9.5

Acidity of Acetylene and Terminal Alkynes

Acidity of Hydrocarbons

In general, hydrocarbons are exceedingly weak acids

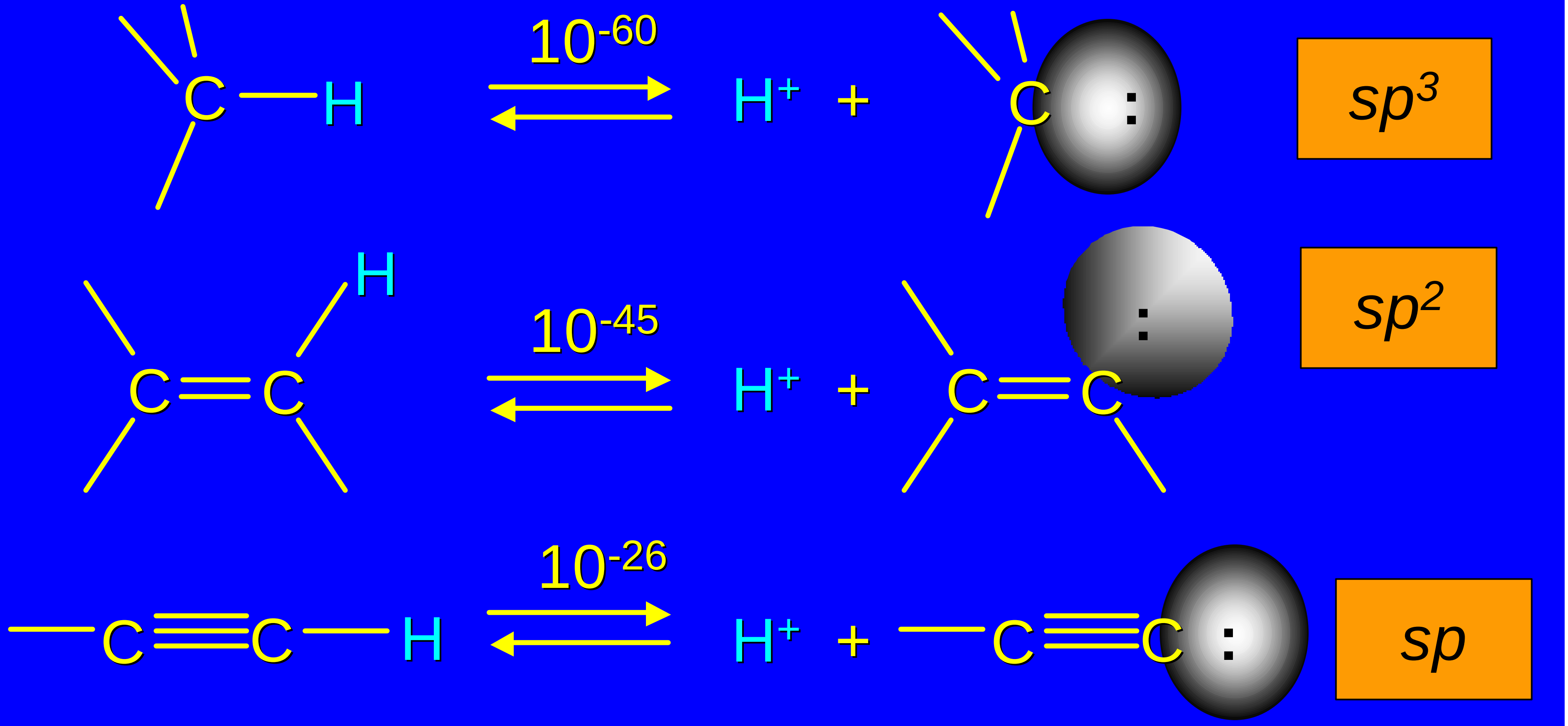
Compound	p*K*$_a$
HF	3.2
H_2O	16
NH_3	36
$H_2C{=}CH_2$	45
CH_4	60

Acetylene

Acetylene is a weak acid, but not nearly as weak as alkanes or alkenes.

