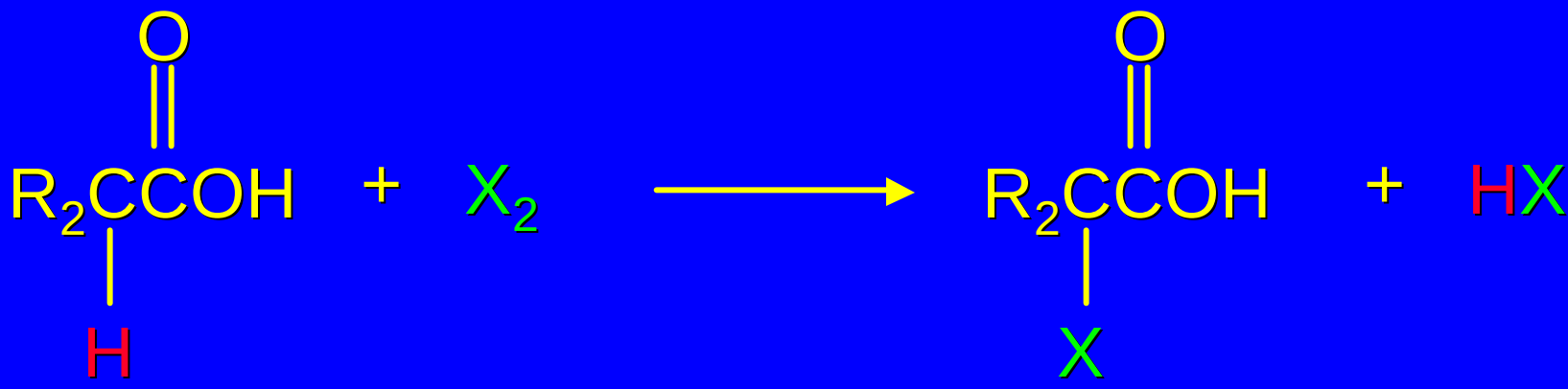
19.16
α-Halogenation of Carboxylic Acids: The Hell-Volhard-Zelinsky Reaction

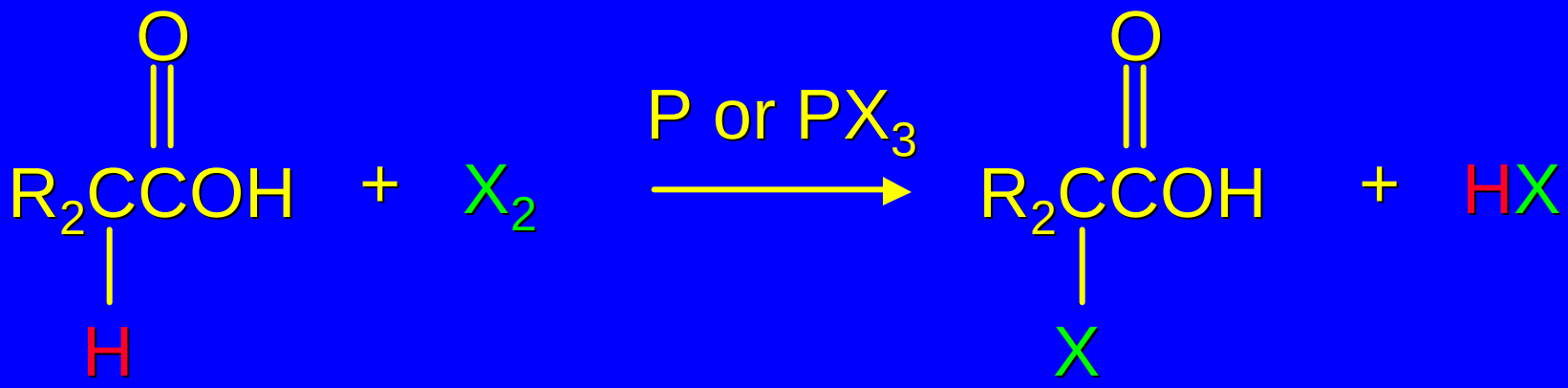
α-Halogenation of Carboxylic Acids



analogous to α-halogenation of aldehydes and ketones

key question: Is enol content of carboxylic acids high enough to permit reaction to occur at reasonable rate? (Answer is NO)

