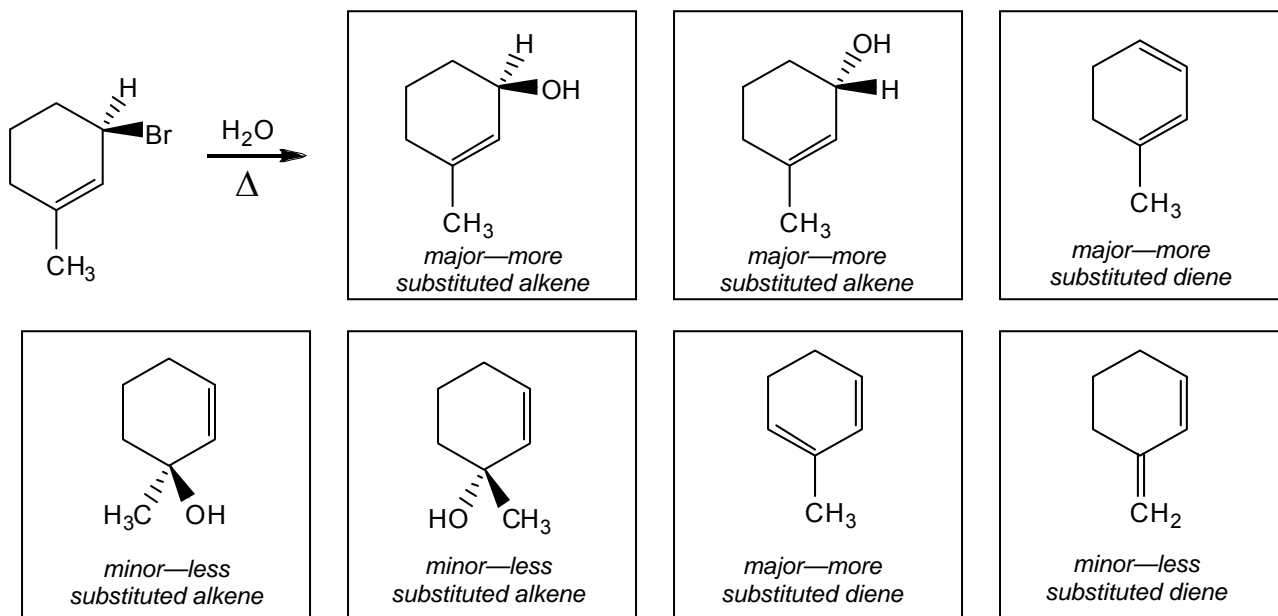
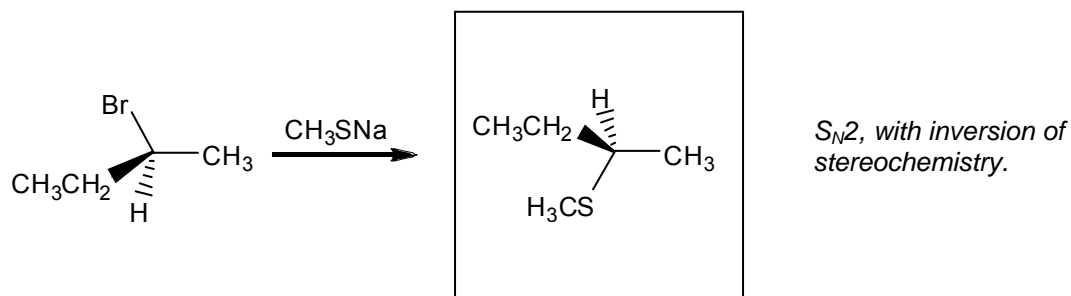
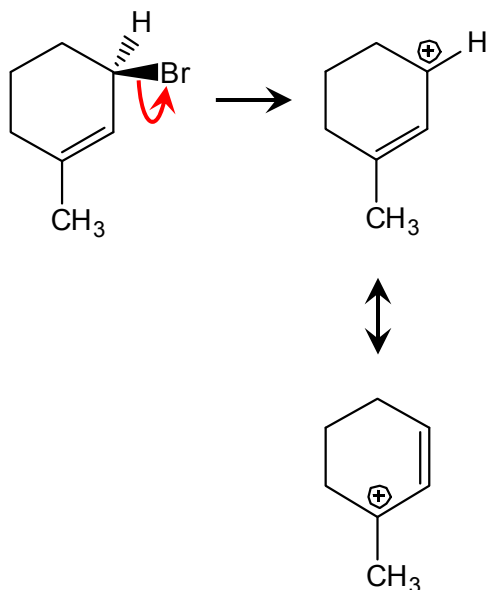


