① WEEK 2: CONJUGATION & AROMATICITY (Chapter 13)

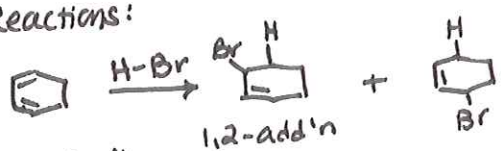
Announcements: Labs start this week!

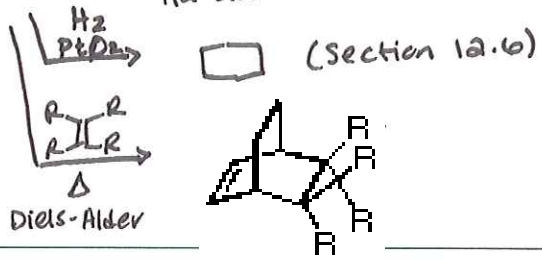
② Recall (last week):

Conjugated Systems

- arrangement of π-bonds in a 1,3- fashion.

Reactions:



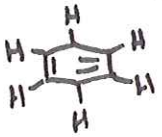


③ This week:

Aromatic Systems

Planar, cyclic, fully conjugated molecules having $4n+2$ π e⁻s, where n = integer (0, 1, 2, 3...)

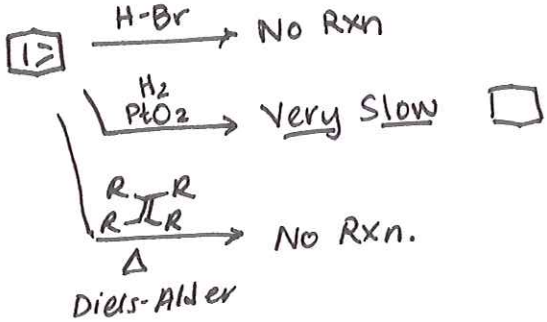
ex: Benzene



$= C_6H_6$

1) Planar
2) Cyclic
3) Fully conjugated
4) 6π e⁻s → $4n+2=6$, $4n=4$, $n=1$

④ Benzene = stable & not very reactive:



We are going to discuss why benzene is so stable (not just a conj. polyene) this week...

⑤ Structure of Benzene?

C_6H_6, first isolated from whale blubber

Proposals:

1) Sir James Dewar — WRONG!

"Dewar" Benzene

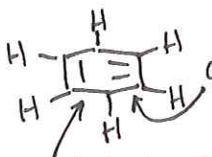
2) Albert Ladenburg — WRONG!

"Ladenburg" Benzene

3) Friedrich Kekulé

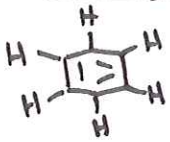
Cyclohexatriene

Almost right.



Alternating single & dbl bonds

⑥ Current Structural Understanding of Benzene



1) Regular hexagon
2) All C-C bond lengths = 1.39Å
3) Each C → sp^2 hybridized.

Resonance Depiction:

Dbl bond character between all C's!

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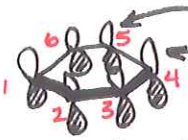
"Quick" Orbital Depiction:



2p orbitals (all parallel)

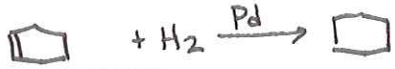
- Orbital overlap among all neighboring C atoms
  - ↳ DELOCALIZATION
- Form circle of e⁻ density above & below ring.