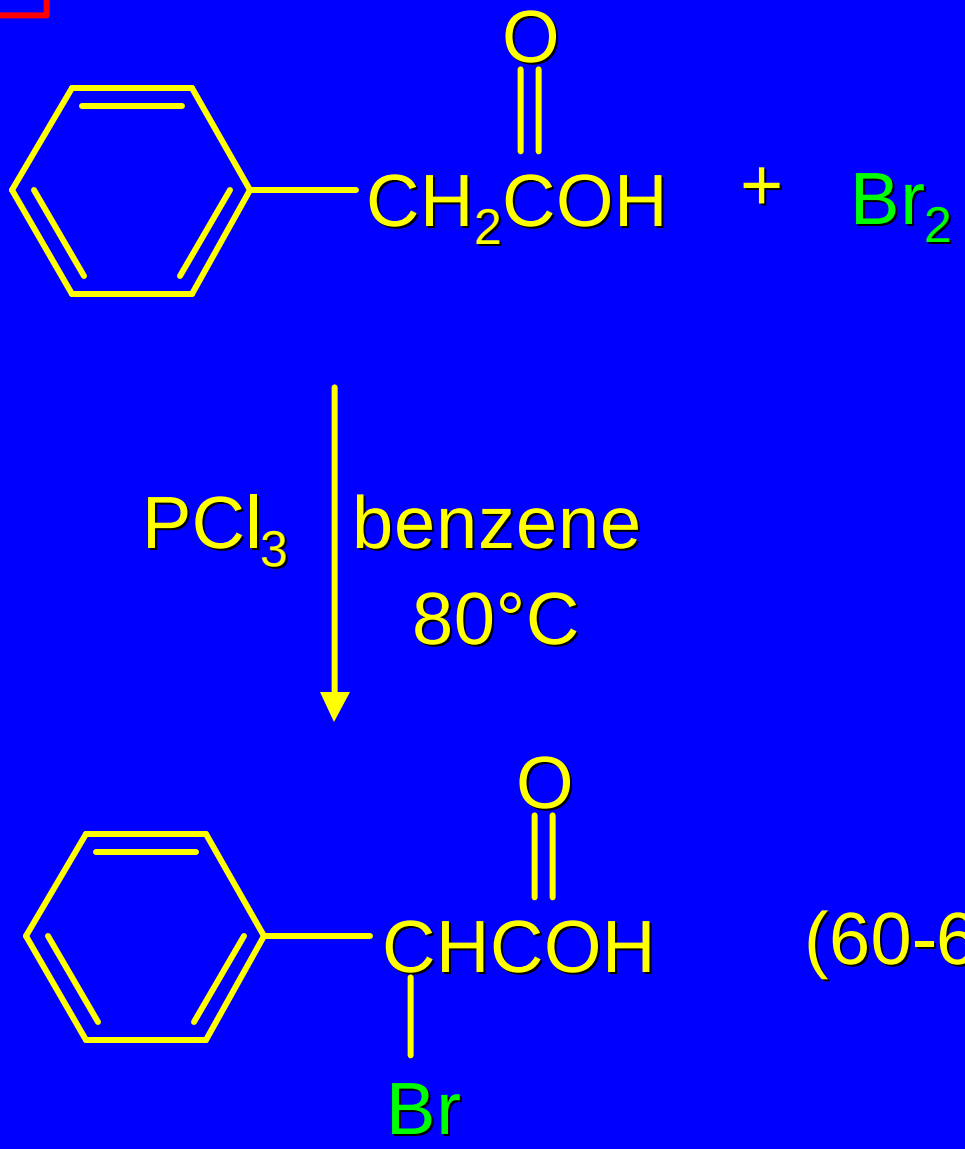
But…



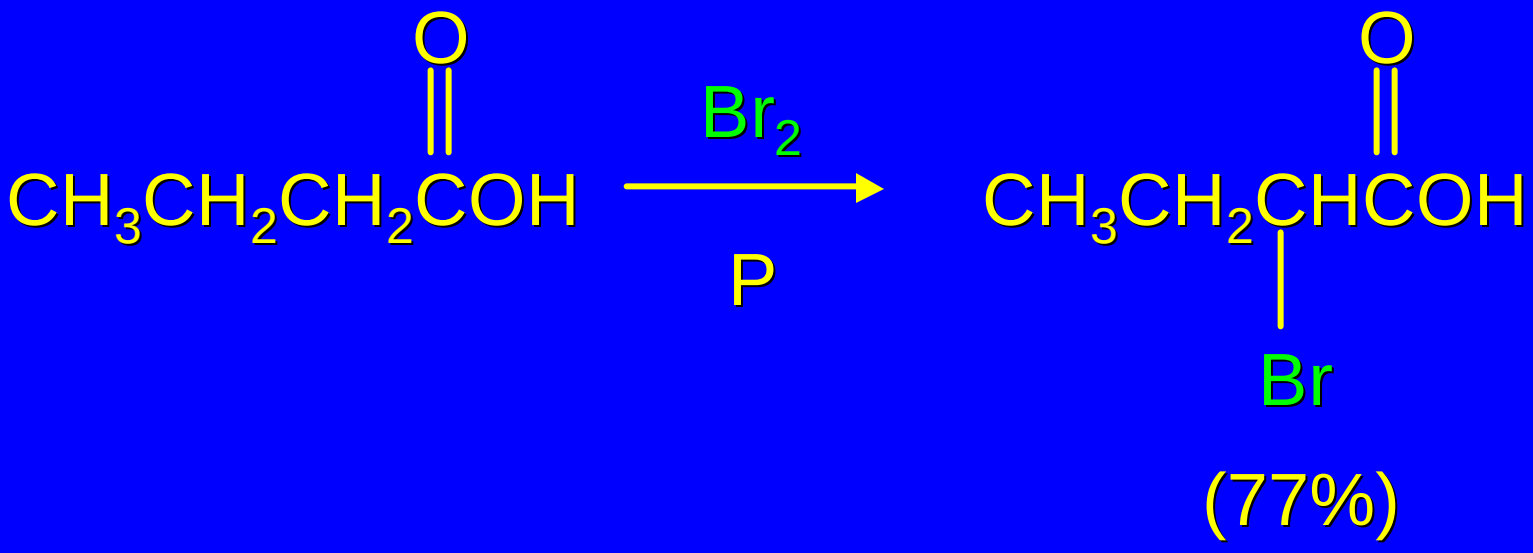
reaction works well if a small amount of phosphorus or a phosphorus trihalide is added to the reaction mixture