Compound	pK_a
HF	3.2
H_2O	16
$HC\equiv CH$	26
NH_3	36
$H_2C=CH_2$	45
CH_4	60

Carbon: Hybridization and Electronegativity



Electrons in an orbital with more *s* character are closer to the nucleus and more strongly held.

Sodium Acetylide

Objective:

Prepare a solution containing sodium acetylide

$$\mathrm{NaC{\equiv}CH}$$

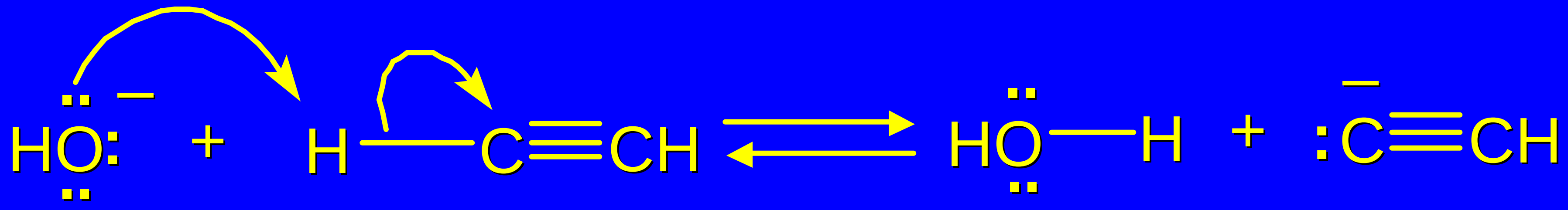
Will treatment of acetylene with NaOH be effective?

$$\mathrm{NaOH} + \mathrm{HC{\equiv}CH} \rightleftharpoons \mathrm{NaC{\equiv}CH} + \mathrm{H_2O}$$

Sodium Acetylide

No. Hydroxide is not a strong enough base to deprotonate acetylene.

$$\mathrm{NaOH} + \mathrm{HC{\equiv}CH} \rightleftharpoons \mathrm{NaC{\equiv}CH} + \mathrm{H_2O}$$



$$\mathrm{H\ddot{\underset{..}{O}}\!:^{-}} + \mathrm{H{-}C{\equiv}CH} \rightleftharpoons \mathrm{H\ddot{\underset{..}{O}}{-}H} + \mathrm{:\overset{-}{C}{\equiv}CH}$$

weaker acid

pK_a = 26

stronger acid

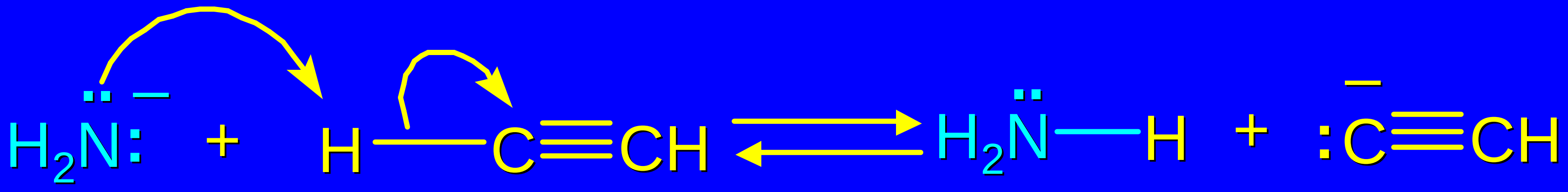
pK_a = 16

In acid-base reactions, the equilibrium lies to the side of the weaker acid.

Sodium Acetylide

Solution: Use a stronger base. Sodium amide is a stronger base than sodium hydroxide.

$$NaNH_2 + HC\equiv CH \rightleftharpoons NaC\equiv CH + NH_3$$



$$H_2\ddot{N}:^{-} + H-C\equiv CH \rightleftharpoons H_2\ddot{N}-H + :\overset{-}{C}\equiv CH$$

stronger acid
pK_a = 26

weaker acid
pK_a = 36

Ammonia is a weaker acid than acetylene.
The position of equilibrium lies to the right.

