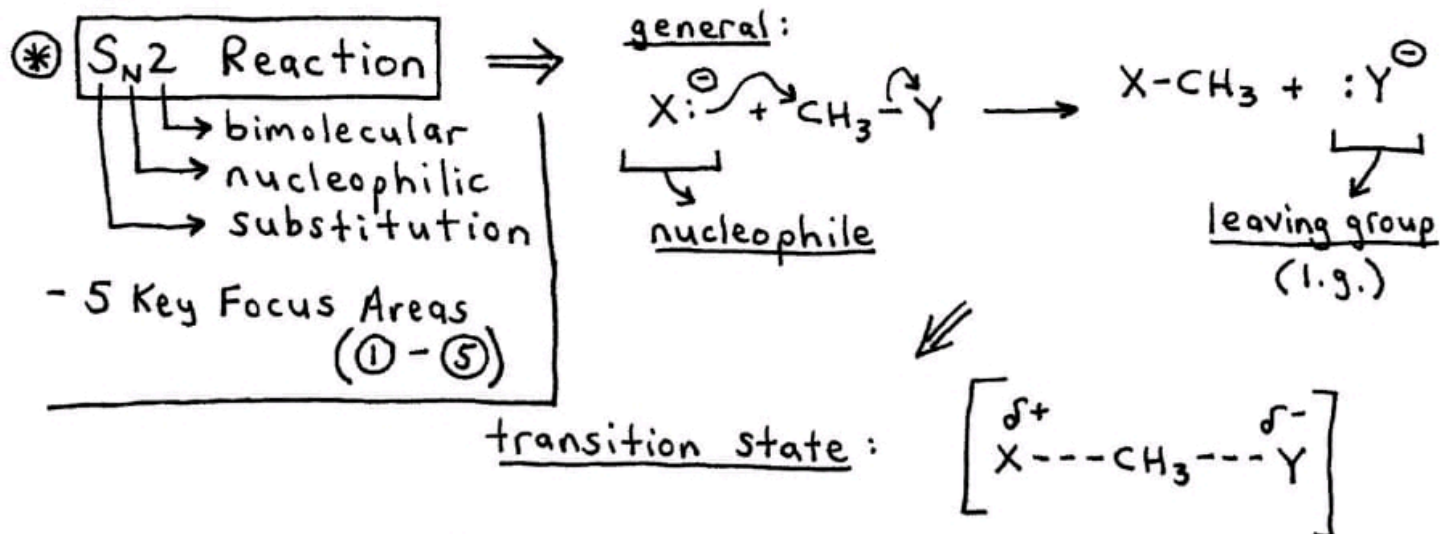


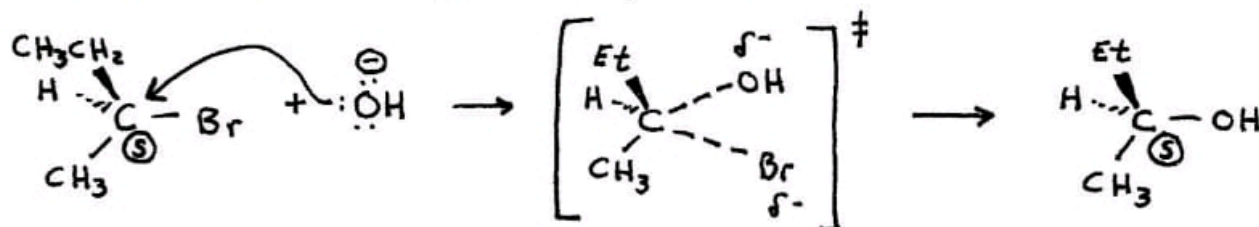


\* carbocations in E1 and S<sub>N</sub>1 reactions are extremely 10<sup>-2</sup> strong acids and desperately want to lose their ⊕ charge.



- rate =  $k[\text{X}^-][\text{CH}_3\text{Y}]$  → consistent with a bimolecular reaction; both reactants involved in rate-determining step (r.d.s.).

① Stereochemistry - 2 possibilities...