### Workshop 14 Solutions Predicting Reaction Outcomes

Predict the starting materials, reagents or products in the following reactions; put one molecule in each box. (Stereoisomers count as separate molecules.) If there are multiple products, state which ones are major or minor.



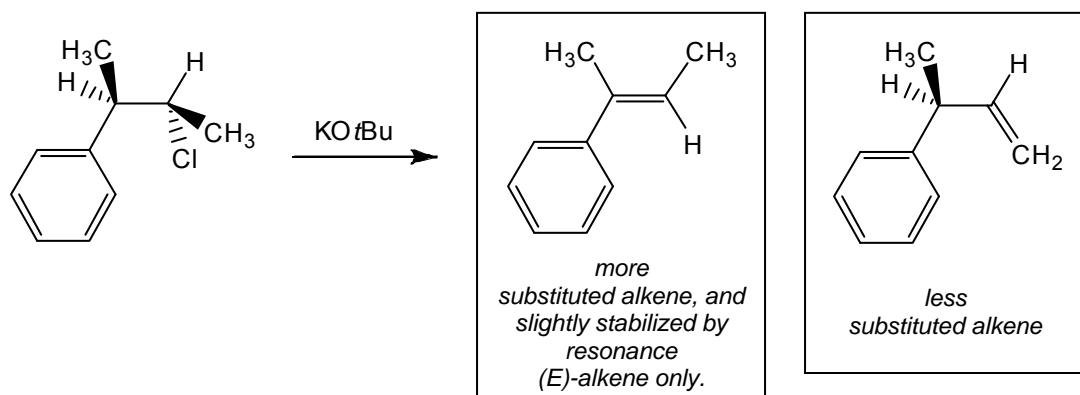
The reaction conditions here are E1/S<sub>N</sub>1 conditions. (The chart we looked at in class shows H<sub>2</sub>O to be a better base than nucleophile, and prefers E1. But as we discussed in class, S<sub>N</sub>1 nearly always accompanies E1.) Both of those mechanisms go through a common cation intermediate:



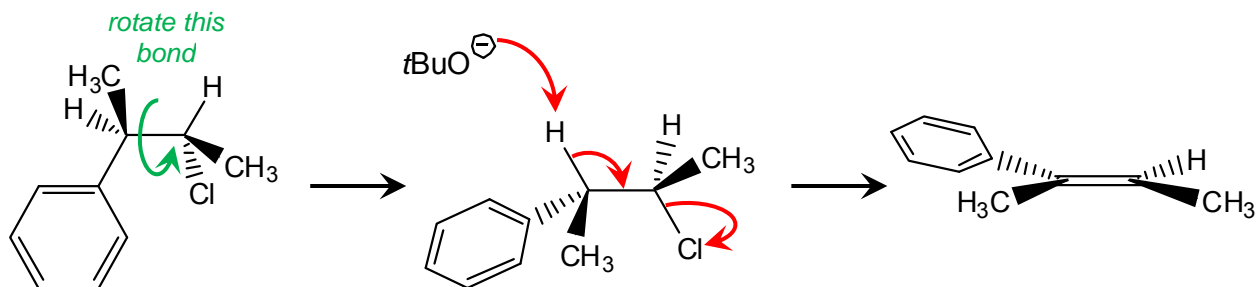
The top three products come from this first cation; the first two via  $S_N1$  using  $H_2O$  as a nucleophile, and the third via  $E1$  using  $H_2O$  as a base. So where do the other products come from? The cation at left is great because it is resonance stabilized, and its resonance structure places the positive charge on a different carbon, which can further react via  $E1$  and  $S_N1$  to make the other four products.

