Tutorial Letter 203/2/2017

General Chemistry 1B

CHE1502

Semester 2

Department of Chemistry

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

Define tomorrow.

UNISA university of south africa

ONLY FOR SEMESTER 2 STUDENTS

ASSIGNMENT 3

Due Date: 5 October 2017
Unique number: 699976

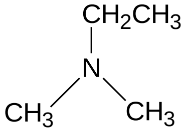
Amines: Nomenclature, classification and structure; Properties; Reactivity / basicity

1. Correct answer: **(1) C only**

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

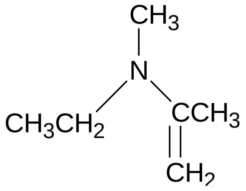
The classification of each amine:

A.



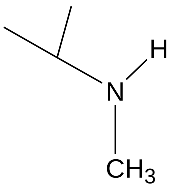
tertiary

B.



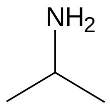
tertiary

C.



secondary

D.



primary

2. Correct answer: (**3**) **1-butanamine has a higher boiling point than butan-1-ol.**

Butan-1-ol, $CH_3CH_2CH_2CH_2OH$, contains an O-H bond and 1-butanamine, $CH_3CH_2CH_2CH_2NH_2$, contains N-H bonds. Because N is less electronegative than O, the O-H bond is more strongly polarized than the N-H bond. The hydrogen bonds that form between a H and the lone pair of electrons on N is weaker than the hydrogen bonds formed between the H and the lone pair of electrons on O. The intermolecular attractions are stronger in butan-1-ol. Therefore, butan-1-ol has a higher boiling point than 1-butanamine.

3. Correct answer: **(3)** $CH_3CH_2CH_2NH_2$

The boiling point of a substance is the temperature at which a liquid is converted to the gas phase.

The boiling point of a compound depends on the intermolecular forces (i.e. the forces that exist between the molecules of the compound).

The stronger the intermolecular forces, the higher the boiling point. All molecules can exhibit van der Waals forces. The given compounds are all amines. The N-H bonds are strongly polarized giving the H atoms a partial positive charge. This electrophilic H has a strong attraction for the non-bonding electrons on N of another amine molecule. This attraction between two amine molecules is called hydrogen bonding. Hydrogen bonding influences boiling points. Tertiary amines do not van the N-H bond and thus cannot form hydrogen bonds. A secondary amine has one N-H bond and a primary amine has two N-H bonds – the extent of hydrogen bonding is thus greater in primary amines. Primary amines will have higher boiling points than secondary amines with comparable molecular weight. The number of carbons in a molecule also influences the boiling point (Section 19.4 in textbook).

(1) Primary amine – the electrons in N involved in resonance delocalization and less available than in (3).

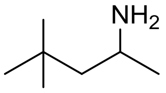
(2) Secondary amine

(3) Primary amine

(4) Tertiary amine- lowest boiling point

4. Correct answer: **(1) 4,4-dimethyl-2-pentanamine**

The above is the correct name for the following compound according to the IUPAC rules:



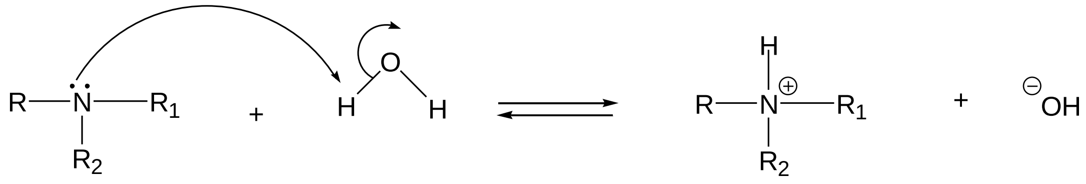
According to the IUPAC convention, the longest continuous carbon chain has 5 C's → pentane. Begin numbering at a branch to give the substituents the lowest possible number; C-2 has a NH_2 group: change ending 'e' to 'amine' → 2-pentanamine; C-4 has two methyl groups → 4,4-dimethyl; add to parent name.

5. Correct answer: **(4) B>A>C**

The above is the order of decreasing basicity (strongest first) of the following compounds:

CH_3NH_2	$(CH_3)_2NH$	H_3N
A	B	C

D is the weakest and B is the strongest base. The basicity of an amine is measured in terms of the ability of the N atom to donate a pair of electrons in the general reaction:



$R, R_1, R_2 \quad = \quad$ H or alkyl

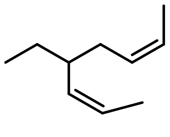
If we compare the bases above, A has one methyl group, B and one more methyl groups, i.e. 2 methyl groups, whereas C has three hydrogen atoms attached to the N atom. An alkyl group is electron-donating towards cations and a methyl group will stabilize the positive charge on N. This stabilization makes A a stronger base than C. When we proceed from A to B, we increase the number of electron-donating groups and therefore increase the basicity. The basicity of a compound is evident when it is dissolved in a solvent. In the reaction above water is the solvent and the ammonium ions becomes solvated with water – this solvation contributes to the stability of the ammonium ions. However, when there are too any groups around the nitrogen like in for example $(CH_3)_3N$, the water molecules are unable to come close to the positively charged atom and can therefore not solvate the ions.

Alkenes: Structure and nomenclature; Physical properties; Geometric isomerism (cis/trans and E/Z configurations); Reactions and mechanisms of hydrohalogenation, acid catalyzed hydration and halogenation of symmetrical and unsymmetrical alkenes and the application of Markovnikov’s rule; Mechanism of hydrohalogenation of unsymmetrical alkenes in the presence of peroxides (anti-Markovnikov’s addition); Hydrogenation of alkenes.

