

Errata

The following list contains the changes that were made in the Preparatory Problems after the January printing. The latest online version was updated with the first three changes.

Problem 12

The table contained standard redox potentials of the $I_2/2 I^-$ system, while the solution used the value as if it belonged to the slightly different $I_3^-/3 I^-$ system. We thank Szilárd Varga of Hungary for pointing this out.

Problem 13

The numerical result in the solution of question h) was incorrect. We thank Yury Halauko of Belarus for pointing this out.

Problem 20

The R/S designations in question c) were swapped. We thank Yury Halauko of Belarus for pointing this out.

Problem 25

The solution of question f) v. had incorrect numerical values and a sign was missing from the formula.

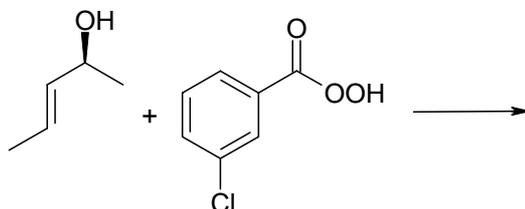
$$t(99\%) = -\ln(1-0.99)/k = 384 \text{ s}$$

$$t(99.99\%) = -\ln(1-0.9999)/k = 768 \text{ s.}$$

We thank Professor Alexander Korobov of Ukraine for pointing this out.

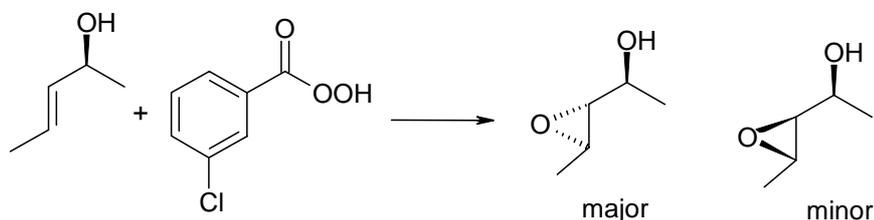
Problem 17 (additional information)

- b) What is the most likely product of the following reactions following work up? How many other stereoisomers might be formed?



Official answer for the Preparatory Problems: The epoxidation of the double bond by meta-chloroperoxybenzoic acid is directed by steric factors. The predominant site of attack is the sterically less hindered side of the double bond giving the „threo” compound as the major product. Attack from the other face of

the molecule is less facile and the „erythro” product is formed only in minor quantities.

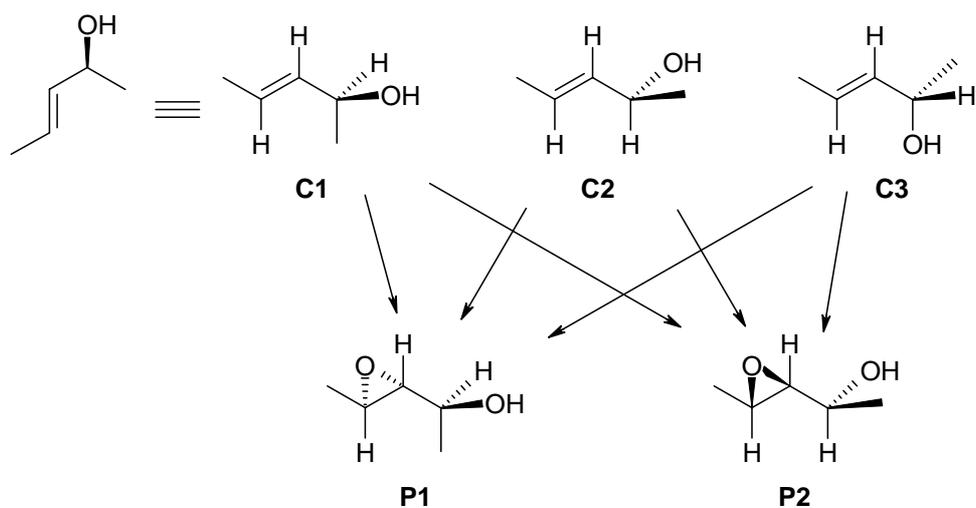


Author's comment:

To answer the above question in detail, one has to understand several issues that are not part of the Curriculum. Although we present a more detailed explanation below, we would like to point out that in this problem students were only expected to realize that there are 2 possible products that can be formed and they are diastereomers. The question “what is the most likely product” in this case relates primarily to constitution and not configuration.

To understand the present reaction in detail one should be aware of the conformational equilibria of allylic systems (WHICH IS NOT REQUIRED OF THE STUDENTS IN THIS PROBLEM) and some unique properties of the *m*-chloroperbenzoic acid catalyzed oxidation reactions.

Below we present 3 possible favored conformers of the starting allylic alcohol (C1, C2 and C3), and the structure of the possible products (P1, P2). Since P1 is the preferred product, it is evident that if one starts from conformer C1 (as hinted by the setting of the problem), then P1 is formed by the attack of MCPBA on the sterically less crowded side of the double bond. If on the other hand one assumes that the dominant conformer is C2 (based on knowledge that the students are not expected to possess), then the attack of MCPBA occurs on the side of the hydroxyl group suggesting that it has a directing effect on the side of the epoxidation by MCPBA. If C3 were the dominant conformer one had a great difficulty answering the product distribution. It is interesting to note that the minor product P2 is preferred by coordination if starting from C1 and preferred by steric factors if starting from C2.



In the everyday practice MOST of the epoxidations by MCPBA occur on the sterically less hindered side of the double bond. EXCEPT for allylic alcohols, where the hydrogen bonding of MCPBA to the hydroxyl group might alter the course of the reaction considerably.

We thank Artiom Cernijenko of Lithuania for pointing out the need of clarification.