

Tutorial letter 201/1/2016

General Chemistry 1B

CHE1502

Semester 1

Department of Chemistry

This tutorial letter contains the answers to the questions in assignment 1.

BAR CODE

FIRST SEMESTER: KEY TO ASSIGNMENT 1

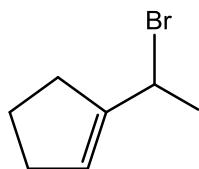
DUE DATE: 1 March 2016

UNIQUE NUMBER: 838537

1. Correct Answer: (2)

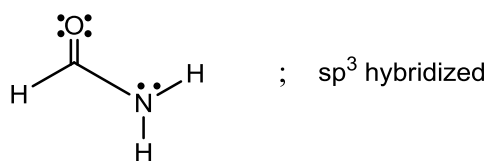
It contains a σ molecular orbital formed by the overlap of one carbon sp^2 hybrid orbitals and one hydrogen sp^3 hybrid orbital.

Based on the structure of the following compound, the above statement is INCORRECT because a hydrogen atom only has a 1s orbital available for overlap with another orbital.



All the other statements are correct.

2. Correct Answer: (1)



The above DOES NOT represent the **appropriate hybridization state of the carbon atom** in the structure shown. The C is part of a C=O bond and therefore it is sp^2 hybridized.

All the other options represent the correct hybridization state of the carbon atom in the respective structure shown.

3. Correct Answer: (2)



The pair of compounds above is constitutional isomers because they have the same molecular formula ($\text{C}_3\text{H}_9\text{N}$).

The other options:

(1) $\text{ClCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ – The SAME COMPOUND

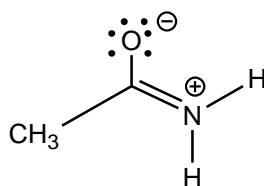
(3) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ and $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$

Compound on the left has a molecular formula of C_4H_{10} and the one on the right has a molecular formula of C_5H_{12} . The compounds have no relationship.

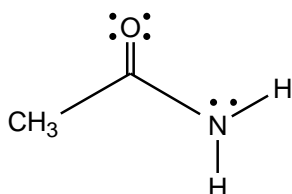
(4) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Compound on the left has a molecular formula of $\text{C}_4\text{H}_{10}\text{O}$ and the one on the right has a molecular formula of $\text{C}_3\text{H}_8\text{O}$ – the compounds have no relationship.

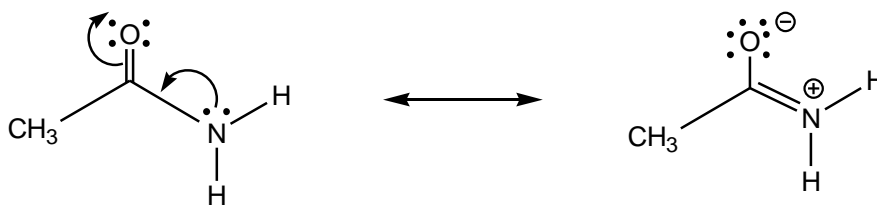
4. Correct Answer: (4)



The structure above is another resonance form of the following organic molecule:



The molecule undergoes resonance delocalization as follows:



5. Correct Answer: (3) 3 < 4 < 1 < 2

The above arrangement represents the compounds shown below in order of increasing Bronsted basicity (weakest first).

1. NH_3 2. OH^- 3. Cl^- 4. H_2O

A Bronsted base is a species that can accept a proton. The proton has no electrons therefore a Bronsted base must contain an electron pair which is available for donation to the proton. The more readily a compound is able to accept a proton, the stronger the base.

If we compare the molecules NH_3 and H_2O , the atoms N and O are both in the same row in the periodic table. Oxygen is more electronegative than N and will therefore attract its lone pair of electrons stronger than nitrogen. The nitrogen will donate its lone pair of electrons more readily to a proton than the oxygen atom, therefore the NH_3 molecule is a stronger Bronsted base than H_2O .

The Cl^- atom has 7 electrons in its outer shell. The Cl^- atom will not accept a proton, it will rather accept an electron in order to obtain an octet structure.

The OH^- ion is the strongest Bronsted base because when it accepts a proton H_2O is formed as the conjugate acid. The water molecule (H_2O) is a weak acid.

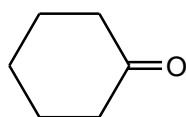
6. Correct Answer: (3)



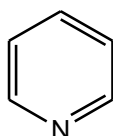
A Lewis base is a species that have a pair of electrons that can be donated to form a new bond. The B atom in BCl_3 does not have any lone pairs of electrons- it has an empty orbital which can accept an electron pair. BCl_3 is therefore a Lewis acid.

