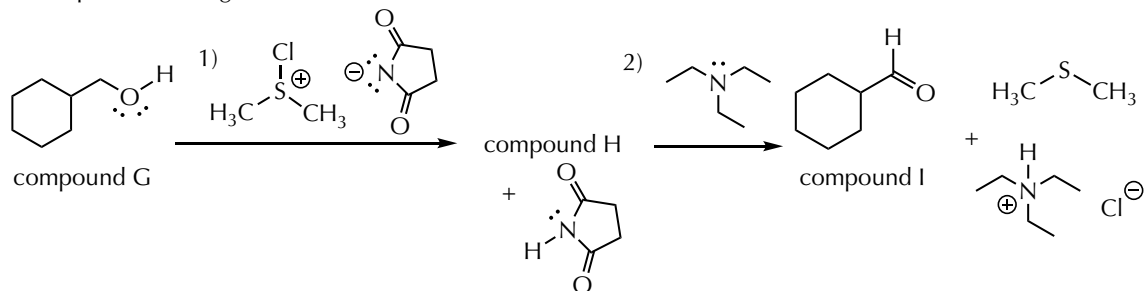
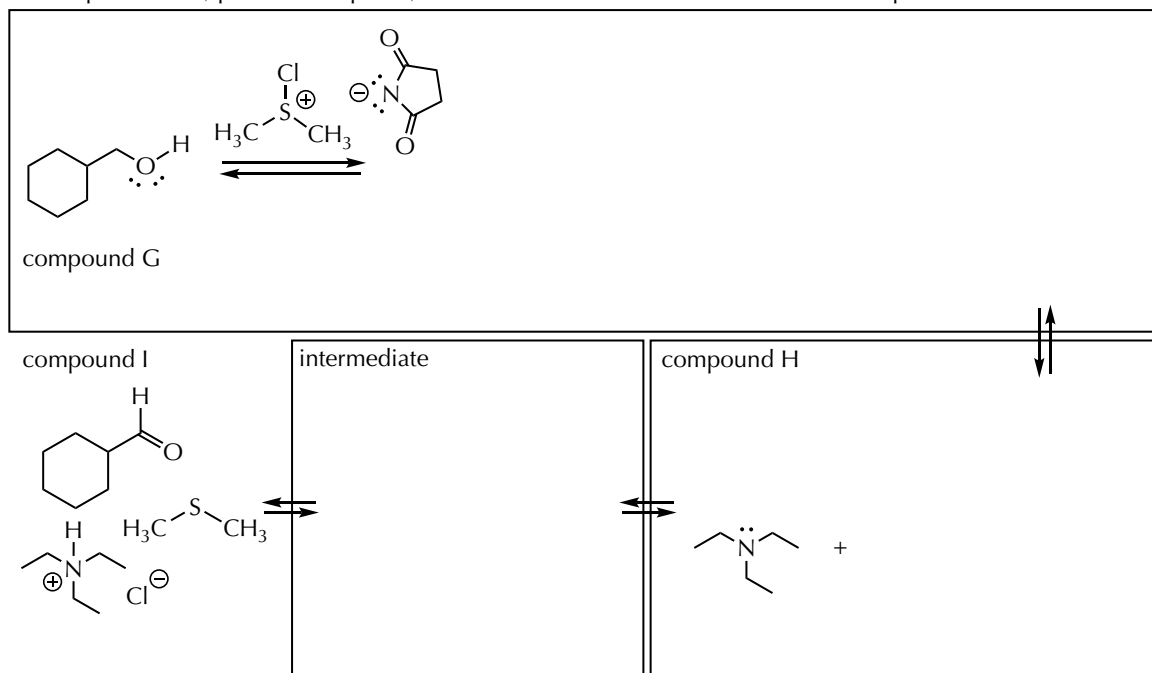


11.11 The Corey-Kim reaction is a mild oxidation reaction that is analogous to the Swern oxidation. In the first part, the hydroxyl group of compound G reacts with the chlorosulfonium reagent to form compound H. The elimination step then occurs upon addition of triethylamine to H, exactly as in the Swern oxidation, leading to compound I through an intermediate.

