

Tutorial letter 203/1/2016

General Chemistry 1B
CHE1502

Semester 1

Department of Chemistry

This tutorial letter contains the answers to
the questions in assignment 3.

BAR CODE

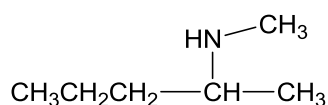
FIRST SEMESTER: KEY TO ASSIGNMENT 3

Due Date: 29 April 2016

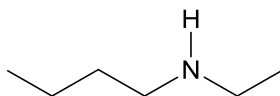
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1. Correct Answer: (3) N-methylpentan-2-amine

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



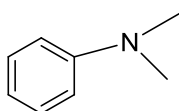
2. Correct Answer: (4)



Amines are classified as alkyl or aryl derivatives of NH_3 . Replacing one H with an alkyl or aryl group gives a primary (1°) amine; replacing two H's with alkyl or aryl group gives a secondary (2°) amine and replacing three H's with alkyl or aryl group gives a tertiary (3°) amine

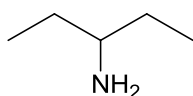
The classification of each amine with its name:

(1) *N,N*-dimethylaniline



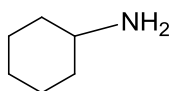
3° amine

(2) 3-pentanamine

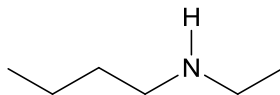


1° amine

(3) cyclohexylamine



1° amine

(4) *N*-ethyl-1-butanamine

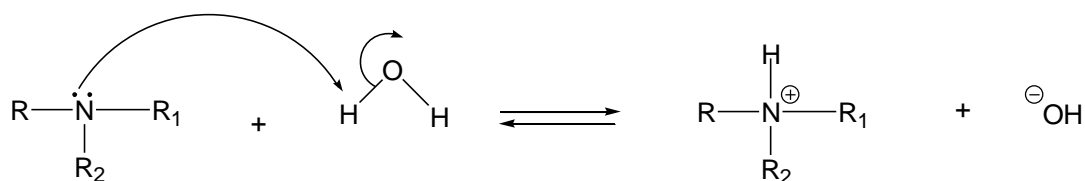
2° amine

3. Correct Answer: (1) IV<II<III<I

The above sequence is the order of increasing basicity (weakest first) of the following compounds:



The basicity of an amine is measured in terms of the ability of the N atom to donate its pair of electrons in the general reaction:

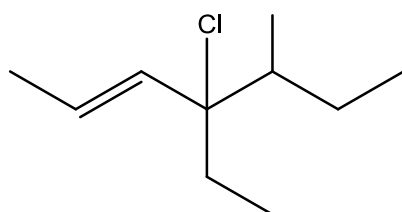


R, R₁, R₂ = H or alkyl

If we compare the bases below, I has one ethyl group, III and one more ethyl groups, i.e. 2 ethyl groups, II has one additional ethyl group (compared to III) whereas IV has 3 isopropyl groups attached to the N atom.

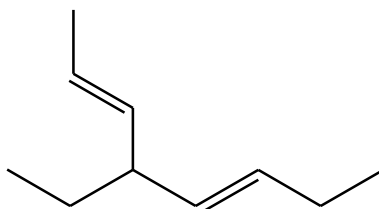
4. Correct Answer: (2) 4-chloro-4-ethyl-5-methylhept-2-ene

The above is the IUPAC name of the following compound:

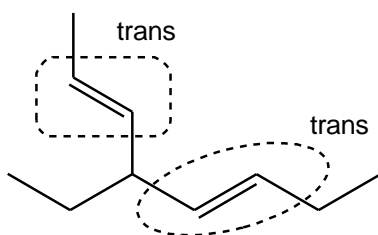


According to the IUPAC convention, the longest continuous carbon chain containing the C=C bond has 7 C's → heptane but since there is a C=C bond in the chain → change the ending from 'ane' to 'ene'. Begin numbering at the end of the C-chain to give the C=C the lowest number → 2-ene. The substituents are: at C-4 a CH₂CH₃ group → 4-ethyl; at C-4 a Cl atom → 5-chloro and at C-5 a CH₃ group → 5-methyl; name the substituents in alphabetical order.

5. Correct Answer: (4)

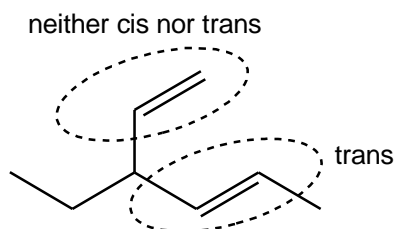


Both double bonds are *trans* double bonds:

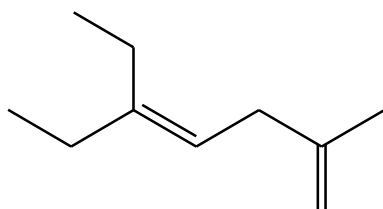


The other options;

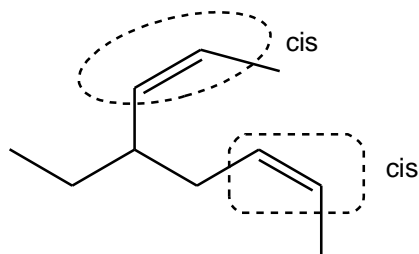
(1)



(2) Both C=C bonds are neither cis nor trans.

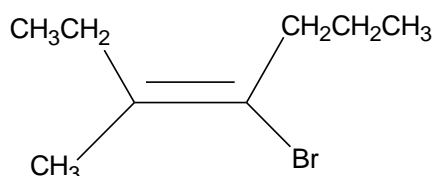


(3)



6. Correct Answer: (1) E-4-bromo-3-methylhept-3-ene

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



According to the IUPAC convention, the longest continuous carbon chain has 7 C's → heptane but there is a C=C bond in the chain → change the ending from 'ane' to 'ene'. Begin numbering at the end of the C-chain to give the C=C the lowest number → 3-ene. The substituents are: at C-3 a CH₃ group → 3-methyl; at C-4 a Br atom → 4-bromo; name the substituents in alphabetical order.