this combination is called the Hell-Volhard-Zelinsky reaction

Example

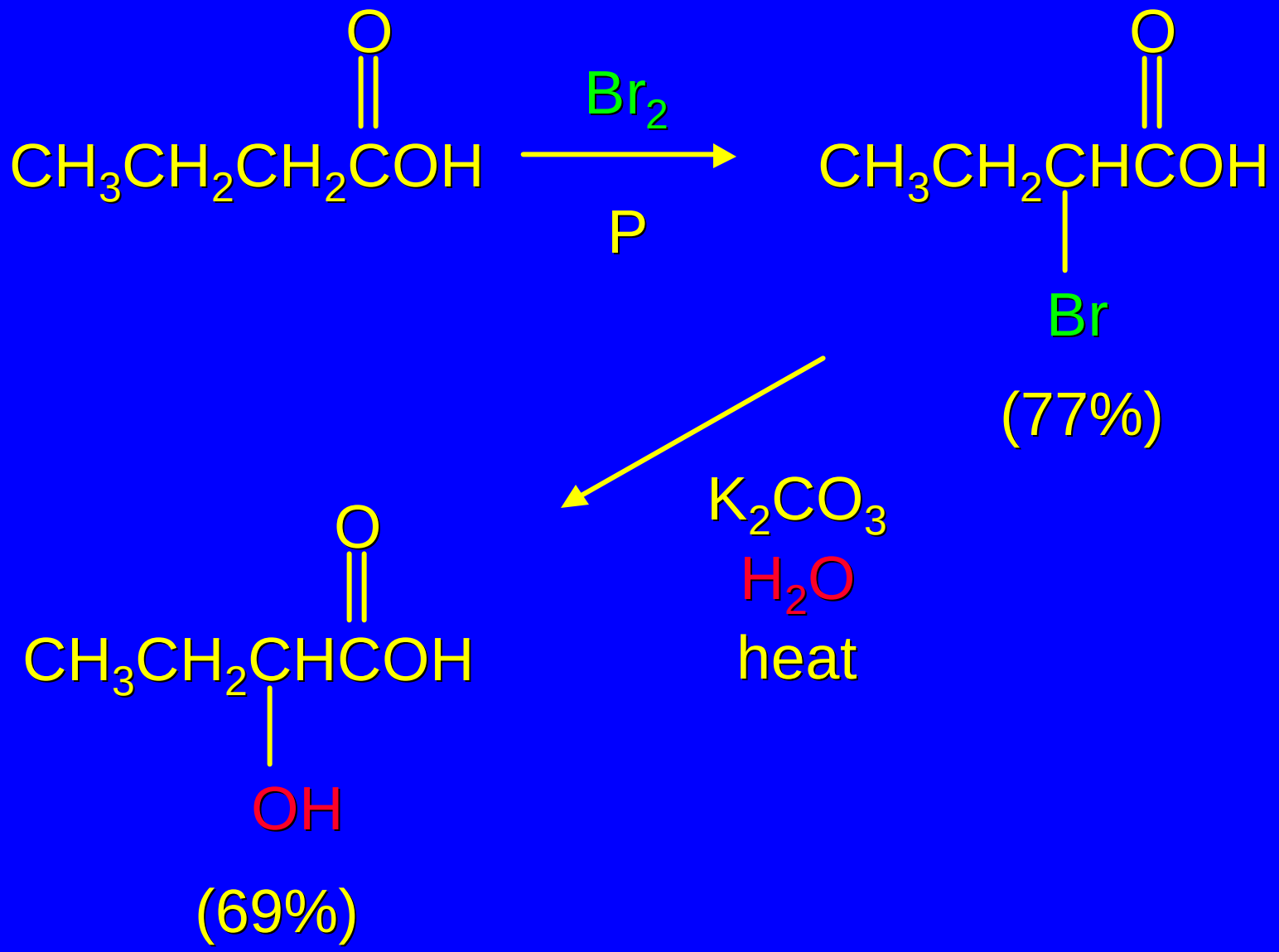


Value

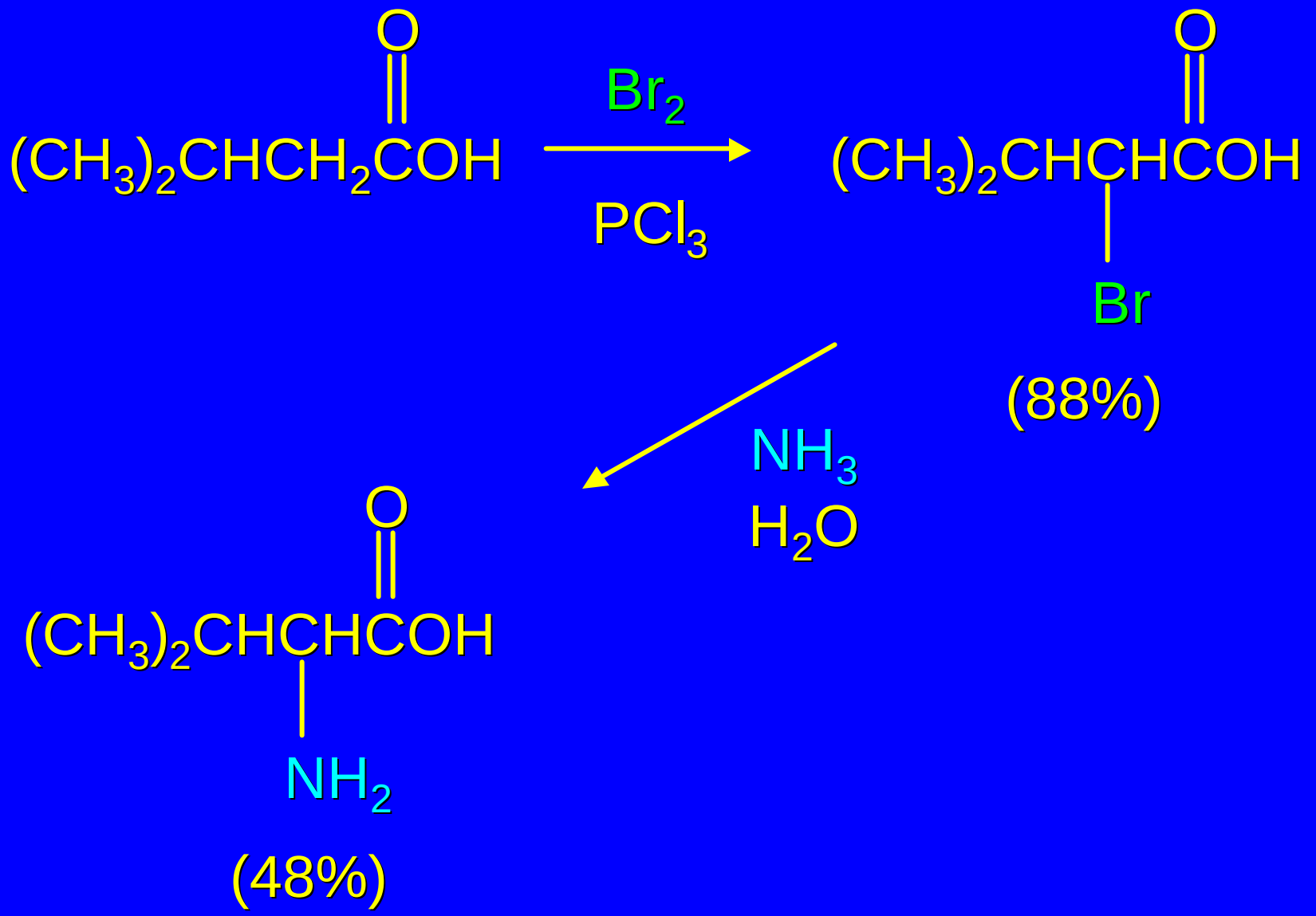


α-Halogen can be replaced by nucleophilic substitution

Value


O
CH3CH2CH2COH
Br2
P
O
CH3CH2CHCOH
Br
(77%)
K2CO3
H2O
heat
O
CH3CH2CHCOH
OH
(69%)

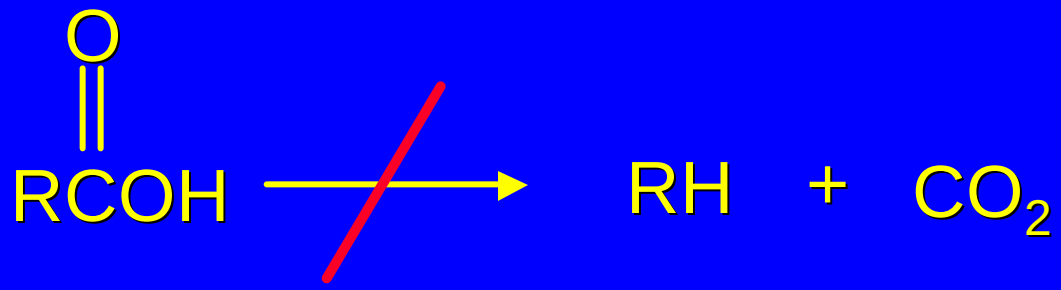
Synthesis of a-Amino Acids



19.17
Decarboxylation of Malonic Acid and Related Compounds

Decarboxylation of Carboxylic Acids

Simple carboxylic acids do not decarboxylate readily.



