

Name Haloalkanes, Halogenation, Radical Reactions



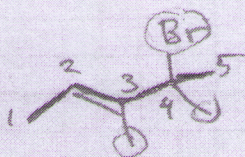
(S)-2-bromo-4-methylpentane

Why NOT

(S)-2-methyl-4-bromopentane? Alphabetical



(R)-4-bromocyclohexene



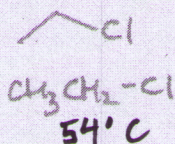
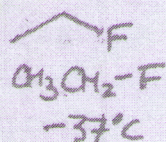
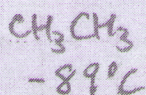
show stereoconfiguration as E/Z or R/S where needed)

(Z)-4-bromo-3,4-dimethyl-2-pentene

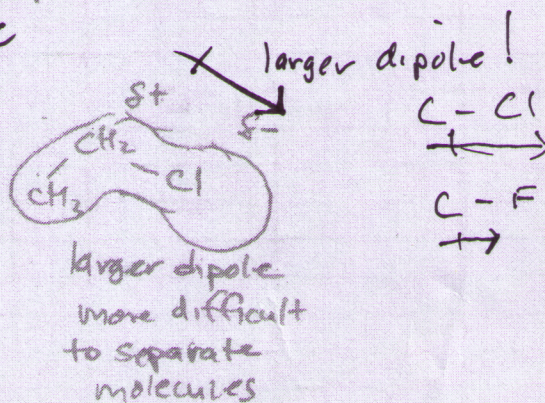
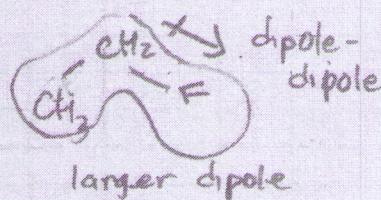
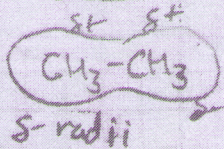
Boiling Points

Why this trend?

bp



Van der Waals forces



bp
°C

-89

-45

36

69

Velcro analogy



longer chain, more overlap

Ball of velcro



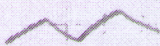
small interface

Look at

 C_5H_{12}

-1

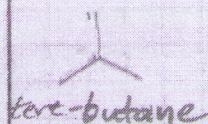
(A)

 C_5H_{12}

36

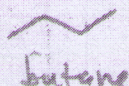
(B)

why is more E (heat) need to separate molecules of (B) than (A)



(C)

-1



(D)

0

same Q as above
(C) vs (D)

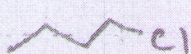
Likewise, haloalkanes follow same trend w/ length.



13



46



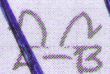
77



108

bp
°C

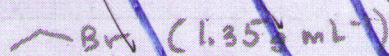
Bond Dissociation Energy



Notice half-headed arrows denote movement of 1 electron

Energy is needed so ΔH° is > 0 (zero)
radical products

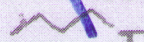
Density (mass-to-volume)

Liquid Alkyl Br and I are denser than H_2O ($1.0 g mL^{-1}$)(1.35 $g mL^{-1}$)

(1.28)

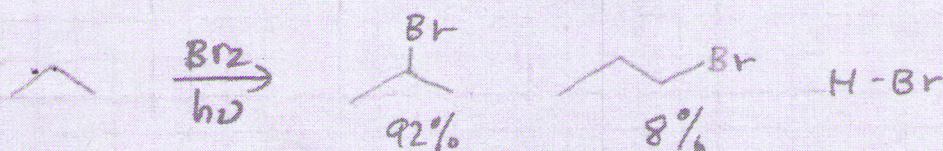


(1.94)