The Z/E nomenclature is used when the groups attached to the C=C are different. Assign priority order to the groups attached to the each carbon of the C=C. Assign priority in terms of atomic number of atom attached to C=C:

On C-3: -CH₃ and -CH₂CH₃; **-CH₂CH₃ has higher priority**

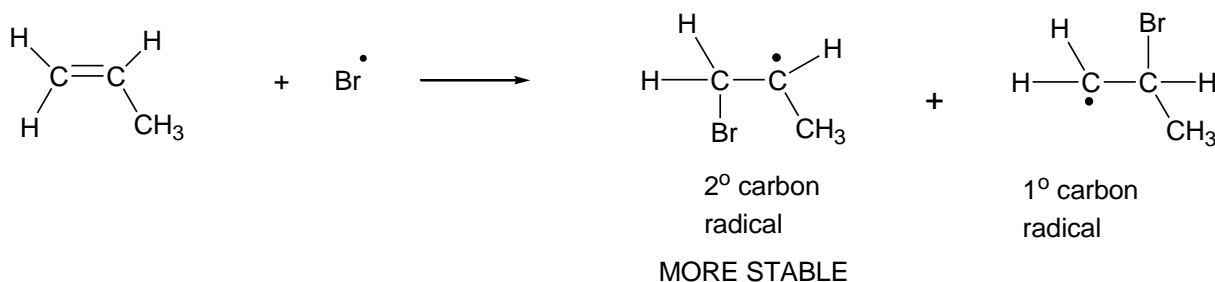
On C-4: -Br and -CH₂CH₂CH₃; **Br has higher priority**

The two priority groups are **on opposite sides of the C=C double bond**, therefore this is an **E-isomer**.

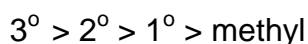
7. Correct Answer: (1)



Alkenes react with hydrogen halides in the presence of peroxides to give alkyl halides via an anti-Markovnikov addition method. In the first step of the reaction, a bromine radical is formed. This bromine radical adds to the carbon-carbon double bond to form an alkyl radical. Propene can form two possible alkyl radicals in the reaction:

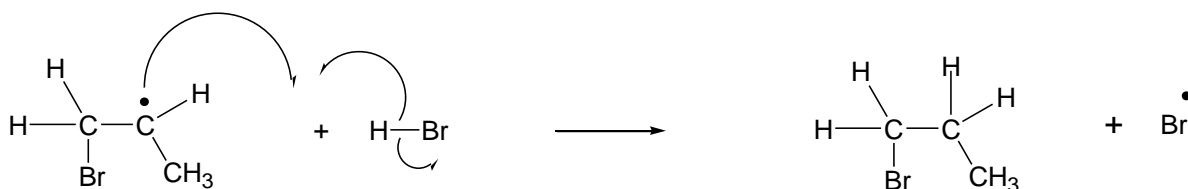


The more stable radical intermediate formed in the reaction gives the major product. Stability of carbon radicals:

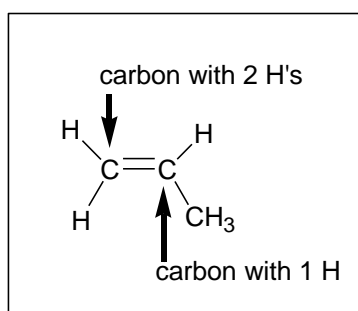


The alkyl radical abstracts a hydrogen atom from H-Br to generate the product and a bromine radical.

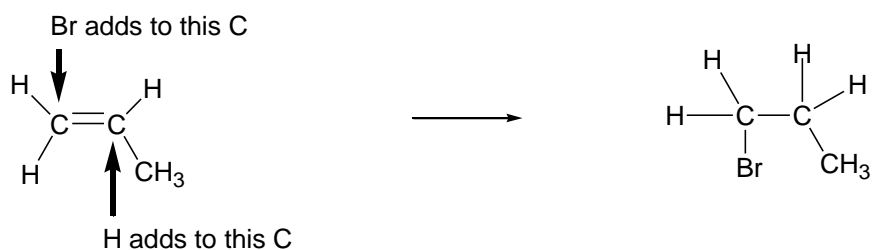
The more stable intermediate is formed in the reaction. This intermediate reacts with HBr to give an alkyl halide as follows:



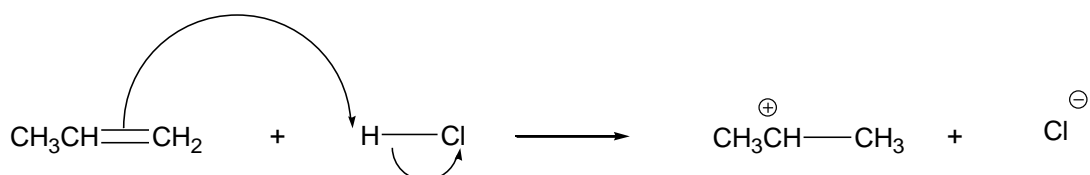
A summary of the reaction:



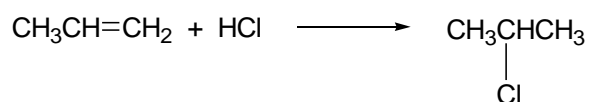
Anti - Markovnikov addition:



8. Correct Answer: (2)

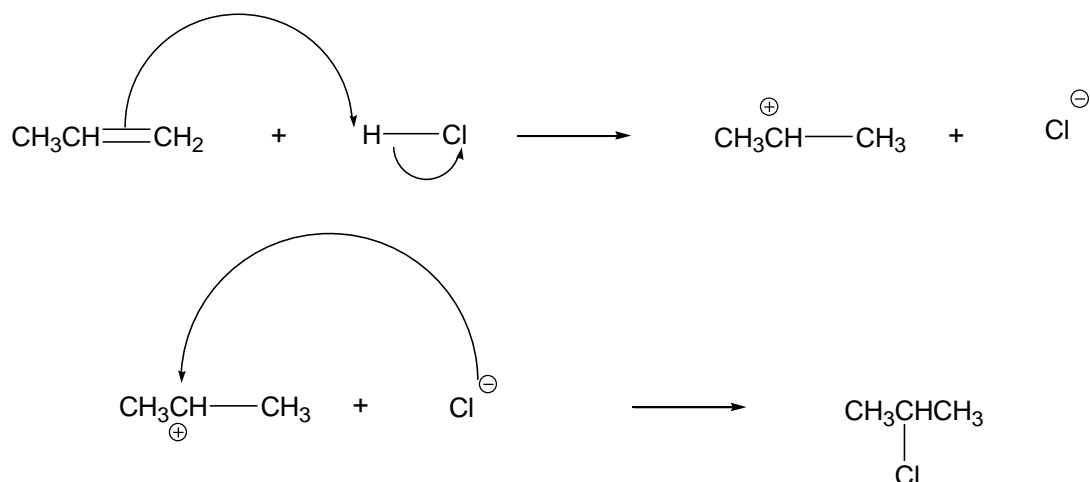


The above is the correct step in the mechanism of the following reaction:

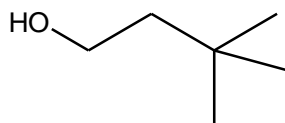


The more stable intermediate is formed in the mechanism of the reaction. In (1) a primary carbocation is formed which is less stable than the secondary carbocation formed in (2).

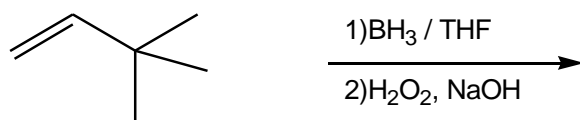
The complete mechanism of the reaction is:



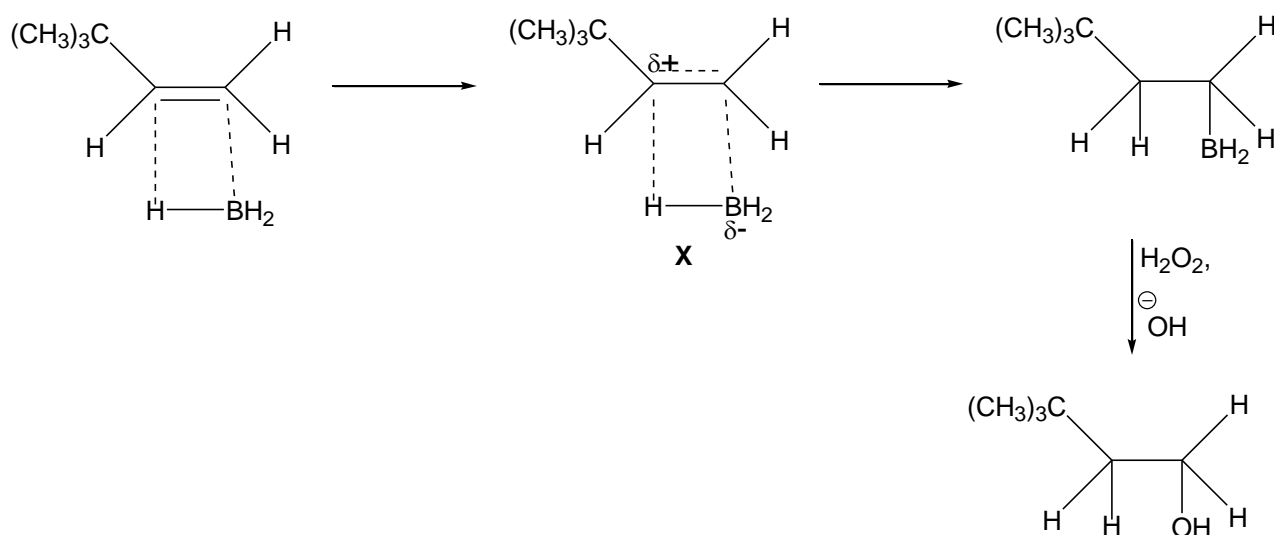
9. Correct Answer: (3)



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



The reaction involves the addition of water to the alkene in an anti-Markovnikov manner which proceeds as shown below. BH_3 is a strong Lewis acid with the B atom having an empty orbital and adds to the $\text{C}=\text{C}$ in the following manner:

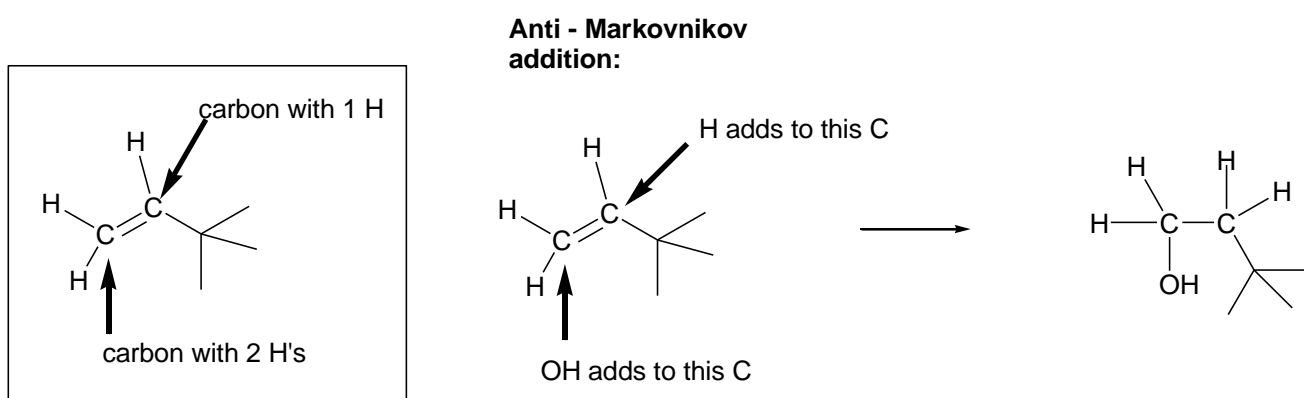


Borane, BH_3 , adds to the $\text{C}=\text{C}$ in a single step with the H adding to the more substituted carbon and the BH_2 to the least substituted carbon to give the more stable transition state – the partial positive charge is on the secondary carbon atom, in **X**. If the H added to the least substituted

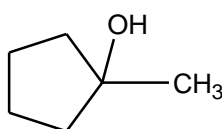
carbon then the partial positive charge would be on the primary carbon atom – producing a less stable intermediate. In the final step the hydroxide ion replaces the BH_2 group to give the product.