6. Correct answer: **(4)** **shorter, stronger**

Carbon-carbon double bonds tend to be shorter and stronger than carbon-carbon single bonds.

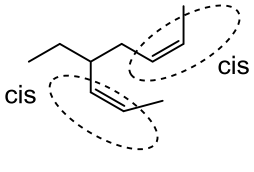
7. Correct answer: **(1)**



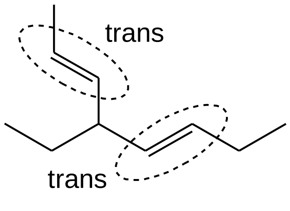
The above structure contains ONLY *cis* double bonds.

Labelling of the double bonds in the options:

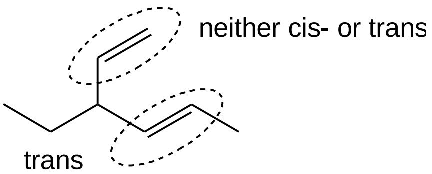
(1)



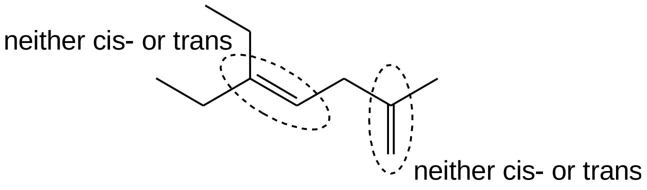
(2)



(3)

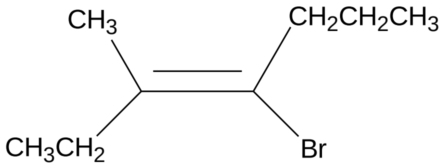


(4)



8. Correct answer: **(2) Z-4-bromo-3-methylhept-3-ene**

The above is the name of the following compound according to the IUPAC rules:



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 CH_3 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: -CH_3 and -CH_2CH_3; **-CH_2CH_3 has higher priority**

On C-4: -Br and -$CH_2CH_2CH_3$; **Br has higher priority**

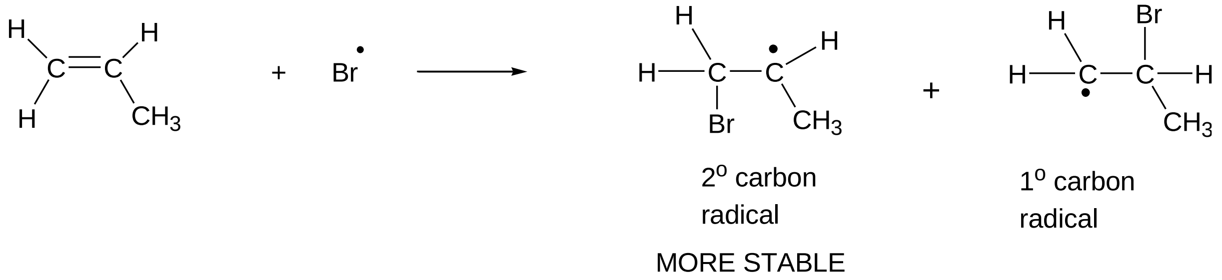
The two priority groups are **on the SAME side of the C=C double bond → Z-isomer**.

9. Correct answer: **(4)**

$CH_3\dot{C}HCH_2Br$

The above intermediate is formed during the reaction of $CH_3CH{=}CH_2$ with HBr in the presence of peroxides.

Alkenes react with hydrogen halides in the presence of peroxides to give alkyl halides via an anti Markovnikov addition method. In the first step, a bromine radical is formed (H-Br → $Br^{\cdot}$ + $H^{\cdot}$). This bromine radical adds to the carbon-carbon double bond to form an alkyl radical. Propene can form two possible alkyl radicals as intermediates in the reaction:

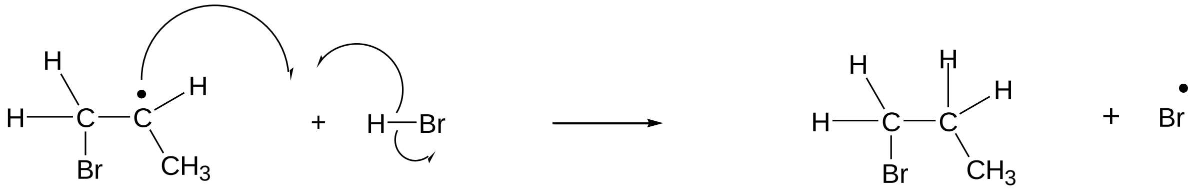


The more stable radical intermediate formed in the reaction gives the major product. Stability of carbon radicals:

$3^o > 2^o > 1^o >$ methyl

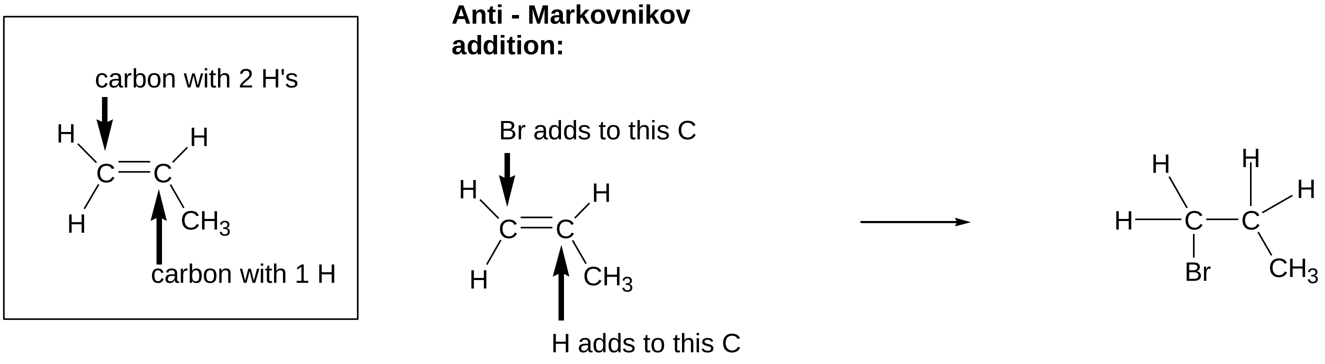
The alkyl radical abstracts a hydrogen atom from H-Br to generate the product and a bromine radical.

