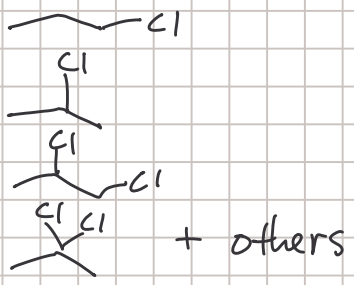
Ch 6

Note Title 11/2/2005

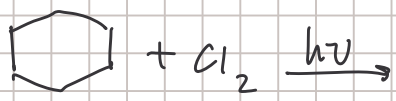
Preparation of alkyl halides

Free-radical halogenation.

$CH_3CH_2CH_3 + Cl_2 \xrightarrow{h\nu}$

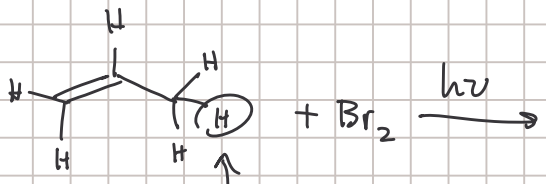


+ others

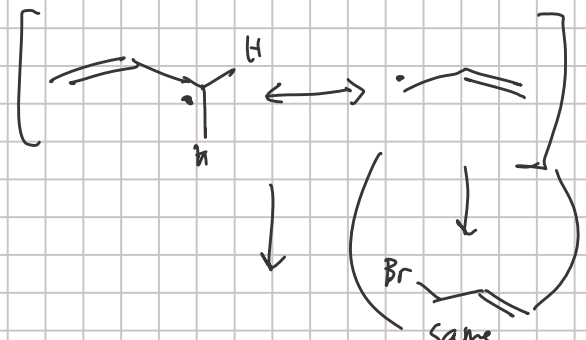


~50%

Allylic bromination



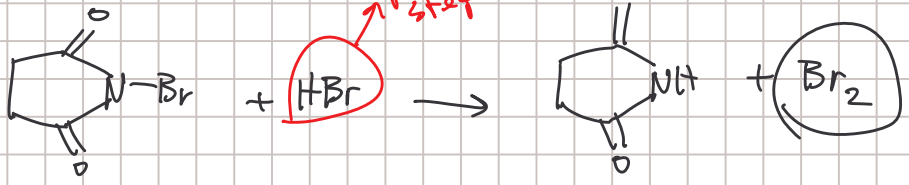
allylic hydrogens (next to double bond)



~80%

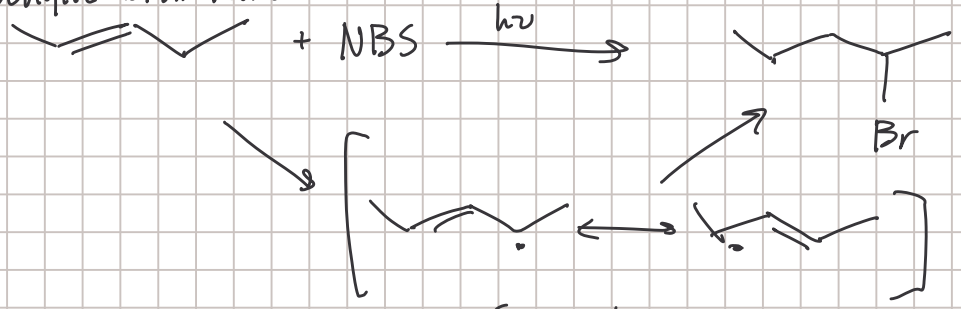
NBS N-bromosuccinimide

comes from propagation step



widely-used Br_2 source — Br_2 production can be carefully controlled

allylic bromination with NBS:



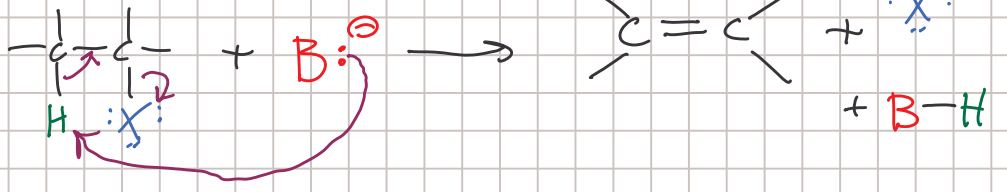
symmetrical radical resonance strs = 1 product!

