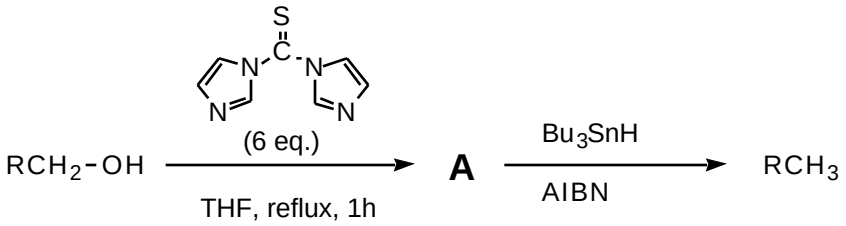

The original exam had schemes and tables added via cut & paste.
Please refer to the original articles cited
when solving this cume as an exercise.

Organic Cumulative Exam

January 1998

Deoxygenation of Alcohols and Other Reactions
(*JACS* **1997**, *119*, 8572)

1. A standard method for converting alcohols to their hydrocarbon derivatives is known as the Barton Deoxygenation Reaction. For the Barton Deoxygenation shown below, show the structure of the intermediate "**A**" and provide a mechanism for the transformation of **A** to the deoxygenation product. (10 pts)



Barton et al. *Synthesis* **1981**, 743.

2. Suggest another reaction or series of reactions (other than the one discussed below) that can be used to effect this transformation (ROH→RH). (5 pts)

Myers and coworkers recently reported (*JACS* **1997**, *119*, 8572) a new, one-step deoxygenation method that they feel represents a useful complement to the Barton Deoxygenation. The overall transformation is shown below:

Note: DEAD = diethylazodicarboxylate
NBSH = *o*-nitrobenzenesulfonylhydrazine

3. The transformation of **1** to **2** is a Mitsunobu displacement reaction. Propose a mechanism for the conversion of **1** to **2**. (10 pts)

4. Let us now consider the second half of Myers' reaction shown in the Scheme on the previous page: the conversion of the alkylsulfonyl hydrazine (**3**) to the alkane derivative (**4**). In their *JACS* paper, Myers and coworkers provided ^{1}H-NMR evidence that, upon warming, the alkylsulfonylhydrazine eliminates *o*-nitrobenzenesulfinic acid to afford a monoalkyl diazene (characterized on the basis of the diazenyl proton at 15.6 ppm and a characteristic long range coupling (2.2 Hz) to the adjacent methylene CH_2).

Look at entries 7-10 in Table 1. The nature of these products clearly tells you something important about the mechanism by which the diazene is transformed to the final product **4**. Show detailed mechanisms for the conversion of the substrates shown in entries 7 and 8 to the products shown in entries 7 and 8 (you need only show the conversion of the diazene to the final product). (15 pts)

5. Entry number 10 in Table 1 is particularly interesting. The substrate does not undergo net deoxygenation, rather the compound undergoes cyclization and *apparent migration* of the hydroxyl group! Importantly, this reaction was performed under O_2 (all the other reactions were performed under inert atmosphere). Also, at the end of the reaction, the products in entry 10 were subjected to a methyl sulfide workup (similar to that used at the end of ozonolysis reactions). When performed under $^{18}O_2$, >96% incorporation of ^{18}O into the product is observed. Provide a mechanism to explain entry number 10. (10 pts)

6. With certain unsaturated substrates, the reaction conditions employed for the "Myers Deoxygenation" give a completely different type of product as shown below. The different product obtained, it turns out, is indicative of a change in mechanism. Suggest a non-radical mechanism for the reaction. (10 pts)

7. In fact, Myers' group originally developed the general reaction shown above for the preparation of allenes (*JACS* **1996**, *118,* 4492). Using this general reaction, and starting with any three carbon alcohol that you like, devise a synthesis for the allene shown below. (10 pts) Even if you can't propose a synthesis that utilizes Myers' reaction, you'll get some credit for any viable route.