Summary of the reaction:

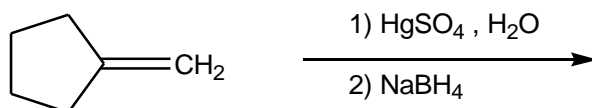
This is a hydration (the addition of water) reaction, i.e. H_2O adds to the $\text{C}=\text{C}$ as follows:



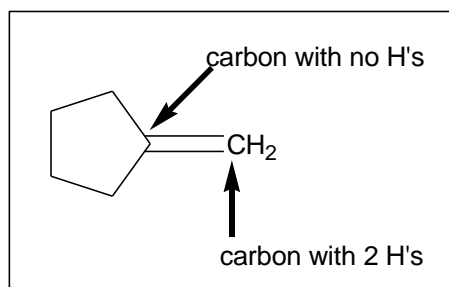
10. Correct Answer: (2)



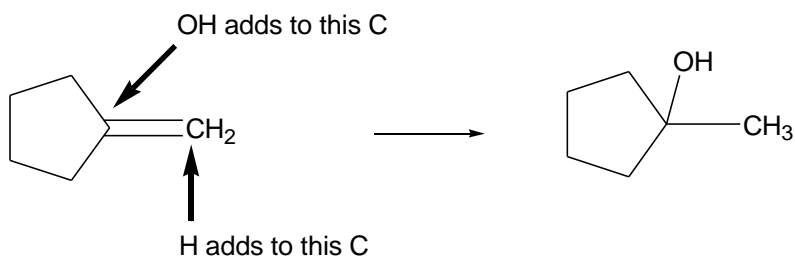
The above compound is the major organic product formed in the following reaction:



In the presence of mercuric ion, Hg^{2+} , an alkene undergoes hydration reaction in a Markovnikov addition manner – i.e. the H adds to the C with the most H's of the double bond and the OH adds to the C with the least H's.

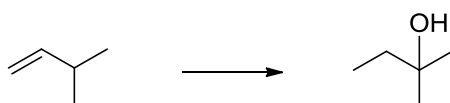


Markovnikov addition:

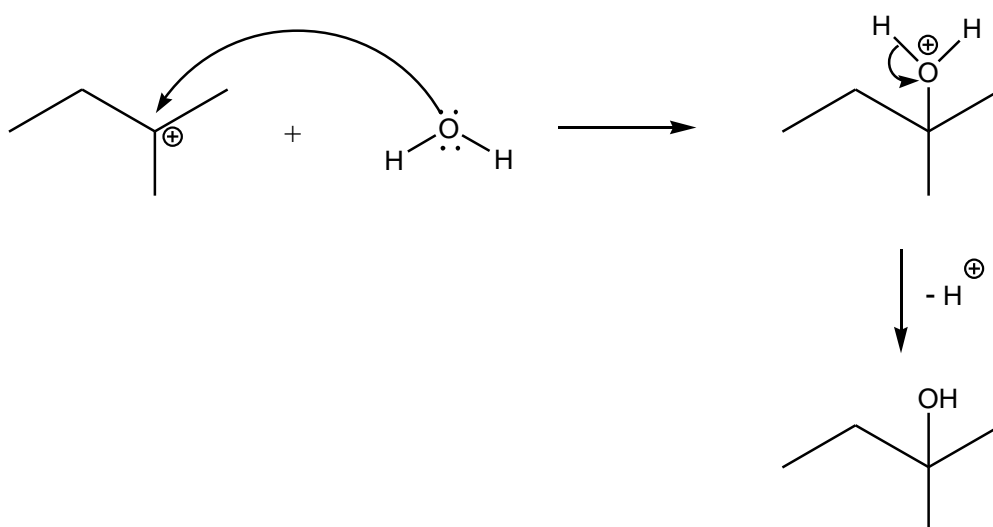
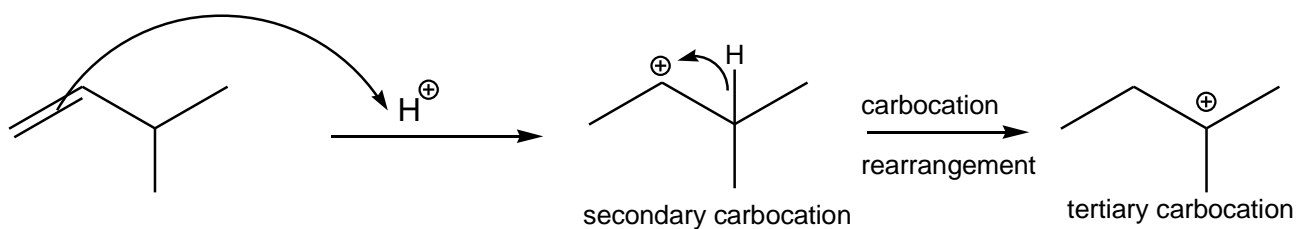


11. Correct Answer: (4) $\text{H}_2\text{SO}_4 \mid \text{H}_2\text{O}$

The above reaction conditions will be the best method to achieve the following conversion:

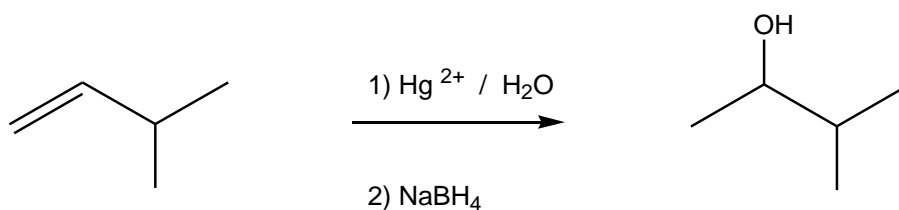


The reaction proceeds via the following steps:

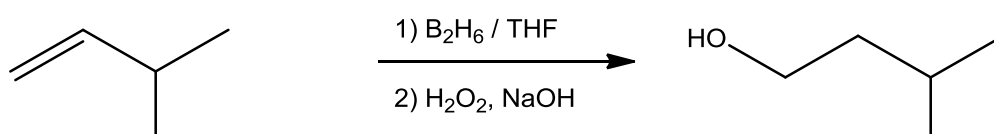


The other options:

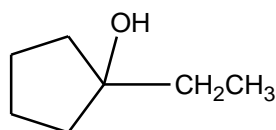
(1) The hydration reaction takes place in a Markovnikov manner (see no. 10 above):



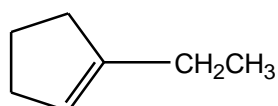
- (2) This reaction will not give the required product.
- (3) Under these reaction conditions, hydration takes place in an anti-Markovnikov manner (see no.9 above):



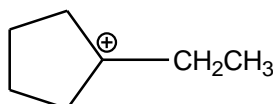
12. Correct Answer: (4)



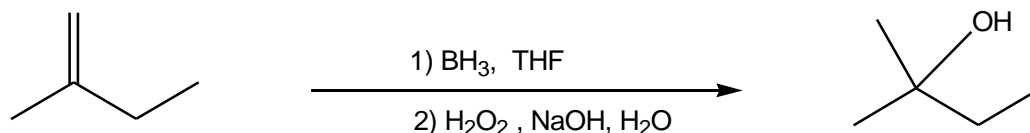
The alcohol above is produced by the acid catalyzed hydration of the following compound:



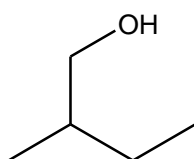
The hydration reaction proceeds in a similar manner to the reaction shown in no 11 above. The reaction proceeds via the following carbocation:



13. Correct Answer: (3)



The reaction in (3) will not take place because the addition of water to the alkene in the presence of borane takes place in an anti-Markovnikov manner which produces the following product:

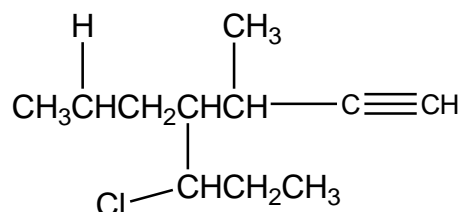


The other options are all correct because:

- (1) The hydration takes place in a Markovnikov manner
- (2) The H_2 adds to the $-\text{C}=\text{C}-$ to give $-\text{CH}_2-\text{CH}_2-$ and the rest of the molecule stays the same.
- (4) The reaction with Br_2 results in a Br atom adding to each C of the $\text{C}=\text{C}$ bond.

14. Correct Answer: (3) 5-chloro-3-methyl-4-propylhept-1-yne

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

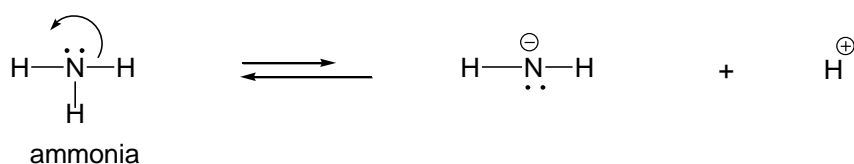


According to the IUPAC convention, the longest continuous carbon chain has 7 C's \rightarrow heptane but there is a carbon-carbon triple bond ('yne') in the chain \rightarrow change the ending from 'ane' to 'yne'. Numbering starts from the end nearest to the multiple bond i.e. the triple bond is at C-1. At

C-3 there is a methyl substituent → 3-methyl; there is a propyl substituent on C-4 → 4-propyl and there is a chlorine on C-5 → 5-chloro, name substituents in alphabetical order.

15. Correct Answer: (2) water and but-1-yne

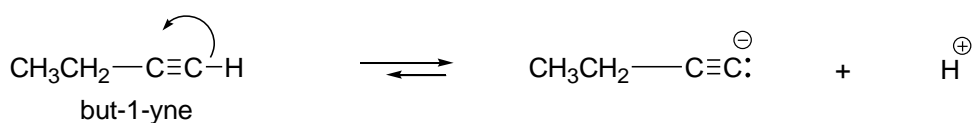
Consider the dissociation reactions shown below. In the case of ammonia, the NH_2^- ion is extremely basic and will react with the H^+ so that the reverse reaction is the predominant reaction.



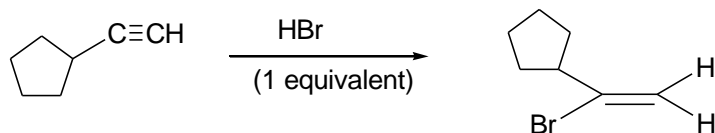
The OH^- ion is less basic than the NH_2^- ion, which is formed in the above reaction, and the reverse reaction of the dissociation of water takes place to a lesser extent than the reverse reaction for ammonia. Water is therefore more acidic than ammonia.



In the reaction of but-1-yne, corresponding anion formed is less basic than the NH_2^- ion formed in the reaction of ammonia. The reverse reaction in the dissociation of but-1-yne takes place to a much lesser extent than the reverse reaction for ammonia. But-1-yne is therefore more acidic than ammonia.