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



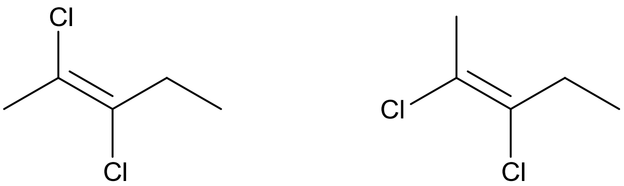
A summary of the reaction:

Anti - Markovnikov addition:

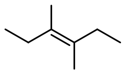


10. Correct answer: **(3)** **2,3-dichloro-2-pentene**

The above alkene can exist as geometric isomers. The two geometric isomers of the alkene are:

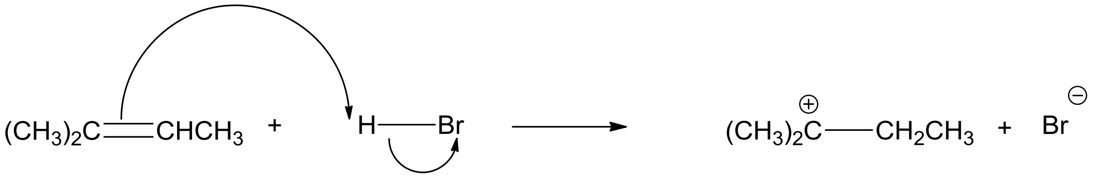


11. Correct answer: **(2)**

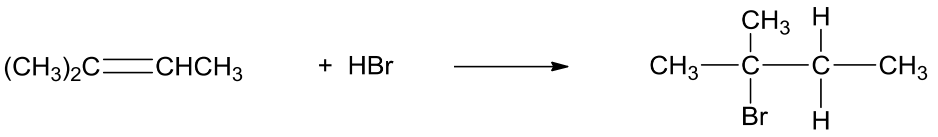


The compound shown above according to Saytzeff's rule, will be the major product in an elimination reaction. According to Saytzeff's rule, the most stable alkene has the most carbons attached to the C=C bond i.e. the C=C with the most alkyl groups attached to it.

12. Correct Answer: **(1)**

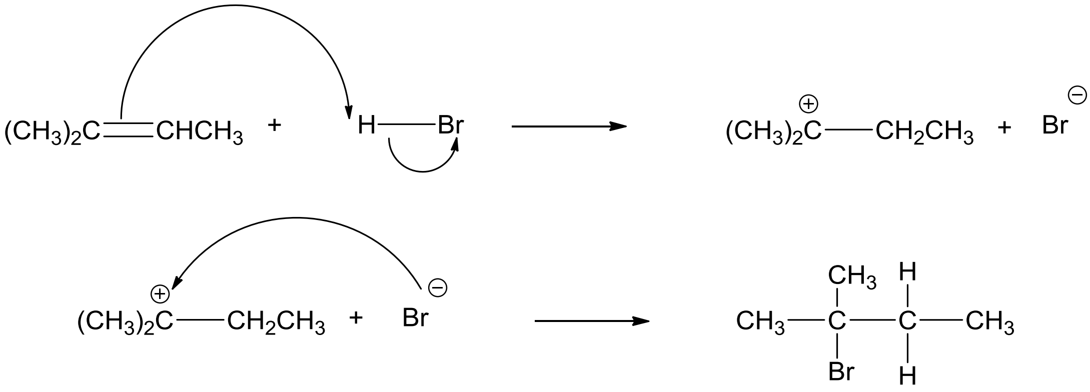


The above is the correct step in the reaction mechanism of the following reaction:

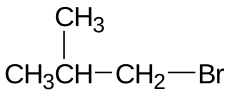


$$(CH_3)_2C{=}CHCH_3 + HBr \longrightarrow CH_3-\overset{CH_3}{\underset{Br}{C}}-\overset{H}{\underset{H}{C}}-CH_3$$

The complete reaction mechanism is:



13. Correct answer: **(1)**

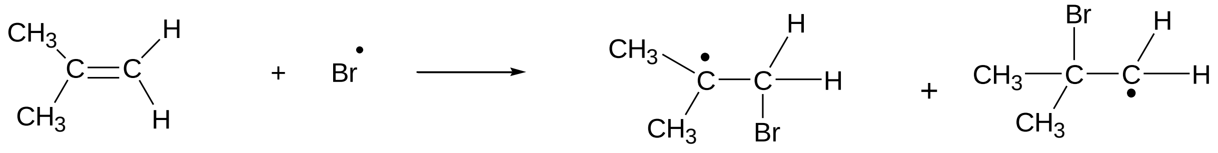


$$\overset{CH_3}{CH_3CH}-CH_2-Br$$

The compound shown above is the product formed in the following reaction:

$$CH_3\overset{CH_3}{C}{=}CH_2 \quad + \quad HBr \quad \xrightarrow{H_2O_2}$$

Alkenes react with hydrogen halides in the presence of peroxides to give alkyl halides via an anti-Markovnikov addition method. A bromine radical is formed in the first step of the reaction. This bromine radical adds to the carbon-carbon double bond to form an alkyl radical. 3-Methylpropene can form two possible alkyl radicals in the reaction:



2^o carbon radical

1^o carbon radical

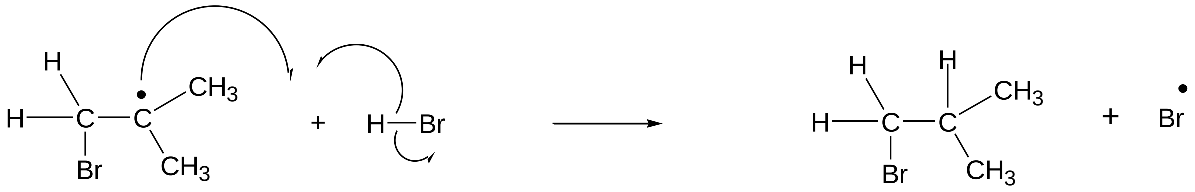
MORE STABLE

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

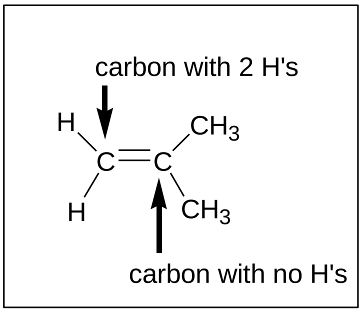
$$3^o > 2^o > 1^o > \text{methyl}$$

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

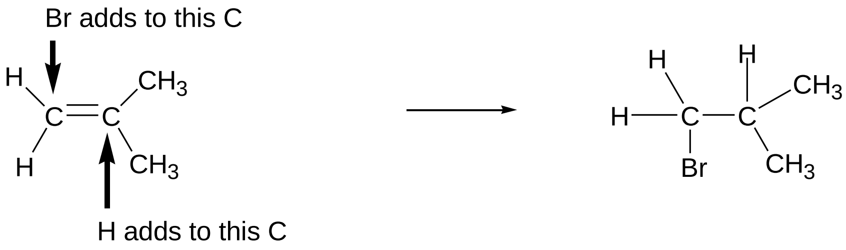
The more stable intermediate is formed in the reaction. This intermediate reacts with HBr to give an alkyl halide as follows:



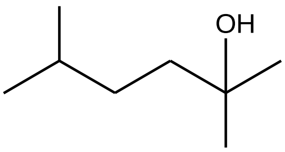
A summary of the reaction:



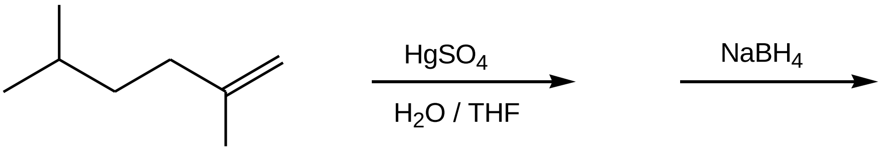
Anti - Markovnikov addition:



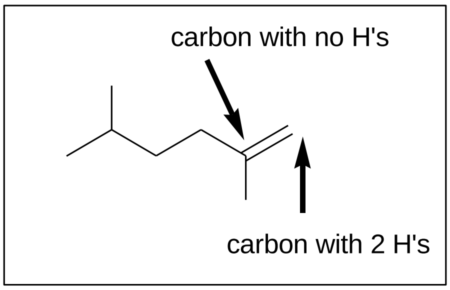
14. Correct answer: **(2)**



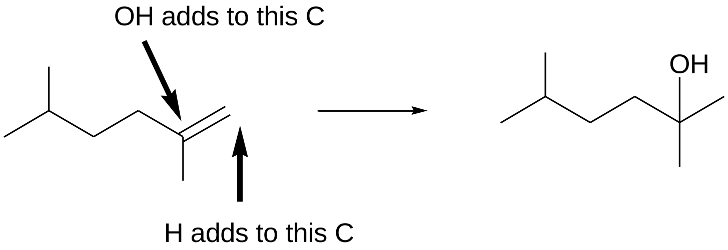
The structure above is the major organic product formed in the following reaction:



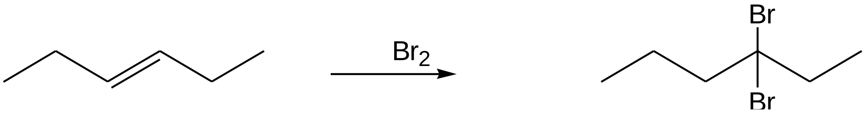
In the presence of mercuric ion, Hg^{2+}, an alkene undergoes hydration reaction in a Markovnikov addition manner – i.e. the H adds to the C with the most H's of the double bond and the OH adds to the C with the least H's.



Markovnikov addition:



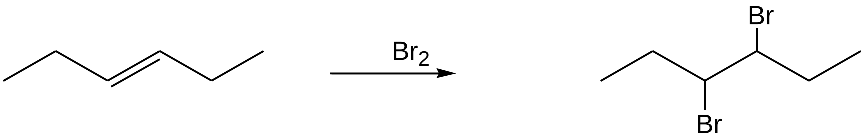
15. Correct answer: **(2)**



The reaction above does NOT produce the product as shown. The options:

(1) This is a hydration reaction (addition of H_2O) in such a way that the OH adds to the C of the C=C with the most H's and the H adds to the C (of C=C) with the most C's.