An important note: many students who work on this problem propose 1,2-hydride shifts (cation rearrangements) to explain other products. This would not happen here. This cation is stabilized by resonance, but shift an H, and you would have a cation that is not resonance stabilized. 1,2-Hydride and 1,2-alkyl shifts only

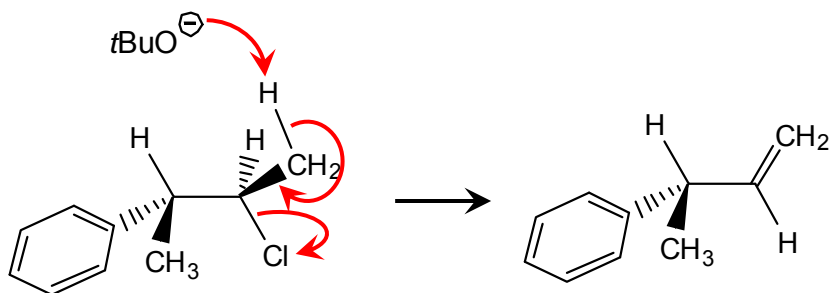
occur when the cation can be made more stable by the rearrangement, not less stable.



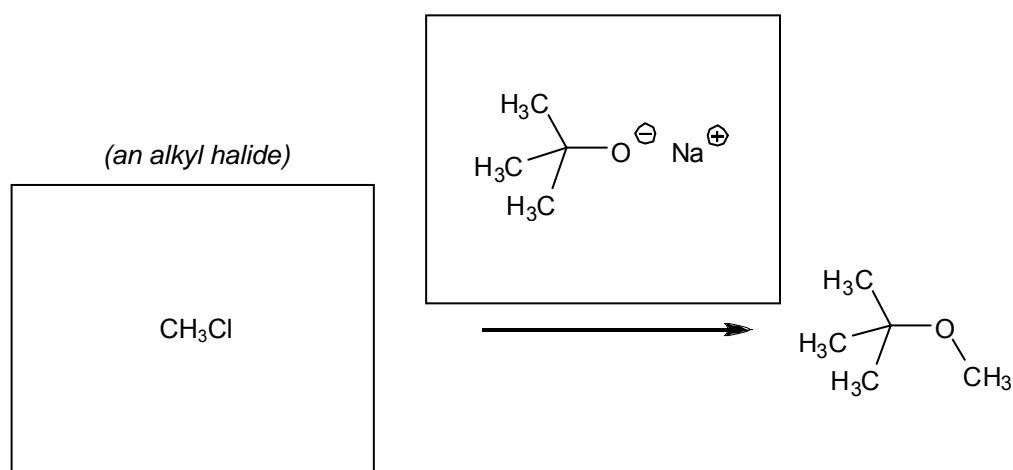
$KOtBu$  is a very strong base and not a great nucleophile, and it will react via  $E2$ . The  $Cl$  leaving group is attached to a carbon with two neighboring carbons, and each neighbor has an  $H$  that could be taken by  $tBuO^-$  anion. In the case of the  $H$  on the left, this is pretty similar to an In-Class Exercise we did, where the central  $C-C$  bond needs to be rotated to satisfy the anti-coplanar requirement of  $E2$ :