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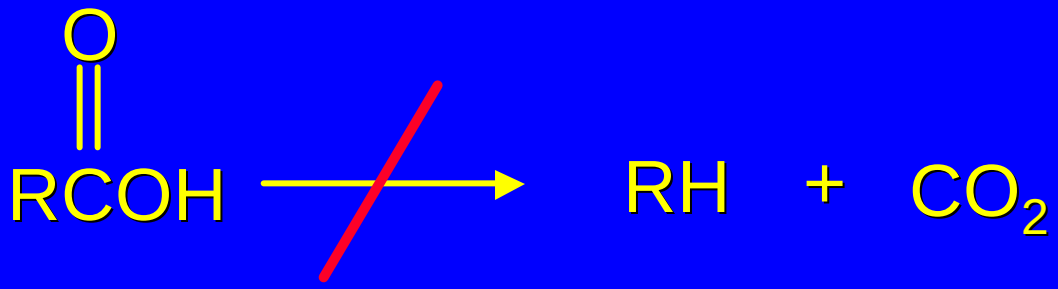
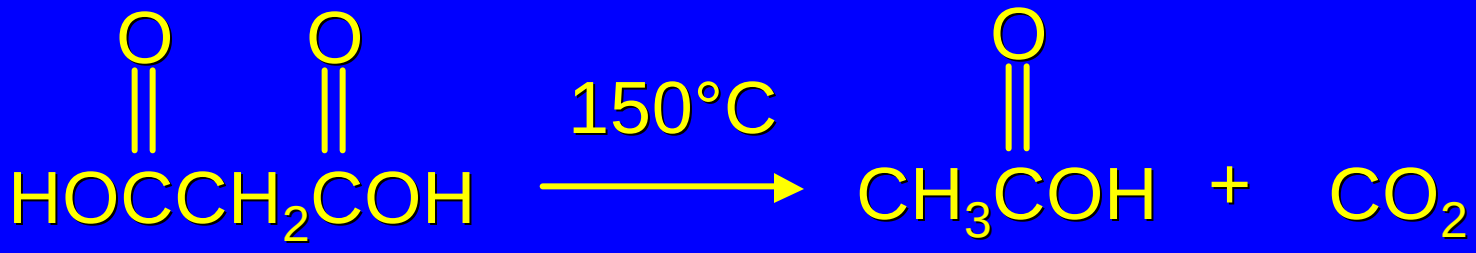
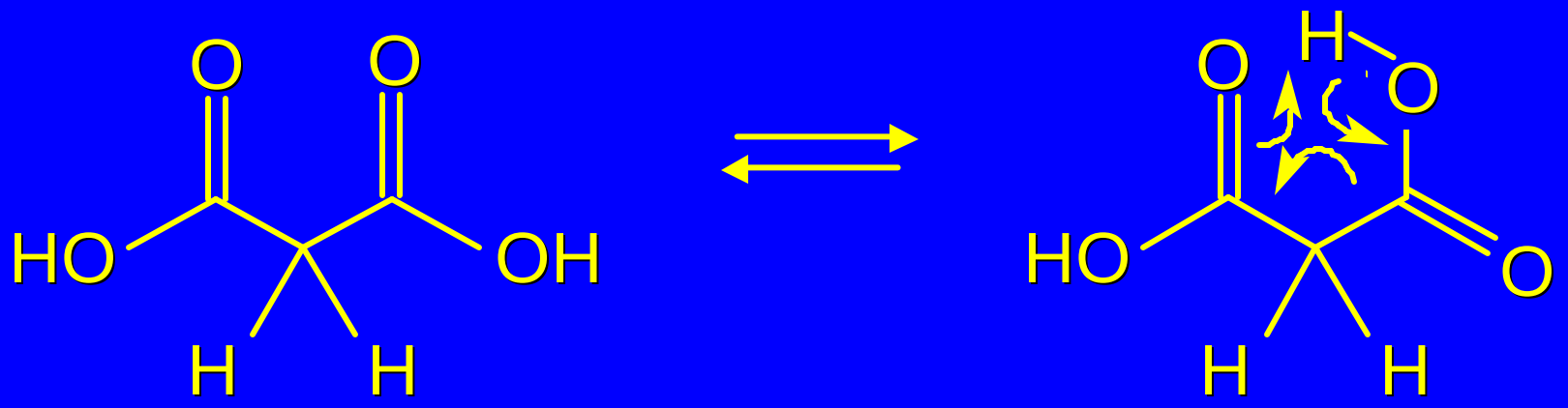


But malonic acid does.



Mechanism of Decarboxylation of Malonic Acid

One carboxyl group assists the loss of the other.



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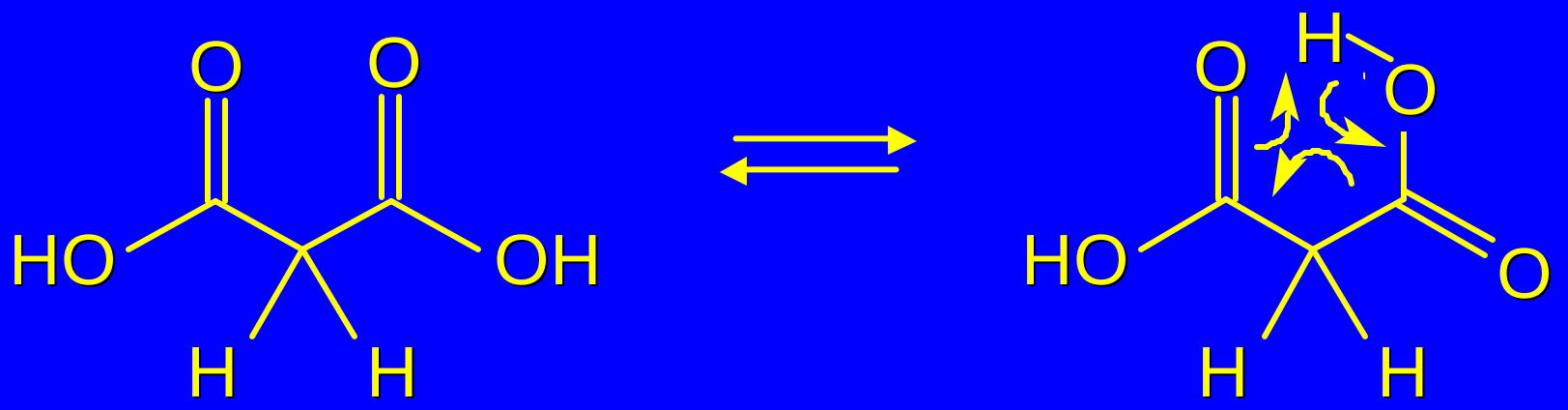
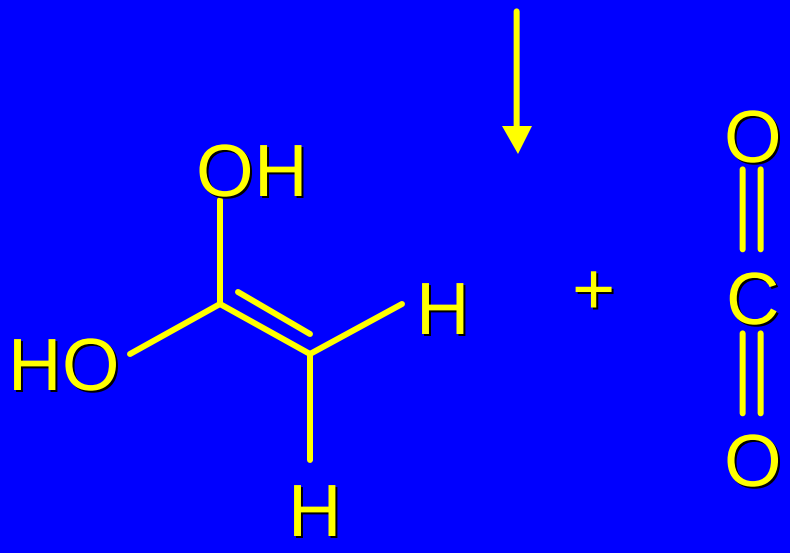


This compound is the enol form of acetic acid.



