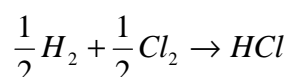


## Autoevaluation TEST N°2 (Topics 6-8)

Family name and name \_\_\_\_\_

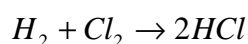
**Important:** Write your name before beginning the test. No additional material will be provided. Books, class notes are not allowed. Calculators are allowed. Use margins for drafts or calculus. **Mark with a cross the correct answer in the box at your left when you are completely sure. No crossings out and no additional comments are allowed. Correct answers mark as +1. Errors mark -0.1. Blanks mark as 0. The final score can not be less than 0.** There is only one correct answer in each question.

- 1) Assuming a molecularity value of 2 for the appearance of HCl in the following reaction, propose a kinetic equation for the rate of appearance of HCl and for the time variation of [HCl].



**Solution:**

Molecularity means number of atoms or molecules that participate in a reaction event, eg. collision. For the appearance of HCl we can write the reaction in equivalent terms



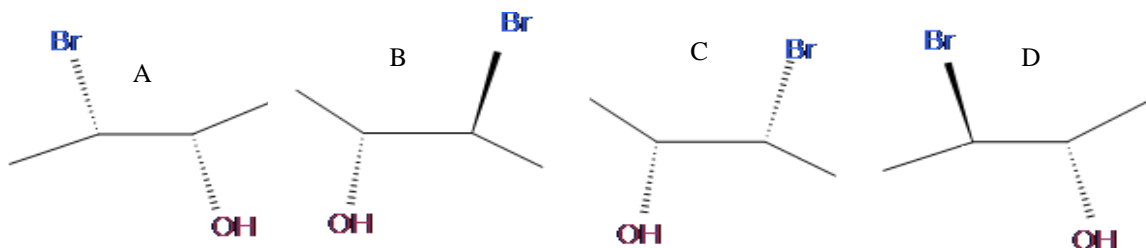
where it becomes clear that the number of molecules that participate in the production of HCl is 2. If molecularity is known that means that the reaction mechanism is also known so the reaction order must be also 2. Therefore the kinetic rate equation is:

$$\frac{1}{2} \frac{d[HCl]}{dt} = k \cdot [H_2] \cdot [Cl_2] = k[HCl]^2$$

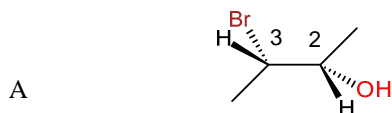
To obtain the time variation of [HCl] we need to integrate the rate equation.

$$\frac{d[HCl]}{[HCl]^2} = 2kdt; \quad \int_{[HCl]=[HCl]_0}^{[HCl]=[HCl]_t} \frac{d[HCl]}{[HCl]^2} = \int_{t=t_0}^t 2kdt; \quad \boxed{\frac{1}{[HCl]_t} - \frac{1}{[HCl]_0} = 2kt}$$

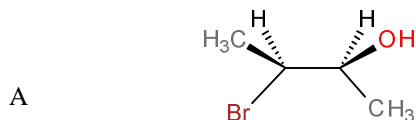
- 2) Unlike enantiomers which are mirror images of each other and non-superimposable, diastereomers are not mirror images of each other and non-superimposable. Here you have some stereoisomers of 3-bromo-2-butanol. Assign their SS, RR, SR, RS configurations and show which are enantiomers and which diastereomers



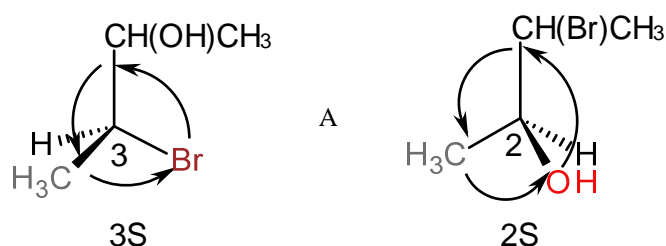
**Solution:** Step by step. Let us begin with A. The complete structure including hydrogen atoms is



We observe that OH has more priority than Br so the carbon atom to which OH is bonded is number 2. We can rotate the C2-C3 bond so as to locate the two hydrogen atoms behind the plane of the page. The resulting structure is



Now we select atoms 2 and 3 and draw two tetrahedrons locating the hydrogen atoms behind the plane of the page



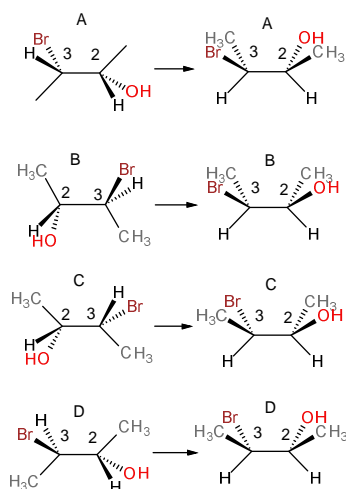
We see therefore that A is (2S,3S)-3-bromobutan-2-ol. The rest of stereoisomers can be named following similar constructions:

B: (2R,3S)-3-bromobutan-2-ol

C: (2R,3R)-3-bromobutan-2-ol

D: (2S,3R)-3-bromobutan-2-ol

To find which are diastereomers and which enantiomers it is convenient to draw Fisher projections. For doing so, and for the purpose of practicing, it is convenient to draw the 3D structures in which bonds have been rotated to locate hydrogen atoms below the plane and in which molecules have been rotated to set carbon 2 (that with OH) in the right. In the next figure we show the initial structures as appear in the exam at the left and the rotated structures at the right:

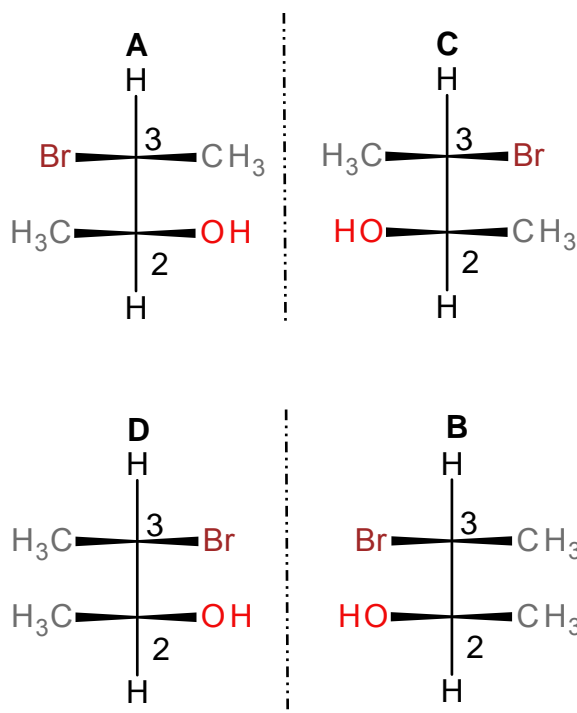


Now the Fisher projections are very simple to draw:

### Autoevaluation TEST N°2 (Topics 6-8)

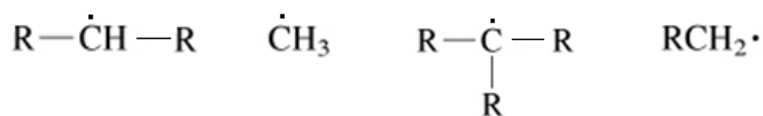
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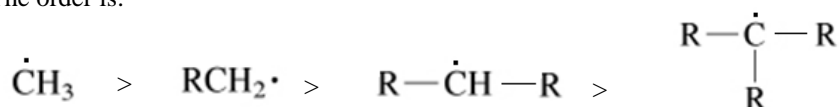
We can observe that A and C are enantiomers as well as D and B. But A and B or D or C and B or D are diastereomers because they are not mirror images.

3) Sort by increasing stability the following radicals. Explain the answer



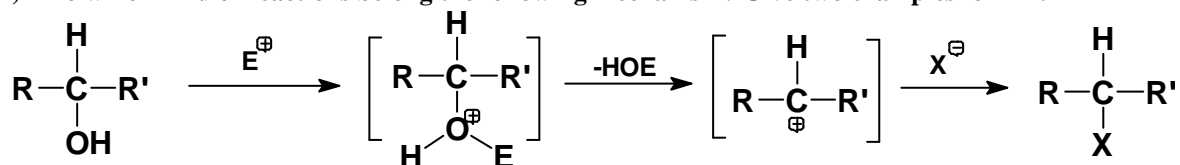
**Solution:**

The order is:



Tertiary radicals are more stable than secondary or primary or even the methyl radical because they have more hyperconjugation structures.

4) To which kind of reactions belong the following mechanism? Give two examples for EX.

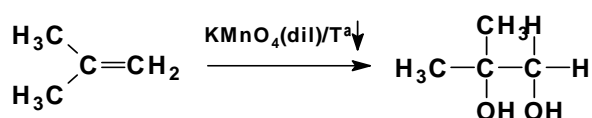


**Solution:**

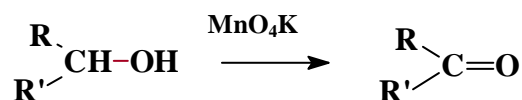
This mechanism corresponds to electrophilic substitutions in alcohols. The electrophilic agents may be binary acids such as HCl or HBr or even halogenating agents such as  $\text{PCl}_3$

5) Give examples of three oxidation reactions and three reduction reactions. Use different functional groups

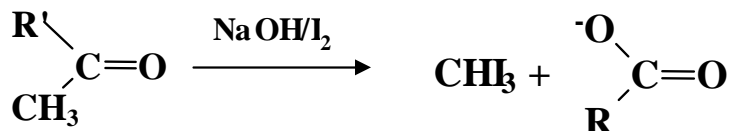
a) Oxidation of alkenes with  $\text{KMnO}_4$  to give glycols



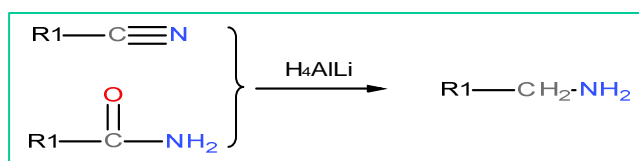
b) Oxidation of secondary alcohols with  $\text{KMnO}_4$  to give ketones



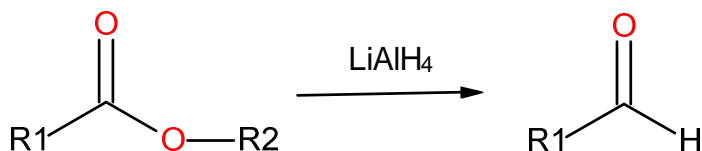
c) Oxidation of methyl ketones with  $\text{NaOH} / \text{I}_2$  to acids (the haloform reaction)



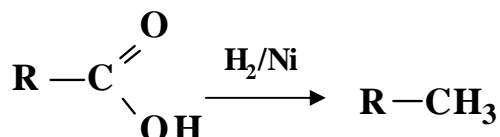
d) Reduction of nitriles or amides with  $\text{AlLiH}_4$  to give amines



e) Reduction of esters with  $\text{AlLiH}_4$  to give aldehydes



f) Reduction of carboxylic acids with  $\text{H}_2$  and a catalyst to give alkanes



**Autoevaluation TEST N°2** (Topics 6-8)

**Family name and name** \_\_\_\_\_

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