The other options are explained below:

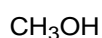
(1) The oxygen atom has two lone pairs of electrons and therefore can act as a Lewis base.



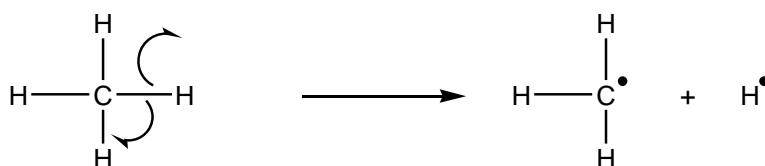
(2) The nitrogen atom has one lone pair of electrons and therefore can act as a Lewis base.



(4) The oxygen atom has two lone pairs of electrons and therefore can act as a Lewis base.



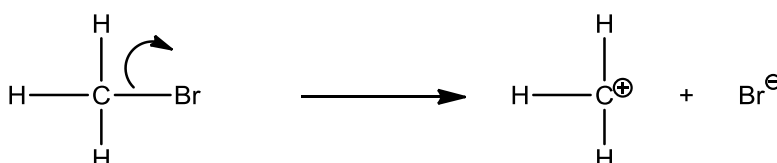
7. Correct Answer: (4)



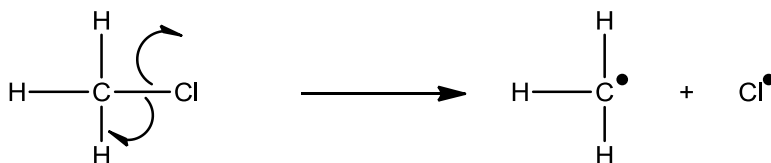
The above is a CORRECT process of bond breaking.

All the other options are incorrect. The corrected versions are shown below:

(1)



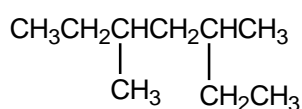
(2)



(3) The process should be the same as in (1) above.

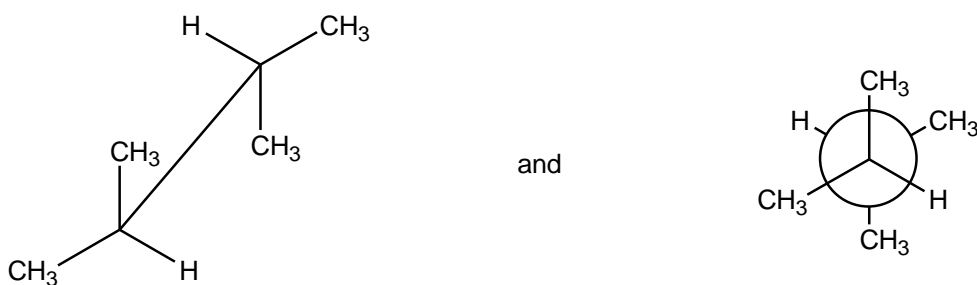
8. Correct Answer: (4) 3,5-dimethylheptane

The above is the correct IUPAC name of the following compound:



According to the IUPAC convention, the longest continuous carbon chain has 7 carbon atoms; 7 C's → heptane. Begin numbering at a branch to give substituents the lowest possible number - in this case, from either side → 3-methyl and 5-methyl. Two methyl groups → 3,5-dimethyl; name the substituents in alphabetical order.

9. Correct Answer: (2)

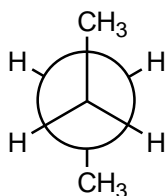


The above pair of drawings represents the identical conformations of the same compound. The first structure is the Sawhorse representation of the conformation and the second structure is the Newman projection of the same compound. The two structures represent the same conformation because the groups and atoms attached to the C-2 and C-3 are in the same

relationship with respect to each other in each structure.

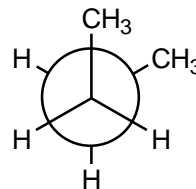
The other options:

- (1) Both conformations are staggered but they are different.



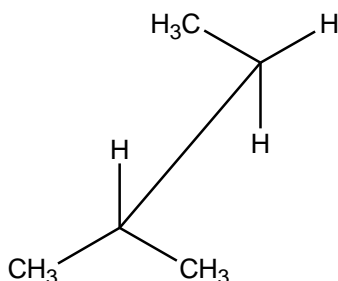
Anti conformation

and

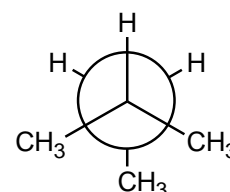


Gauche conformation

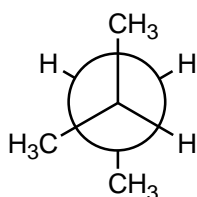
- (3) The two structures represent different conformations - in the structure of the left, the CH_3 group (in top C) is between a CH_3 group and a H atom of the other C atom. In the structure of the right, the CH_3 group of the one C is between a CH_3 group and another CH_3 group of the other C atom.