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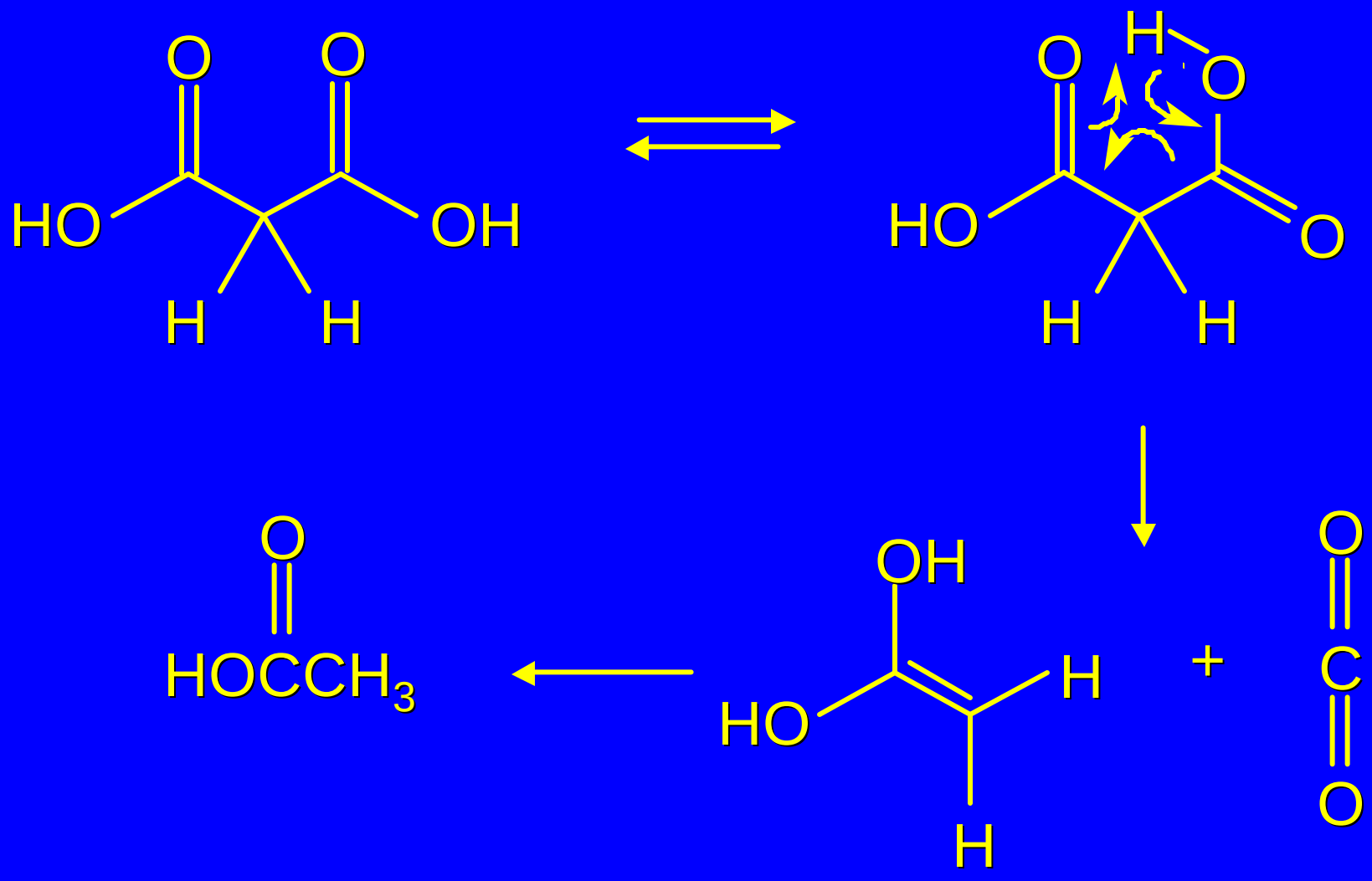

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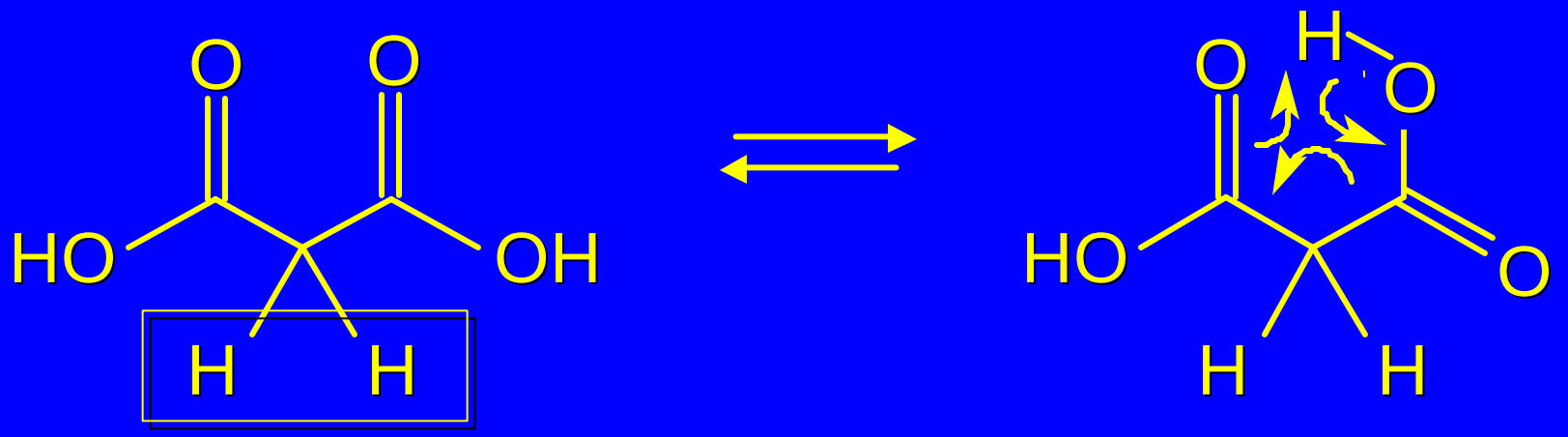
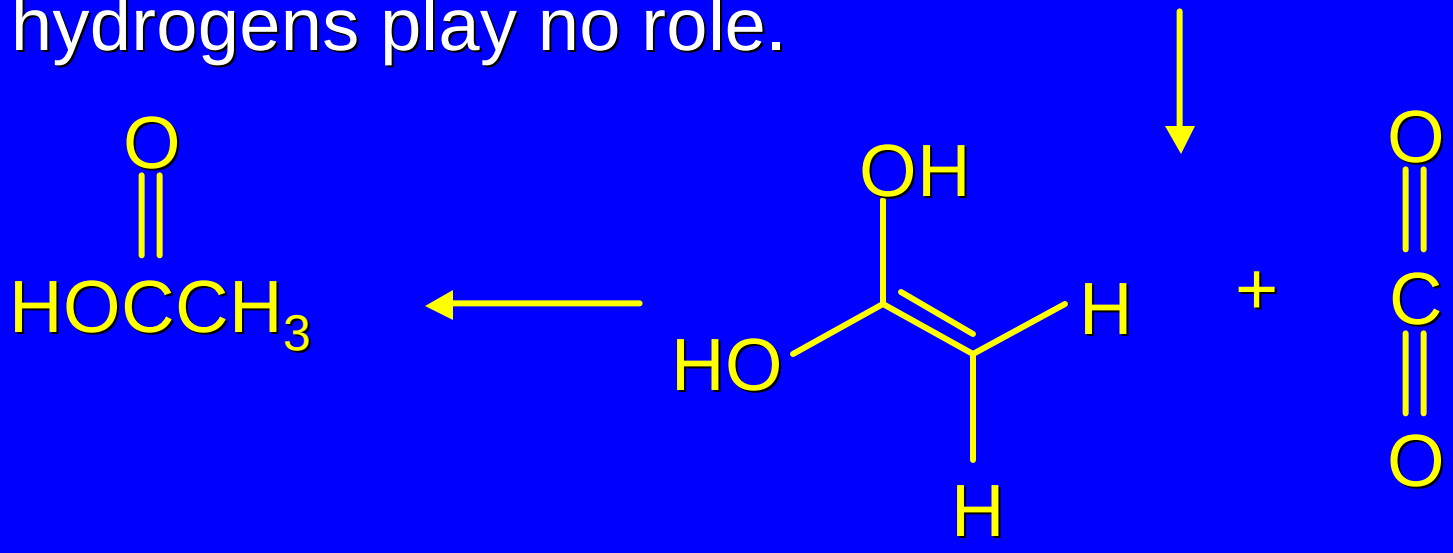


