$$
2 \sigma \text { bonds }
$$

Alkynes $-C \equiv C-$ sp hybridized $\left\{\begin{array}{l}2 x \text { sp-hybridized onsitals } \\ 1 \sigma \text { bond, } \\ 2 \times 2 p \text {-unhybridized orbitals }\end{array}\right.$
linear $2 \pi$ bonds.

$$
2 \pi \text { bonds }
$$

$\pi$-bonds (overtapping 2p-orsitals)
L) Nudeophile $\rightarrow \underset{\substack{\text { isolated }}}{\boldsymbol{u}} \pi-e^{\theta}$ density is reactive no resonave

2-types of Alkynes:

Terminal Alkgnes

$$
\text { r }-C \equiv c-H
$$

$$
R=\operatorname{cor} H
$$

Internal Alkynes

$$
\begin{aligned}
& R-C \equiv C-R \\
& R \neq H, R=\text { Carbon-Containing Stulf }
\end{aligned}
$$

Recall; the $\uparrow s$-character, the more stasle the anion. so $\rightarrow$ the terminal alkgne is relafively acidic.

$$
\begin{aligned}
& 1 \text { allayne for / NaNHI }= \\
& R-C \equiv C-H \xrightarrow{=} \xrightarrow{\text { NaqO } O: N H_{2}} \quad R-C \equiv C: \Theta+H-\ddot{N} H_{2} \\
& \text { pka } \sim 25 \quad \text { Pka } \sim 38
\end{aligned}
$$

Belause $p K_{a}=38>p K_{a} \approx 25$, the e.9. will faver the risht side

$$
10^{13}=10^{(88-28)}
$$

Terminal Alkyne anion:

The ONLY reaction to make a new $c-c$ bond (yet)

$$
\mathrm{H}_{3} \mathrm{C}-\mathrm{C} \equiv \mathrm{C}-\mathrm{H} \xrightarrow{\mathrm{Br}} \text { No } \mathrm{R}_{x n} \text { ! }
$$

we need a base to make $R-C \equiv C::^{\theta}, \pi$-bonds along cannot make a $c-c$ bond!

$$
R-C \equiv C-H \overbrace{2) R^{\prime}-\mathrm{Br}}^{\text {1) } 1.0 \mathrm{NaNH}_{2}} \quad R-C \equiv C-R^{\prime}
$$

order of addition matters!
Hydroboration- oxidation of alkynes
Recall:

$$
\approx \frac{1) \mathrm{BH}_{3}}{2) \mathrm{H}_{2} \mathrm{O}_{2} / \mathrm{NaOH}} \sim \mathrm{OH}
$$

$$
\text { (sic) }{ }_{2} B H=H-\underset{\text { B }}{\substack{\text { 'Antler" }} \text { Sterically hindered. }}
$$

$$
\mathrm{H}_{3} \mathrm{C}-\mathrm{C} \equiv \mathrm{C}-\mathrm{H}
$$

2) $\mathrm{H}_{2} \mathrm{O}_{2} / \mathrm{NaOH}$

Time out:

Time out:
Enols are not stable $\rightarrow$ they" react" further through a process called "tantomerization"
when we generate the end form, it will spontaneansly "tantomerize" to generate the more stable keto form
$c=0$ is stronger than $c=C$

Nomenclature for $c=0$ :

| 0 | $0_{0}^{0}$ |
| :---: | :---: |
| $-C_{-H}$ | ,$c_{-1}^{-C_{C}} C_{1}$ |
| aldehyde | ketone |

Tine in:

$$
\left.\left.\underset{\mathrm{H}_{2} \mathrm{O}}{\mathrm{H}_{2}-4} \underset{\mathrm{HO}}{\mathrm{H}_{\mathrm{H}}}\right] \stackrel{\mathrm{M}_{0}}{ }\right]
$$

making Alkynes
$L \underbrace{\text { vicinal }}_{\text {next to }} \underbrace{\text { Dihalides }}_{2 "}$



$$
R-C \equiv C-R^{\prime}
$$

Internal Alkyne


1) 3.0

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

pk $050 \quad$ H
2) $\mathrm{HCl} / \mathrm{H}_{2} \mathrm{O}$

$$
\downarrow_{1} \mathrm{St}_{:-\mathrm{NH}_{2}}
$$

mild
$\downarrow^{2 n d} \theta_{: \ddot{N}} H_{2}$
$R-C \equiv C-H \rightarrow W$ holt stop there! $b / c$ the $H$ is more pka~25 acidic than the H -atoms in
e. 9

2 molecules:
 starting material
$L_{1 s t}$
$L_{2 n}$ 有

$$
\begin{array}{r}
R-C \equiv C-H \\
\quad 3^{3-d O}: \ddot{N} H_{2} \\
\mid R-C \equiv C: \theta\rceil
\end{array}
$$

$$
[R-C \equiv C: \theta]
$$




Radicals
$c \cdot \stackrel{C}{C}$
: Br 。

7 valence $e^{0} s$

- Partially filled $2 p$ orbital $\rightarrow$ unpaired $e^{\theta}$
- neutral formal chase
- Reactive
making Radicals: break a weak bond $w /$ heat $(\Delta)$ or light (Lv)
radical reactions start (initiate) when a radical forms

Es.:

 bond

Radical stability $\rightarrow$ Think stability of Catsoletion, but no inductive effect
$\rightarrow$ Hyper Conjugation
$\rightarrow$ Resonance $($ es. $\quad \rightarrow$ V $)$
Radicals: $-\mathrm{CH}_{3} \xrightarrow[\mathrm{H}^{2}]{\mathrm{H}} \mathrm{C}-\mathrm{CH}_{3}$



$\frac{\text { methyl } 1^{10} 3^{\text {more substituted }} 2^{00}}{\text { mole stable }}$

Hyperconjugation: overlap of nearby $\sigma$-bonds and the empty/partialy filled up orbital