Can draw as 

↑ Circle denotes 2p overlap

(8) Quantifying Delocalization Energy:

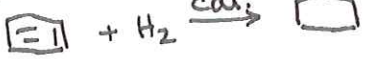
Heats of Hydrogenation:



cyclohexene

$\Delta H = -28.6 \frac{kcal}{mol}$ "exothermic"

Hypothesize/Guess:



$\Delta H \approx 3 \times (-28.6 \frac{kcal}{mol}) = -85 \frac{kcal}{mol}$

Actual:

$\Delta H = -49.3 \frac{kcal}{mol}$

$\Delta\Delta H$ (guess vs. actual) $= 32.9 \frac{kcal}{mol}$

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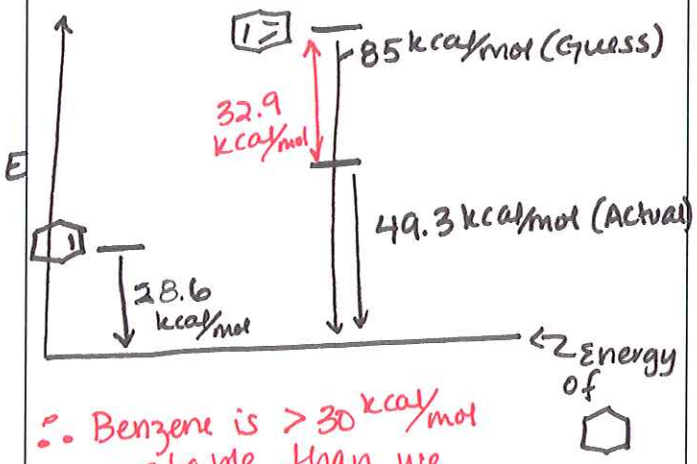
Energy Diagram:



∴ Benzene is > 30 kcal/mol more stable than we would expect. This 30 kcal/mol = delocalization energy (stabilizing)

(10) Aromaticity: Aromatic compounds are stable b/c of this delocalization energy.

Is benzene the only aromatic cmpd?

NO.

Criteria for Aromaticity:

1) Molecule must be cyclic.
2) Fully conjugated (2p orbital on every atom in ring)
3) Molecule is planar

ex)  Benzene is planar. 2p orbitals can overlap. Delocalization ✓

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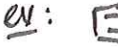
ex:  not aromatic. not planar

cyclooctatetraene

lost overlap; broke connectivity.

(12)

4) Must have $(4n+2)$ π electrons, ⇒ Hückel's Rule n = integer $(0, 1, 2, \ldots)$

ex:  → 6 π e⁻s

$4n + 2 = 6$

$4n = 4$

$n = 1$ OK!

Cyclic ✓ Fully conj ✓ Planar ✓

ex:  cyclobutadiene

Cyclic ✓ Fully conj ✓ Planar ✓

4 π e⁻s ⇒ $4n+2 = 4$

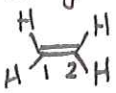
$4n = 2$

$n = 1/2$

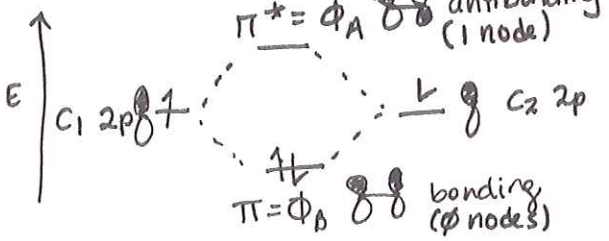
Not an integer → NOT AROMATIC!!!

(13) **Why does Hückel's Rule work?**

Molecular Orbital Diagrams:

Recall: Ethylene 

π-bond: $2p_{C_1} + 2p_{C_2}$



2 2p orbitals ⇒ 2 MO's (π, π*)

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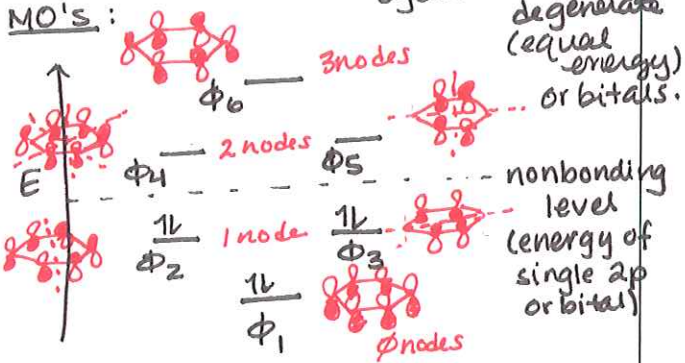
Benzene (6 π e-s) 1:

6 2p orbitals ⇒ 6 MO's

Cyclic ⇒ some degenerate (equal energy) orbitals.

