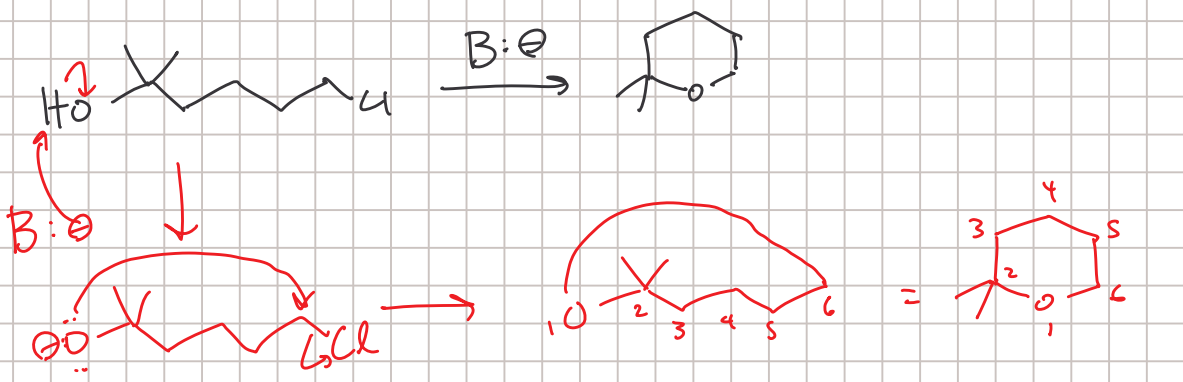
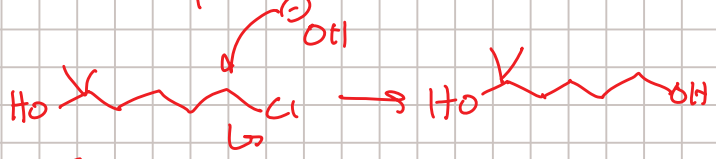
Ch 14 Group Work

Note Title 1/25/2006

① Show the mechanism. Which type of base would be best? Why? What are a few examples?



A Bulky base is best, to prevent S_N2 on the primary halide.

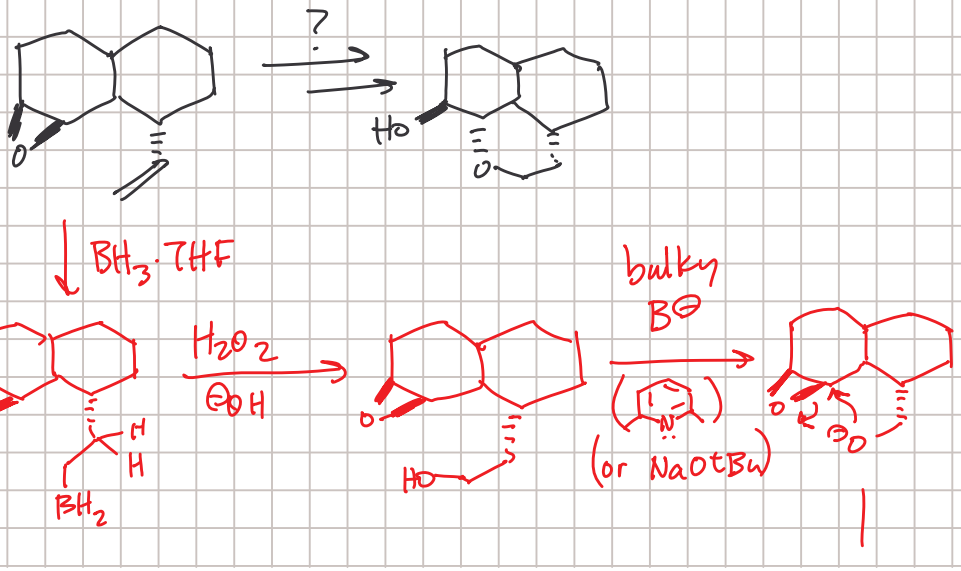


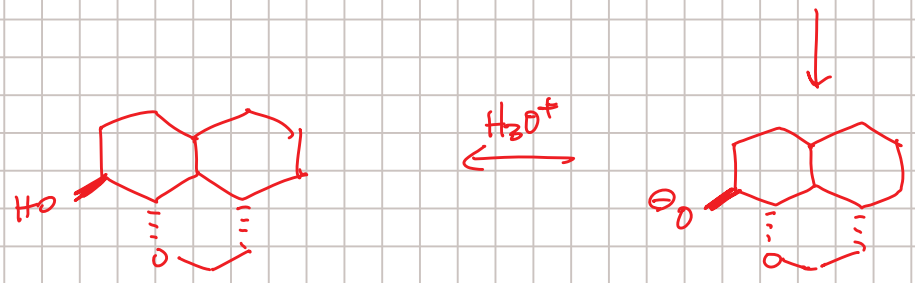
2,6-lutidine is good: (and about the right strength)

otherwise t-Butoxide would work too

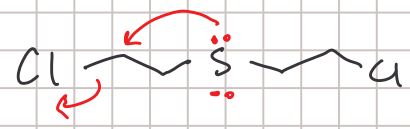
$(CH_3)_3CO^{\ominus}$ (Na^+ or K^+)

