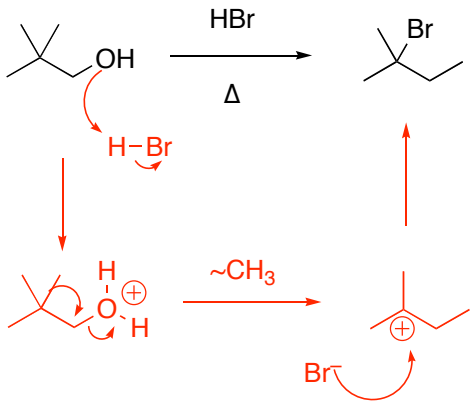
Chem 2061 Fall 2005
Ch 6 Homework

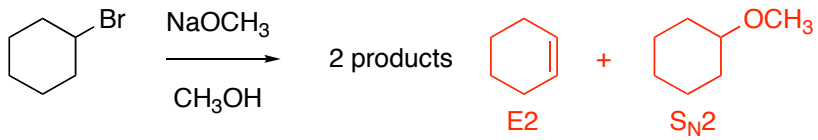
1. 2,2-dimethyl-1-propanol reacts slowly with HBr when heated to produce 2-bromo-2-methylbutane as the major product. Draw a full stepwise mechanism with all curved arrows to account for this product.




Remember, neopentyl leaving groups will methyl shift while the leaving group is leaving, forming a tertiary carbocation. This is then attacked by bromide (which is too weak of a base to eliminate). This is an $S_N1$ mechanism.

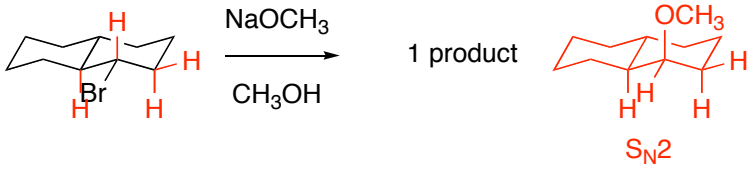
2. Predict the mechanism the following conditions will react with ($S_N1$, $S_N2$, E1, or E2), and draw major product(s) with correct stereochemistry where applicable. Briefly explain your rationale.

a.

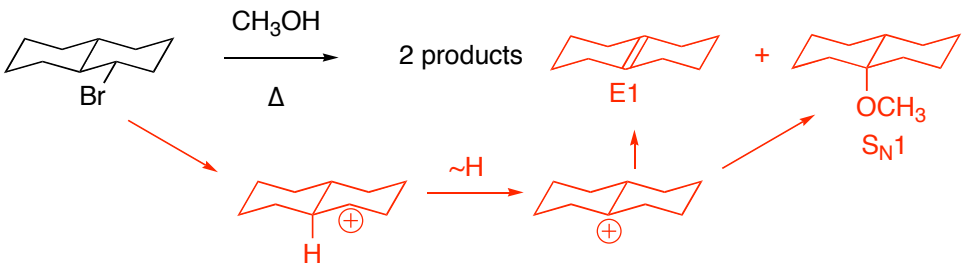



Since $NaOCH_3$ is a strong nucleophile and base, it will force a 2nd-order mechanism. It is not a bulky base, so the 2° alkyl halide will give a mixture of E2 and $S_N2$ products.

b.

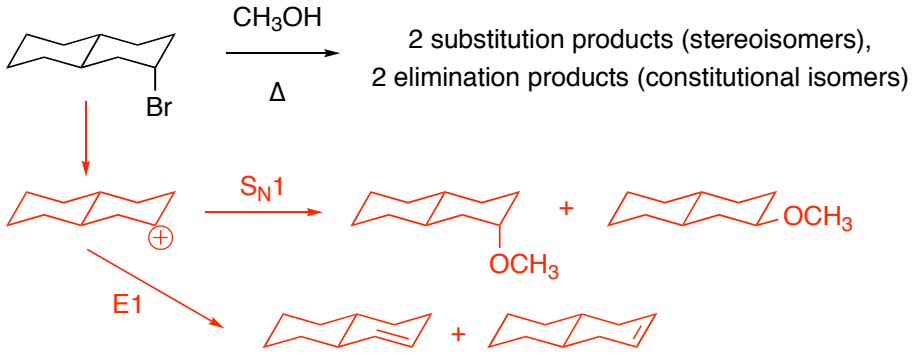



This bicyclic compound is locked into a single chair-flipped conformation, which has no adjacent hydrogens anti-coplanar to the bromine. Therefore E2 is impossible. The only product will be $S_N2$, with corresponding inversion of configuration.




c.

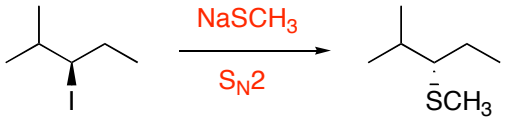
Lack of a strong nucleophile/base means the reaction is 1st order. The carbocation adjacent to the tertiary carbon will undergo hydride shift, and then elimination (Saitseff) and substitution products will be observed.




d.

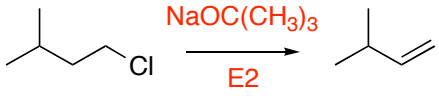
There are two substitution products resulting from attack of either side of the flat carbocation, and two elimination products, both disubstituted double bonds.

3. Predict the reagents and conditions necessary to complete the following reactions, and, as always, briefly explain your rationale.



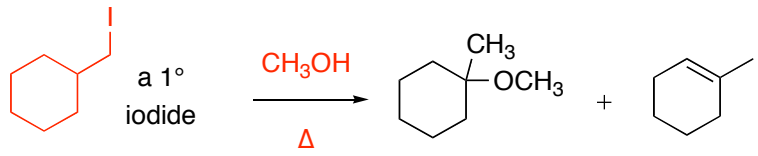

a.

$NaSCH_3$ (or $KSCH_3$ – any source of $SCH_3^-$) is a strong enough nucleophile and a weak enough base to give this single major product. Stereochemistry is inverted because of the concerted 2nd-order reaction




b.

The only way to get this single major product is to force elimination by using a very bulky base like t-butoxide. Diisopropylamine or triethylamine would have also worked. The bulky base prevents the 1° alkyl halide from substituting.




c.

There must be substitution and elimination competing. Since both products could only be formed by a tertiary carbocation on the ring, there must have been a hydride shift in order to have started with the primary iodide. Methanol and heat gives us these first-order conditions necessary.