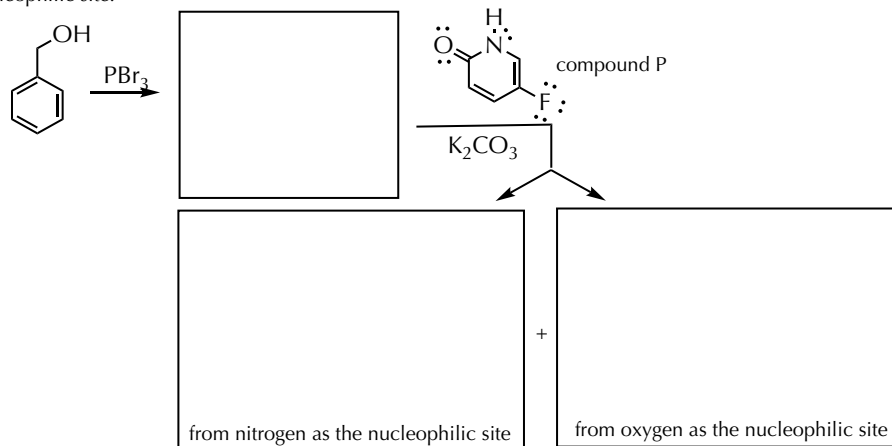


In the space below, provide a stepwise, curved arrow mechanism for this reaction sequence.



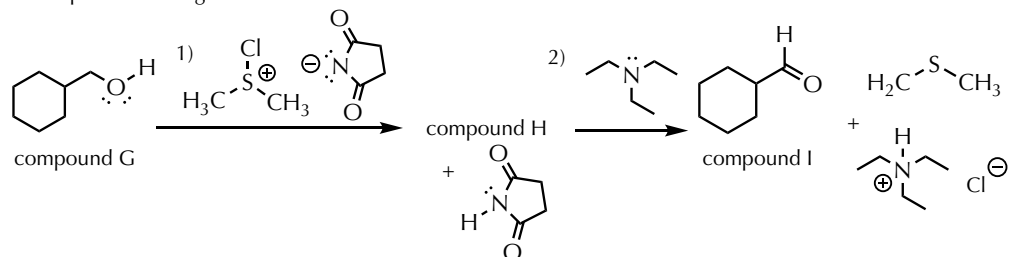
Question not used in the text:

Fill in the missing product(s) in the reaction scheme below. Using K_2CO_3 as the base and compound P as the nucleophile, two regioisomers (constitutional isomers) of the final product are formed. These result from either the oxygen or nitrogen atom of compound P serving as the nucleophilic site.