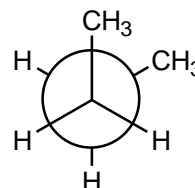
and



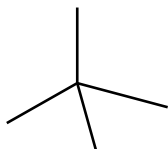
- (4) The conformations below do not have the same molecular formula – each conformation represents a different compound. The first Newman projection is a conformation of 2-methylbutane and the second Newman projection represents a conformation of *n*-butane.



and



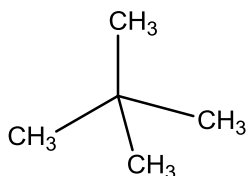
10. Correct Answer: (1)



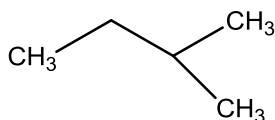
The above molecule has the MOST 1° hydrogens.

A discussion of all the options where the hydrogens, attached to primary carbons, are shown below:

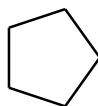
- (1) A primary C (1° C) is attached to one other C atom – the hydrogens attached to a primary C are called 1° hydrogens. There are four methyl groups and there are therefore twelve, (4x3 = 12), 1° hydrogens.



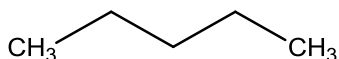
- (2) There are three methyl groups and there are therefore nine, (3x3 = 9), 1° hydrogens.



- (3) There are no primary C's – all C's are secondary, 2°, carbons and the compound has zero 1° hydrogens.



- (4) There are two methyl groups and there are therefore six, (2x3 = 6), 1° hydrogens.



N.B. You should be able to identify the secondary and tertiary carbons/ hydrogens.

11. Correct Answer: (2) secondary free radicals are more stable than primary free radicals

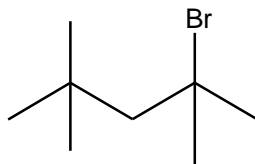
The reaction of chlorine with butane in the presence of light gives primarily 2-chlorobutane and not 1-chlorobutane as the reaction product because secondary free radicals are more stable than primary free radicals.

Butane can form primary and secondary carbon radical intermediates in the reaction.

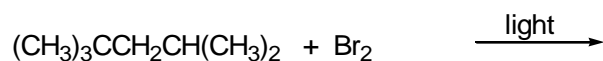


The more stable carbon radical intermediate forms the major product.

12. Correct Answer: (2)

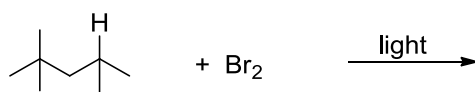


The above compound is the major monosubstituted organic product formed in the following reaction:

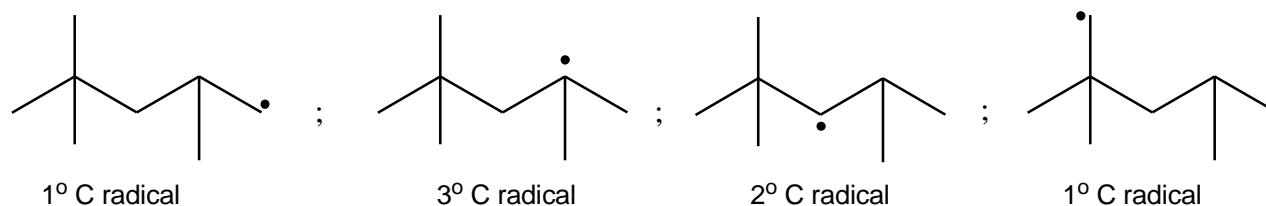


Explanation:

The above chemical equation can be rewritten as:



The halogenation reaction of alkanes proceeds via a radical intermediate. Possible radicals that can form in the reaction are:

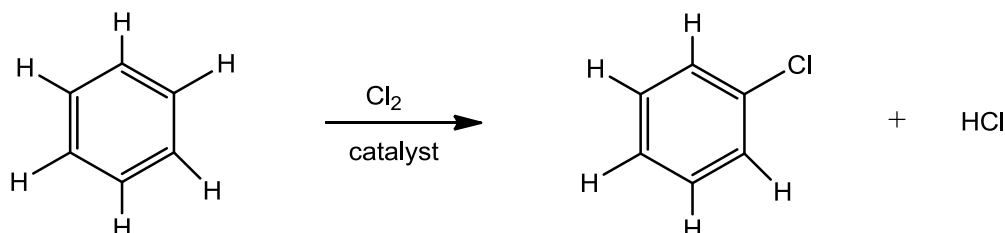


The tertiary carbon radical is the most stable radical and will produce the major product.