9.6

Preparation of Alkynes

by

Alkylation of Acetylene and Terminal Alkynes

Preparation of Alkynes

There are two main methods for the preparation of alkynes:

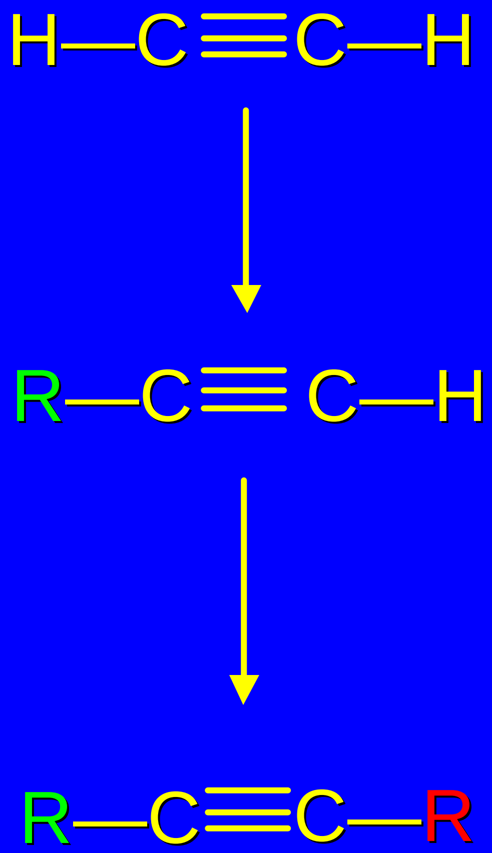
Carbon-carbon bond formation

alkylation of acetylene and terminal alkynes

Functional-group transformations

elimination

Alkylation of Acetylene and Terminal Alkynes



$$H-C\equiv C-H$$

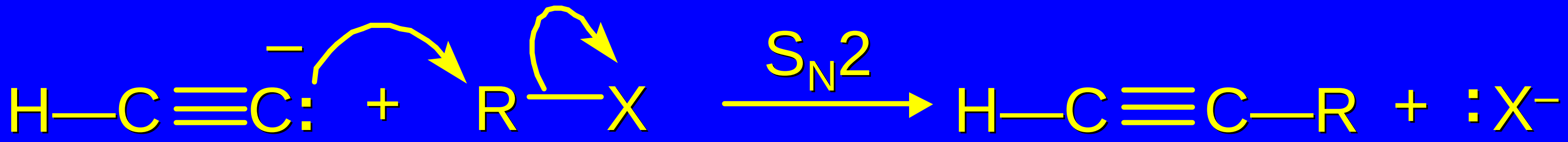
$$\downarrow$$

$$R-C\equiv C-H$$

$$\downarrow$$

$$R-C\equiv C-R$$

Alkylation of Acetylene and Terminal Alkynes



$$H{-}C{\equiv}\overset{-}{C}{:} + R{-}X \xrightarrow{S_N2} H{-}C{\equiv}C{-}R + {:}X^{-}$$

The alkylating agent is an alkyl halide, and the reaction is nucleophilic substitution.

The nucleophile is sodium acetylide or the sodium salt of a terminal (monosubstituted) alkyne.