These hydrogens play no role.



Mechanism of Decarboxylation of Malonic Acid

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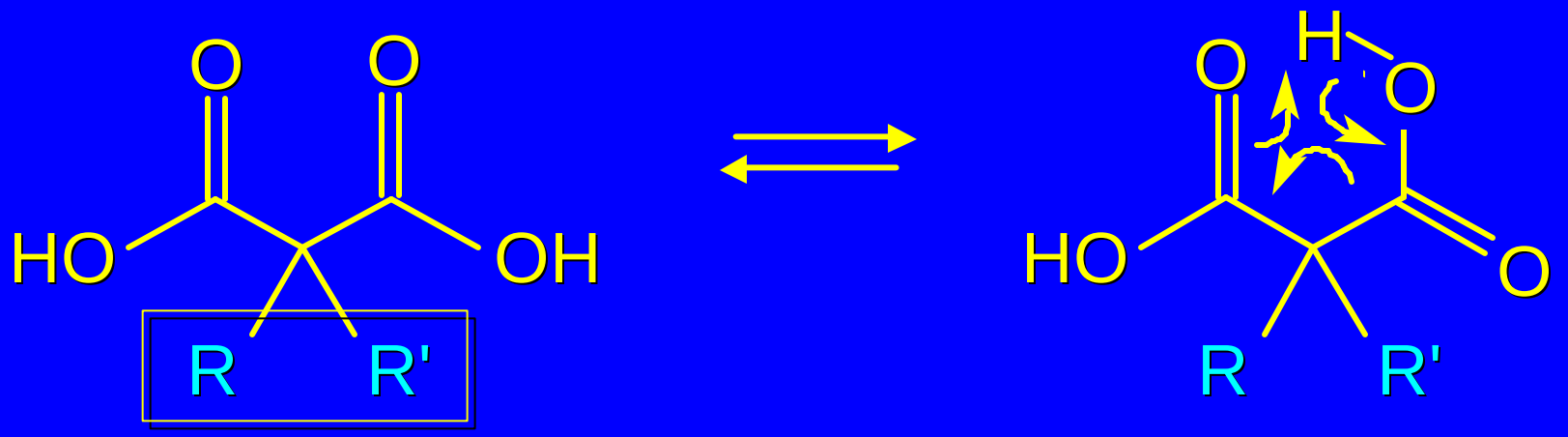
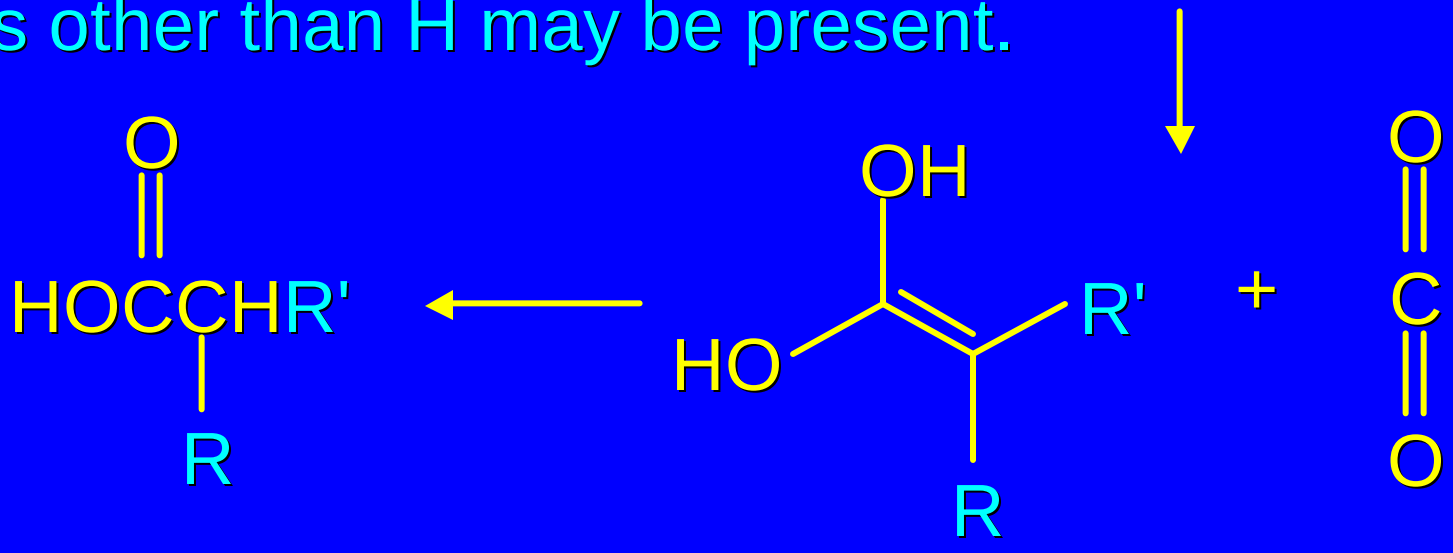
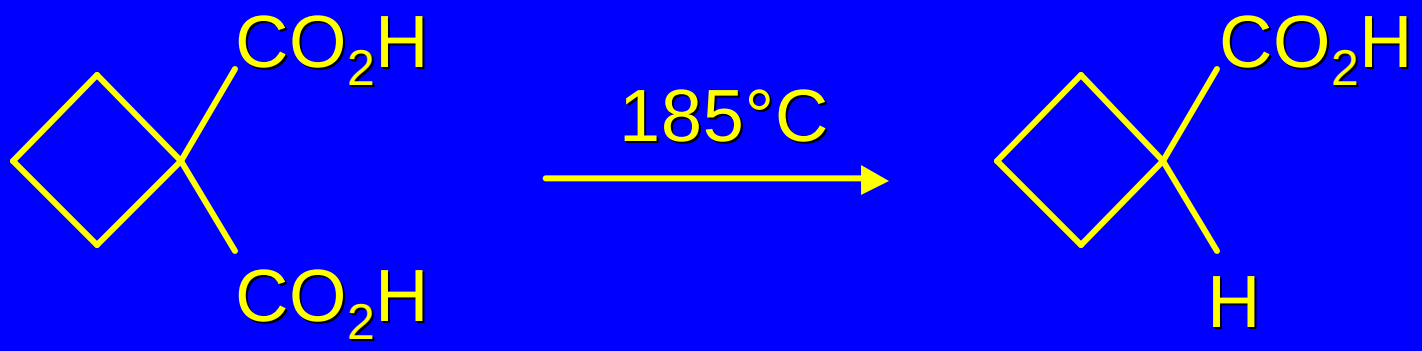