MO's:



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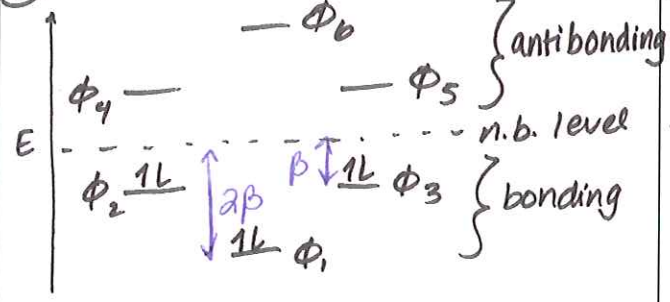


New unit for energy:

$\beta = -18$ kcal/mol

Note: All bonding orbitals filled & no e-s in antibonding orbitals.

(16) **Frost Circle**: easily generates molecular π orbitals for planar, cyclic, fully conjugated molecules.

ex: benzene 1:

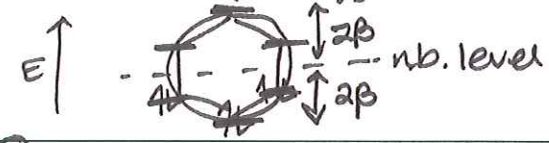
① Draw Circle

② Draw ring correspondingly to molecule inside circle w/ vertex down.

③ where ring meets Frost's Circle = π molecular orbital!

④ Cut Frost's circle in half = n.b. level

Radius = 2β energy units



(17)

⑤ Put in e-s (above) (bottom up).

Frost Circle/MO's for cyclobutadiene: 1:1

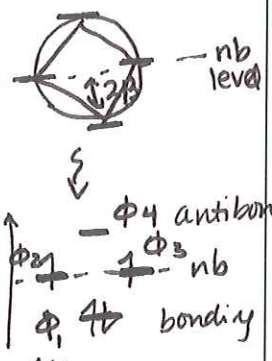
① Draw circle

② Ring w/ vertex down

③ Intersections = Φ's.

④ Find nb level.

⑤ Put in e-s (4 π e-s)



Not stable!

Unpaired e-s @ nonbonding level ⇒ Radical Character.

$4n+2 \neq 4 \Rightarrow n = 1/2$

NOT AROMATIC.

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Hückel's Rule w/ MO's in Mind:

When $4n+2$ & n = integer: all e-s will be in bonding MO's (stable). ⇒ AROMATIC.

When $4n+2$ & $n \neq$ integer, there will be unpaired e-s @ the nonbonding level (unstable).

↳ ANTIAROMATIC!

(19) Examples: Aromatic or Not?

① Neutral Compounds

Substituted Benzenes

Toluene

① cyclic ✓
② Fully conj ✓
③ Planar ✓
④ Hückel's Rule: ✓
$4n+2=6$
$n=1$

AROMATIC

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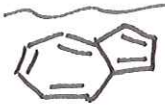
Polynuclear Aromatics

naphthalene

① cyclic ✓
② Fully conj ✓
③ Planar ✓
④ Hückel's Rule
$4n+2=10$
$n=2$

AROMATIC



① cyclic ✓
② Fully conj ✓
③ Planar ✓
④ $4n+2=10$ ✓
$n=2$

AROMATIC

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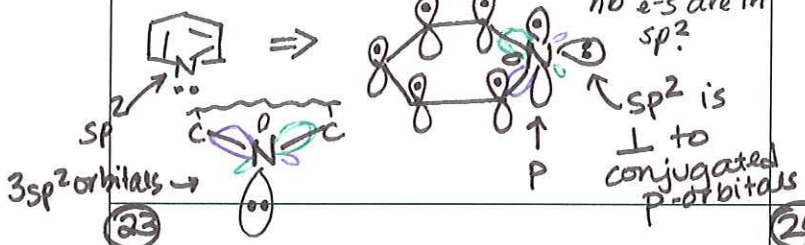
Heteroaromatics

pyridine

① Cyclic ✓
② Fully conj ✓
③ planar ✓
④ $4n+2=6$; $n=1$ ✓

AROMATIC.