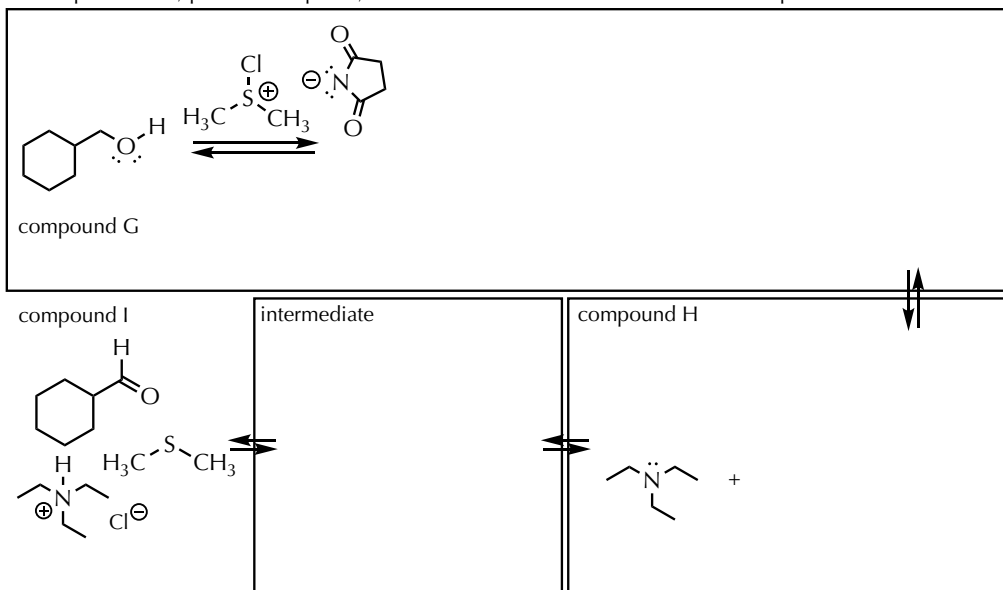


Chemistry 215 • Thinking in Blue • Week 02

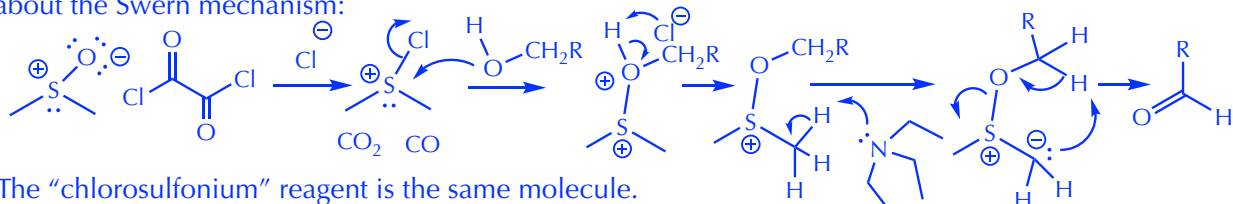
11.11 The Corey-Kim reaction is a mild oxidation reaction that is analogous to the Swern oxidation. In the first part, the hydroxyl group of compound G reacts with the chlorosulfonium reagent to form compound H. The elimination step then occurs upon addition of triethylamine to H, exactly as in the Swern oxidation, leading to compound I through an intermediate.



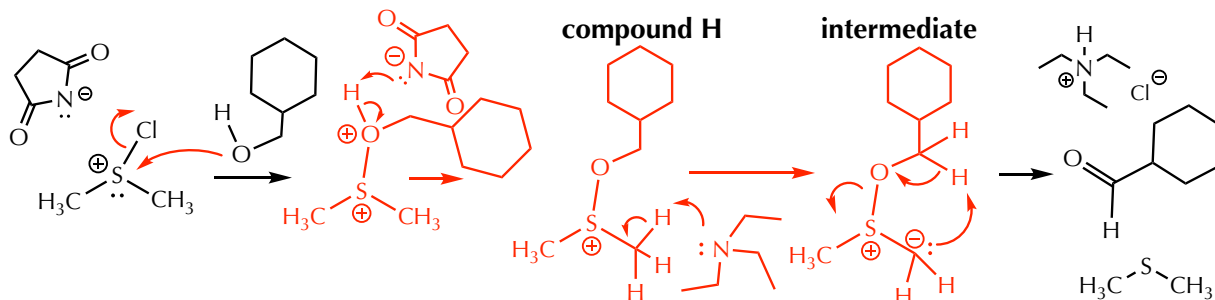
In the space below, provide a stepwise, curved arrow mechanism for this reaction sequence.