Example: Alkylation of Acetylene

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}CNa$$

$$\Big\downarrow \; CH_3CH_2CH_2CH_2Br$$

$$HC{\equiv}C{-}CH_2CH_2CH_2CH_3$$

(70-77%)

Example: Alkylation of a Terminal Alkyne

$$(CH_3)_2CHCH_2C{\equiv}CH$$

$$\Big\downarrow \; NaNH_2,\ NH_3$$

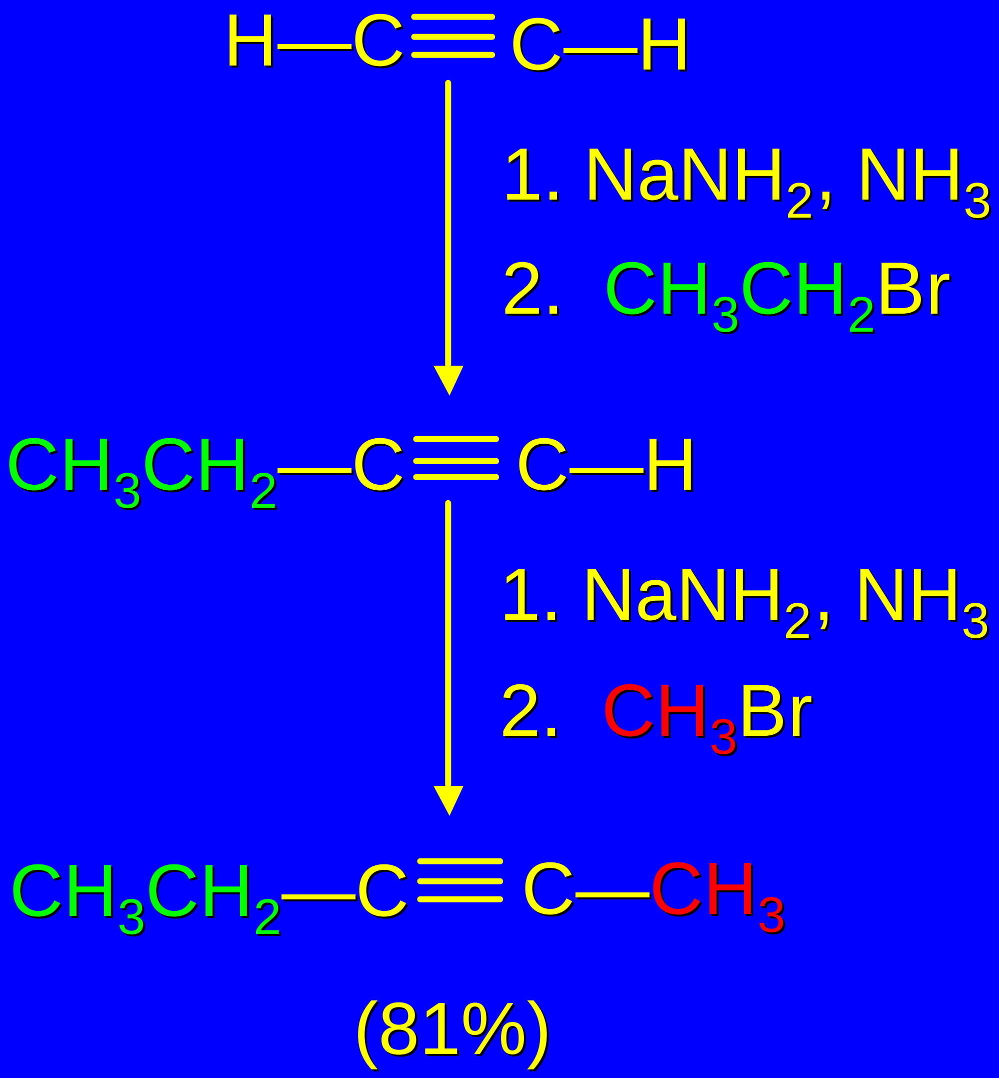
$$(CH_3)_2CHCH_2C{\equiv}CNa$$

$$\Big\downarrow \; CH_3Br$$

$$(CH_3)_2CHCH_2C{\equiv}C{-}CH_3$$

(81%)

Example: Dialkylation of Acetylene



$H—C{\equiv}C—H$

1. $NaNH_2$, NH_3
2. CH_3CH_2Br

$CH_3CH_2—C{\equiv}C—H$

1. $NaNH_2$, NH_3
2. CH_3Br

$CH_3CH_2—C{\equiv}C—CH_3$

(81%)