13. Correct Answer: (1)



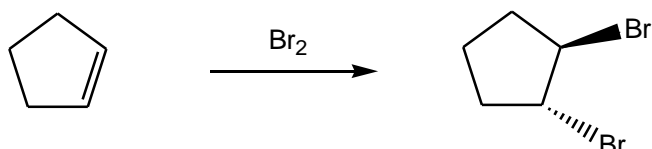
The above reaction is a substitution reaction. The chemical equation is redrawn below:



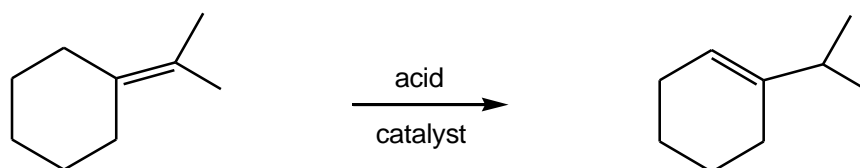
In the above reaction a Cl replaces/substitutes a H atom.

The other options:

(2) The reaction below is an addition reaction:



(3) In this reaction isomerization takes place.

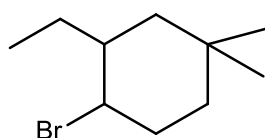


(4) The reaction below is an elimination reaction:



14. Correct Answer: (1) 1-bromo-2-ethyl-4,4-dimethylcyclohexane

Of the options given, above is the correct IUPAC name of the following compound:

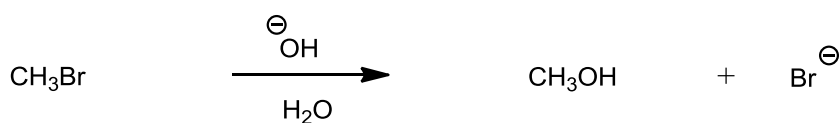


According to the IUPAC convention, the longest continuous carbon chain is a ring with 6 C's → cyclohexane. Begin numbering at a position on the ring to give substituents the lowest possible number. There are two possibilities:

- 1) Begin numbering at the C attached to the methyl groups- then there are substituents on C-1, C-1, C-3 and C-4
- 2) Begin numbering at the C attached to the Br atom - then there are substituents on C-1, C-2, C-4 and C-4

On C-1 there is a bromine atom → 1-bromo; on C-2 there is an ethyl group → 2-ethyl; on C-4 there are two CH₃ substituents → 4,4-dimethyl; name substituents in alphabetical order.

15. Correct Answer: (3)

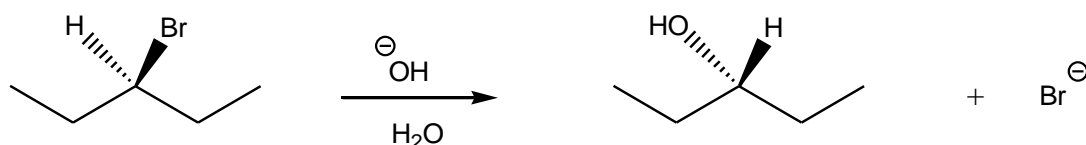


The above nucleophilic substitution reaction takes place THE FASTEST.

The nucleophile, OH^- , is a strong nucleophile which promotes nucleophilic substitution reaction via the $\text{S}_{\text{N}}2$ reaction mechanism. The alkyl halide is a methyl alkyl bromide which can easily react in such a reaction.

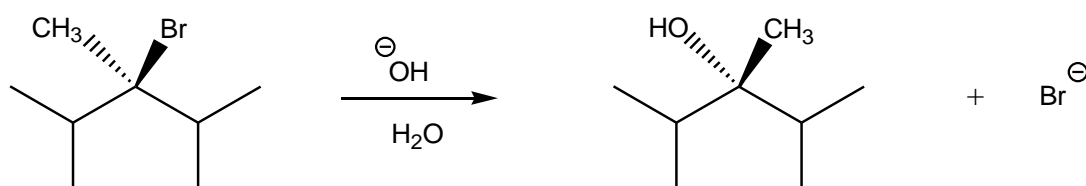
The other options:

(1)



