Haloalkanes, Alcohols and Amines. Problem Sheet 1

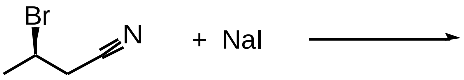
1. Arrange these compounds in order of increasing reactivity for S_N2 displacement:

(a) 1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane
(b) 1-bromopentane, 1-bromo-2,2-dimethylpropane, 1-bromo-3-methylbutane.

2. In the following nucleophilic substitution reactions, predict the product and provide the mechanism. In each case state whether the mechanism proceeds by S_N1 or S_N2.

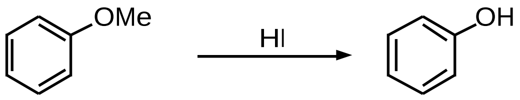
Bu_3P + EtI $\longrightarrow$

$PhMe_2CCl$ + EtOH $\longrightarrow$

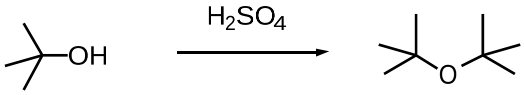


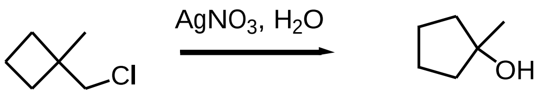
3. When optically active 2-iodooctane was allowed to stand in acetone solution containing $Na^{128}I$ (radioactive iodine), the alkyl halide was observed to lose optical activity and to exchange its ordinary iodine for radioactive iodine. The rate of these reactions depended on both [RI] and $[^{128}I^-]$, but the loss of optical activity was exactly *twice* as fast as gain of radioactivity. This unambiguously establishes that in the S_N2 mechanism, each molecule undergoing substitution suffers inversion of configuration. Explain.

4. Provide a mechanism for the following transformation. What is the by-product from the reaction? Classify the key carbon-oxygen breaking step as S_N1 or S_N2.

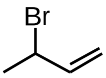


5. Provide mechanisms for the following transformations.

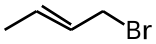




6. When either but-2-en-1-ol ***OR*** but-3-en-2-ol is allowed to react with HBr, the *same* product distibution of 1:4 of **A**:**B** is produced. Explain.

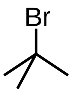


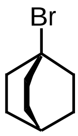
A

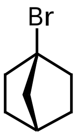


B

7. Explain the observed reaction rates when the bromides below where solvolysed in EtOH.







rel. rate: 1 10^{-6} 10^{-14}

8. What is the usual stereochemical consequence of the S_N2 mechanism if the attacked carbon centre is chiral? Rationalise the following.