Why not $4n+2=8$? Geometry of orbitals; 2 nb e-s are in sp^2?



(22)

pyrrole

① Cyclic ✓
② Fully conj ✓
③ Planar ✓
④ $4n+2=6$ ✓
$n=1$

Aromatic

Now, why do we count n.b. e-s? Geometry of orbitals:

lp in N p-orbital is // parallel to C p-orbitals.

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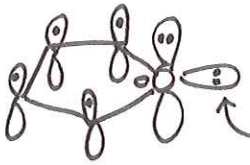
Furan

① Cyclic ✓
② Fully conj ✓
③ Planar ✓
④ $4n+2=6$ } Why?
$n=1$



sp^2 orbital is perpendicular to conj. p-orbitals.

• = 6 in parallel, conjugated p-orbitals

(24)

Polynuclear Containing a Heteroatom

quinoline

① Cyclic ✓
② Fully conj ✓
③ Planar
④ $4n+2=10$; $n=2$ ✓
Aromatic.

(25) Annulenes : monocyclic, fully conjugated molecule.

ex: benzene = [6]annulene

ex:

[14]-annulene

① cyclic ✓
② Fully conj ✓
③ Planar ✓ (Build Model)
④ $4n+2=14$; $n=3$ ✓

} Aromatic

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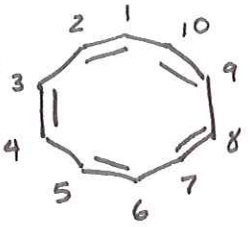
ex:



[10]-annulene (all cis bonds)

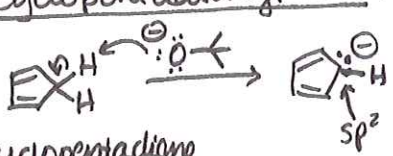
① cyclic ✓
② fully conj ✓
③ Planar? NO Make Model.

NOT AROMATIC.

(27)

Aromatic Ions

Cyclopentadienyl Anions

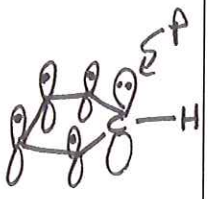


cyclopentadiene not aromatic

pKa 16 (relatively acidic b/c aromatic system obtained upon deprotonation)

anion

Aromatic (cyclic, fully conj., planar, $4n+2=6$; $n=1$)



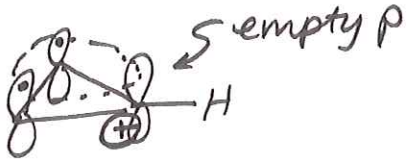
stable for anion (not as stable as benzene)

(28)

Cyclopropenyl Cation

① cyclic ✓
② fully conj. ✓
③ Planar ✓
④ $4n+2=2$ ✓
$n=0$

AROMATIC



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Tropylium Ion

Aromatic
1) cyclic ✓
2) fully conj. ✓
3) planar ✓
4) $4n+2=6$; $n=1$ ✓

empty p.

(30)

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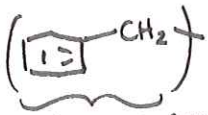
Substituted Benzenes

Benzene =  =  = PhH

Ph = phenyl

monosubstituted benzenes:

phenyl group = $C_6H_5 = \phi$



benzyl group = $C_6H_5CH_2 = Bn$

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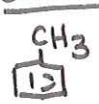
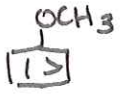
Common Monosubstituted Benzenes



