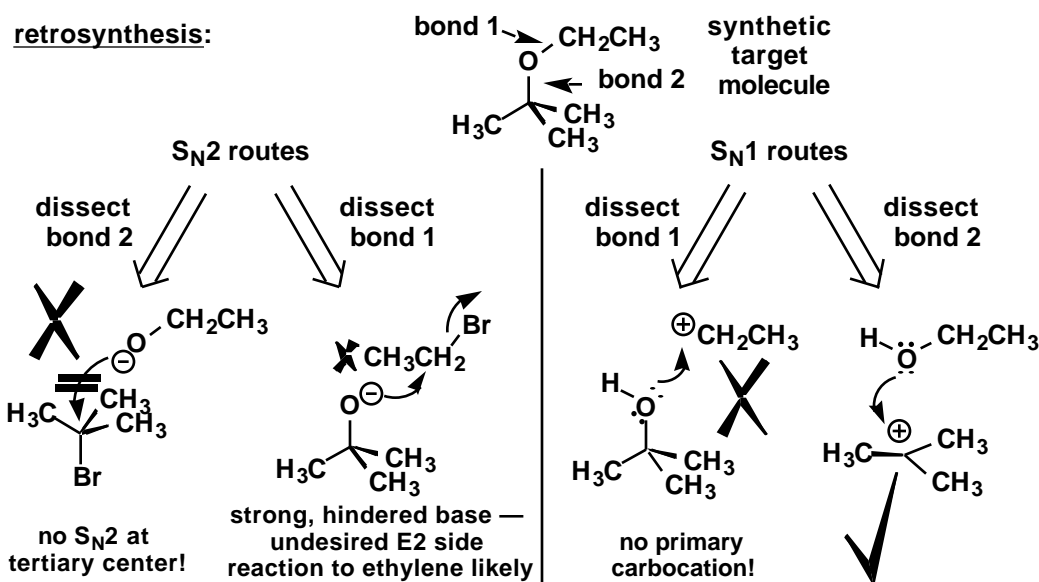


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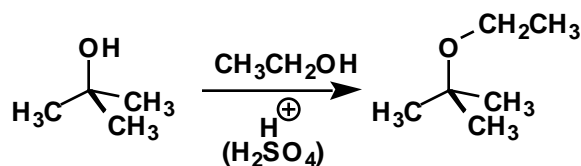
At the conclusion of our discussion of reactions that proceed by the S_N2 mechanism (Segment 13.07), we examined the chemical synthesis of isopropyl methyl ether from isopropanol and methanol by S_N2 routes, using as an aid the procedure of retrosynthetic analysis. Our arsenal of reactions now has been enhanced. It will be fruitful to reconsider the exercise in this light, and particularly instructive to modify the structure of the target somewhat: now we will consider the chemical synthesis of ethyl t-butyl ether from ethanol and t-butanol by S_N2 and S_N1 routes. Among the former, the reaction of ethylate anion with t-butyl bromide will give only elimination, yielding ethanol and isobutylene; there can be no S_N2 reaction at the tertiary center. However, in this case if we alter our approach, using t-butylate anion and ethyl bromide, we again can expect poor results. Formally we seem not to be breaking any of the rules which we have established: ethyl bromide is a primary bromide. However, the t-butylate anion is so encumbered that there is, in fact, hindrance by its methyl groups even at its front (oxygen) side. In addition, t-butylate anion is an extremely strong base. The net result is that even in this primary case much elimination (to yield ethylene), rather than substitution, can be expected when t-butylate anion is the base.

Examination of S_N1 routes to ethyl t-butyl ether also proves, at first, disappointing. We should not invoke a primary carbocation (as per S_N1 dissection 1, below) as an intermediate that we can hope to employ. However, this time when we vary the bond to be dissected, we uncover an excellent possibility. If we can produce the t-butyl carbocation in ethanol solution, it should collapse to give an oxonium ion that, upon loss of a proton, should yield the target. Indeed, this approach has brought us to a workable synthesis: we need only add t-butyl alcohol to an ethanolic solution containing strong acid, for example, sulfuric acid, to obtain the desired product. Our figure uses several notations to outline not only the

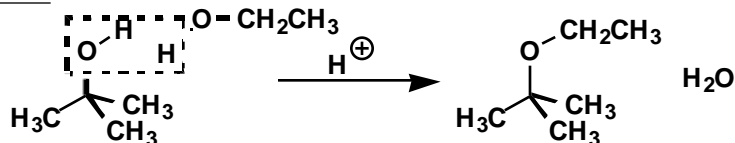
retrosynthetic analysis, but also the synthesis in the forward direction, the overall stoichiometry, and the solvolysis mechanism.



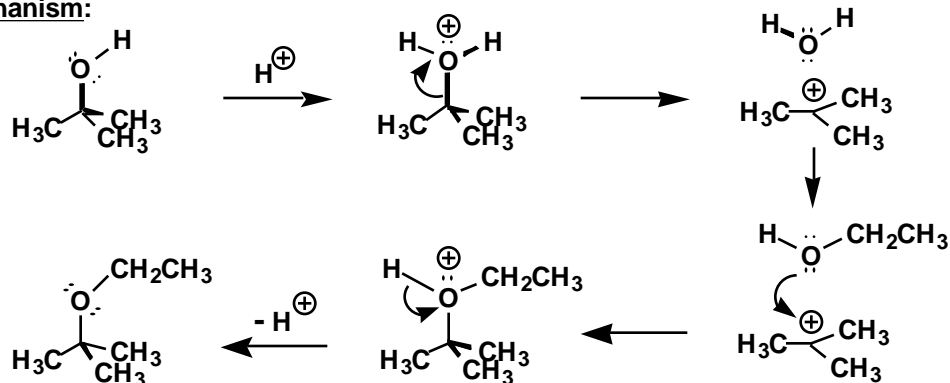
synthesis:



overall reaction:



mechanism:



retrosynthesis and synthesis of ethyl t-butyl ether
 from alcohols by both S_N2 and S_N1 routes

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