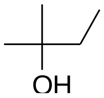
(2) A Br atom adds to each C of the C=C:



(3) The H_2 in the presence of the catalyst adds a H atom from the same side to each C of the C=C; the rest of the molecule remains the same

(4) Reaction takes place in a similar manner as described in no 14 above.

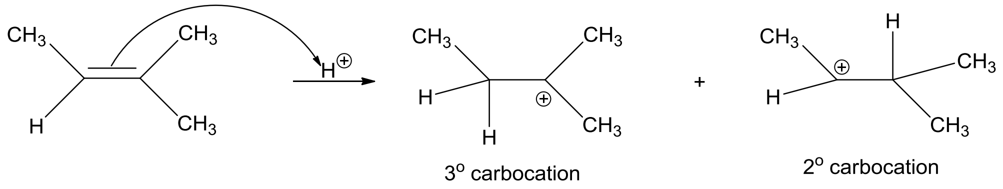
16. Correct answer: **(1)**



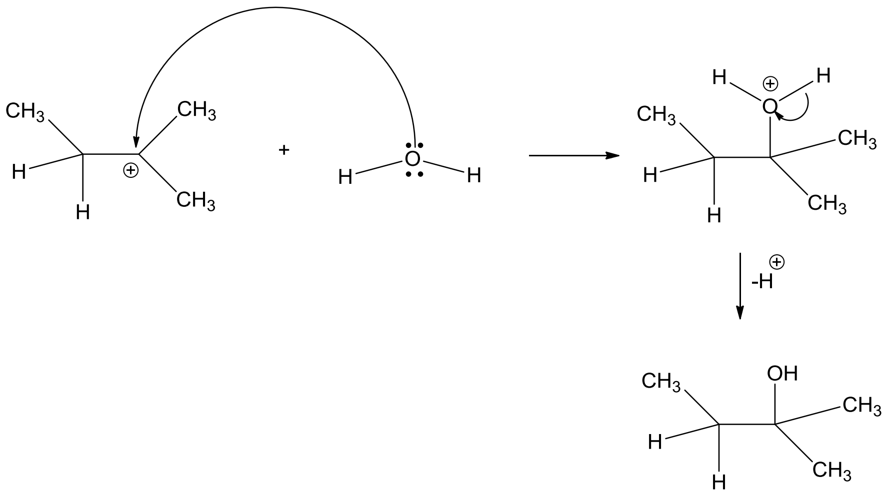
The above alcohol is produced by the acid catalyzed hydration of 2-methyl-2-butene.

The reaction mechanism

The first step in the acid catalyzed hydration of 2-methyl-2-butene with 2-methyl-2-butene redrawn is:



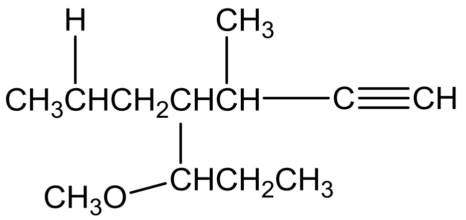
The most stable carbocation is the tertiary carbocation, which is lower in energy than the secondary carbocation and is mainly formed. The reaction of the tertiary carbocation will give the predominant / major product.



Alkynes: Structure and nomenclature; Physical properties; Reactions and mechanisms of hydration, halogenation and hydrohalogenation of symmetrical and unsymmetrical alkynes (Markovnikov's rule); Hydrogenation of alkynes; Acidity / Reactivity of terminal alkynes.

17. Correct answer: **(3)** **5-methoxy-3-methyl-4-propylhept-1-yne**

The above is the correct name the following compound according to the IUPAC rules.



$$\mathrm{CH_3\overset{\overset{H}{|}}{C}HCH_2\underset{\underset{CH_3O-CHCH_2CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{C}H-C\equiv CH}$$

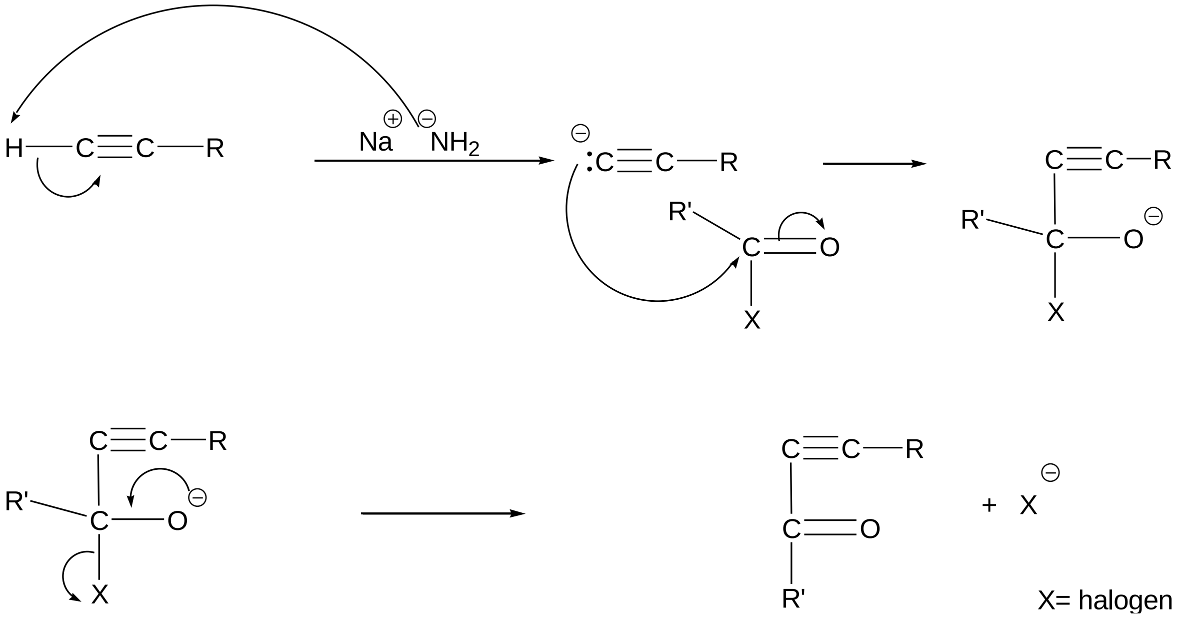
According to the IUPAC convention, the longest continuous carbon chain has 7 C's → heptane but there is a carbon-carbon triple bond ('yne') in the chain→ change the ending from 'ane' to 'yne'. Numbering starts from the end nearest to the multiple bond i.e. the triple bond is at C-1 in such a way that the most substituents are attached to the parent chain . At C-3 there is a methyl substituent → 3-methyl; there is a propyl substituent on C-4 → 4-propyl and there is an OCH_3 group on C-5 → 5-methoxy; name substituents in alphabetical order.