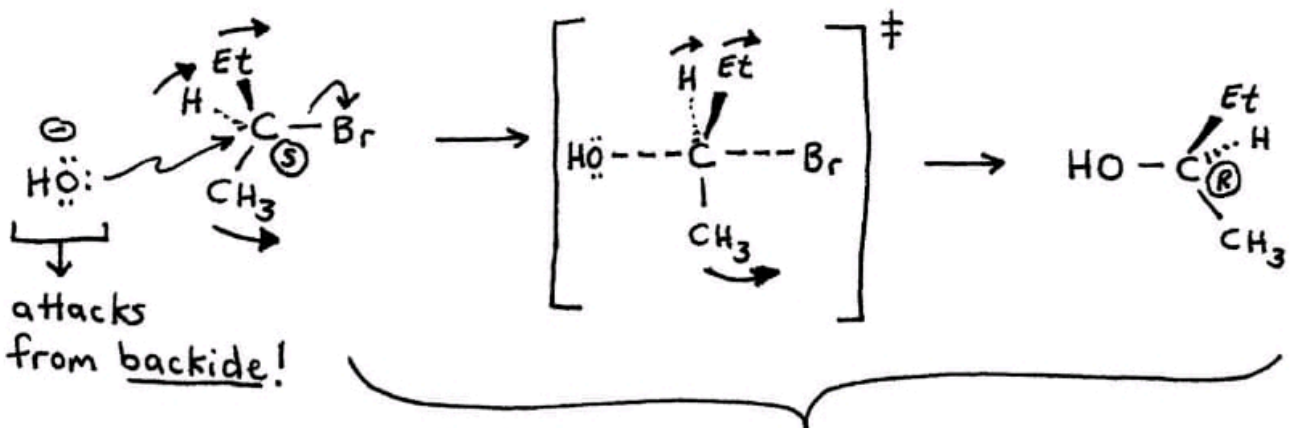


- front-side displacement = retention of absolute configuration (S).

↳ NOT OBSERVED experimentally!

\* ↳ instead, inversion of absolute configuration is observed.

↳ details on next page...

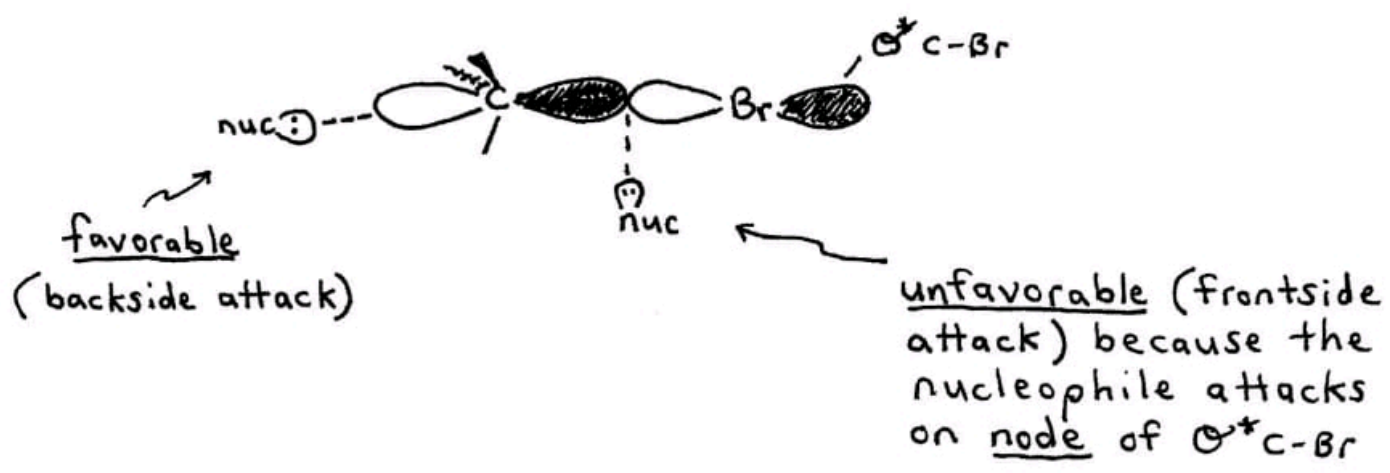


- this is observed!

- "backside displacement"
- inversion of configuration ( $S \rightarrow R$ ).

Q: Why does the  $S_N2$  reaction occur by way of "backside displacement"?

A: Because of an unfavorable interaction between the lone-pair orbital of the nucleophile (filled) and the antibonding  $\sigma^*$  C-Br molecular orbital of the alkyl bromide (empty).



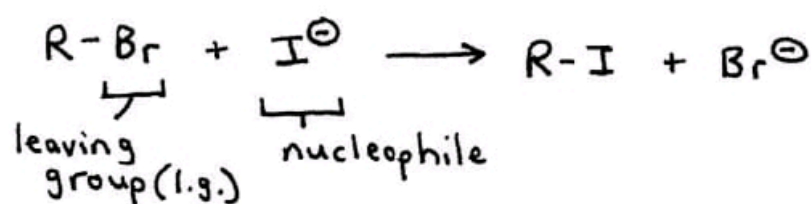
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## ② Effect of Alkyl Halide Structure