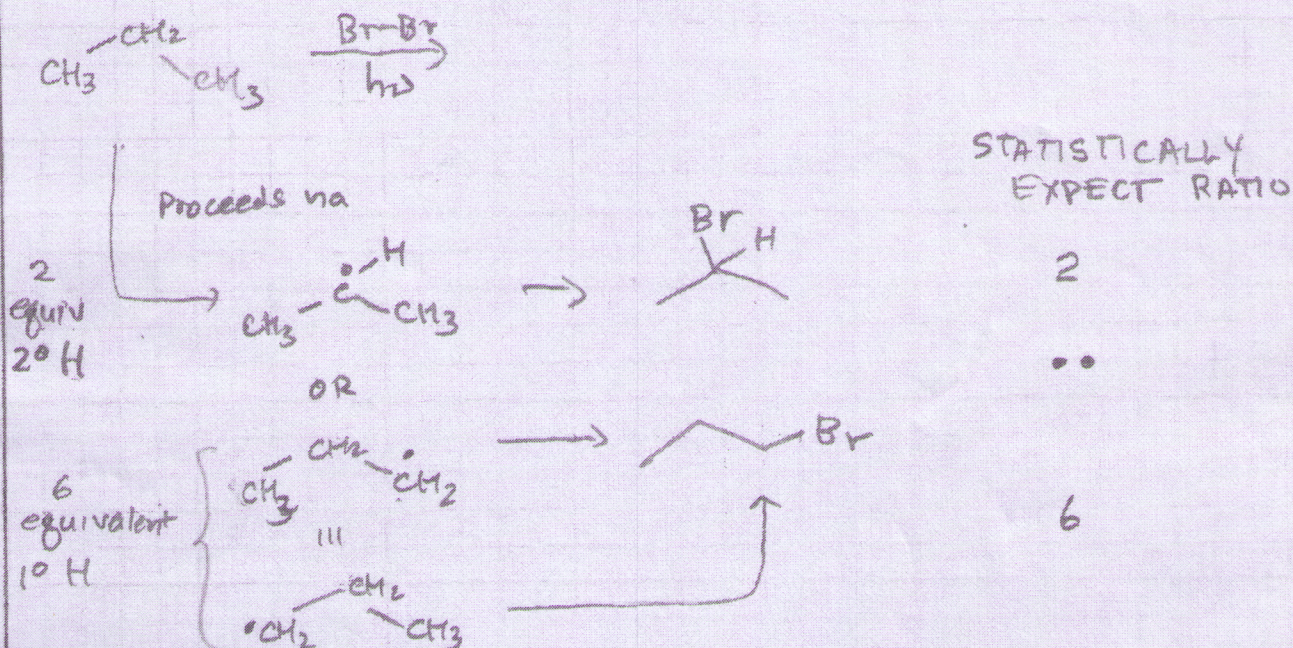


(1.615)

Regioselectivity of Radical halogenation



What you expect



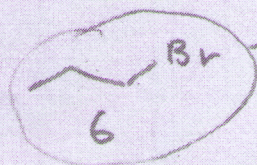
That is

$\frac{2}{8}$

||

25%

92%



$\frac{6}{8}$

||

75% expected

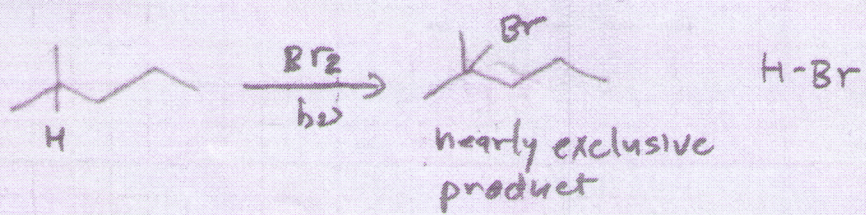
8% observed

Expected to be more abundantly made!
Why is it not?