18. Correct answer: **(3)**

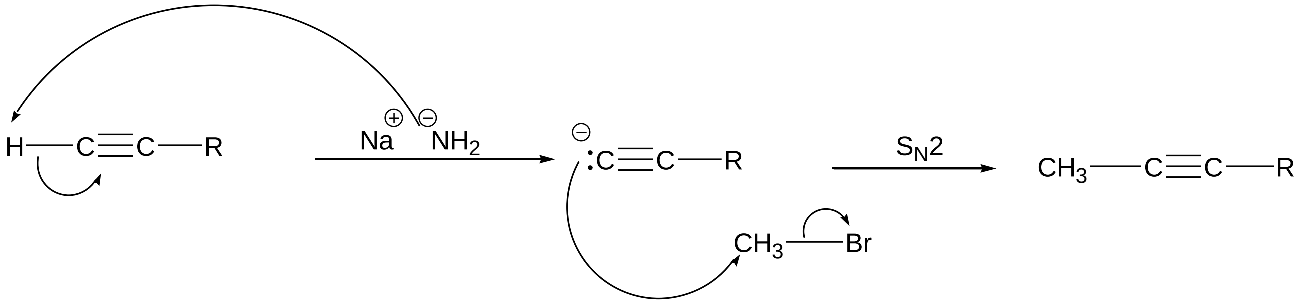
$$CH_3CH_2C{\equiv}CCH_3 \xrightarrow{NaNH_2} \xrightarrow{CH_3CH_2Br} CH_3CH_2C{\equiv}C\,CH_2CH_2CH_3$$

The above reaction does not take place because the alkyne is not a terminal alkyne and therefore will not form an acetylide ion. The other options:

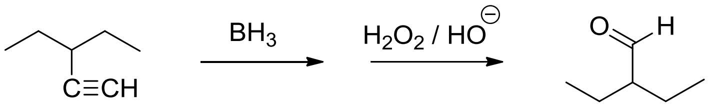
(1) and (4)



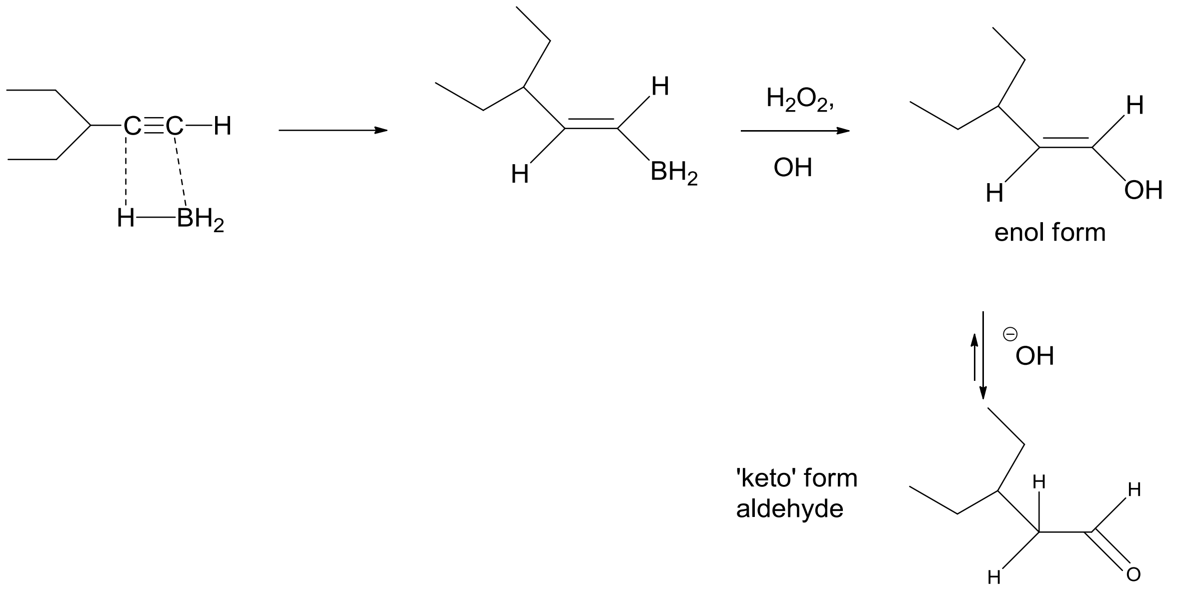
(2) The reaction takes place as follows, where R=CH_3 group:



19. Correct answer: **(4)**

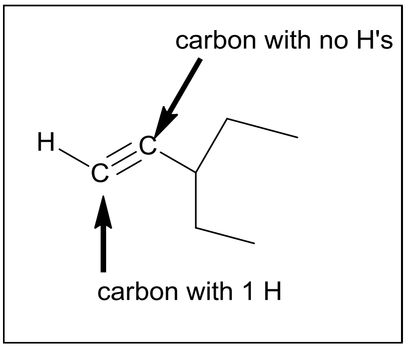


The product above will not form in the reaction. The hydroboration-oxidation reaction involves the addition of water to the carbon-carbon triple bond of the alkyne in an anti-Markovnikov manner, which proceeds as shown below. BH_3 is a strong Lewis acid with the B atom having an empty orbital and adds to the C≡C bond in the following manner:

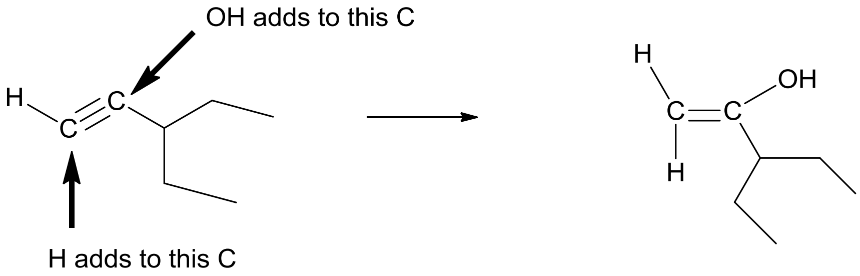


Borane, BH_3, adds to the C≡C in a single step with the H adding to the more substituted carbon and the BH_2 to the least substituted carbon. In the final step, the hydroxide ion replaces the BH_2 group to give the product. Summary of the reaction:

This is a hydration (the addition of water) reaction, i.e. H_2O adds to the C≡C as follows:

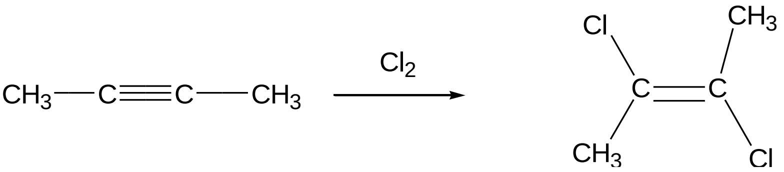


Anti - Markovnikov addition:

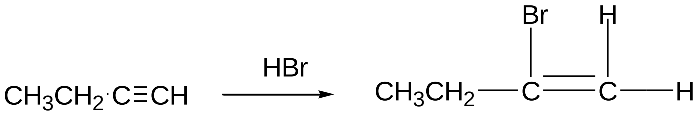


Other Options:

(1) In the reaction, the equivalents are not stated and it is assumed thus the product shown is possible which will be the same for 2 equivalents or excess of Cl_2 . If only one equivalent of Cl_2 is used – the reaction produces the following product:



(2) If only one equivalent of HBr is given, then the reaction takes place as follows:



If excess or 2 mole equivalents of HBr were used, then the reaction takes place as shown.

(3) The reaction involves hydration of the alkyne where the water adds to the C≡C in a Markovnikov manner.

20. Correct answer: **(4)** ***trans*-2-pentene**

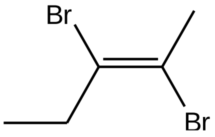
The reaction of 2-pentyne with Na/NH_3 gives ***trans*-2-pentene** as the product.

The reaction of 2-pentyne with Na/NH_3 involves the addition of two H's in such a way that the H atoms add to opposite sides of the C=C bond.

21. Correct answer: (**3)** **hydroboration/oxidation**

Hydroboration/oxidation below involves an enol intermediate. The reaction is similar to the reaction in no 19 (4) above.

22. Correct answer: **(4)**

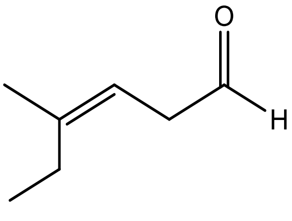


In the reaction, each Br atom adds to a carbon of the C≡C bond.

Carbonyl compounds and derivatives: Structure and nomenclature of ketones and aldehydes; Properties and reactivity of ketones and aldehydes.

23. Correct answer: **(3)** **4-methylhex-3-enal**

The above is the IUPAC name for the following compound:

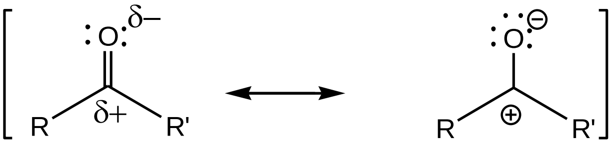


According to the IUPAC convention, the longest continuous carbon chain has 6 C's → hexane.

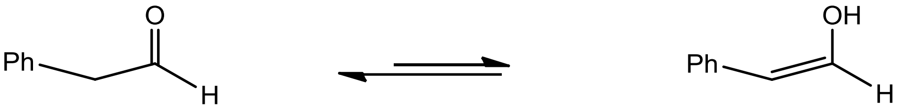
The compound has an aldehyde carbonyl group at the one end; so the ending ‘ane’ changes to ‘al’ → hexanal. Begin numbering at the CH=O group. At C-4 there is a methyl group → 4-methyl; and C-3 has a C=C → normally the ‘ane’ is changed to ‘3-ene‘; change parent name to → hex-3-enal.