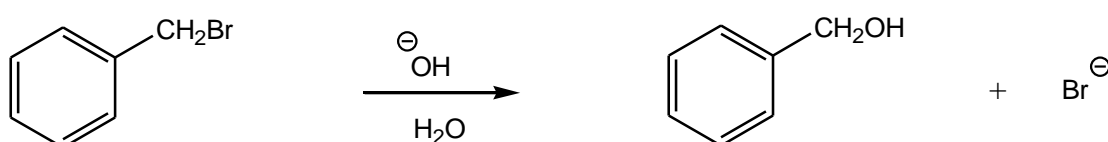
This alkyl halide is a secondary alkyl bromide which can undergo $\text{S}_{\text{N}}2$ reaction. However, the reaction of primary alkyl halides is always faster than the reaction of primary alkyl halides under similar reaction conditions

(2)



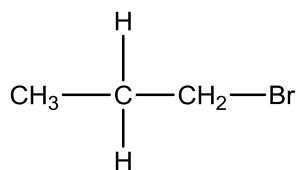
The alkyl halide is a tertiary alkyl halide which, due to crowding at the tertiary C, cannot undergo $\text{S}_{\text{N}}2$ reaction to give the product as shown.

(4)



The alkyl halide is a primary alkyl halide which, compared to the alkyl halide in (3), has a larger group attached to the C where the nucleophile, OH^- , must attack. This $\text{S}_{\text{N}}2$ reaction will therefore take place at a slower rate than the reaction in (3).

16. Correct Answer: (3)

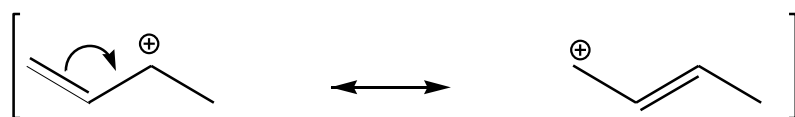


Under the given reaction conditions, the nucleophilic substitution reaction will proceed according to the S_N1 reaction mechanism. Thus each reaction will proceed via a carbocation intermediate.

In the compound shown above, the Br group is the leaving group and will produce a primary carbocation which is the least stable carbocation.

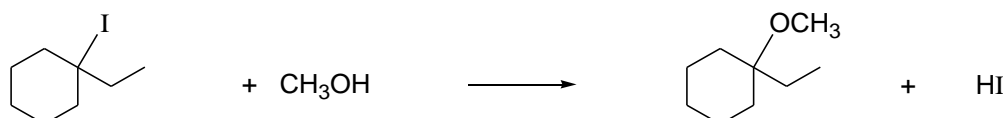
In the other examples:

- (1) S_N1 reaction takes place readily with this substrate although this is a secondary alkyl halide. This compound will form the following carbocation which is stabilized by resonance.



- (2) A resonance stabilized carbocation is formed in the reaction. (Draw resonance structures and redraw the Ph group as a ring structure)
- (4) A tertiary carbocation is formed which is also stabilized by resonance.

17. Correct Answer: (1)



In the above reaction, the alkyl halide is a tertiary alkyl iodide which, due to steric hindrance (crowding), cannot undergo S_N2 reactions easily. Also, CH_3OH is a poor nucleophile which promotes S_N1 reactions.

The other options:

- (2) The substrate is a primary alkyl halide and SH^- is a strong nucleophile – both reagents promote $\text{S}_{\text{N}}2$ reactions.
- (3) The substrate is a secondary alkyl halide and CN^- is a strong nucleophile – both reagents promote $\text{S}_{\text{N}}2$ reactions.
- (4) The $\text{S}_{\text{N}}2$ reaction can take place.

18. Correct Answer: (4) PhS^-

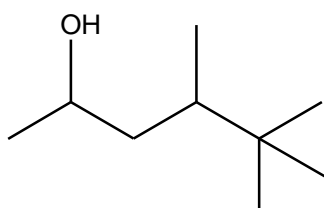
The above anion has an excess of electrons which can easily be donated when it reacts as a nucleophile in an $\text{S}_{\text{N}}2$ -type reaction.

The PhS^- ion will react the fastest with for example, $\text{CH}_3\text{CH}_2\text{-I}$ in a substitution reaction because it is the strongest nucleophile.

- (1) H_2O is a weak nucleophile – it has lone pairs of electrons on the electronegative O atom and the electrons are not readily donated.
- (2) The compound, CH_3Cl , has a polar C-Cl bond and tends to be electrophilic. It will thus not act as a nucleophile.
- (3) The structure of the anion, CH_3COOH^- , does not make sense.

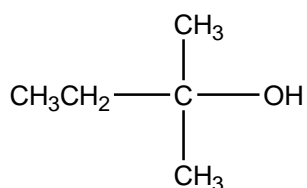
19. Correct Answer: (2) 4,5,5-trimethyl-2-hexanol

The above is the correct IUPAC name for the following compound:



According to the IUPAC convention, the longest continuous carbon chain that contains the OH group has 6 C's → hexane. Begin numbering at the end that will give the OH substituent the lowest possible number; i.e. OH is on C-2, change the ending from -e to -ol → 2-ol; three methyl groups on C-4, C-5, C-5 → 4,5,5-trimethyl. Name the substituents in alphabetical order.

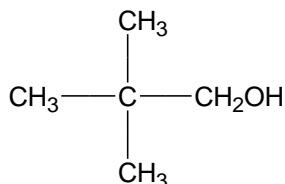
20. Correct Answer: (1)



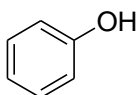
In a tertiary alcohol the OH group is attached to the tertiary carbon.

The other options

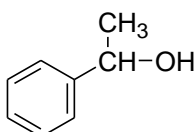
(2) A primary alcohol:



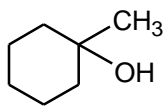
(1) An aromatic alcohol – phenol:



(2) A secondary alcohol:



21. Correct Answer: (1)

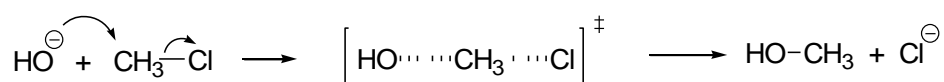


Alcohols undergo dehydration in the presence of a strong acid. In the presence of acid the O atom of becomes protonated to form the oxonium ion. The OH group which is a poor leaving group is converted to a good leaving group. Loss of water gives a carbocation and the reaction which produces the most stable carbocation which will react the fastest.

Intermediates formed in the options:

- (1) This compound leads to the formation of a tertiary carbocation which is very stable.
- (2) This compound leads to the formation of a primary carbocation which is very unstable.
- (3) This compound leads to the formation of a secondary carbocation which is less stable than a tertiary carbocation.
- (4) This compound forms of a secondary carbocation which is less stable than a tertiary carbocation.

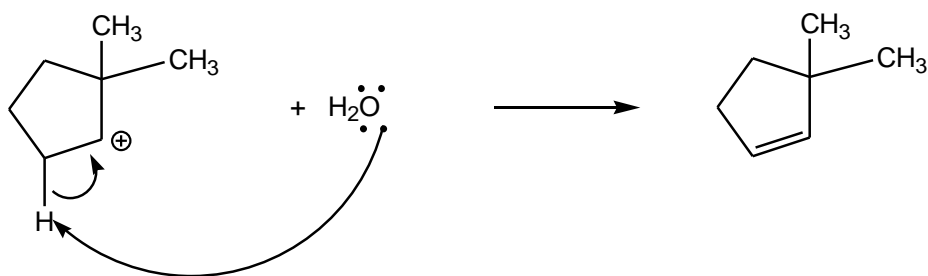
22. Correct Answer: (3)



The above represents the CORRECT mechanism for a nucleophilic substitution reaction – specifically for a S_N2 reaction.