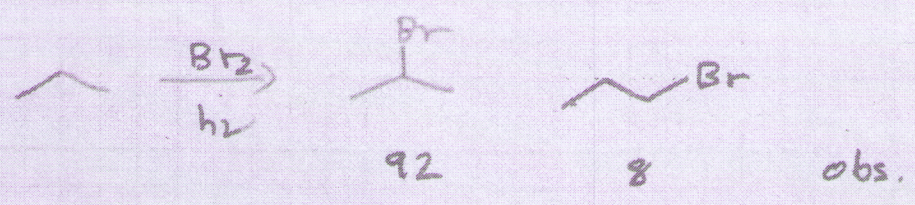
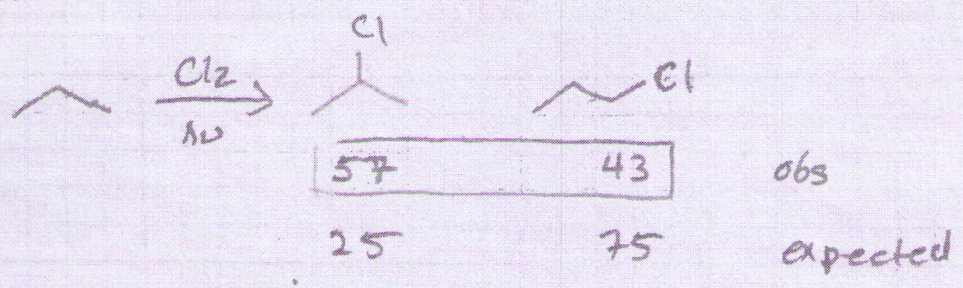
$\text{H} \rightarrow \text{Br}$ replacement is favored for 2°H over 1°H

Actually

$3^\circ \text{H} > 2^\circ \text{H} > 1^\circ \text{H}$ for replacement by Br



For Cl

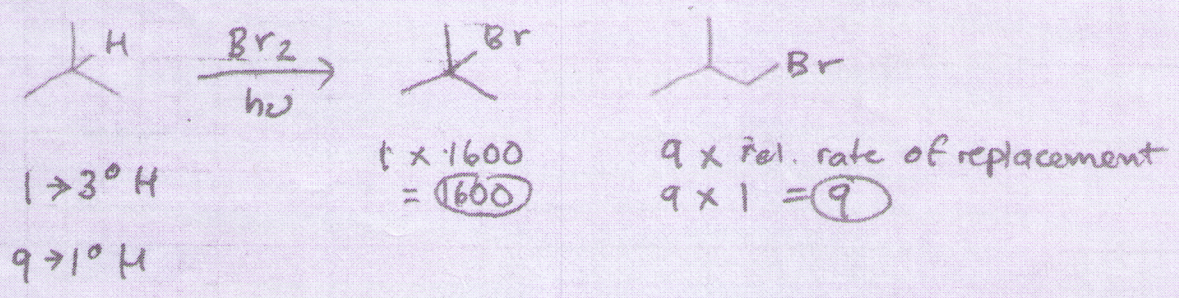


Br_2 is far more regioselective than Cl_2 in monohalogenation

The regioselectivity per hydrogen of bromination for

3°H	2°H	1°H	replacement is
1600	80	1	

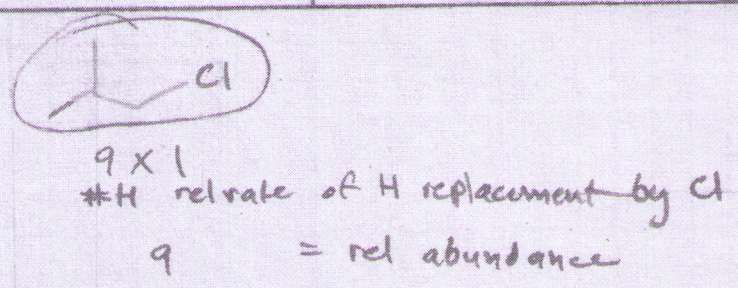
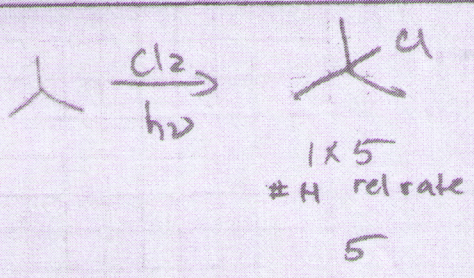
$\therefore$