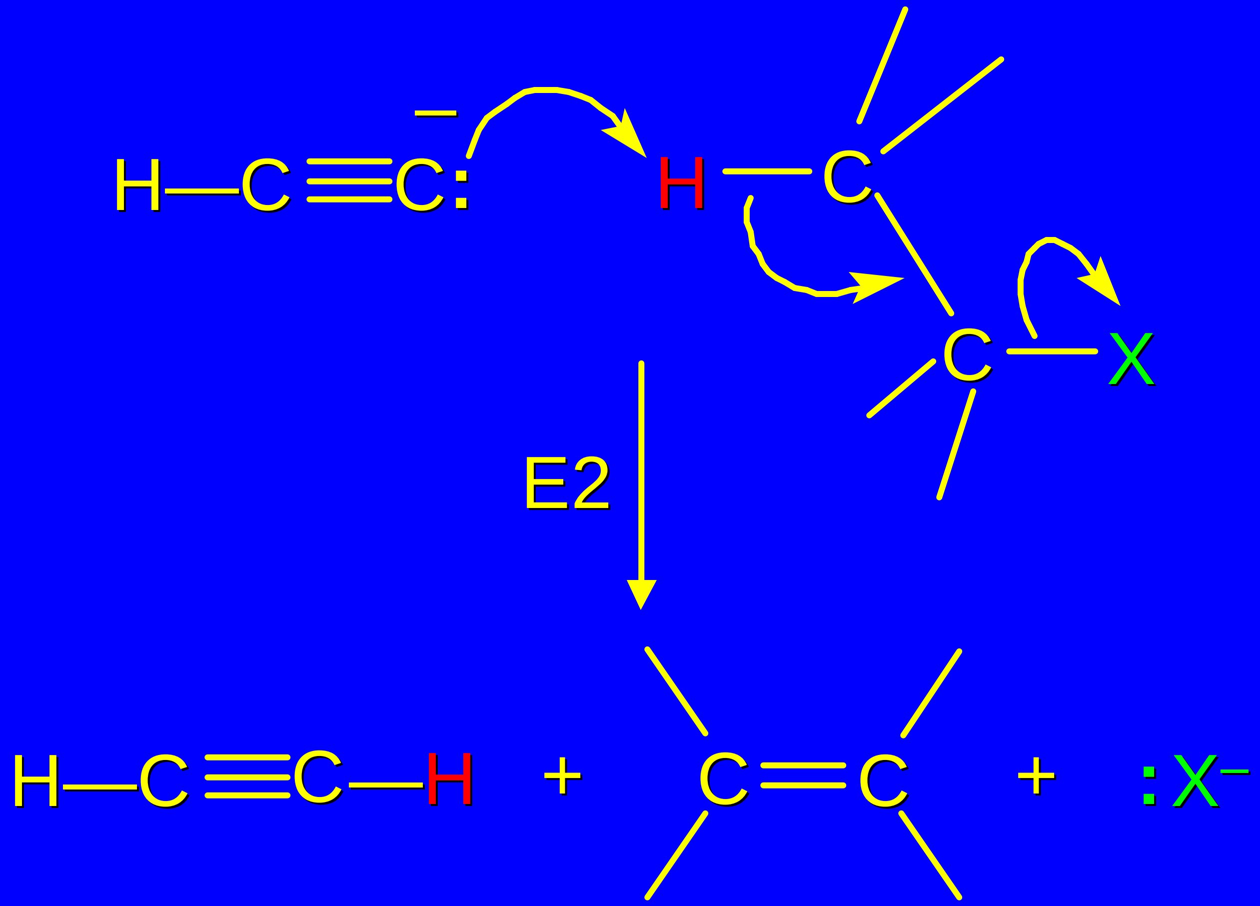
Limitation

Effective only with primary alkyl halides

Secondary and tertiary alkyl halides undergo elimination

Acetylide Ion as a Base

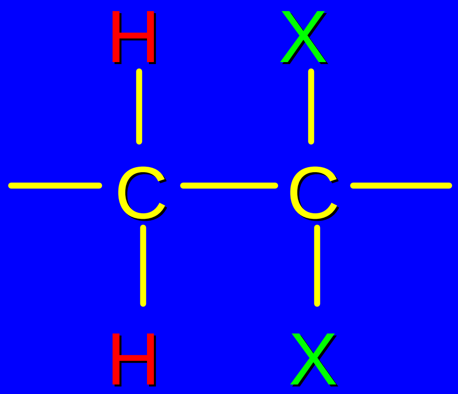
E2 predominates over S_N2 when alkyl halide is secondary or tertiary



