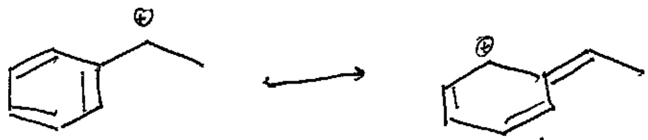
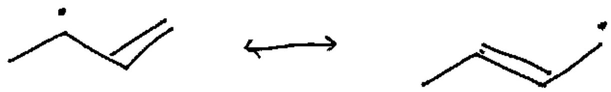
Recall: Special reactivity patterns @ allylic & benzylic positions



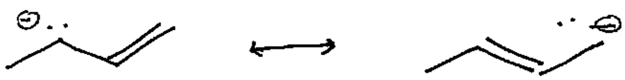
etc.

resonance stabilization of ⊕

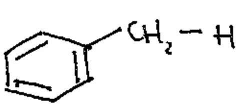


... or ·

Comparable effects for carbanions:



manifestation: pK_a values

	pK_a
$CH_3CH_2CH_2CH_2-H$	≥ 50
$CH_3CH=CH-CH_2-H$	43
	41

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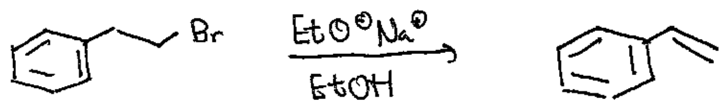
Allylic/benzylic effects on reactivity even if no reactive intermediate ($\oplus$, $\cdot$, $\ominus$)

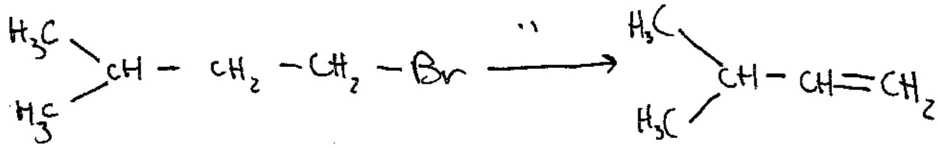
These effects manifested at transition state.

Example 1

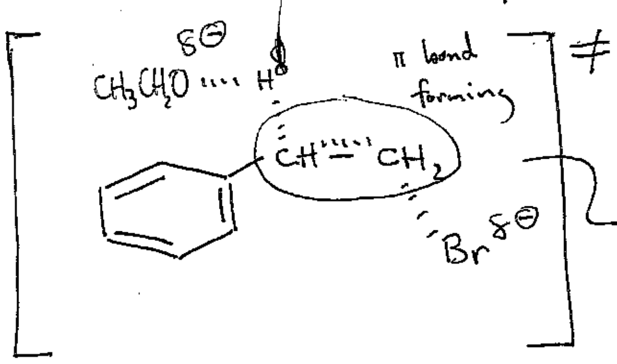
E2 (elimination)



> 100× faster than



Mechanistic rationale (hypothesis): (transition state



∴ partial resonance of alkene w/ aromatic ring π-system.

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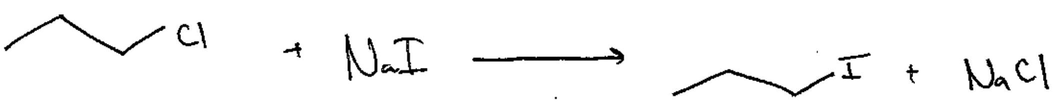
Example 2 - S_N2