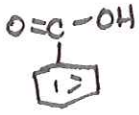
toluene (PhMe)

aniline

phenol



anisole



benzoic acid

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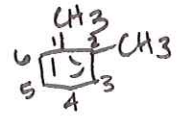
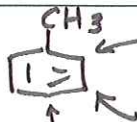
Disubstituted:

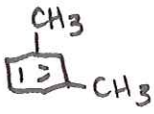


o-xylene

1,2-dimethylbenzene

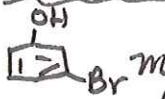


- ortho (o)
- meta (m)
- para (p)
- Denote position relative to methyl group



m-xylene

p-xylene



m-bromophenol or 3-bromophenol

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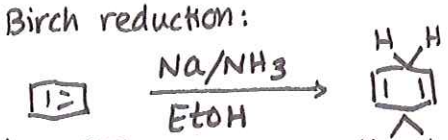
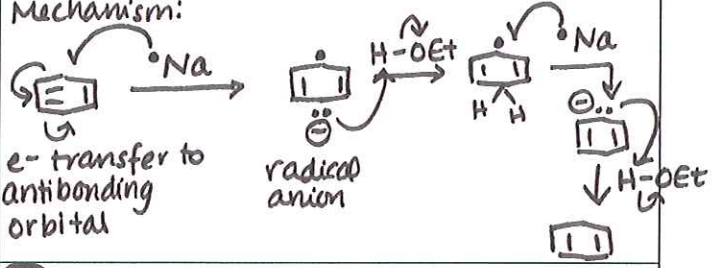
Reactions of benzene derivatives

① Birch reduction:



benzene → diene

Mechanism:



e- transfer to antibonding orbital

radical anion

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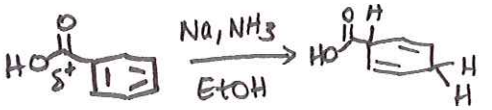
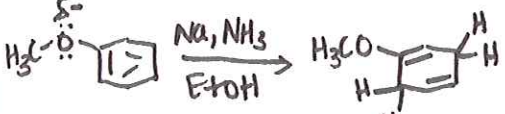
Substituent Effects:

A) Electron-withdrawing groups (EWG):



Diene w/ EWG substituent in between 2 dbl bonds

B) Electron-donating groups (EDG):



Diene w/ EDG substituent on dbl bond.

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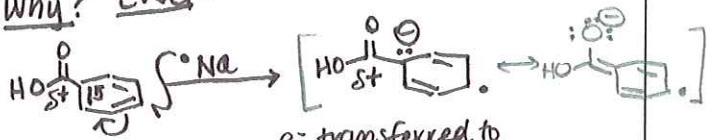
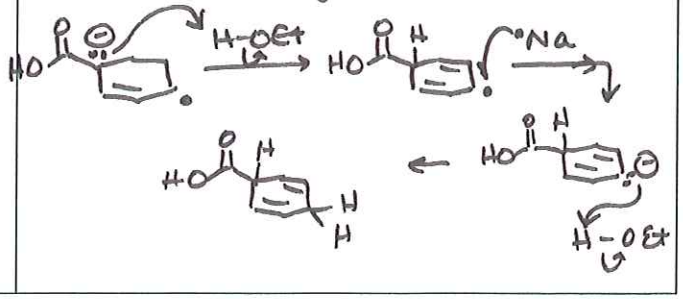
Why? EWG:



e- transferred to para position.

∴ neg. charge stabilized adjacent to δ+



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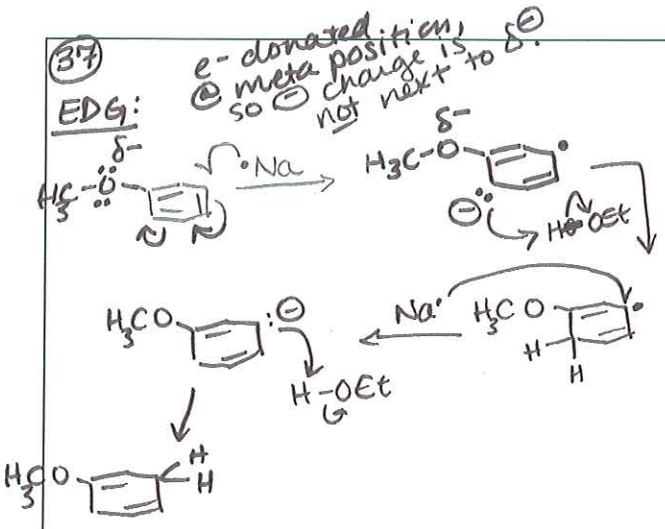
EDG: e- donated @ meta position, so ⊖ charge is not next to δ⊖



