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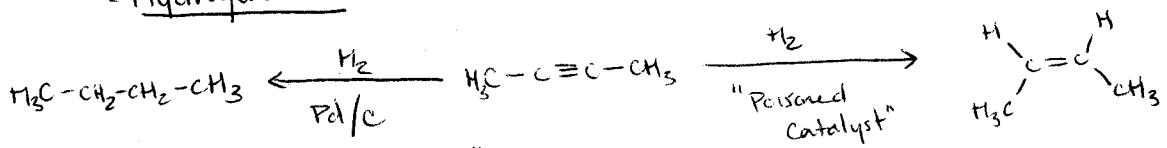
EXAM 3: MONDAY - ROOM ASSIGNMENTS AS BEFORE

RECALL: Reactions of Alkynes

- Hydrogenation



Syn Addition

Alternative Method to produce trans-alkenes (Anti-addition of H_2)

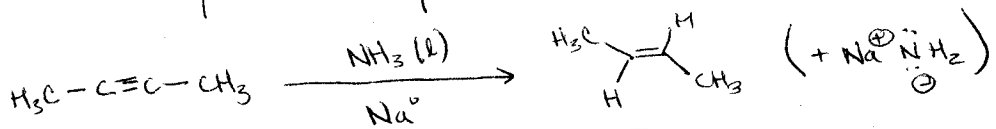
"Dissolving Metal Reduction"

$Na^\circ + NH_3(l) \longrightarrow Na^\oplus + e^\ominus(NH_3)_n$

↑ Sodium Metal

└ "solvated electrons" - electrons stabilized by a number (n) of ammonia molecules

Use this reagent for Alkyne Reduction



trans

See text for mechanism

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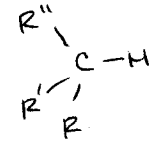
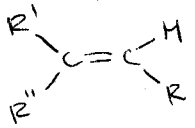
Hydrocarbon pka values:

Alkane (sp^3)



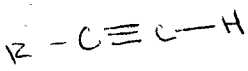
pka ~55

Alkene (sp^2)



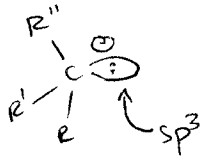
pka ~42

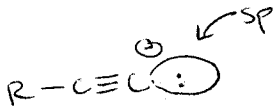
Alkyne (sp) *



pka ~25

Rationale: Consider Conjugate Bases





Least stable carbanion ⟵ Most stable Carbanion

Least 's'-character in orbital bearing the lone-pair ⟵ Most 's'-character in orbital bearing the lone-pair

* More 's'-character in lone-pair orbital leads to greater stability

→ 's' orbitals are closer to nucleus ("more electronegative")

Sp → "Happier" bearing lone-pair compared to sp^2 or sp^3 orbitals

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Practical Ramification: We can generate alkyne carbanions (aka. "acetylide" anions) via deprotonation (ex: with $Na^{\oplus}\ {}^{\ominus}NH_2$)

Recall: H_2NH ← pka ~35

Thus:

$R-C\equiv C-H \xrightarrow[(\text{"sodium amide"})]{NaNH_2} R-C\equiv C^{\ominus}\ {}^{\oplus}Na + (NH_3)$

[Use as nucleophile to form C-C bonds with Alkyl halides!!]

WOOHOO!!!

Ex: $H_3C-C\equiv CH \xrightarrow[2)\ \sim\!\!-Br]{1)\ NaNH_2} CH_3-C\equiv C-\sim$ (New C-C bond)

(S_N2 Rxn) ($H_3C-C\equiv C-CH_2CH_2CH_3$)

LIMITATION: • Requires 1° Alkyl halide electrophile
• The use of 2° Alkyl halides results in elimination ⇒ E2

*NOTE: Deprotonation to generate $C^{\ominus}$ vs. Metal-halogen exchange for making grignard (R-MgX) or organolithium (R-Li) reagents.