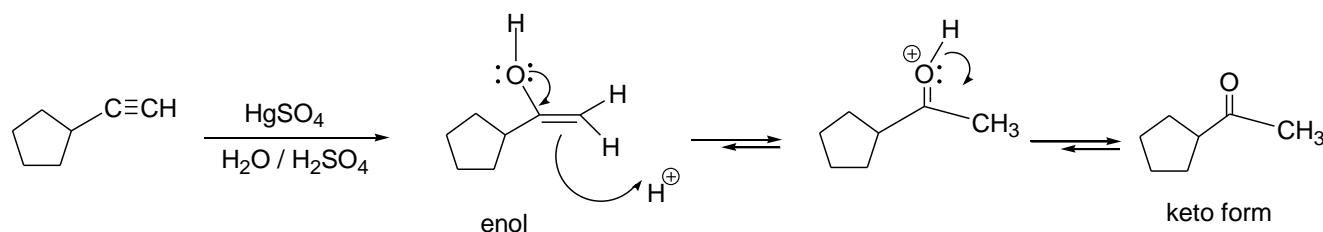
16. Correct Answer: (2)



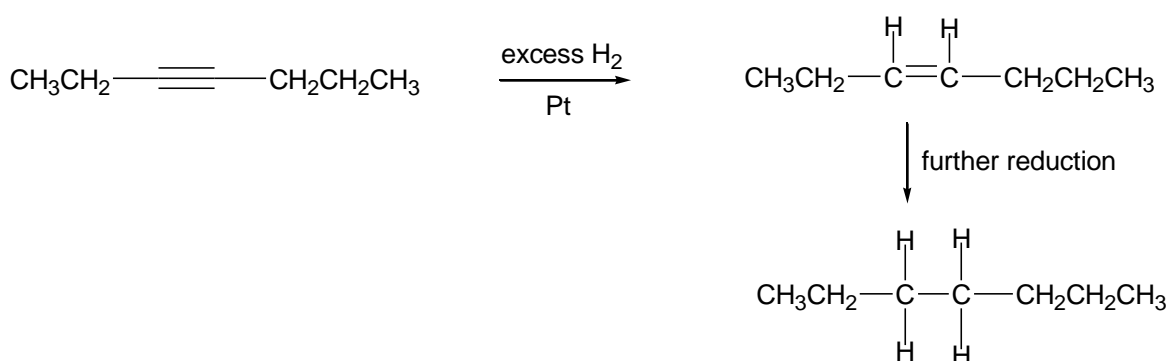
The reaction is an addition reaction where the electrophile (H^+) adds to the triple bond to give the more stable carbocation intermediate – a Markovnikov type of addition takes place in the above reaction.

The other options:

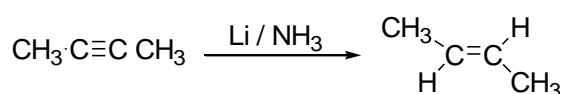
(1) Mercuric ion hydration takes place with Markovnikov orientation. The enol that is formed undergoes isomerization to give the corresponding ketone (keto-enol tautomerism):



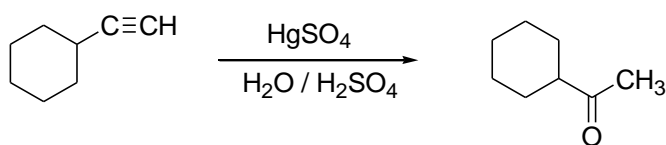
(3) With excess hydrogen the alkyne is first reduced to an alkene and then the alkene is reduced to an alkane.



(4) Metal-ammonia reductions normally produce the trans alkene:



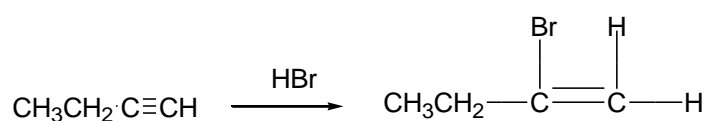
17. Correct Answer: (4)



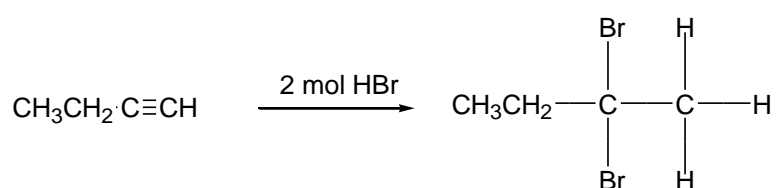
The reaction is similar to the reaction shown in no. 16 (1) above.

The other options:

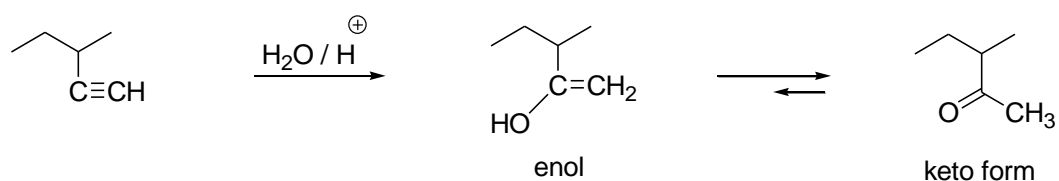
(1) Only one equivalent of HBr is given in the reaction, product formation:



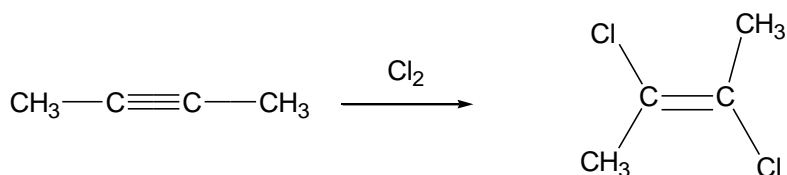
If excess or 2 mole equivalents of HBr were used, then the reaction would be:



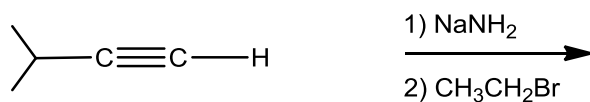
(2) The addition of water to the carbon-carbon triple bond produces an enol which undergoes rapid interconversion to form the keto form of the product.



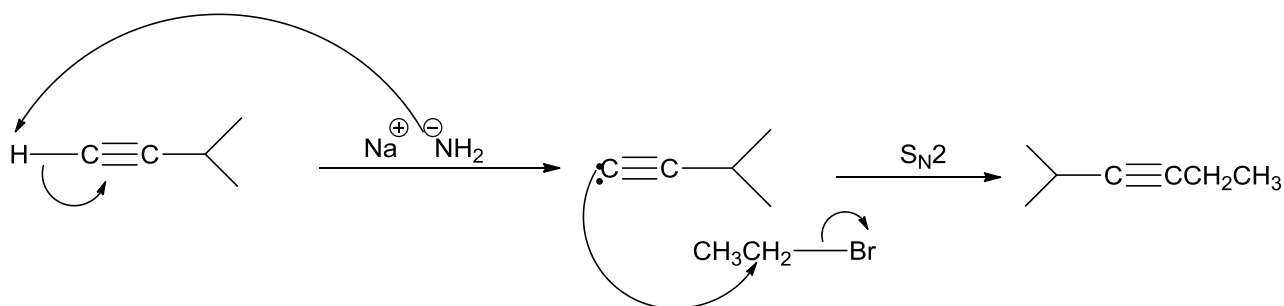
(3) In the reaction, only one equivalent of Cl_2 is used.



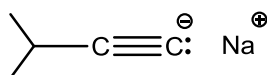
Consider the following reaction sequence for questions 18 and 19 below:



The reaction takes place as follows:

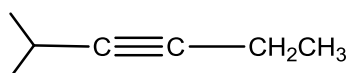


18. Correct Answer: (1)



The structure above is the major organic species formed in STEP 1.

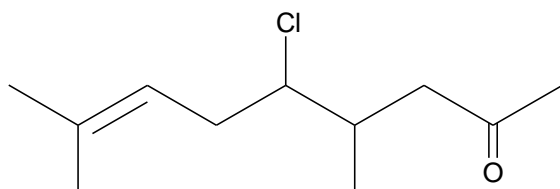
19. Correct Answer: (1)



The structure represents the major organic product in the reaction sequence.

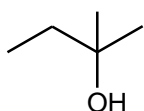
20. Correct Answer: (3) 5-chloro-4,8-dimethylnon-7-en-2-one

The above is the IUPAC name for the following compound:



According to the IUPAC convention, the longest continuous carbon chain has 9 C's → nonane. The compound has a carbonyl group (is a ketone); begin numbering at the end of the C-chain to give the C=O the lowest number i.e. at C-2; so the ending 'e' changes to 'one' → nonan-2-one. But there is a C=C bond in the chain at C-7 → change the 'an' to 'en' → non-7-en-2-one. At each of C-4 and C-8, there is a methyl group → two methyl's: 'di-methyl' → 4,8-dimethyl and at C-5 there is a chlorine atom → 5-chloro. Write the substituents in alphabetical order

21. Correct Answer: (1)

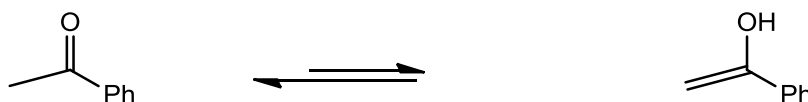


An alcohol can only be oxidized if the C that is attached to the OH has a hydrogen atom attached to it. The compound in (1) is a tertiary alcohol with no H attached to the C bearing the OH group and therefore cannot be oxidized to a ketone by chromic acid.

The other options can all be oxidized:

- (2) Compound is a primary alcohol
- (3) Compound is a secondary alcohol
- (4) Compound is a primary alcohol

22. Correct Answer: (4)

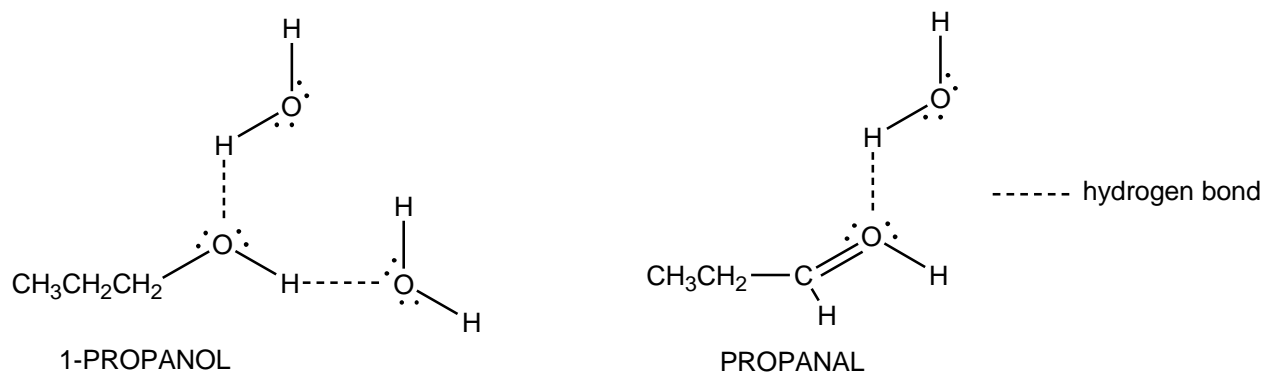


The mechanism of keto-enol tautomerism is shown in no. 16 (1) above. Remember, **the only change is the location of the H atom and the pi-electrons – all the other groups are atoms remain the same.**

23. Correct Answer: (2) 1-butene < propanal < 1-propanol

The above sequence represents the correct ranking in terms of increasing solubility in water.