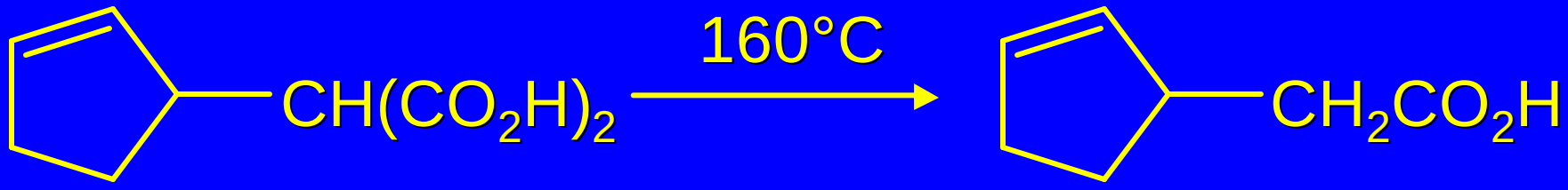
Groups other than H may be present.



Decarboxylation is a general reaction for 1,3-dicarboxylic acids



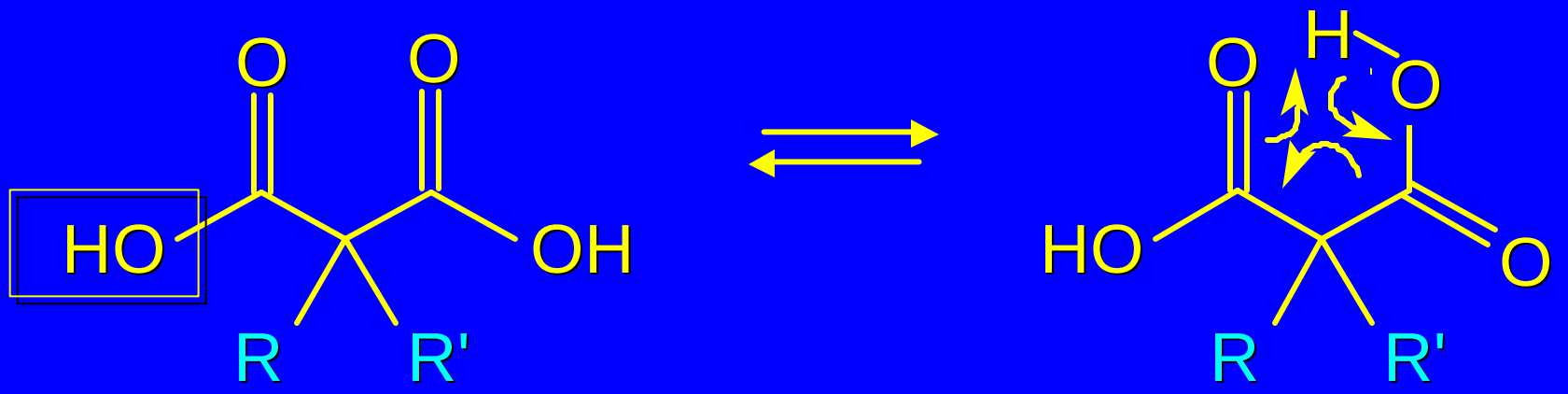
(74%)



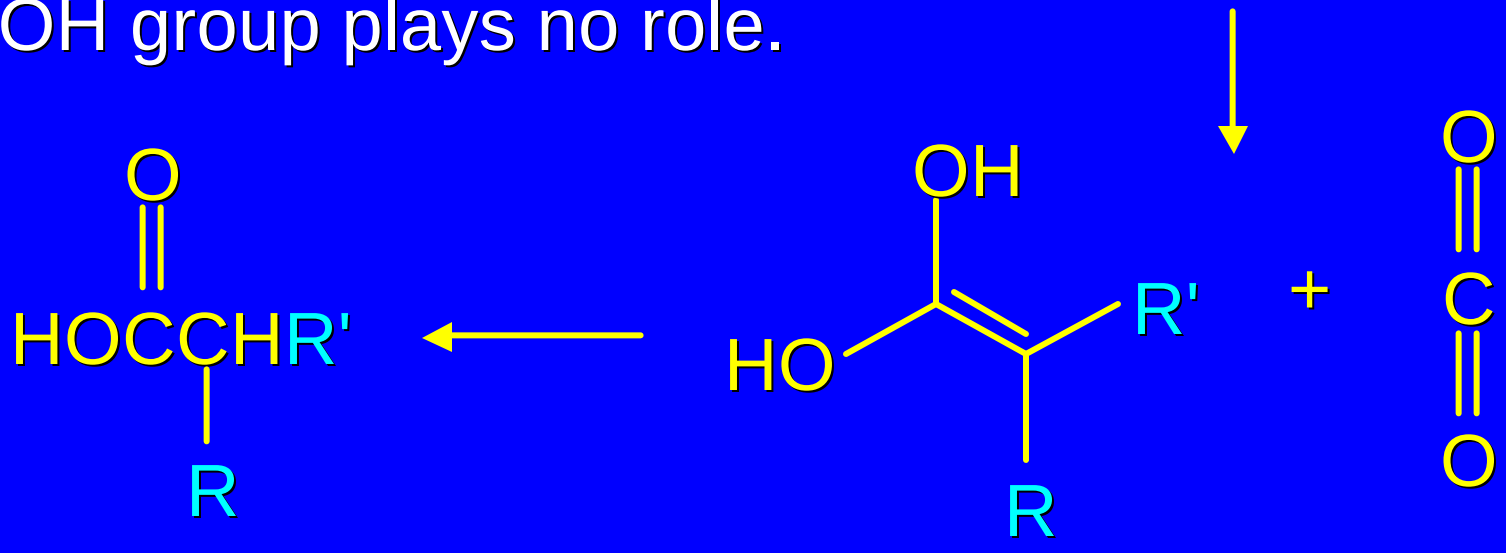
(96-99%)

Mechanism of Decarboxylation of Malonic Acid

One carboxyl group assists the loss of the other.