② Give reagents for this series of transformations

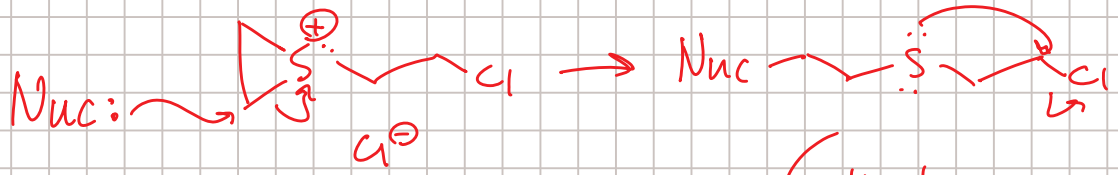




③ Mustard gas is a strong alkylating agent. Show how it forms a sulfonium salt & show the salt alkylating a Nuc.

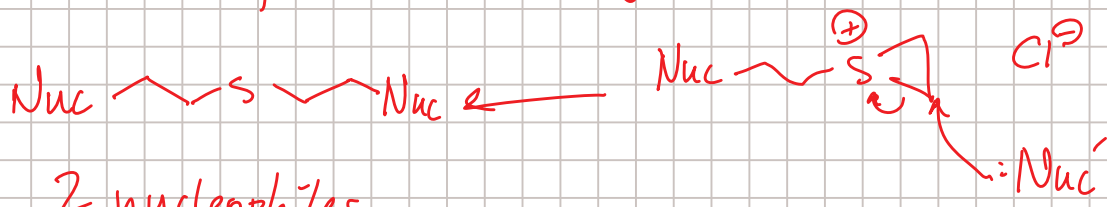


Mustard gas



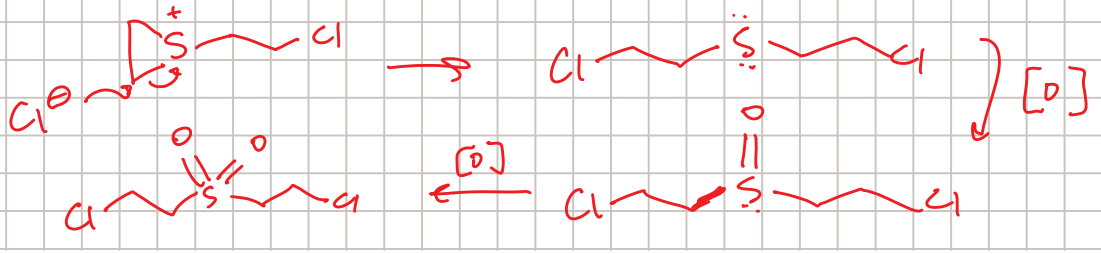
- sulfonium salt formed intramolecularly
- Attack by nuc relieves ring strain

alkylation can continue!

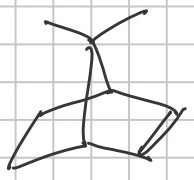


2 nucleophiles Cross-linked!

Bleach (NaOCl) oxidizes & deactivates mustard gas.



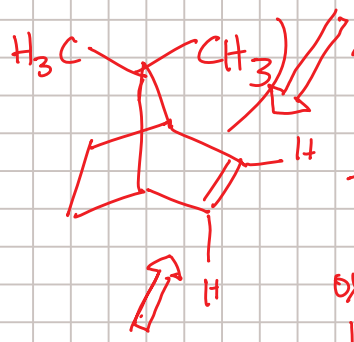
(sulfoxides & sulfones can no longer form electrophilic sulfonium salt)

④  $\xrightarrow{MCPBA}$ epoxide A

$\downarrow$ 1) Br_2/H_2O 2) $B\ominus$ — show struct of A & B

— which (A or B) will be opened faster by a strong Nuc?