relative abundance 1600 to 9

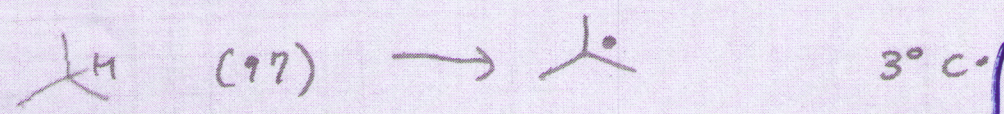
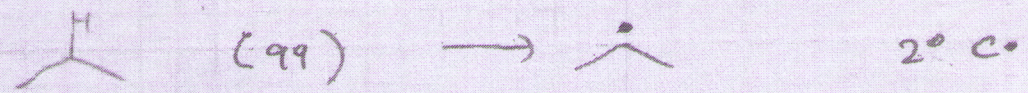
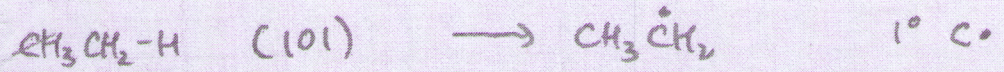
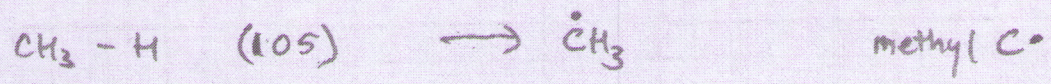
The regioselectivity per hydrogen of chlorination for

3°H	2°H	1°H
5	4	1

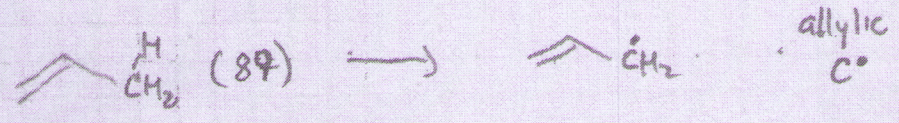
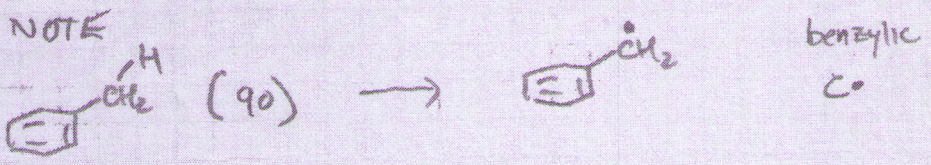