This OH group plays no role.



Mechanism of Decarboxylation of Malonic Acid

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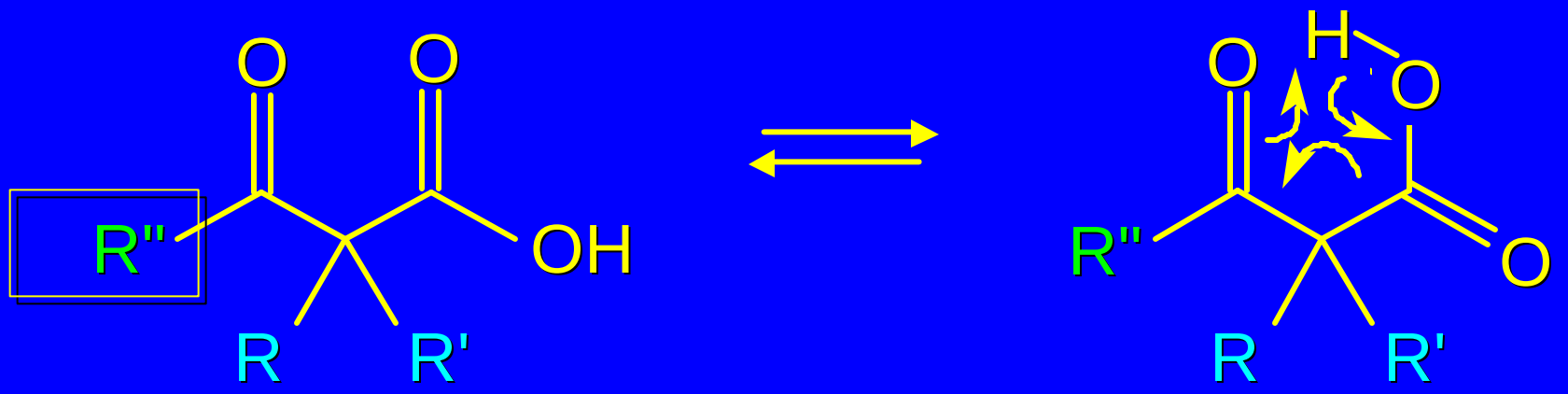
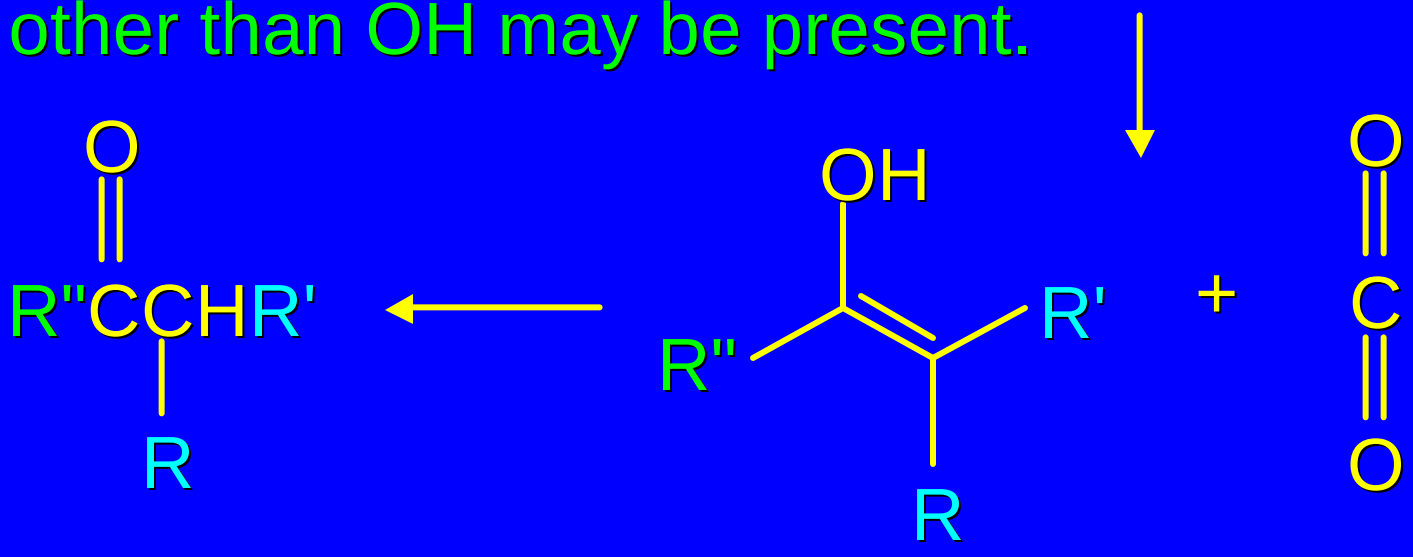
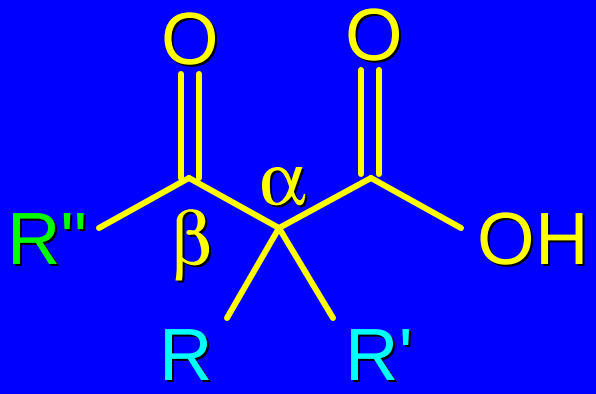


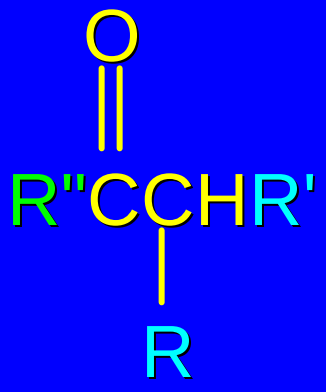
Groups other than OH may be present.



Mechanism of Decarboxylation of Malonic Acid



This kind of compound is called a β-keto acid.



Decarboxylation of a β-keto acid gives a ketone.

Decarboxylation of a b-Keto Acid