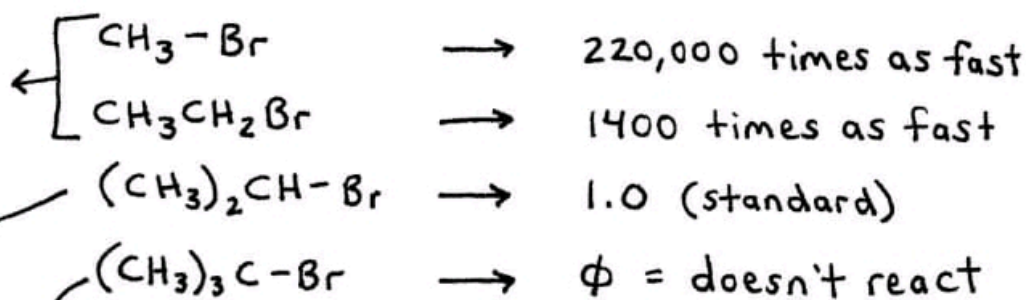
10-4

↳ in  $S_N2$  reactions, not all alkyl halides react the same.



\*  $\text{R-Br} \Rightarrow$  Relative rates of an  $S_N2$  reaction with  $\text{I}^\ominus$ .

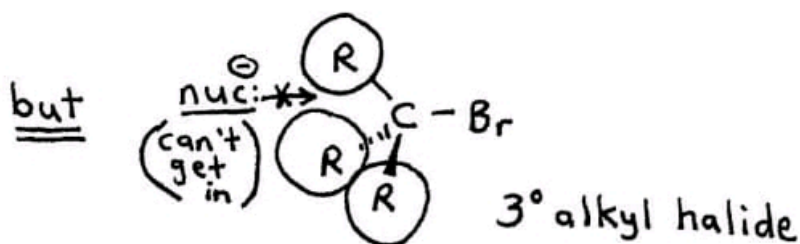
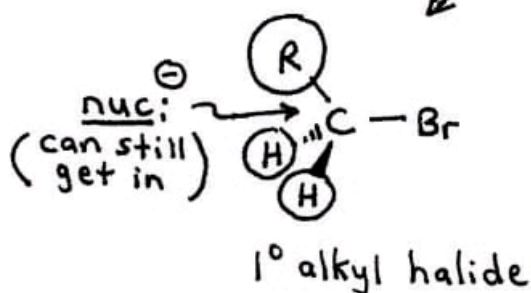
Methyl and  $1^\circ$  alkyl halides react fast by  $S_N2$  method.



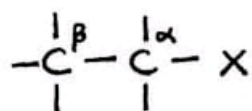
$2^\circ$  alkyl halides react slowly.

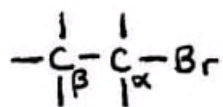
$3^\circ$  alkyl halides do not react by  $S_N2$ .

\* reason: steric hindrance to backside attack.



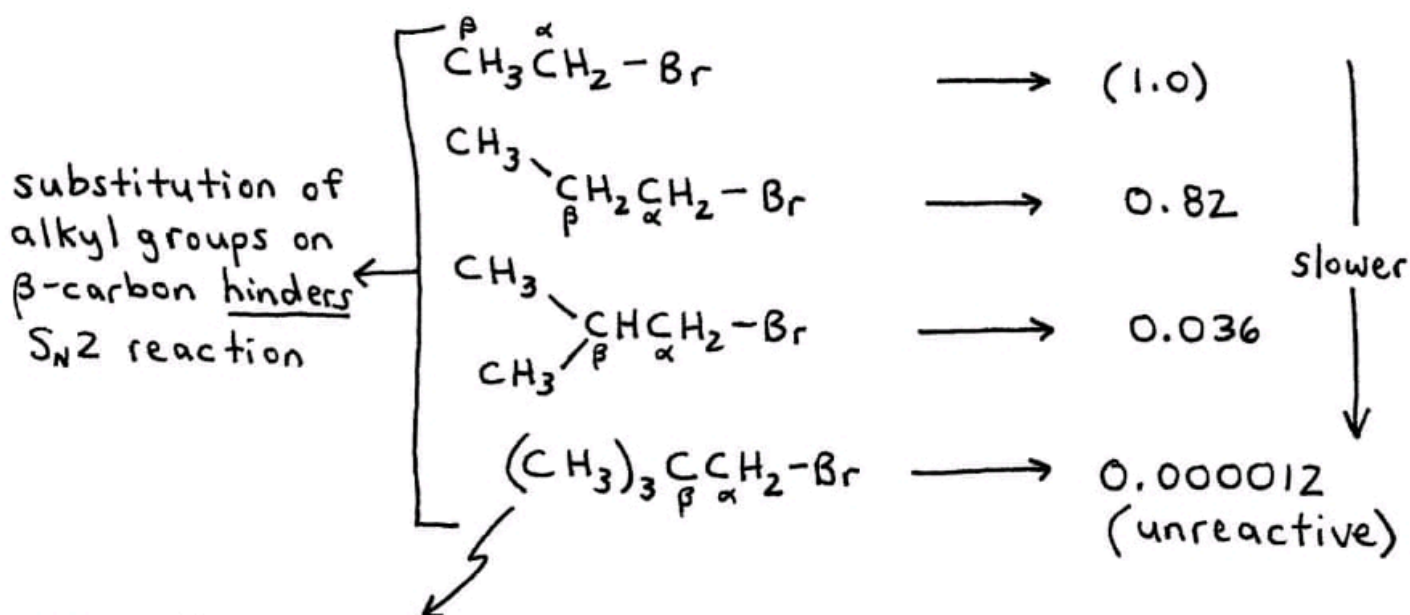
\* Branching at next carbon (the  $\beta$ -carbon) also hinders the approach of the nucleophile in an  $S_N2$  reaction.