Nucleophilic substitution & elimination

Substitution reaction

X = halogen

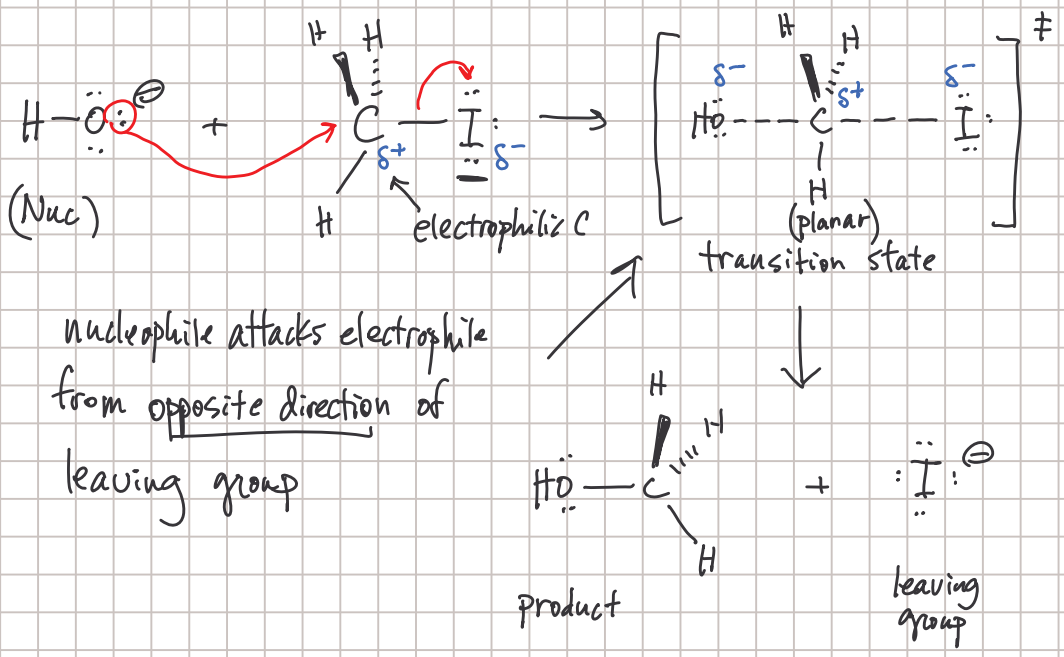
Elimination reaction:



S_N2 reaction

Substitution – nucleophilic – 2nd-order

nucleophile — substrate — product — leaving group



Single-step concerted mechanism.

↳ bonds broken & formed simultaneously

Nuc + substrate must meet in order to react

$$\text{rate}_{S_N2} = k[CH_3I][OH^-]$$

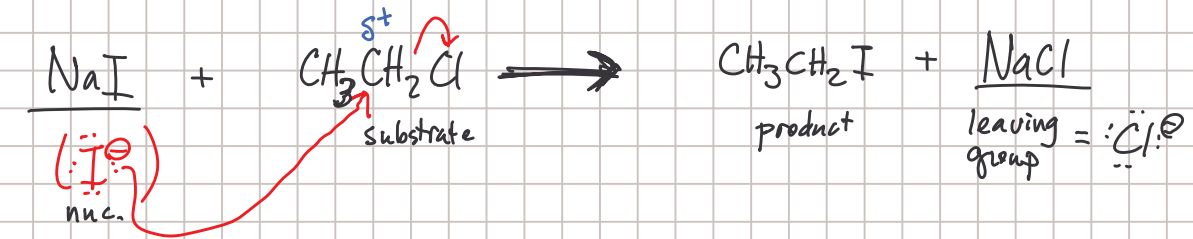
substrate, nuc.

2nd order overall

S_N2

Halogen exchange

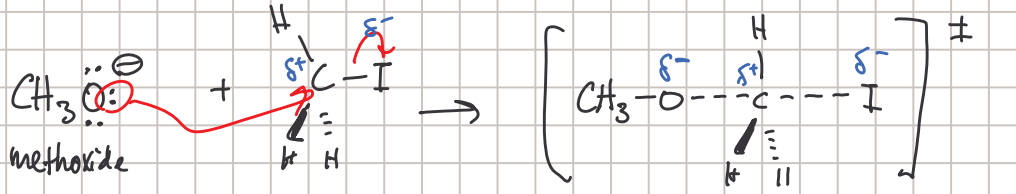
$$R\text{-}X + I^\ominus \longrightarrow R\text{-}I + X^\ominus$$

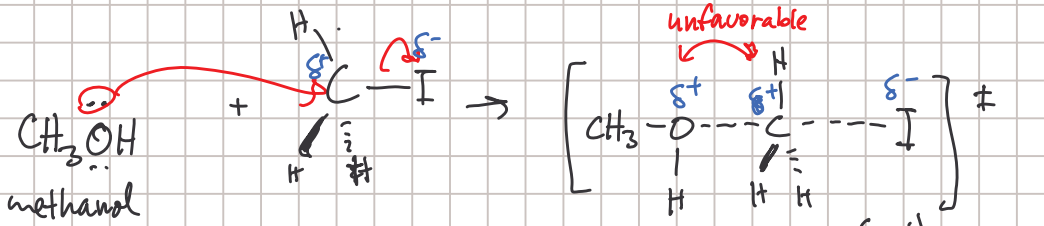


really only works when $I^\ominus$ is nucleophile.

Nucleophiles a strong nuc. is required for S_N2

1. a <u>base</u> is always a stronger nucleophile than its <u>conjugate acid</u>.





higher E_a = (much) slower reaction

nucleophiles $^{\ominus}OH > H_2O$, $^{\ominus}SH > H_2S$, $^{\ominus}NH_2 > NH_3$

2. nucleophilicity decreases from left → right on periodic tbl.

$^{\ominus}OH > F^{\ominus}$ more electronegative atoms hold their e^- more tightly

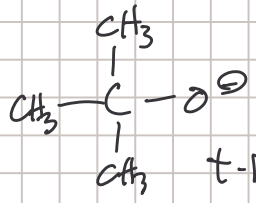
$NH_3 > H_2O$

3. nucleophilicity increases down the periodic table b/c of increased <u>polarizability</u> (squishiness)

$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} >> F^{\ominus}$

large e^- clouds form <u>new</u> <u>bonds</u> easier

(4.) bulkiness can control nucleophilicity vs. basicity



t-butoxide

bulky

unable to attack $C^{\delta+}$

is able to attack small H's

strong base weak nucleophile

steric hindrance when attacking C

$CH_3CH_2-O^{\ominus}$

ethoxide

less bulky

reacts w/ $C^{\delta+}$ faster

strong nucleophile