MORE ABUNDANT CIRCLED

BDE of 1°, 2°, 3°, methane Hydrogens



Lowest BDE
∴ easier to form because radical is more stable

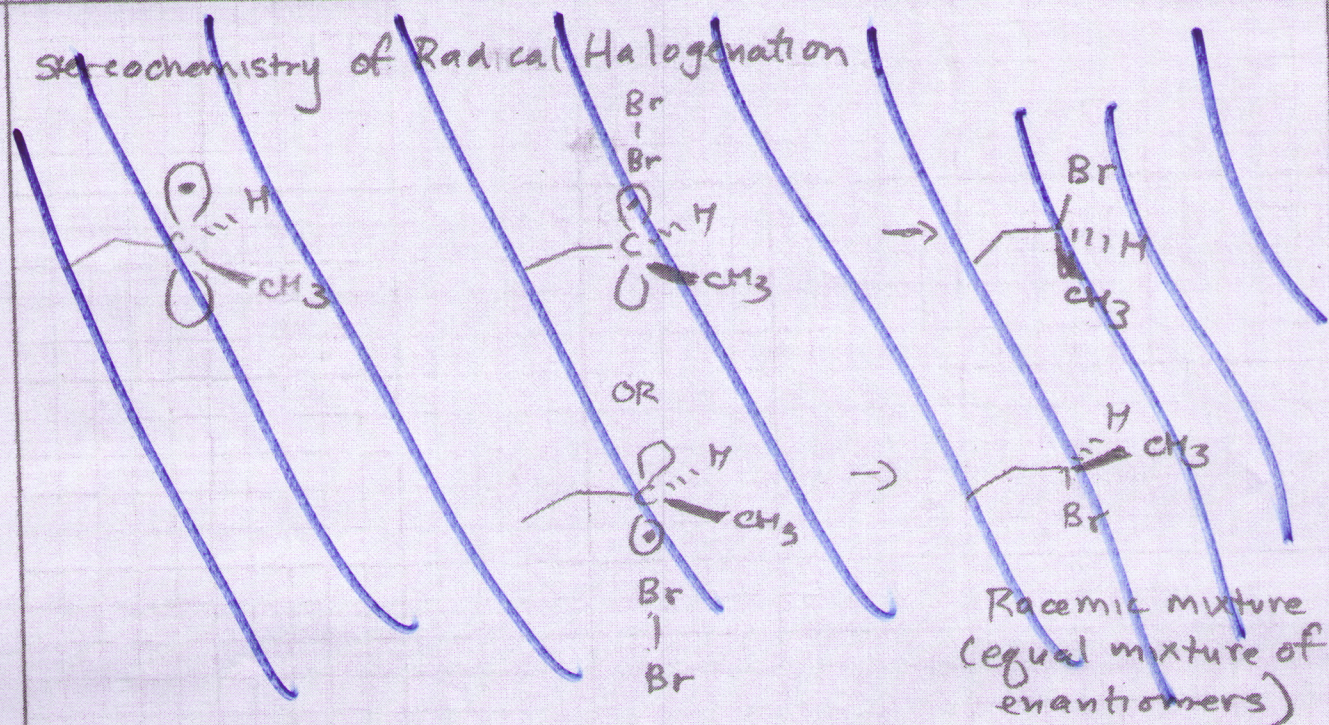


similar stability

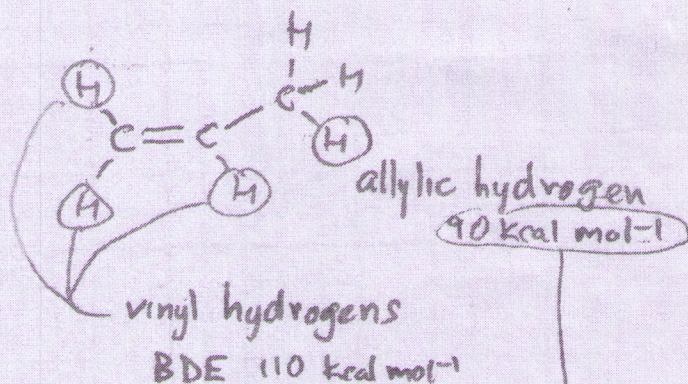
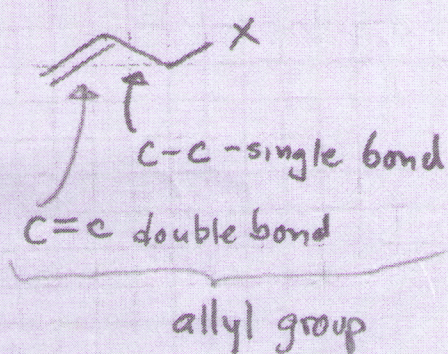
NOTE these follow the same order of stability as C⁺
 3° C⁺ more stable than 2° C⁺ > 1° C⁺ > methyl C⁺

Let's look at ΔH° values to assess the energetics of bromination regioselectivity.