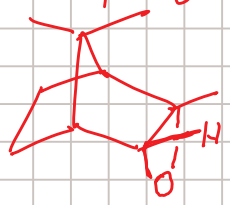
epoxide B



attack from top hindered by CH_3

clear down here

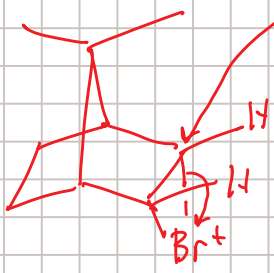
MCPBA → (delivers an oxygen atom to less-hindered face of dbl bond)



epoxide A

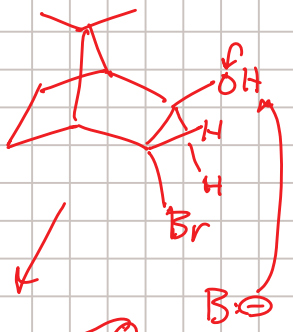
epoxide formed on bottom face.

Br_2

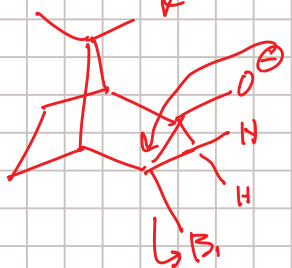


$H_2\ddot{O}$: attacks opposite face from bromonium

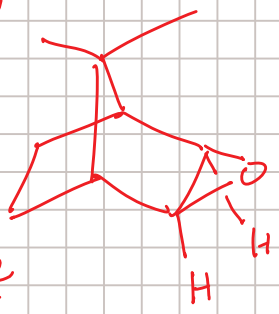
$-H^+$

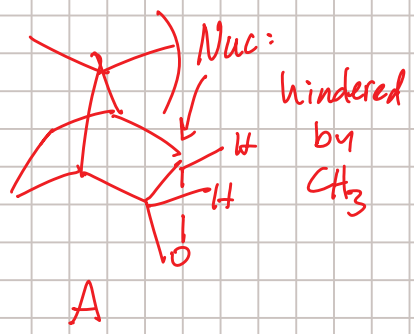


bromine atom delivered on less-hindered face to form bromonium ion (like epoxide A)

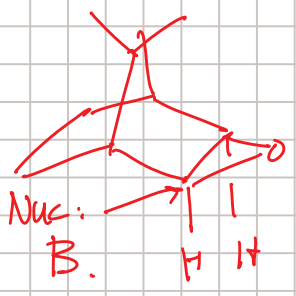


epoxide B on top face





A

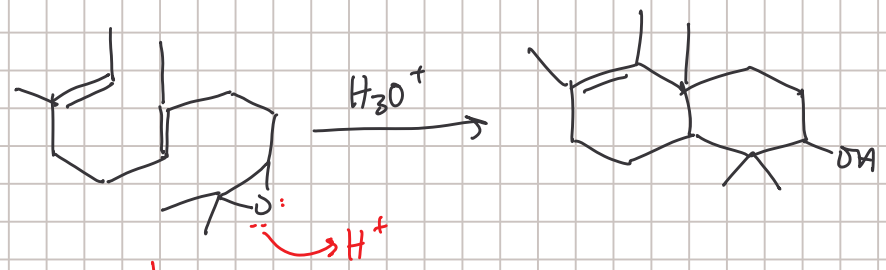


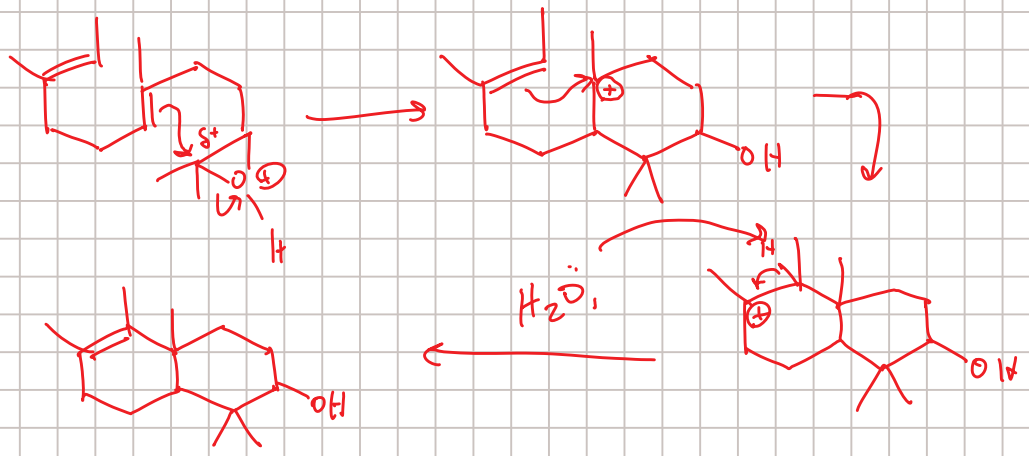
B.

Nuc must attack from back side of epoxide

B could be opened faster by Nuc.

(5) Show the mech.





an acid-catalyzed cyclization cascade (like biosynthesis of steroids)