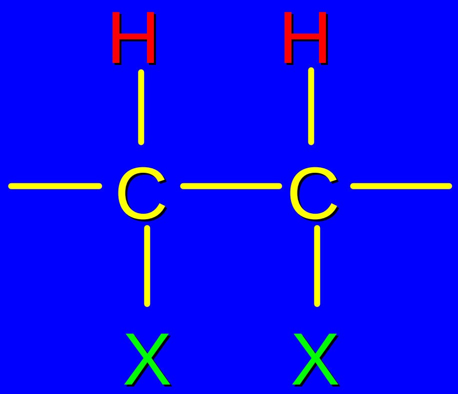
9.7

Preparation of Alkynes by Elimination Reactions

Preparation of Alkynes by "Double Dehydrohalogenation"



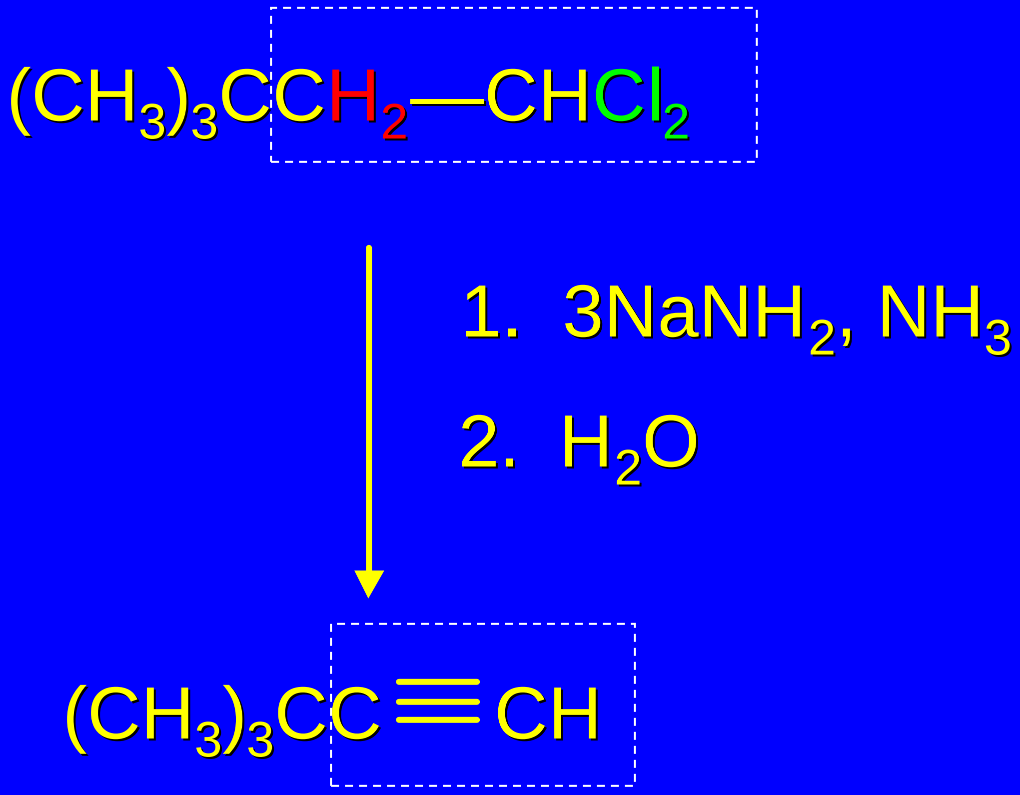
Geminal dihalide



Vicinal dihalide

The most frequent applications are in preparation of terminal alkynes.