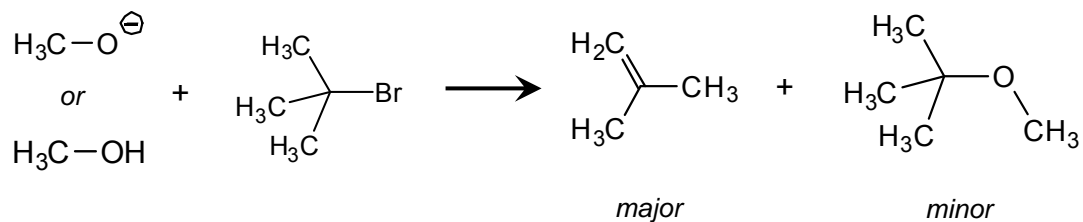
The base could also take an H from the methyl group:



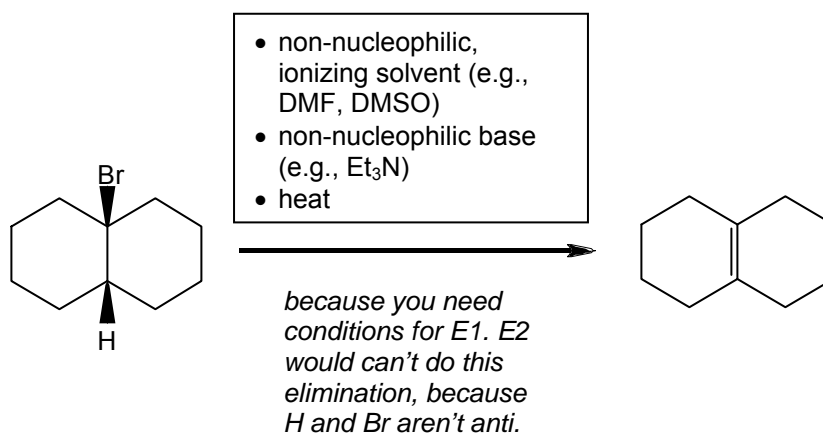
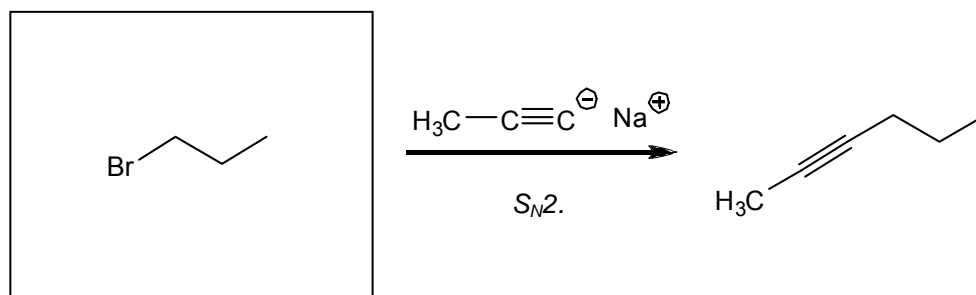
Which of these would be preferred? The more substituted alkene is the more stable alkene, and Zaitsev's rule says that this would normally be the preferred product. But *tert*-butoxide is a large, hindered base, and so it prefers to take a hydrogen from the least-hindered position--producing the less-substituted alkene. I think this drives selectivity in this reaction.



You would think that there would be another possible answer to this problem, where the roles of the two segments of the molecules were reversed (in which the methyl group is the alkoxide or alcohol and the *t*-butyl group is the halide). The problem with this combination is that it will react E2 rather than  $S_N2$ , or E1 rather than  $S_N1$ :



By contrast, the combination I've put in the boxes cannot do elimination;  $\text{CH}_3\text{Cl}$  only has one carbon, so it can't get converted to an alkene.



Not only would  $\text{E}2$  not work here, it would actually give you different products than the one you want. If a strong base needed to take an  $\text{H}$  from the underside of the molecule in order to accommodate the anti-coplanar requirement of  $\text{E}2$ , it could find one on a different carbon:

