201 2015 1 b - Tutorial Letter 201 Semester 1

Chemistry B (University of South Africa)

Tutorial letter 201/1/2015

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: 23 February 2015**
- **UNIQUE NUMBER: 594282**

1. Correct Answer: (4) In a carbon atom, the 2s and 2p orbitals are equal in energy.

The above statement is INCORRECT because 2p orbitals are higher in energy than 2s orbitals.

All the other options as stated are correct.

2. Correct Answer: (1) Most of the electron density in a π molecular orbital is centered above and below the internuclear axis.

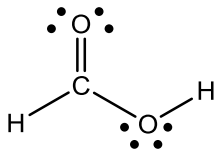
The above statement about π molecular orbitals is CORRECT.

The other options are corrected as follows:

(2) When two atoms are connected by a double bond, one of the bonds is a σ (sigma) bond and one is a π (pi) bond.

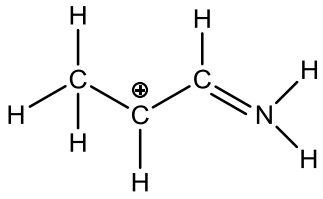
(3) The σ molecular orbitals are cylindrically symmetric.

3. Correct Answer: (3)



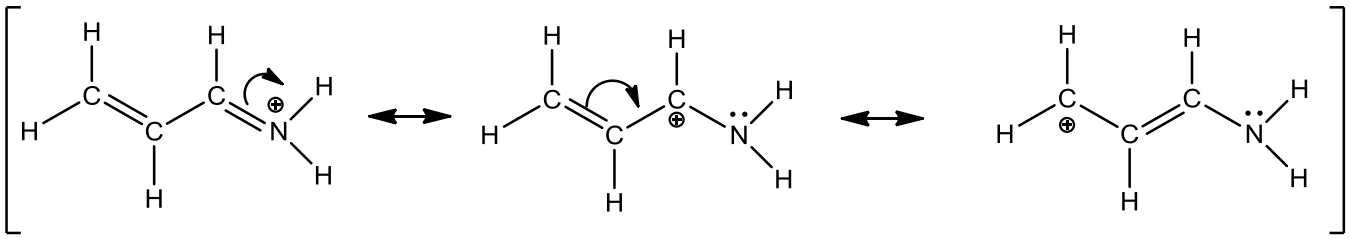
The above structure is the correct Lewis structure of a molecule with molecular formula CH_2O_2.

4. Correct Answer: (1)

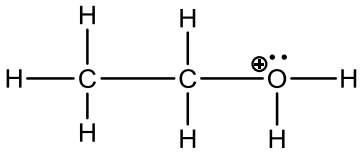


The structure shown above is not a resonance structure of the cation below:

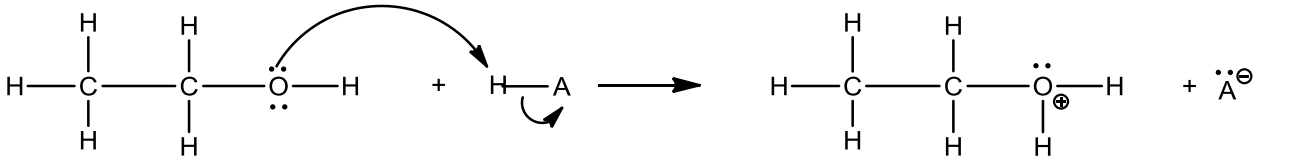
All the other options are correct. Resonance structures of the cation. The resonance delocalization takes place as follows:



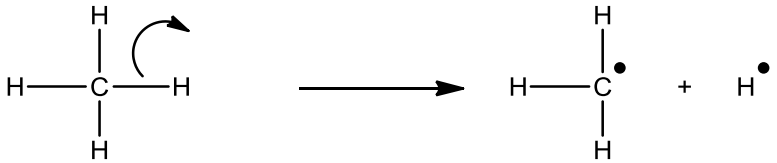
5. Correct Answer: (4)



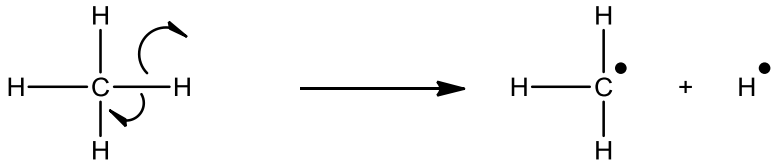
The compound, CH_3CH_2OH, is a Lewis base and the above is the Lewis structure of the conjugate acid of CH_3CH_2OH. When a Lewis base donates pair of electrons to a Lewis acid, the conjugate acid and conjugate base pairs are formed in a process shown below:



6. Correct Answer: (3)

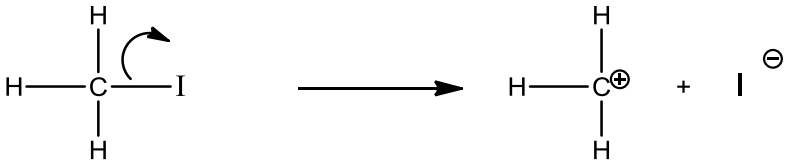


The above process is an INCORRECT representation of bond breakage because the arrow indicates that the bond breaks in such a manner that the hydrogen leaves with both bonding electrons which should result in the formation of $^{+}CH_3$ and $H:^{-}$ ions. This mode of bond breaking is called heterolysis or heterolytic cleavage. However, the difference in electro-negativity between a C and H is small enough for the C-H bond to break so that each atom departs with one electron. The correct representation of the bond breaking process is:

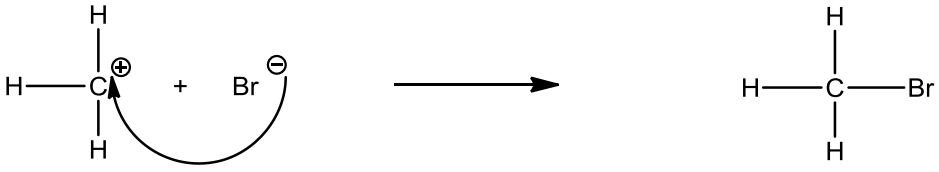


All the other options are correct as explained below:

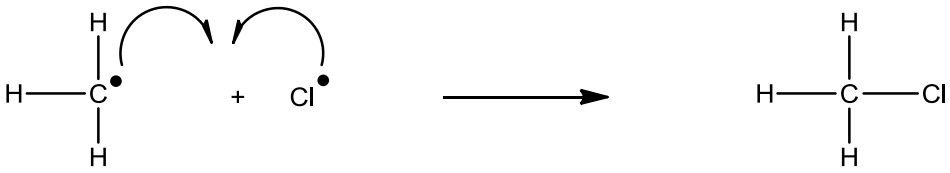
(1) The arrow shows that the bond breaks in such a manner that the iodine leaves with both bonding electrons (because the difference in electronegativity between C and I plays a role). This heterolytic bond breaking results in the formation of ions as shown below:



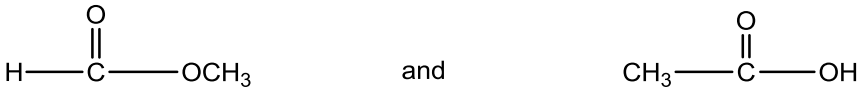
(2) In this bond formation process the bromide ion donates an electron pair to the positively charged carbon.



(4) In the bond formation process, known as homolytic bond formation, the chlorine radical and the methyl radical each donate an electron to form a single bond between the C and Cl.



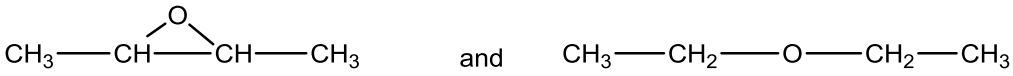
7. Correct Answer: (2)



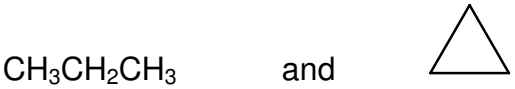
The two compounds above are constitutional isomers because they have the SAME MOLECULAR FORMULA ($C_2H_4O_2$) but some of the atoms / groups are connected at different positions

The other options do not represent structural / constitutional isomers, as explained below:

(1) The first structure has a molecular formula of C_4H_8O and the second structure has a molecular formula, $C_4H_{10}O$.

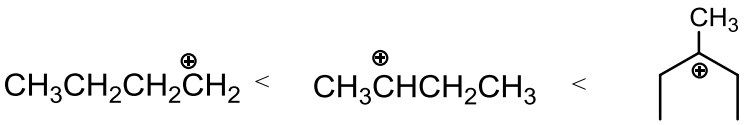


(3) The first structure has a molecular formula of C_3H_8 and the second structure has a molecular formula, C_3H_6.



(4) The first structure has a molecular formula of C_4H_8O and the second structure has a molecular formula, C_3H_6O.

8. Correct Answer: (2)



A **B** **C**

The set of carbocations shown above represent an order of increasing stabilities, i.e. from the least stable to the most stable.

In **A**, the C^+ is attached to one carbon atom and is a primary carbocation.

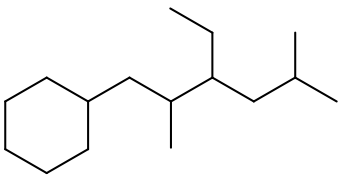
In **B**, the C^+ is attached to two carbon atoms and is a secondary carbocation.

In **C**, the C^+ is attached to three carbon atoms and is a tertiary carbocation.

A secondary carbocation is more stable than primary carbocation and a tertiary carbocation is more stable than secondary carbocation.

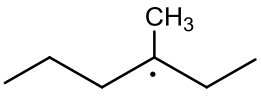
9. Correct Answer: (3) 3-ethyl-1-cyclohexyl-2,5-dimethylhexane

The above is the correct IUPAC name of the molecule shown below.

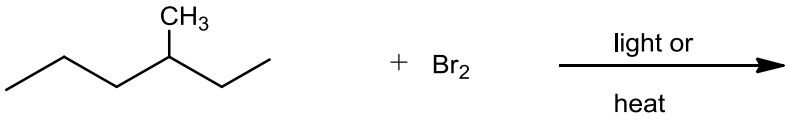


According to the IUPAC convention, the longest continuous carbon chain has 6 carbon atoms; 6 C's → hexane. Begin numbering at a branch to give substituents the lowest possible number - in this case, numbering from the left: on C-1 is a ring with 6 C's → 1-cyclohexyl; the other substituents are on C-3: ethyl → 3-ethyl; C-2 :methyl and C-5: methyl. Two methyl groups → 3,5-dimethyl; name the substituents in alphabetical order.

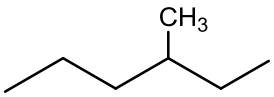
10. Correct Answer: (2)



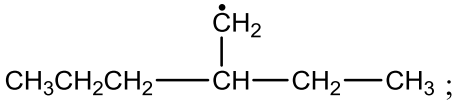
The above is a tertiary carbon radical and is the MOST STABLE radical formed in the reaction:



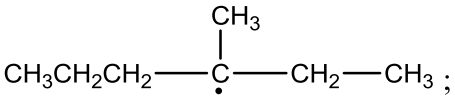
In the reaction of bromine with 2-methylbutane,



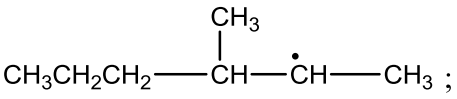
may form the following radical intermediates :



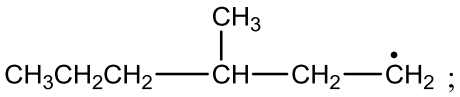
1° C radical ;



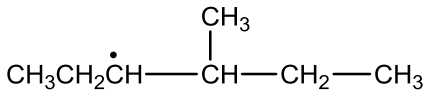
3° C radical ;



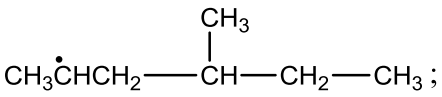
2° C radical ;



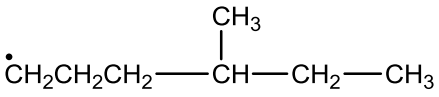
1° C radical ;



2° C radical ;



2° C radical ;

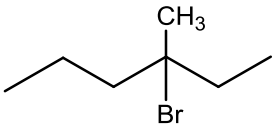


1° C radical

The tertiary free radicals are more stable than primary and secondary free radicals.

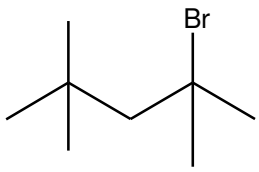
Therefore, the more stable carbon radical that is formed in the reaction is the tertiary carbon radical shown in (2).

11. Correct Answer: (3)



The more stable carbon radical that is formed in the reaction, i.e. the tertiary carbon radical shown as the answer on question 10 above, will form the major monobrominated product in the reaction. This product is given in option (3).

12. Correct Answer: (1)



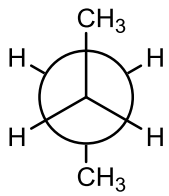
The above molecule is a tertiary alkyl halide (**C**-Br bonded to 3 other C's.

(2) The molecule is a secondary alkyl halide because the C attached to Br is bonded to two other C's.

(5) The molecule is a primary alkyl halide because the C attached to Br is bonded to only one other C atom.

(6) The molecule is a primary alkyl halide because the C attached to Br is bonded to only one other C atom.

13. Correct Answer: (2)



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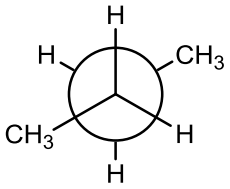


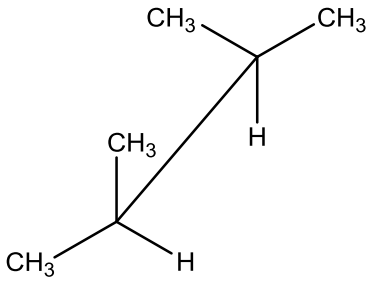
The above Newman projections represent the identical conformations of the same compound, $CH_3CH_2CH_2CH_3$.

Conformations are the different arrangements formed by rotations about a single bond in a molecule. The two structures represent the same conformation because the groups and atoms attached to the C-2 and C-3 are in the same and they represent a staggered

(anti) conformation (the two methyl groups are on opposite sides.

The other options:

(1)



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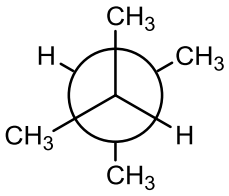
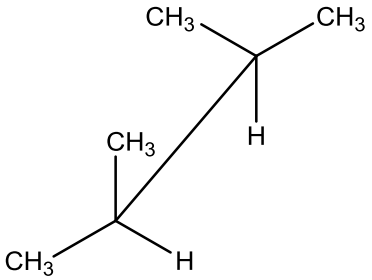


The two conformations above represent different conformations as indicated below.



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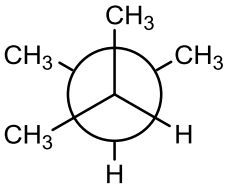

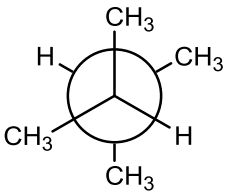

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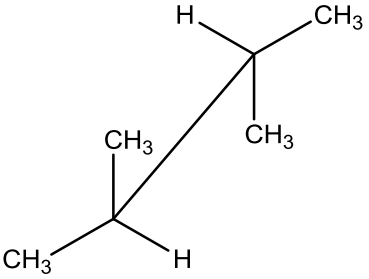
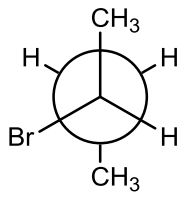


(3) The structures below represent Newman projections of 2-bromobutane and both conformations represent staggered conformations. However, the conformation on the left has the two methyl groups anti to each other and the conformation on the right has the largest group on C-2 (Br) and the largest group on C-3 (CH_3) on opposite sides – called the anti-conformation of the molecule.



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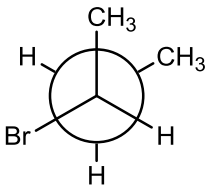
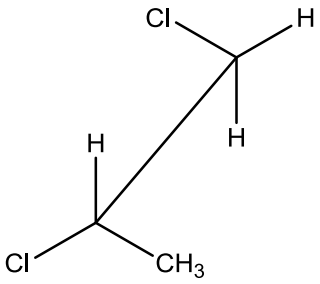
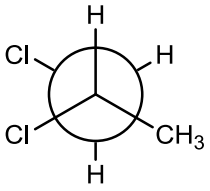


(4) The two structures represent different conformations of the 1,2-dichloropropane as illustrated below.





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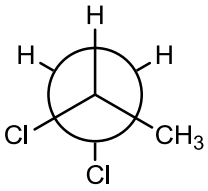
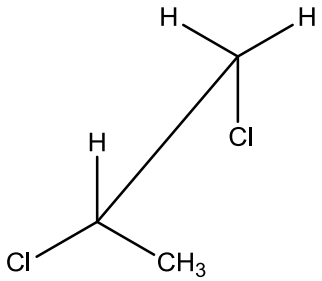
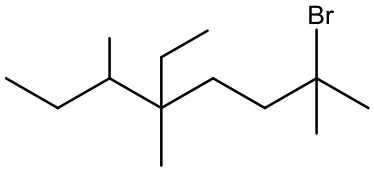




14. Correct Answer: (1) 2-bromo-5-ethyl-2,5,6-trimethyloctane

The above is the IUPAC name of the molecule shown below.

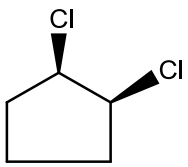


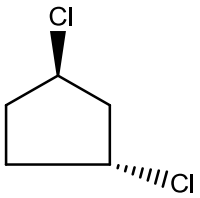
According to the IUPAC convention, the longest continuous carbon chain contains 8 C's → octane. Numbering at the end of the carbon chain to give the substituent(s) the lowest possible number; on C-2 there is a bromine atom → 2-bromo; on C-2, C- 5 and C-6 there are CH_3 substituents; three CH_3 substituents → trimethyl → 2,5,6-trimethyl and on C-5 there is a

CH_2CH_3 substituent → 5-ethyl; name substituents in alphabetical order.

15. Correct Answer: (2) structural /constitutional isomers

The above best described the structural relationship between *cis*-1,2-dichlorocyclopentane and *trans*-1,3-dichlorocyclopentane.





cis-1,2-dichlorocyclopentane *trans*-1,3-dichlorocyclopentane

Both compounds have the same molecular formula, $C_5H_8Cl_2$, but the Cl atoms are attached to different carbon atoms.

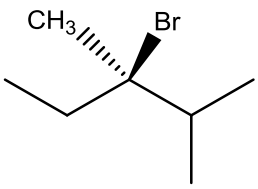
A description of the other options:

(1) Two compounds are stereoisomers when the atoms have the same bonding sequence but different arrangement of their atoms in space. Enantiomers are compounds that have non-superimposable mirror images.

(3) Two compounds are geometric isomers when the atoms have the same bonding sequence but different arrangement of their atoms in space.

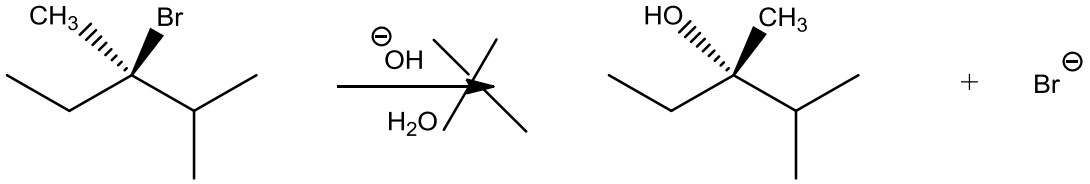
(4) Conformers are structures of the same compound that are the result of rotations about single bonds.

16. Correct Answer: (4)



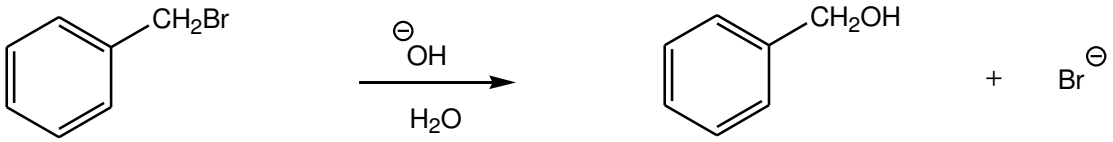
The above substrate reacts the slowest in the following nucleophilic substitution reaction:

The nucleophile, $^{-}$OH, is a strong nucleophile which promotes nucleophilic substitution reaction via the S_N2 reaction mechanism. The alkyl halide in (4) is a tertiary alkyl halide which, due to crowding at the tertiary C atom, **does not undergo S_N2 reaction easily t**o give the product as shown below:

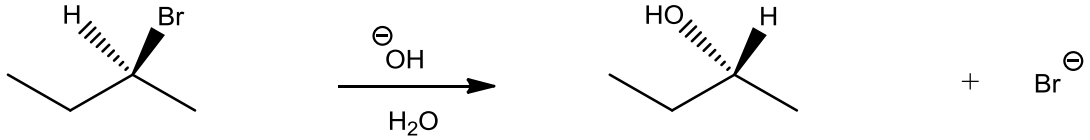


The other options:

(1) The alkyl halide is a primary alkyl halide which, compared to the alkyl halide in (3), this alkyl halide has a larger group attached to the C where the nucleophile, $^{-}$OH, must attack. This S_N2 reaction will therefore take place at a slower rate than the reaction in (3) and it will be faster than the reaction in (2).

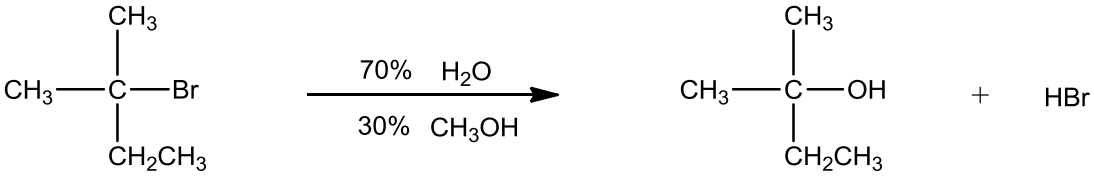


(2) This alkyl halide is a secondary alkyl bromide which can undergo S_N2 reaction.
However, the reaction of primary alkyl halides is always faster than the reaction of secondary alkyl halides under similar reaction conditions.



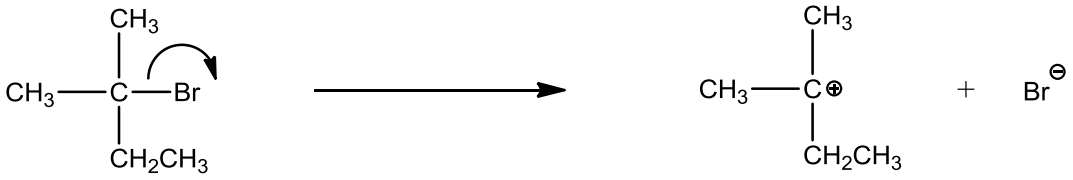
(3) The alkyl halide is a primary alkyl bromide which can easily react in such a reaction. The reaction below takes place the fastest.

17. Correct Answer: (2)

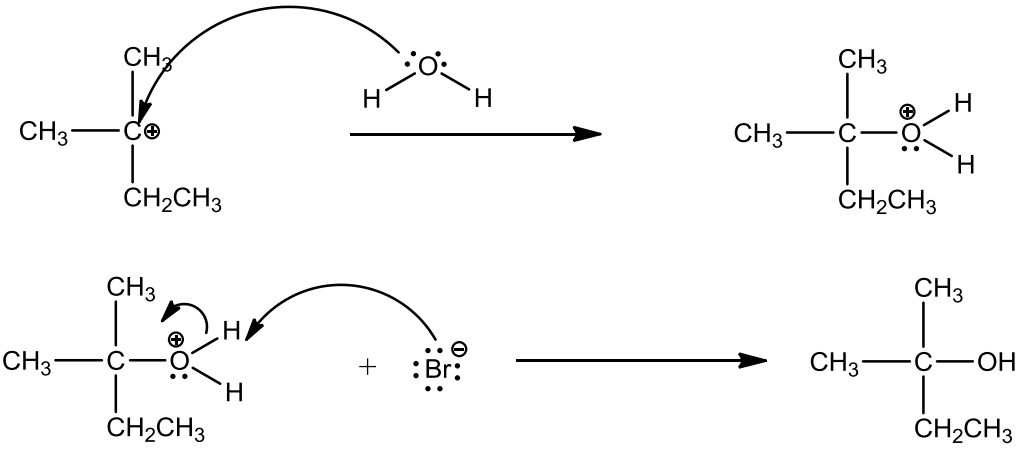


Under the given reaction conditions, the nucleophilic substitution reaction will proceed according to the S_N1 reaction mechanism (H_2O is a poor nucleophile). Thus each reaction will proceed via a carbocation intermediate. The reaction that produces the most stable carbocation will react the fastest under these conditions.

The option (2) will form a stable tertiary carbocation intermediate in the first step of the reaction mechanism:

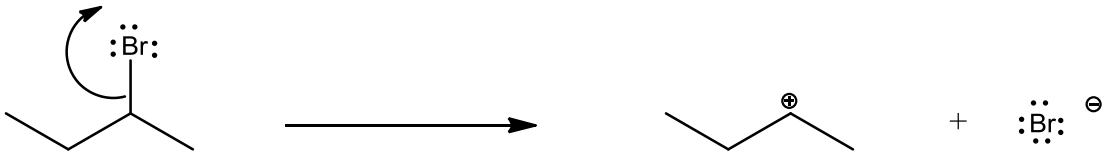


The final alcohol product is formed by the nucleophilic attack of H_2O on the carbocation. The second and third steps of mechanism for product formation:



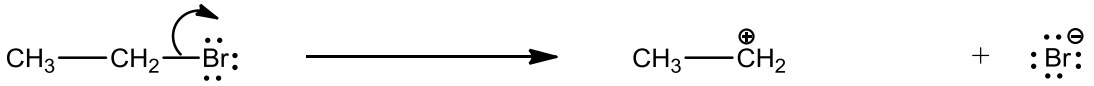
The other options:

(1)



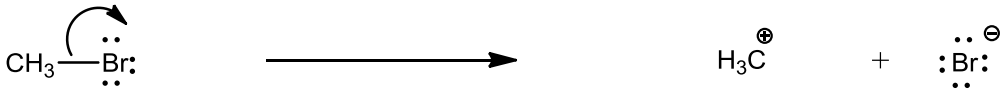
This reaction which proceeds via the secondary carbocation intermediate takes place at a slower rate than the reaction which goes via the tertiary carbocation intermediate.

(3) Will form a primary carbocation intermediate which is less stable than a tertiary carbocation:



This reaction which proceeds via the primary carbocation intermediate takes place at a slower rate than the reaction which goes via the secondary carbocation intermediate.

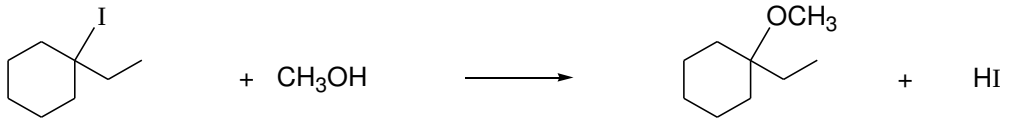
(4) The alkyl bromide will form a primary carbocation intermediate which is less stable than a secondary carbocation:



This reaction which proceeds via the methyl carbocation intermediate takes place at a slower rate than the reaction which goes via the primary carbocation intermediate.

NB. The final alcohol product is formed in each reaction by the nucleophilic attack of H_2O on the carbocation. Do the second and third steps of the mechanism for alcohol formation of the other options.

18. Correct Answer: (2)



The above reaction proceeds via an S_N1 reaction mechanism. 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, tertiary alkyl iodide produces a stable carbocation intermediate and CH_3OH is a poor nucleophile – both reagents promote S_N1 reactions.

(1) The substrate is a secondary alkyl halide and ^-CN is a strong nucleophile – both reagents promote S_N2 reactions.

(3) The S_N2 reaction can take place – reaction of a primary alkyl halide with the I^- ion as the nucleophile proceeds via the S_N2 reaction mechanism.

(4) The substrate is a primary alkyl halide and ^-SH is a strong nucleophile – both reagents promote S_N2 reactions.

NB. As exercise, try to write the reaction mechanism for each reaction.

19. Correct Answer: (1)

$$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH, \quad S_N2$$

The above reaction is a correct representation of the major products formed and the mechanism for the reaction. The product indicates that a substitution reaction took place. Ethyl bromide is a primary alkyl halide and OH is a good nucleophile – both reagents promote S_N2 reactions.

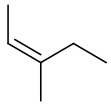
The other options:

(2) The product indicates that a substitution reaction took place. The substrate is a secondary alkyl halide and ^-SH is a strong nucleophile – both reagents promote S_N2 reactions.

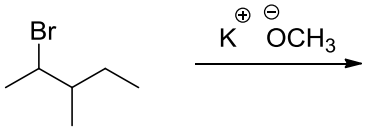
(3) The product indicates that an elimination reaction took place. The alkyl bromide is a tertiary alkyl halide which reacts with a strong base – both reagents promote E2 reactions.

(4) The product indicates that a substitution reaction took place. The alkyl bromide is a tertiary alkyl halide and ethanol, CH_3CH_2OH, is a poor nucleophile – both reagents promote S_N1 reactions.

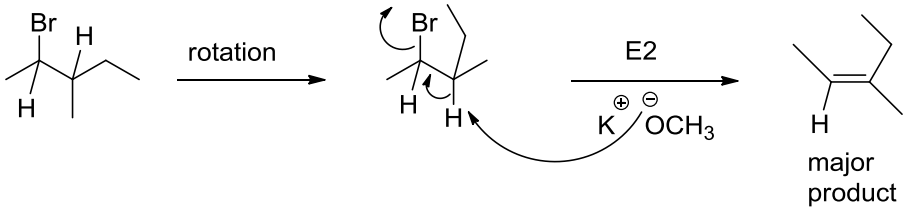
20. Correct Answer: (3)



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

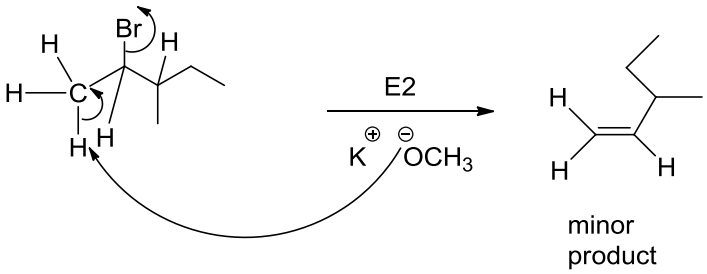


The methoxide ion is a strong base and it therefore predominantly participates in an E2 elimination reaction with the alkyl halide. The mechanism for the E2 elimination reaction is:

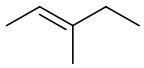


In the structure of the alkyl halide given in the question, the Br and H (H on C next to C-Br) to be eliminated are not anti and coplanar. Rotation around the C-C bond occurs so that the H and Br (anti and coplanar) are in the correct orientation to enable E2 reaction.

There is another C with H's next to the C-Br which may lead to another elimination product:



The product in option (2) may also be correct – since the stereochemistry of the groups around the C-Br carbon was not specified, the product formation to get option (3) may not be so evident.

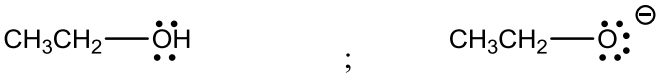


According to Zaitsev's rule, the product with the most substituted double bond will predominate.

Therefore, the product formed [shown as option (3)] is the major product. The product formed in option (1) is a minor elimination product. The product shown in option (4) is as a result of a nucleophilic substitution reaction.

21. Correct Answer: (2) Ethanol is a weaker nucleophile than ethoxide

The above statement is correct.



ethanol ; ethoxide

Both species have lone pairs of electrons and act as a nucleophile. The ethoxide ion has a negative charge and is a stronger nucleophile than the neutral ethanol molecule.

The corrected statements of the other options are shown below:

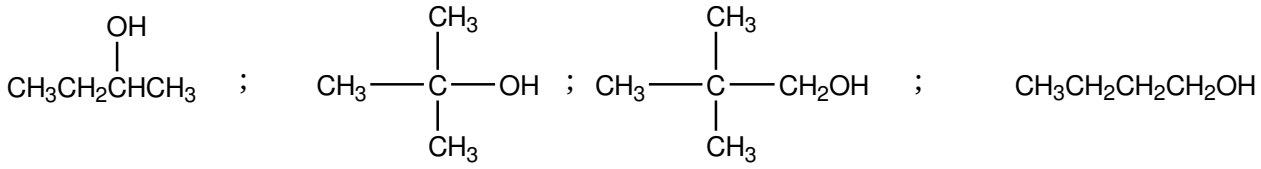
(1) Ethoxide has a negative charge and is a nucleophile.

(3) Ethoxide promotes nucleophilic substitution reaction via the S_N2 mechanism because ethoxide is a good nucleophile.

(4) Ethanol and ethoxide can act as Lewis bases.

22. Correct Answer: (3) All of the compounds contain a good leaving group.

The above statement regarding the following compounds (shown below) is incorrect because each compound contains an OH group which is a poor leaving.



A **B** **C** **D**

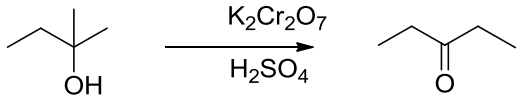
All the other options are correct.

(1) The compound, **A**, is chiral; C-2 has 4 different groups / atoms attached to it.

(2) **C** and **D** are primary alcohols.

(4) **B** is a tertiary alcohol – the C bearing the OH groups is also attached to three other carbon atoms i.e. that C is a chiral centre.

23. Correct Answer: (2)

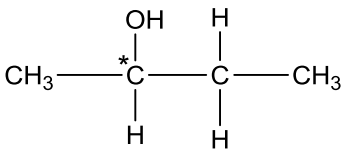


The above reaction will **NOT** take place. The alcohol is not oxidized to pentan-3-one. An oxidation reaction normally involves the conversion of C-OH bonds to C=O bonds with the removal of hydrogens (one from the OH and one from the C-OH, carbinol carbon). Therefore, tertiary alcohols do not undergo oxidation reactions.

All the other options are correct and will produce the product as shown.

24. Correct Answer: (4) 2-butanol

Structure of 2-butanol:

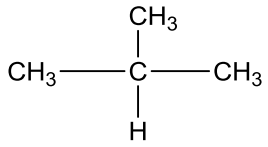


The above molecule has a chiral (asymmetric) carbon atom. It has a carbon with 4 different groups/atoms attached to it – i.e. the carbon that is marked by an * - it is attached to a CH_3, H, CH_2CH_3 and OH groups.

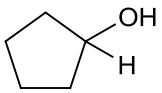
The other options do not have a carbon with 4 different groups / atoms attached to it.

(1) 2-Methylpropane: there is no carbon atoms with 4 different groups attached to it –

Therefore it DOES NOT have a chiral (asymmetric) carbon atom.

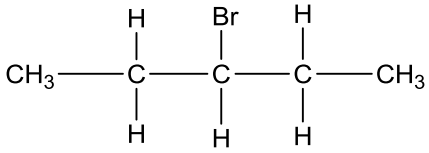


(2) cyclopentanol



The carbon attached to the OH group is also attached to a H atom and the two carbons attached to it are identical. Hence the molecule does not have any carbon atoms with 4 different groups attached to it. It therefore does not have a chiral (asymmetric) carbon atom.

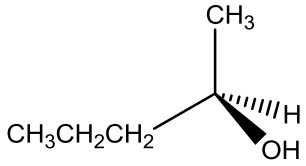
(3) 3-Bromopentane has the structure:



Each C does not have 4 different groups/atoms attached to it and the molecule does not have a chiral (asymmetric) carbon atom.

25. Correct Answer: (3) (R)-pentan-2-ol

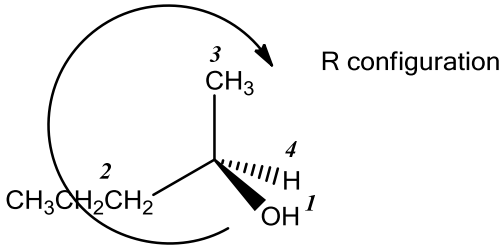
The above is the correct name according to the Cahn-Ingold-Prelog rules for the following compound:



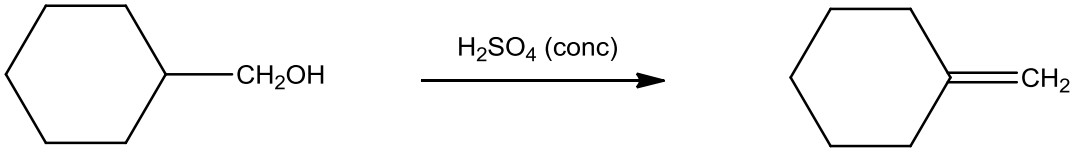
According to the IUPAC convention, the longest continuous carbon chain that contains the OH group has 5 C's→ pentane. Begin numbering at the end that will give the OH substituent the lowest possible number; i.e. OH is on C-2, change the ending from *–e* to *-ol*→ 2-ol; there are no other substituents attached to the carbon chain. Name: pentan-2-ol

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

Group	**Priority**
OH	1
$CH_2CH_2CH_3$	2
CH_3	3
H	4

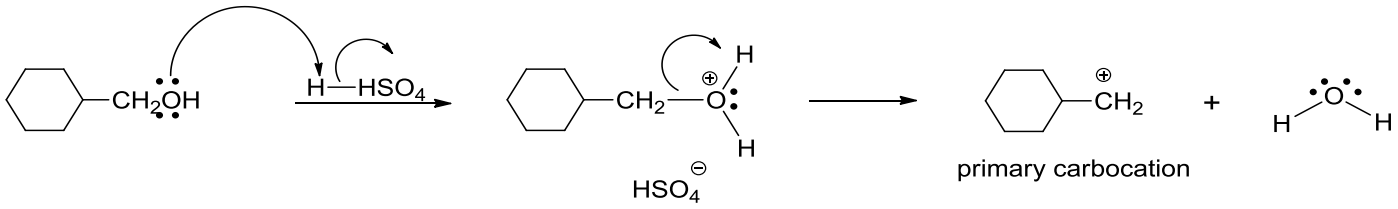


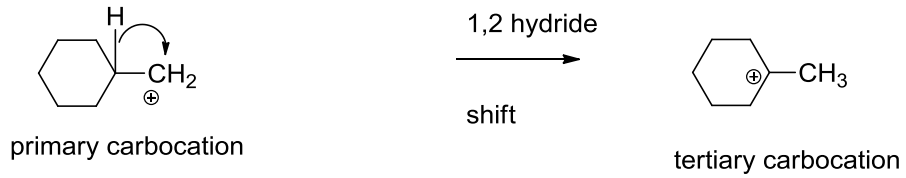
26. Correct Answer: (2)



The above reaction will NOT PRODUCE THE MAJOR PRODUCT as shown.

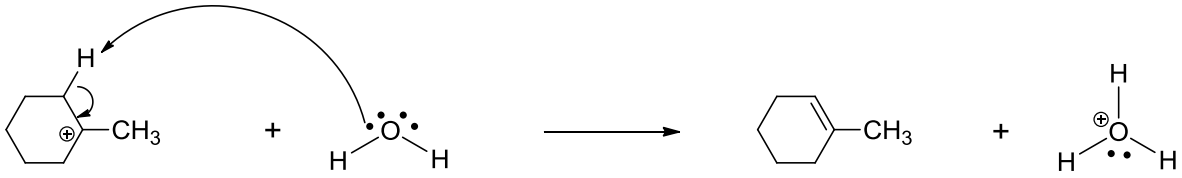
Alcohols undergo dehydration in the presence of a strong acid. In the reaction, protonation of the OH group gives in an oxonium ion. The loss of water results in a carbocation. The compound that forms the more stable carbocation will undergo dehydration at the fastest rate.





Carbocation stability: $3^{o}\ C^{+} > 2^{o}\ C^{+} > 1^{o}\ C^{+} > {}^{+}CH_3$

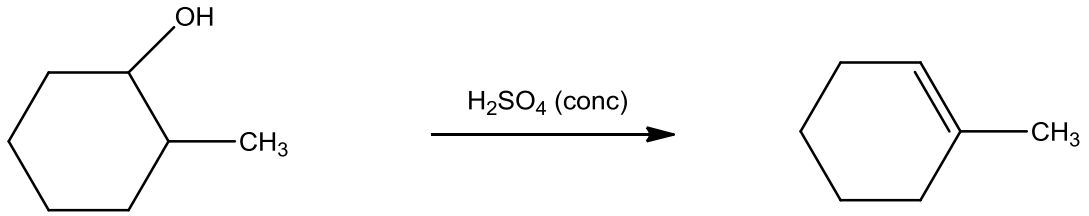
Abstraction of the H on one of the secondary carbons (of the ring) which is adjacent to the carbocation produces the major product:



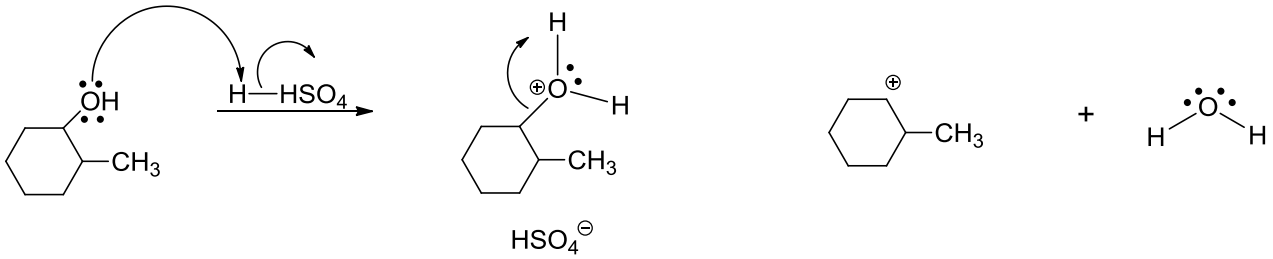
According to Zaitsev's rule, the product with the most substituted double bond will predominate.

All the other options are correct and will produce the product as shown in the chemical equation.

(1)



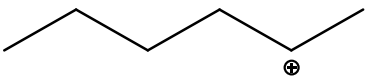
Carbocation formed:



Abstraction of the H on the C attached to the methyl group will give the major product as given.

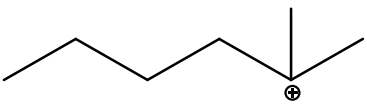
It is possible for the abstraction of the hydrogen on the other α-C will give the least substituted product which is the same as the product in option (2).

(3) The reaction proceeds via the carbocation:



Subsequent abstraction of the H on the α-carbon takes place to give the more substituted alkene.

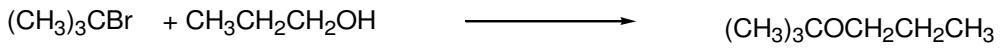
(4) The reaction proceeds via the carbocation:



Subsequent abstraction of the H on the α-carbon takes place to give the more substituted alkene.

27. Correct Answer: (2) Remain the same.

If the concentration of 1-propanol is doubled in the reaction below, than the rate of the reaction remains the same.



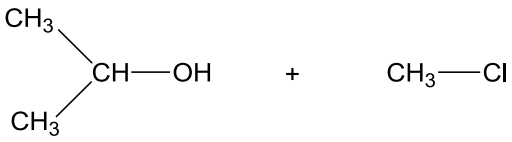
This is an S_N1 reaction, the C-Br bond in the tertiary alkyl bromide breaks and a stable tertiary carbocation is formed in the rate determining step. In the next step, the 1-propanol reacts fast with the carbocation via the donation of an electron pair on the O atom to the positively charged carbon atom.

28. Correct Answer: (1) Molecules of dimethyl ether form hydrogen bonds with each other.

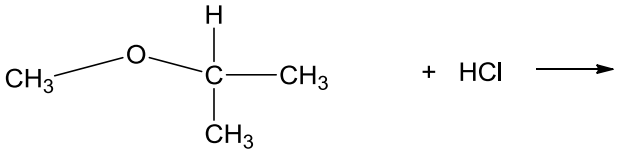
The above statement is incorrect because ethers do not have O-H groups and therefore cannot take part in hydrogen bonding.

All the other options are correct.

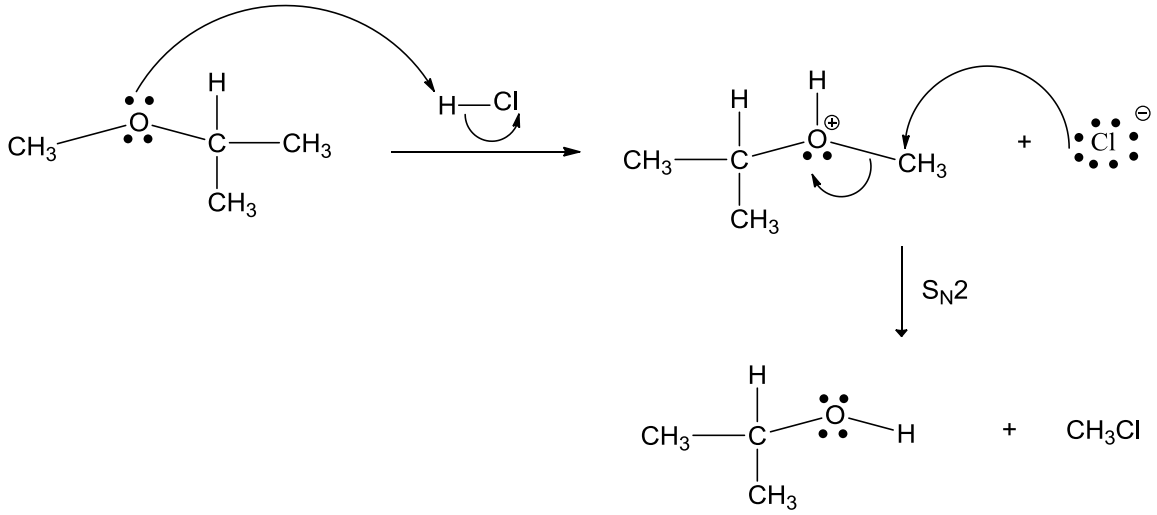
29. Correct Answer: (2)



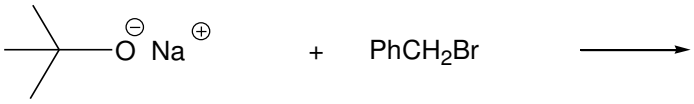
The above compounds are the major products in the cleavage reaction of the ether with HCl below:



The reaction above proceeds as follows:



30. Correct Answer: (1)



The reaction using the above reagents is the most appropriate to prepare $(CH_3)_3COCH_2Ph$.

(1) The best way to prepare $(CH_3)_3COCH_2Ph$ by the Williamson ether synthesis via a S_N2 reaction is to use a methyl or primary alkyl halide in a reaction with an alkoxide. The alkoxide ion ($^-OCH(CH_3)_2$) above will react with $PhCH_2I$ via a S_N2 reaction. [Try to write this mechanism]

The other options:

(2) The reaction of $(CH_3)_2COH$ with $PhCH_2OH$ will not produce an ether molecule as product. Each reagent can function as a weak nucleophile due to the presence of the electron pairs on oxygen. In order for the two reagents to react, one of the reagents must become electrophilic. An alcohol can only become electrophilic if the OH group is protonated in strongly acidic solutions.

(3) With the reagents given, $(CH_3)_3CO^- K^+$ with $PhCH_2OH$, the $(CH_3)_3CO^- K^+$ is a better nucleophile and may react with an electrophile. The $PhCH_2OH$ molecule cannot act as an

electrophile since it has lone pairs of electrons on the O atom making it a poor nucleophile. Hence nucleophilic substitution reaction with these reagents will not take place. The $(CH_3)_3CO^- K^+$ is also a strong base which can abstract the weakly acidic hydroxyl proton in $PhCH_2OH$ to give the alkoxide, $PhCH_2O^-$ and $(CH_3)_3COH$. The $PhCH_2O^-$ may react with an electrophile but the $(CH_3)_3COH$ molecule is not electrophilic. Hence ether formation is not possible.

(4) The reaction of $(CH_3)_3CI$ with $PhCH_2O^-Na^+$ i.e. the Williamson ether synthesis takes place via a S_N2 reaction mechanism. The S_N2 reaction of the alkoxide ion with $(CH_3)_3CI$ as the alkyl halide, will not take place. This is because the leaving group, I, is attached to a tertiary carbon atom (three CH_3 groups attached to the C linked to I) and steric hindrance severely slow down the S_N2 reaction. Since the alkoxide is a strong base, this reaction will rather give an elimination product instead of the substitution product.