Geminal dihalide Æ Alkyne



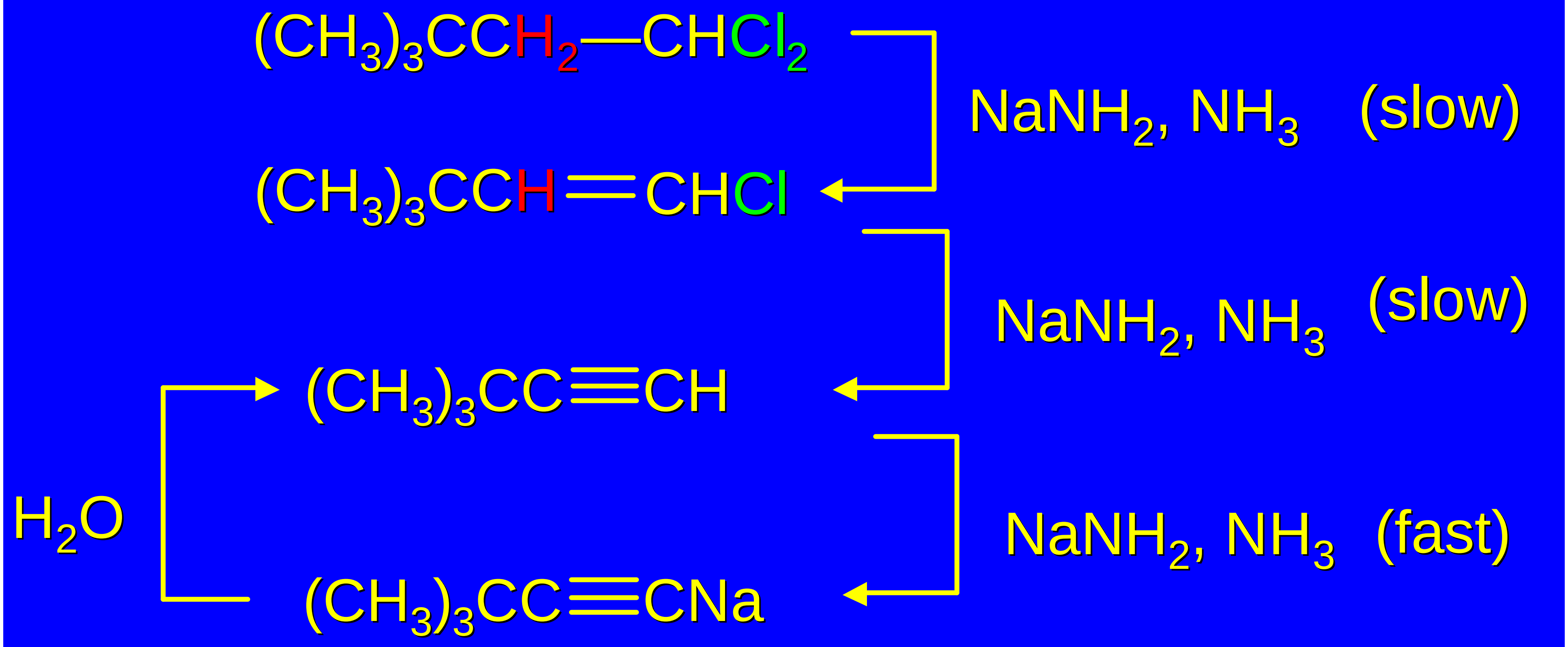
$$(CH_3)_3CCH_2\text{—}CHCl_2$$

1. $3NaNH_2$, NH_3
2. H_2O

$$(CH_3)_3CC\equiv CH$$

(56-60%)

