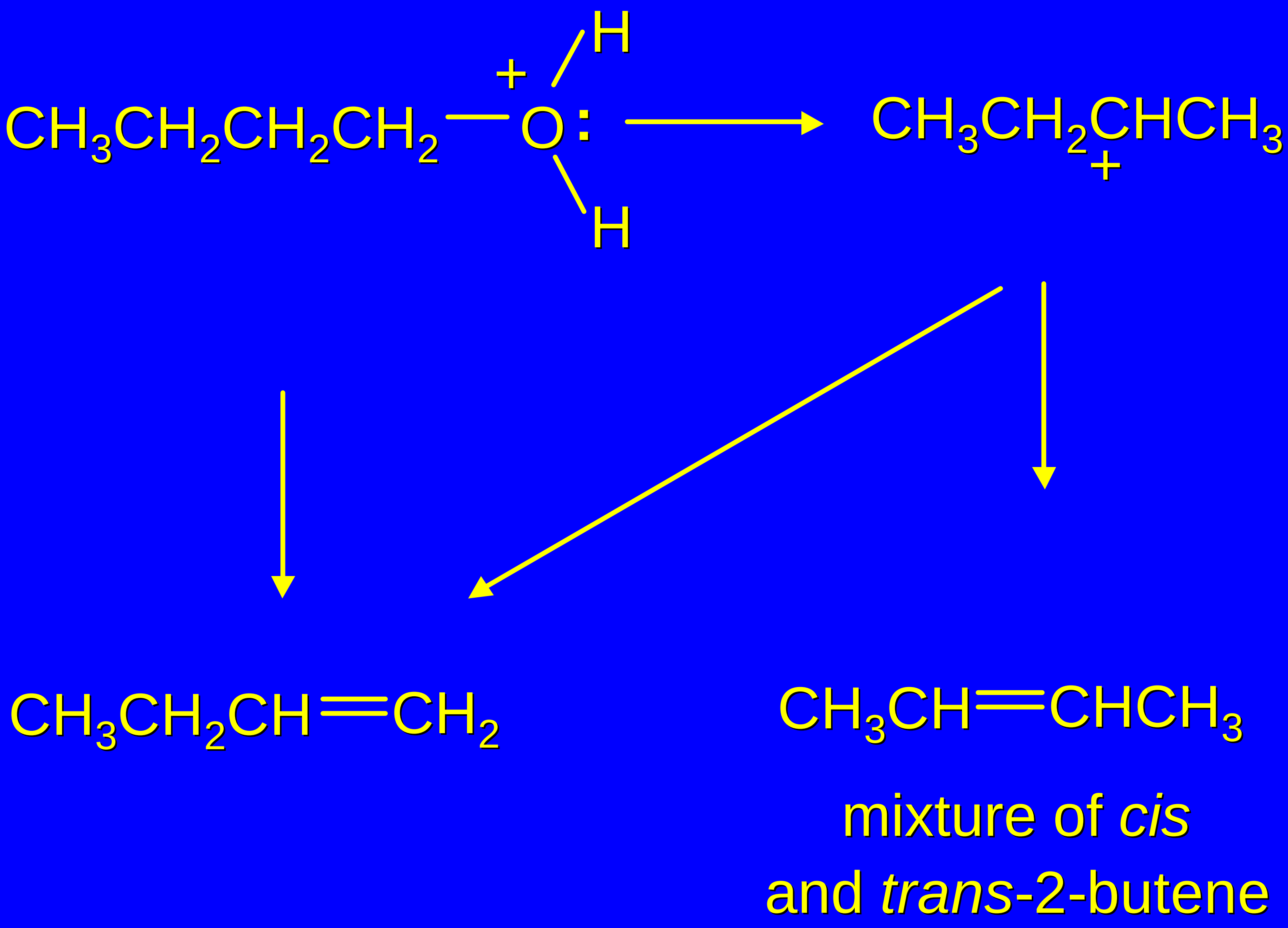
$$\downarrow$$

$$CH_3CH_2CH{=}CH_2$$

hydrogen migrates with its pair of electrons from C-2 to C-1 as water is lost

carbocation formed by hydride shift is secondary

Rearrangement involves hydride shift



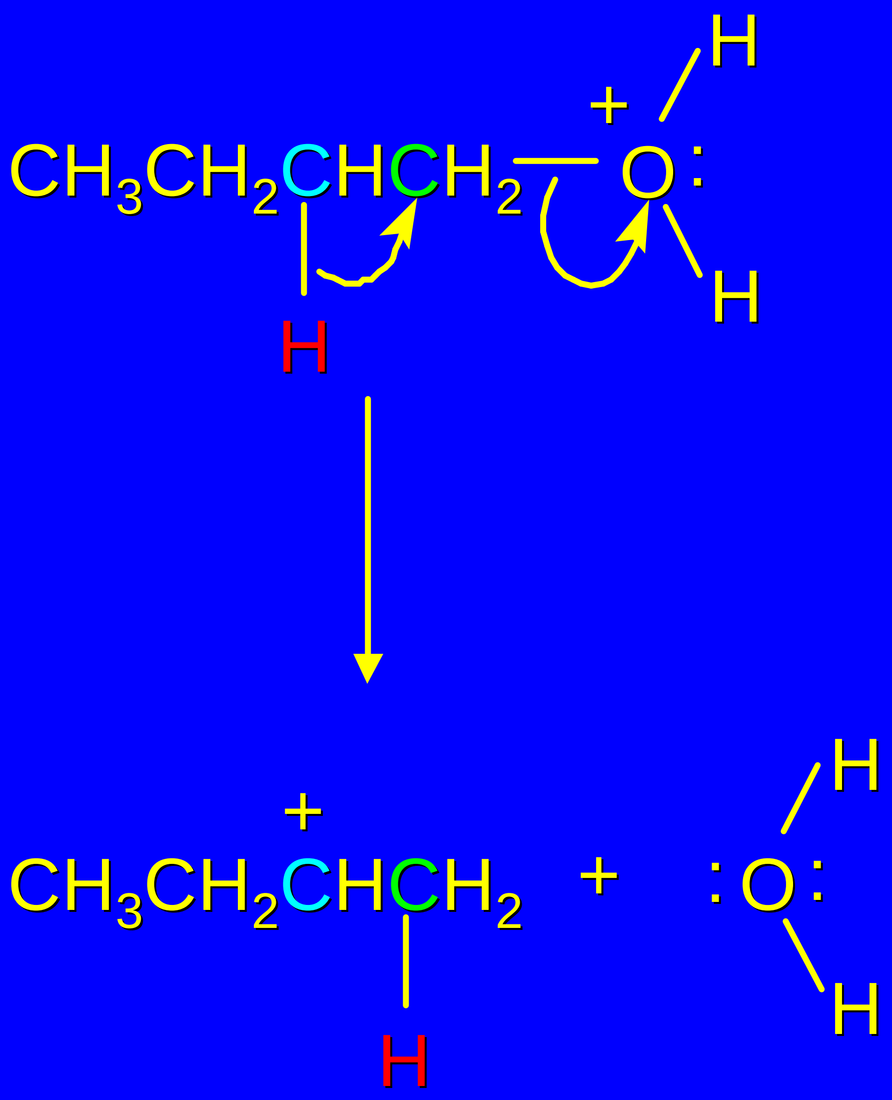
$CH_3CH_2CH_2CH_2-\overset{+}{O}H_2 \longrightarrow CH_3CH_2\underset{+}{C}HCH_3$

$CH_3CH_2CH{=}CH_2$

$CH_3CH{=}CHCH_3$

mixture of *cis*
and *trans*-2-butene

Hydride Shift



$$CH_3CH_2CHCH_2{-}\overset{+}{O}H_2 \longrightarrow CH_3CH_2\overset{+}{C}HCH_2 + H_2O$$

Carbocations can...

- react with nucleophiles
- lose a proton from the β-carbon to form an alkene
- rearrange (less stable to more stable)