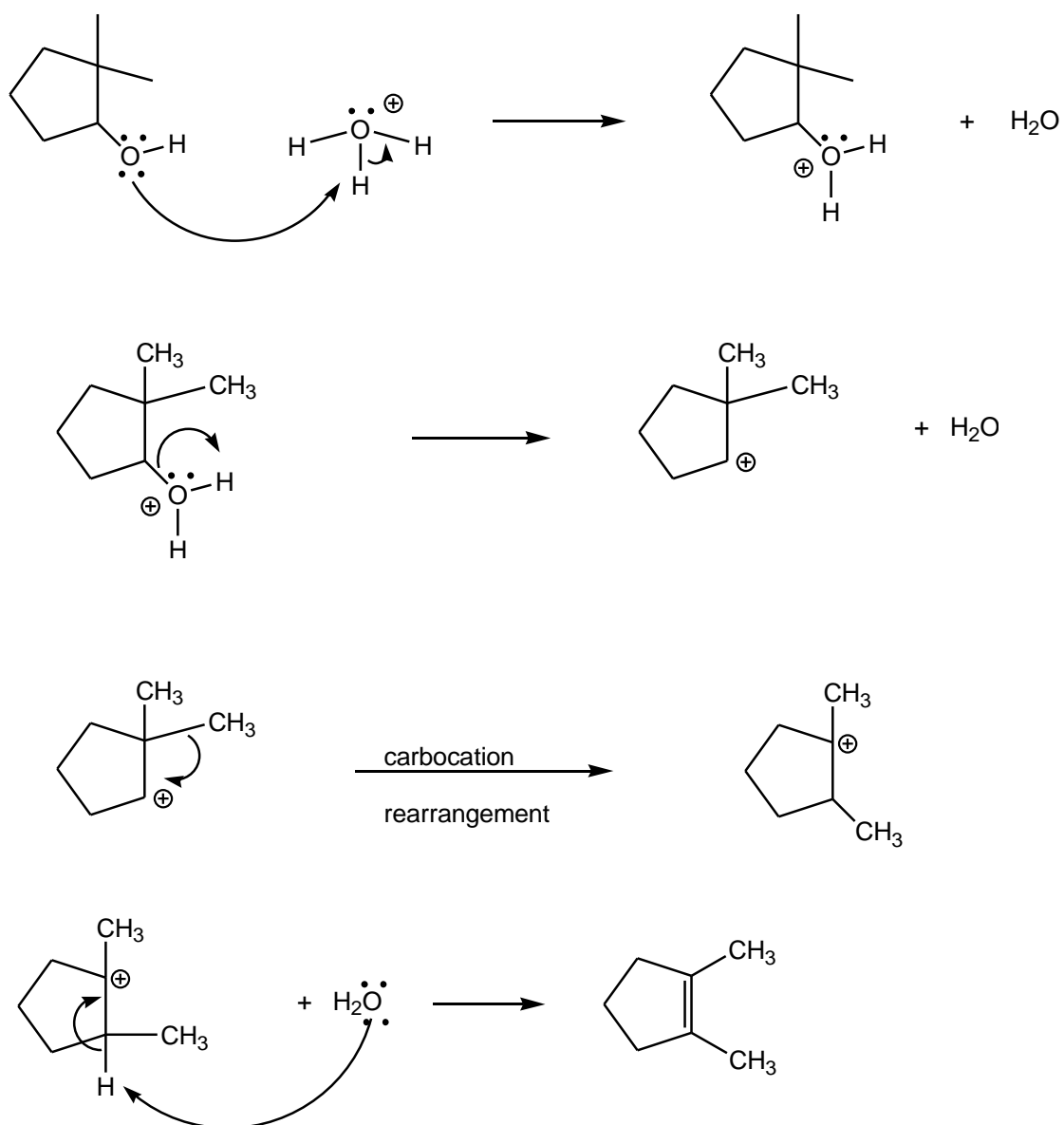
All the other options are incorrect.

23. Correct Answer: (4)



The above step is not part of the mechanism of the dehydration reaction.

The reaction mechanism is:



24. Correct Answer: (4)

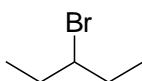


The above compound has the highest boiling point because its molecules can undergo hydrogen bonding due to the presence of the O-H bond.

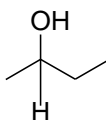
25. Correct Answer: (2) 2-butanol

According to the structure of each compound, below, the compound shown in (3) has a chiral (asymmetric) carbon atom because there are 4 different groups or atoms attached to C-2.

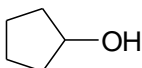
(1) 3-Bromopentane



(2) 2-butanol



(3) cyclopentanol

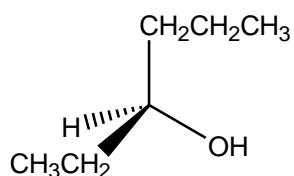


(4) 2-Methylpropane



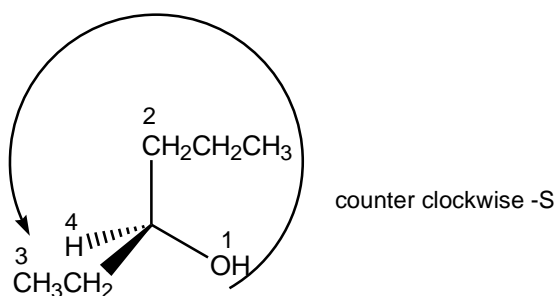
26. Correct Answer: (2) (S)-hexan-3-ol

The above name is the correct one according to the Cahn-Ingold-Prelog rules of the following compound:

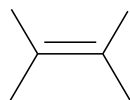


According to the Cahn-Ingold-Prelog rules, assigning priorities to the groups/atoms around the chiral center:

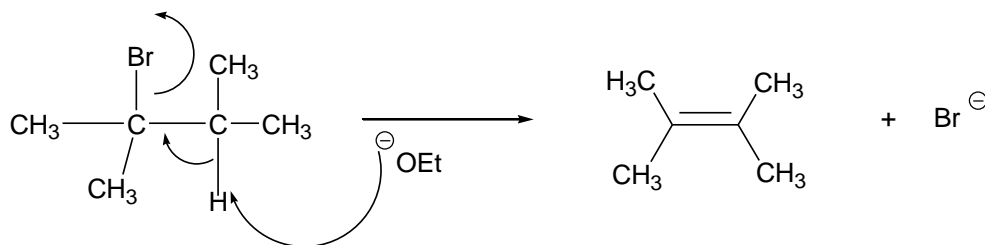
Group	Priority
OH	1
CH ₂ CH ₂ CH ₃	2
CH ₂ CH ₃	3
H	4



27. Correct Answer: (3)

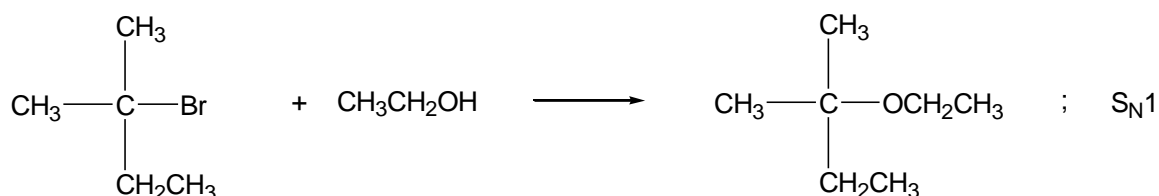


Sodium ethoxide is a strong base and in the reaction with the tertiary alkyl bromide, E2 elimination occurs:



According to Zaitsev's rule, the product with the most substituted double bond will predominate. Therefore, the product formed above is the major product. The product formed (1) is a minor elimination product. The product shown in (2) is as a result of a nucleophilic substitution reaction. The product shown in (3) will not form in this reaction.

28. Correct Answer: (3)



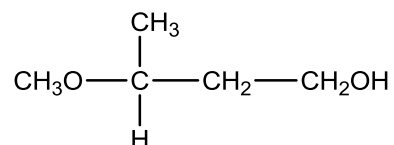
The alkyl halide is a tertiary alkyl bromide which will produce a stable carbocation intermediate. Therefore, the S_N1 reaction will occur.

Explanation of the options:

- (1) This reaction is not an elimination reaction but a substitution reaction.
- (2) The reaction is an elimination reaction not a substitution reaction – proceeds via the E2 mechanism.
- (3) This is the reaction of a tertiary alkyl halide and a poor nucleophile, $\text{CH}_3\text{CH}_2\text{OH}$. These reagents undergo nucleophilic substitution reaction via the S_N1 reaction mechanism.
- (4) This is a substitution reaction and not an elimination reaction (it does not proceed via an E2 reaction mechanism). A primary alkyl halide forms an unstable carbocation and the reaction of a primary alkyl halide with a strong nucleophile like OH^- goes via the

29. Correct Answer: (1) 3-methoxybutan-1-ol

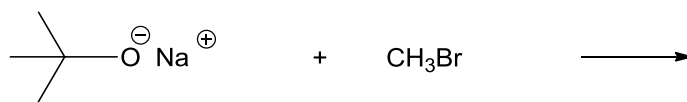
The above name corresponds to the following compound according to the IUPAC nomenclature:



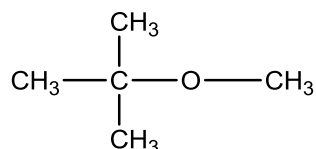
This compound has an OH group and an OCH₃ group – this is an alcohol and the OCH₃ group is a substituent.

According to the IUPAC convention, the longest continuous carbon chain that contains the OH group has 4 C's → butane. Begin numbering at the end that will give the OH substituent the lowest possible number; the OH is on C-1, change ending -e to -ol → 1-ol; the OCH₃ group is on C-2 → 2-methoxy. Write the name in alphabetical order.

30. Correct Answer: (4)



The above reaction is the most appropriate to prepare the following compound:



The reaction of an alkoxide with an alkyl halide proceed is a S_N2 reaction. Evaluation of the S_N2 reaction with each option:

(1) This is a tertiary alkyl halide which undergoes S_N1 reaction instead of S_N2 reaction

- (2) Under the reaction conditions, both reagents contain a poor leaving group which makes substitution to form the product very difficult.
 - (3) The nucleophile cannot attack the carbon attached to the OH group because the OH group is a poor leaving group. The nucleophile is also a strong base and will abstract the H from the OH group.
 - (4) This is a reaction between a strong nucleophile and a primary alkyl halide which contains a good leaving group, Br, therefore, the desired product will form.
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