Geminal dihalide Æ Alkyne



$(CH_3)_3CCH_2{-}CHCl_2$

$NaNH_2, NH_3$ (slow)

$(CH_3)_3CCH{=}CHCl$

$NaNH_2, NH_3$ (slow)

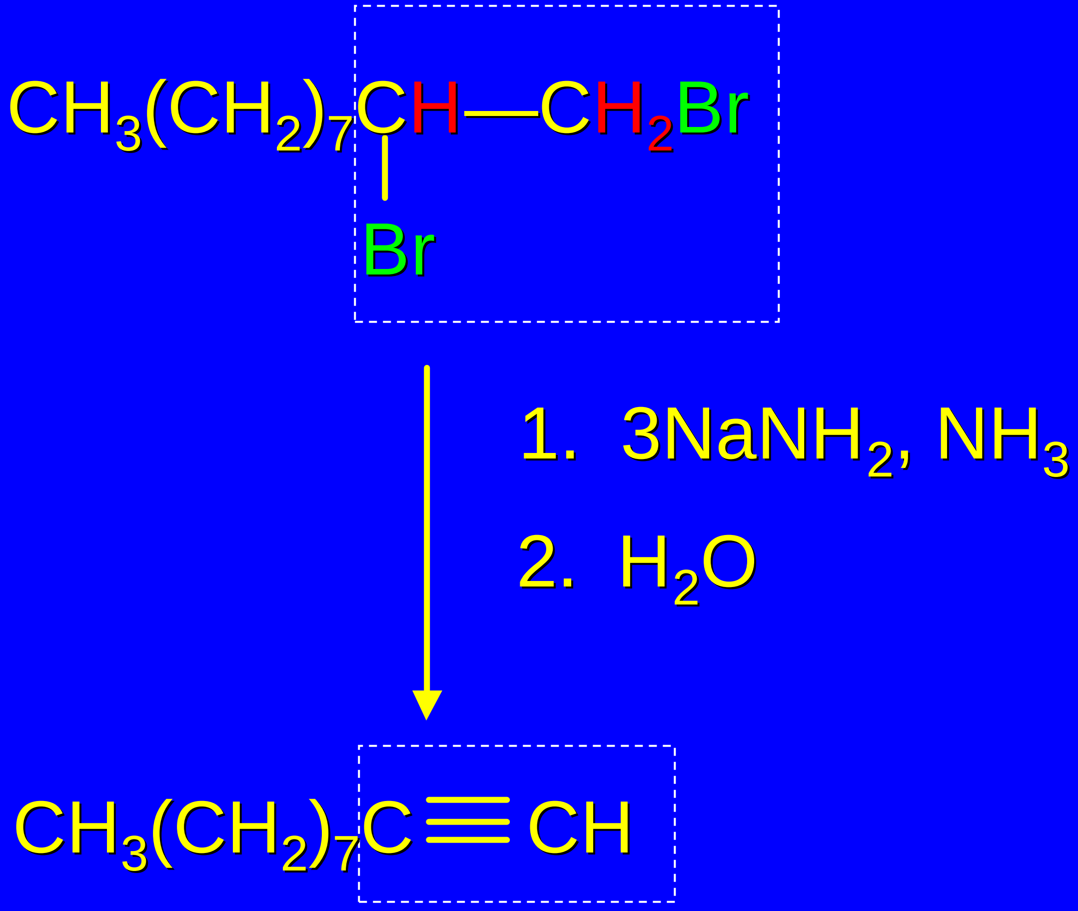
$(CH_3)_3CC{\equiv}CH$

H_2O

$NaNH_2, NH_3$ (fast)

$(CH_3)_3CC{\equiv}CNa$

Vicinal dihalide Æ Alkyne



$$\mathrm{CH_3(CH_2)_7}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}}\mathrm{H{-}CH_2Br} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. } \mathrm{3NaNH_2,\ NH_3}} \mathrm{CH_3(CH_2)_7C{\equiv}CH}$$

(54%)