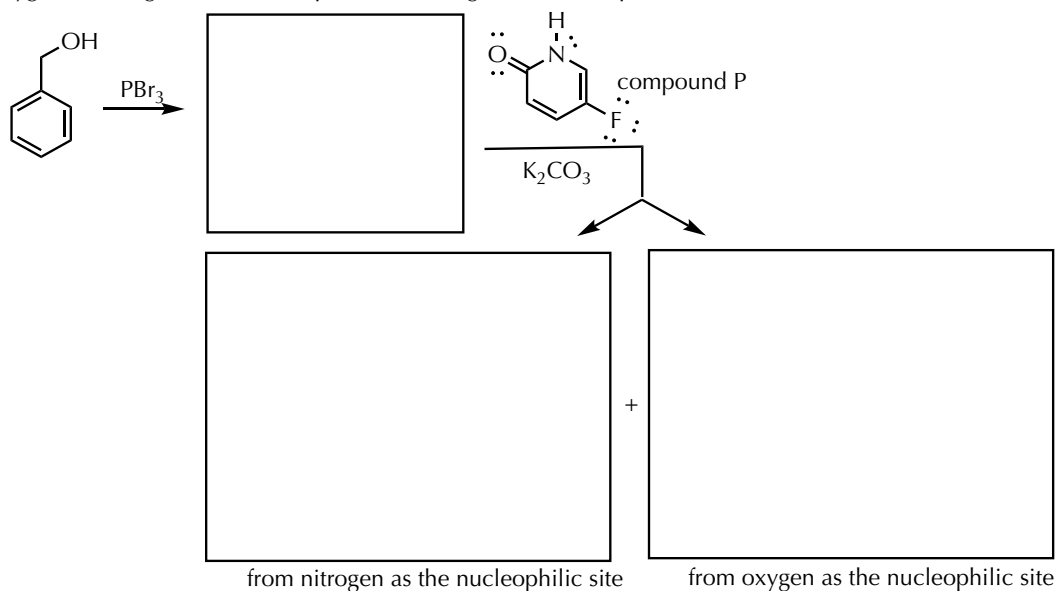
The first sentence states that the details of the Swern oxidation mechanism are required to be familiar. The second and third sentences make reference to the Swern steps as an analogy; without the Swern details coming in, however, the analogy is not meaningful. First, you need to remember the details about the Swern mechanism:



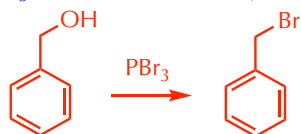
The "chlorosulfonium" reagent is the same molecule. The anionic nitrogen will deprotonate the HO⁺ intermediate.



Fill in the missing product(s) in the reaction scheme below. Using K_2CO_3 as the base and compound P as the nucleophile, two regioisomers (constitutional isomers) of the final product are formed. These result from either the oxygen or nitrogen atom of compound P serving as the nucleophilic site.

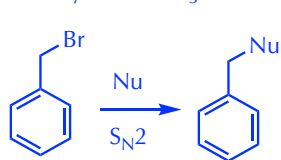


There is no getting around it: reagent-based chemistry must be specifically remembered for its general application. In this case, the reagent “ PBr_3 ” is one of the one-step “ ROH -to- RX ” reagents, which can be applied to thousands of alcohol substrates.

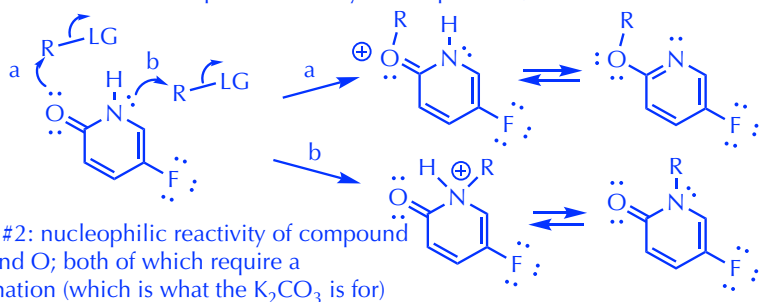


As compound P is described as a nucleophile, there is a bit of information there because the “ OH ” group of the alcohol is not a leaving group, so the inference is that the first reaction is producing one. This may be subtle, but it is a real reminder about the PBr_3 reaction that can be inferred from the text.

The rest of the problem derives strongly from the text, as compound P is specifically described as a nucleophile and that both its nitrogen atom and oxygen atom are potential nucleophilic sites. Conceptually, the result from the PBr_3 reaction can undergo nucleophilic reactions according to the S_N2 concept. Thus, these two pieces of information (about the reactivity of the PBr_3 reaction product, and about the nucleophilic reactivity of compound P) need to be combined.



concept #1: S_N2 reactivity of the alkyl bromide



concept #2: nucleophilic reactivity of compound P, at N and O; both of which require a deprotonation (which is what the K_2CO_3 is for)