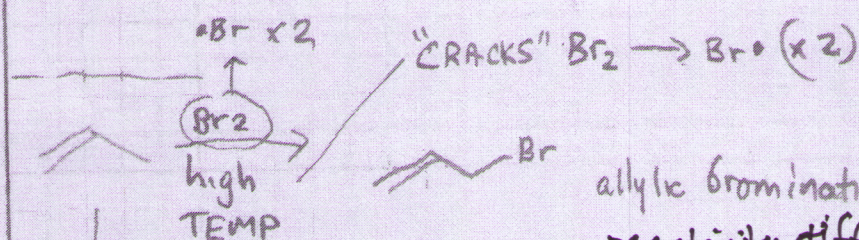
Stereochemistry of Radical Halogenation



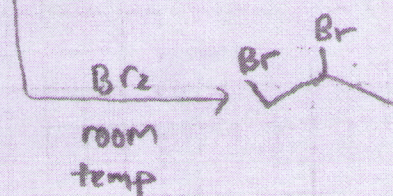
Allylic Halogenation



easier to break

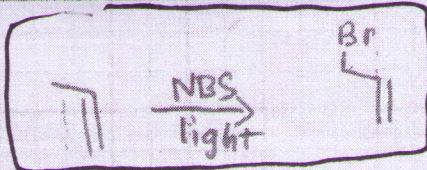


allylic bromination, but uncontrolled reactivity difficult to stop at mono Br₂

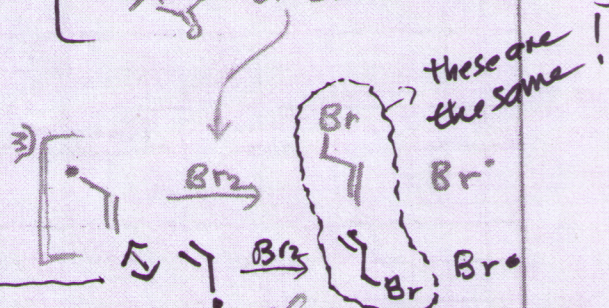
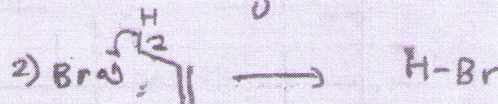
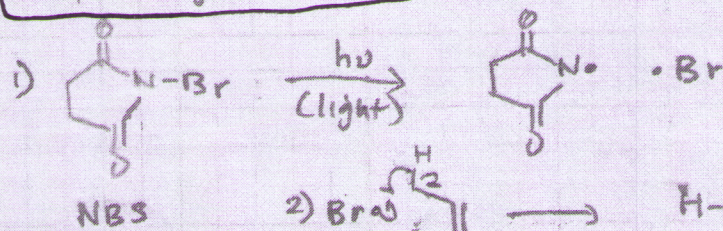
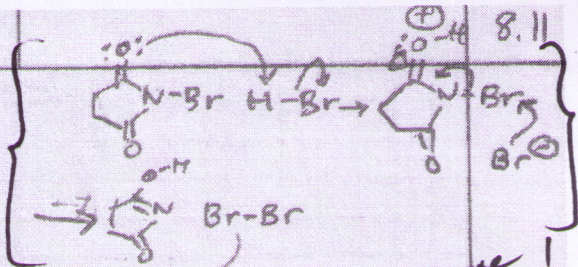


TO AVOID THIS DIBROMINATION AT ROOM TEMP AND TO REPLACE THE HIGH TEMP ALLYLIC BROMINATION RXN ABOVE N-bromosuccinimide (NBS) is used

NBS bromination continued

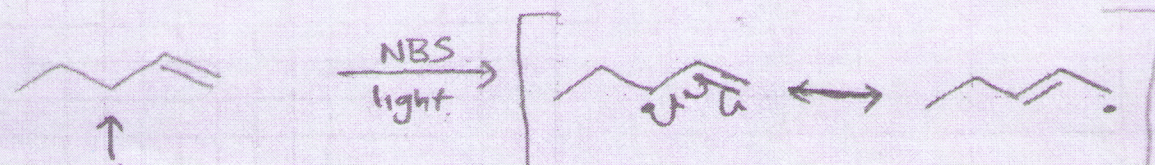


IMPORTANT



← is resonance arrow.

Sometimes allylic Bromination gives a mixture of unique products due to resonance.

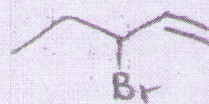
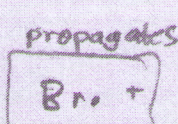


↑ allylic C with allylic H

radical intermediate

Br₂ from NBS

Br₂ from NBS



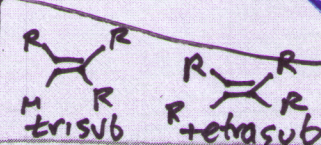
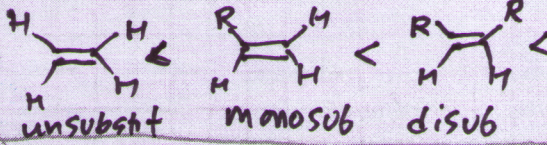
MAJOR PRODUCT

[MORE SUBSTITUTED] ALKENE

more stable Alkene predicts most abundant

More about this in Chapter 9

NOTE!



alkene stability