The solubility of a compound in water depends on the extent of hydrogen bonding that is formed by a molecule of the compound and water. As seen below, 1-propanol forms more hydrogen bonds with water than propanal and therefore 1-propanol is more soluble in water. 1-Butene does not have any electronegative atoms that can undergo hydrogen bonding with water and is therefore insoluble in water.



24. Correct Answer: (2) I < IV < II < III

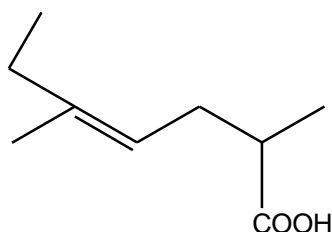
The above sequence ranks the following compounds in order of their tendency to undergo nucleophilic addition reaction (i.e, starts with the compound that reacts the slowest with a nucleophile):



Normally because of steric crowding around the carbonyl carbon (C=O), ketones are less reactive than aldehydes. Compound, I, is the least reactive and of the other compounds, an increase in the positive nature of the carbonyl carbon (C=O) will result in an increase in the reactivity to react with water. IV has an electron-donating ethyl group and will therefore be the least reactive of the aldehydes. Compound III has a CCl₃ group which contain strongly electron-withdrawing Cl atom which makes the carbonyl carbon very electron poor and therefore the most reactive.

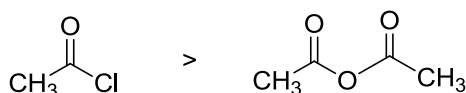
25. Correct Answer: (3) 2,5-dimethylhept-4-enoic acid

The above is the IUPAC name for the following compound:



According to the IUPAC convention, the longest continuous carbon chain has 7 C's → heptane. The compound has a carboxyl group, COOH at the end of the chain; so the ending 'e' changes to 'oic acid'. Start numbering from the carboxylic acid functional group and consider the chain that contains the most substituents. But there is a C=C bond in the chain at C-4 → change the 'an' to 'en' → -4-enoic acid. At C-2 and C-5 there are methyl groups → 2,5-dimethyl. Name substituents in alphabetical order.

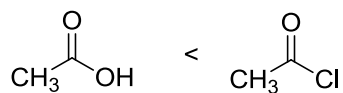
26. Correct Answer: (1)



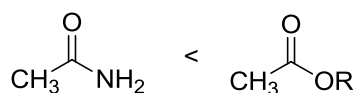
The above represents the correct order of reactivity of carboxylic acids derivatives with nucleophiles. The compound that has the best leaving group with react the fastest. Cl is a better leaving group than the OR group and NH₂ is a very poor leaving group.

The corrected version of the other options:

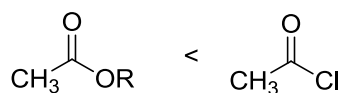
(2)



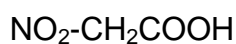
(3)



(4)



27. Correct Answer: (3)

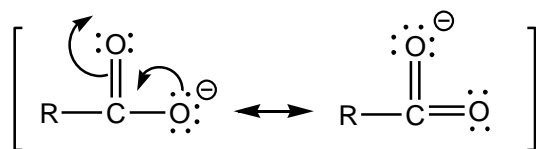


The compound above is the strongest acid.

The strength of the acid depends on its ability to donate an H^+ according to the general reaction:

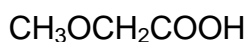


A strong acid will readily donate an H^+ and the forward reaction predominates – in order for that to happen the conjugate base which forms must be stable. In the reaction above, the stability of the conjugate base, i.e. the carboxylate ion, determines the stability of the carboxylic acid. The more stable carboxylate ion that is formed, the more acidic the acid. The resonance stabilization of the carboxylate ion is shown below:



Draw the carboxylate ions for the given acids.

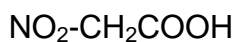
- (1) The CH_3O group is electron-donating and will make the carboxylate ion less stable. This group is a stronger electron-donating group than the methyl group in (4) – acid in (4) is stronger.



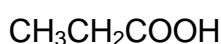
- (2) The CH_3 groups are electron-donating and will make the carboxylate ion less stable.



- (3) The NO_2 group is a strong electron-withdrawing group and will stabilise the carboxylate ion.

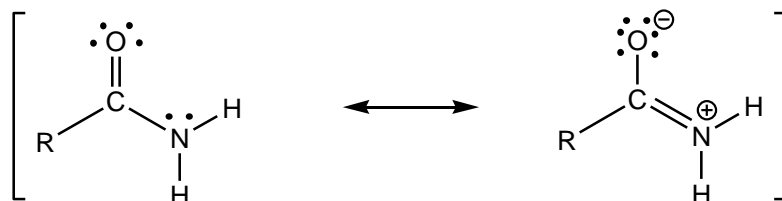


- (4) The CH_3 group is electron-donating and will destabilise the carboxylate ion. There is only one methyl group and this compound is more acidic than the compound in (2).



28. Correct Answer: **(4) the carbonyl group withdraws electrons by resonance.**

Amides are less basic than amines because the carbonyl group withdraws electrons by resonance.



In the reaction of an amide with a strong acid, protonation takes place at the oxygen instead of the nitrogen atom because in the resonance structure the O has a partial negative charge and N a partial positive charge – electrons on O are available for donation to the proton.

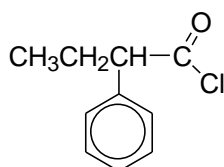
29. Correct Answer: (4)

all of the above

When the carbonyl group of a neutral ketone is protonated,

- (1) the resulting species has a positive charge
- (2) the resulting species is activated toward nucleophilic attack
- (3) the resulting species becomes more electrophilic

30. Correct Answer: (1)



The above is the correct structure of 2-phenylbutanoyl chloride.

2-Phenylbutanoyl chloride: butanoyl → longest C chain which includes the C=O has 4 carbons; chloride → acid chloride Cl-C=O, 2- phenyl → on C-2 there is a Ph substituent (start numbering at the C=O carbon atom)