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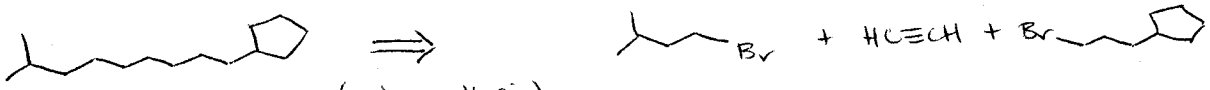
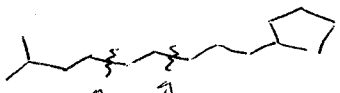


(Retrosynthesis)

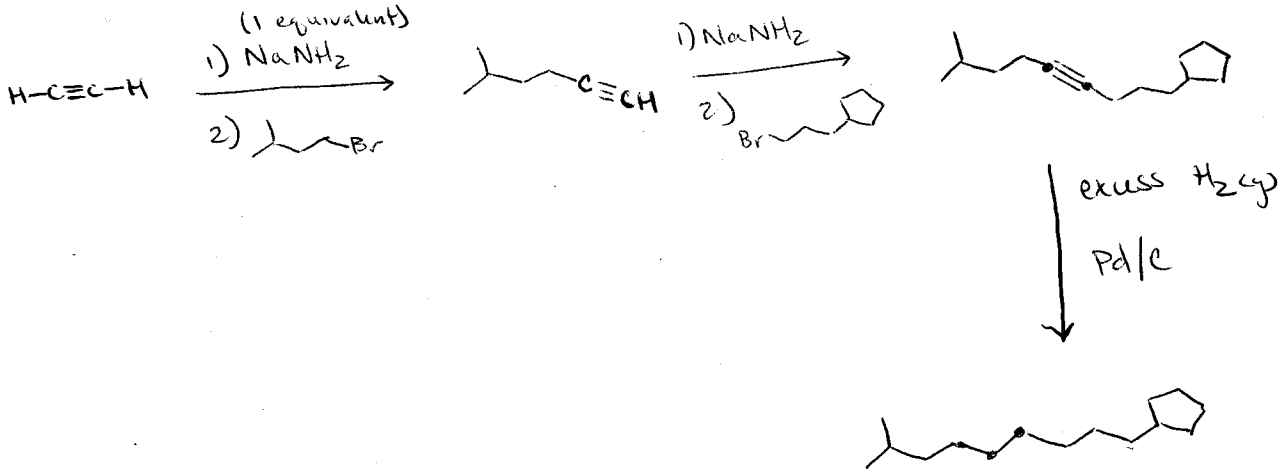
"could come from"
"working backwards"

I.e:



Make these C-C bonds by acetylide S_N2 rxn with alkyl-halide

So, in the forward direction, our proposed synthetic route looks like:



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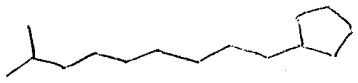


other routes are possible...?

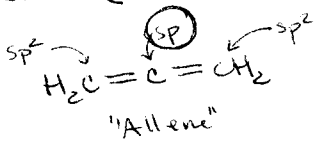
Chapter 15 - Dienes, Resonance, Aromaticity

Rec. Problems: 3-5, 11-24, 27-30, 33-45, 50-73

"Diene" = Molecule with 2x double bonds (C=C)
("di-alkene")

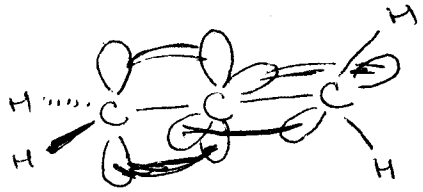
* 3 classes of dienes - Based on spacing between C=C units

① Allenes (or cumulenes)



"Allene"

Consider:



"Twist" along the length of the Allene!

(* see text for ramifications of this twist for chirality)

② Conjugated Dienes - C=C units are immediately adjacent

ex. 1,3-butadiene

$H_2C=C-C=CH_2$

(Note: Sometimes structure prevents conjugation)

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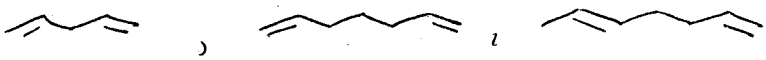
③ "ordinary Dienes" - At least one sp^3 carbon between the 2 C=C units

ex:  etc...