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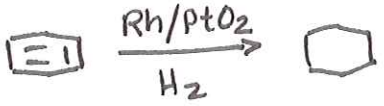
Total Red'n of benzene:

"Super" Catalyst:



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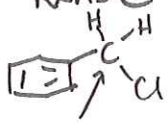
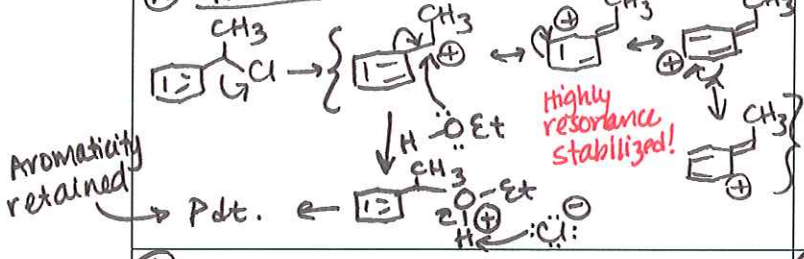
The Benzylic Position

Rxns @ benzylic position = facile.



benzylic position/carbon

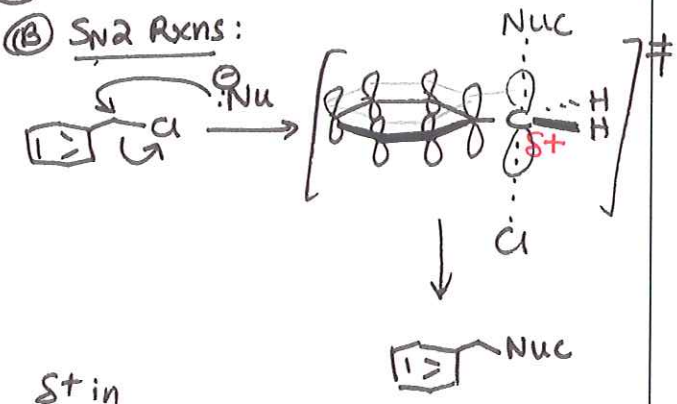
(A) S_N1 Rxns:



Aromaticity retained → Pdt.

(40)

(B) S_N2 Rxns:



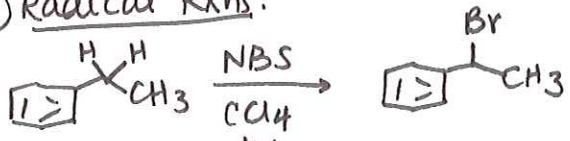
δ+ in T.S. is delocalized.

↓

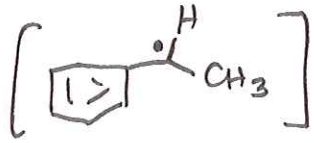
Lower energy barrier for this rxn.

(41)

(C) Radical Rxns:



via

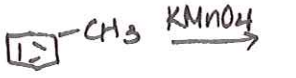


"resonance-stabilized" intermediate.

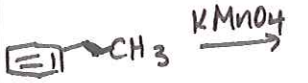
(42)

(D) Oxidation

- benzylic position highly prone to oxid.
- mechanism is vague (not fully known)

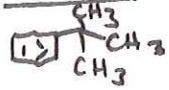


benzoic acid



longer chains "chewed" down

However:



Fully substituted benzylic carbons don't react! Must be ≥1 H @ benzylic position for rxn to proceed.