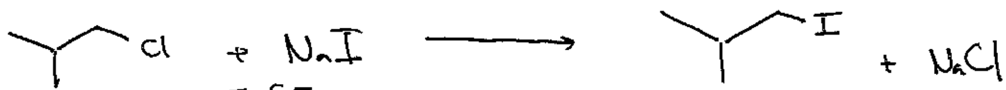
- no int.; focus on TS

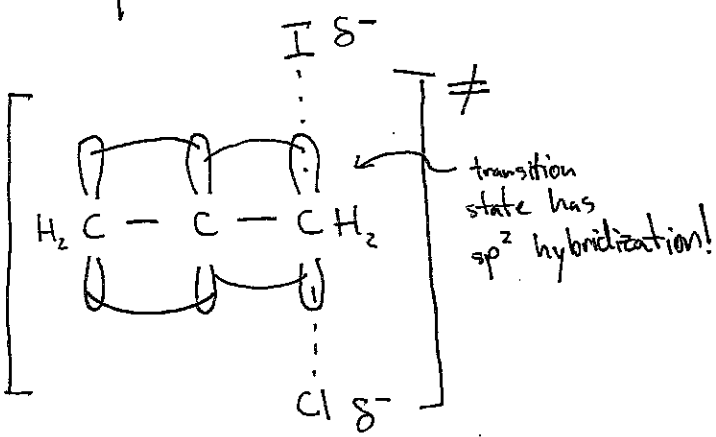
Observe:

~ 100x faster than



~ 100,000x faster than





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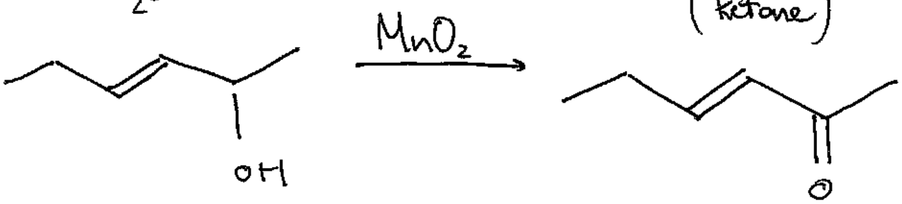
Example #3 - Selective oxidation at allylic & benzylic positions.

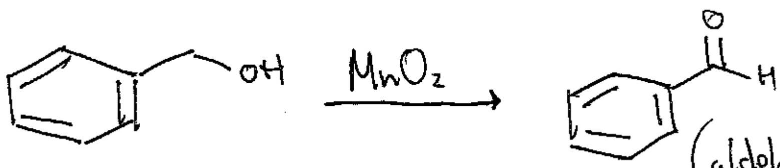
(Alcohol → carbonyl)

⇒ MnO_2

2°

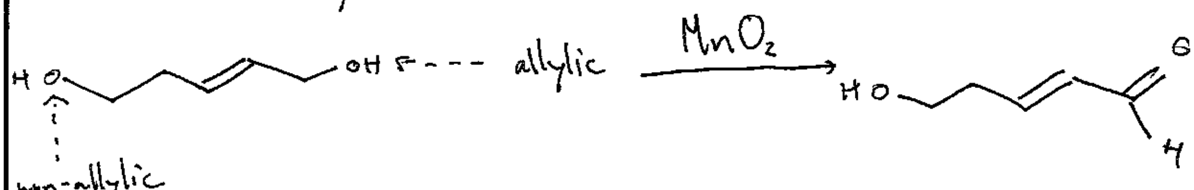
(ketone)



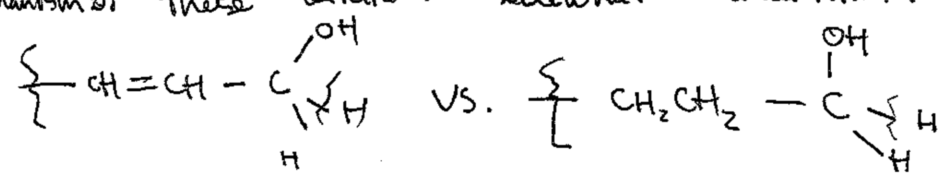


(1°) (aldehyde)

Note selectivity:



Mechanism of these oxidations somewhat uncertain...



- should be easier to break allylic C-H bond than non-allylic