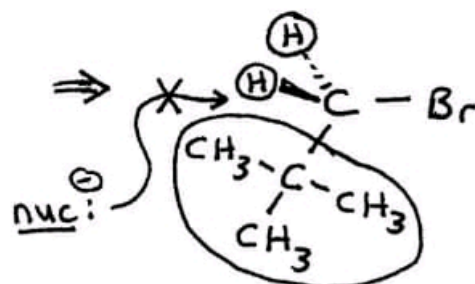


10-5

\* R-Br  $\Rightarrow$  Relative rates of an  $S_N2$  reaction with  $I^\ominus$  (nuc).

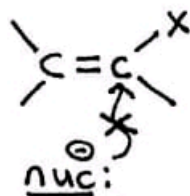


neopentyl bromide reacts  $10^5$  times slower than ethyl bromide ( $CH_3CH_2-Br$ ).



\* neopentyl halides are unreactive

note: aryl and vinyl halides do not undergo  $S_N2$  reactions:



③ Nucleophilicity - a "better nucleophile" leads to a faster reaction.

$\rightarrow$  4 points to make

$\rightarrow$  (a) - (d) on next pg...

$\rightarrow$  = more willing to donate an  $e^-$ -pair.

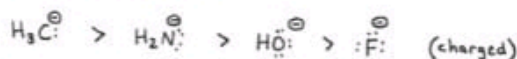
→ (a) - (d) on next pg...

donate an e<sup>-</sup> pair.

a) in general, stronger bases are better nucleophiles than weaker bases. 10-6

↳ this is true in aprotic solvents, but not in protic solvents. See (c) below.

b) nucleophilicity decreases going from left to right in a row of the Periodic Table.



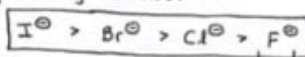
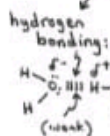
— decreasing nucleophilicity —→



\* charged species are better nucleophiles than their related neutral species (above).

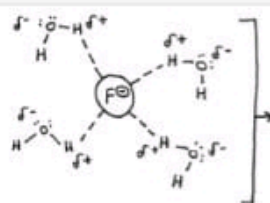
c) Nucleophilicity depends on the solvent.

- in protic solvents (solvents with -OH or >NH<sub>2</sub> groups), nucleophilicity follows:



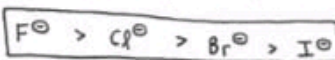
↳ fluoride (F<sup>-</sup>) is tied up with solvent molecules, while iodide (I<sup>-</sup>) does not form strong hydrogen bonds with the solvent.

↳ F<sup>-</sup> is stabilized due to interactions with protic solvent, so it has a longer way to go than I<sup>-</sup> when conducting its nucleophilic attack on an alkyl halide.



F<sup>-</sup> has high charge density <sup>10-7</sup> and forms strong hydrogen bonds to protic solvents; so its nucleophilicity is decreased.

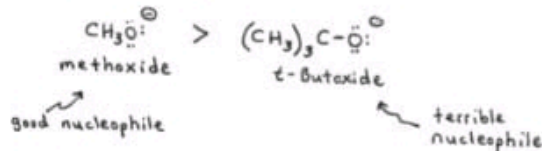
- in aprotic solvents (solvents that can't form hydrogen bonds), nucleophilicity follows basicity:



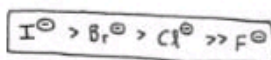
stronger base  
stronger nuc:<sup>-</sup>

weaker base  
weaker nuc:<sup>-</sup>

d) Steric bulk of nucleophile decreases its nucleophilicity because its approach to halide is impeded.



④ Leaving group = weaker bases = better leaving groups



best l.g.  
(weakest base).

worst l.g.  
because it's  
the best base.

↳ willing to accept a negative charge.