24. Correct answer: **(4)** **nucleophiles**

The positively polarized carbon atom of a carbonyl group is electrophilic and therefore reacts with the nucleophile, that has electrons available for donation. The carbonyl group has the resonance forms:



25. Correct answer: **(4)**



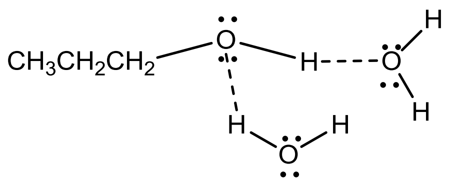
A ketone or aldehyde can undergo keto-enol tautomerism if the carbon atom which is adjacent to the carbonyl group has at least one H atom attached to it. In the compound above, there are two H’s attached to the adjacent C (the α-carbon) – hence it will exhibit keto-enol tautomerism.

Each of the other representations of keto-enol tautomerism is not possible.

26. Correct answer: **(4) 1-butene < propanal < 1-propanol**

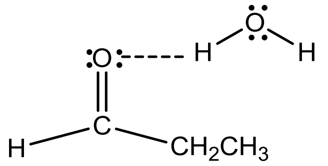
The above represents the correct ranking in terms of increasing solubility in water. Increase in solubility in water from left to right: 1-butene least soluble and 1-propanol the most soluble.

The compound that forms the strongest hydrogen bonds with water will be the most soluble and the one that do not form hydrogen bonds with water will be the least soluble.



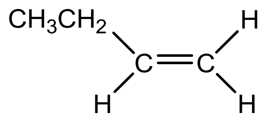
Propan-1-ol

;



Propanal

;

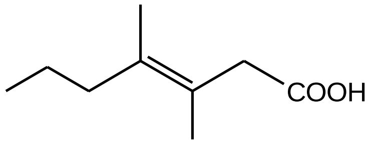


Buten-1-ene

------ are hydrogen bonds

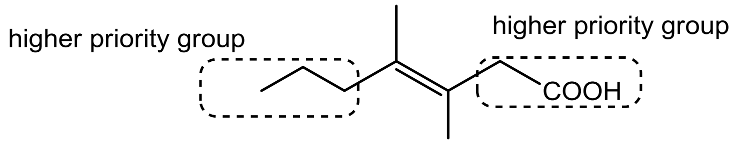
Carboxylic acids and derivatives: Structure and nomenclature carboxylic acids and carboxylic acid derivatives (esters and amides); Properties and reactivity of carboxylic acids and carboxylic acid derivatives.

27. Correct answer: **(1)**



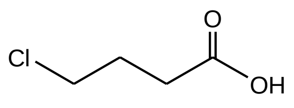
The above is the correct structure of (E)-3,4-dimethylhept-3-enoic acid.

‘Hept’ → Carbon chain of 7 C’s; ‘3-hepten’ → at C-3 there is a C=C; ‘oic acid’ → a COOH group on C-1; ‘3,4-dimethyl’ → there are two CH_3 groups: on C-3 and on C-4. The ‘E’ indicates that the higher priority groups around the C=C are on the opposite side.

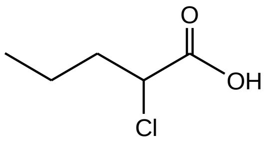


28. Correct answer: **(1)** **C < A < B < D**

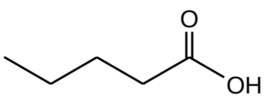
The above is the order of increasing acidity (from lowest to highest) of the following weak acids:



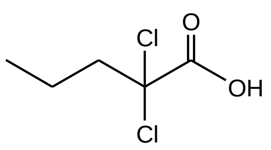
A



B

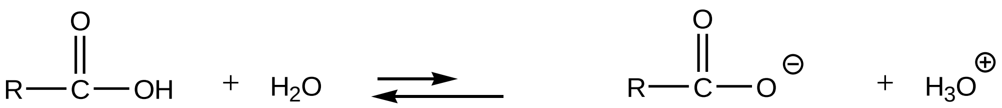


C



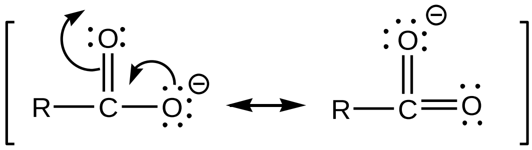
D

Carboxylic acids may dissociate in water as follows:

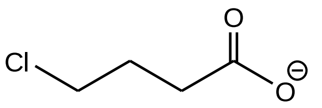


$$R{-}\overset{\overset{\displaystyle O}{||}}{C}{-}OH + H_2O \rightleftharpoons R{-}\overset{\overset{\displaystyle O}{||}}{C}{-}O^{\ominus} + H_3O^{\oplus}$$

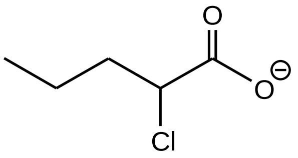
The strength of the acid depends on its ability to donate an H^+. A strong acid will readily donate an H^+ and the forward reaction predominates – in order for that to happen the conjugate base which forms must be stable. In the reaction above, the stability of the conjugate base, i.e. the carboxylate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



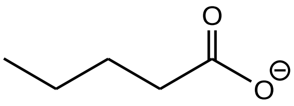
All of the acids, **A** to **D**, form carboxylate ions that are resonance stabilized. The corresponding carboxylate ions for the given acids are:



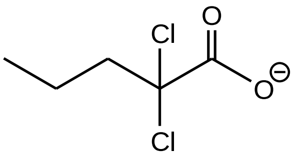
A



B



C

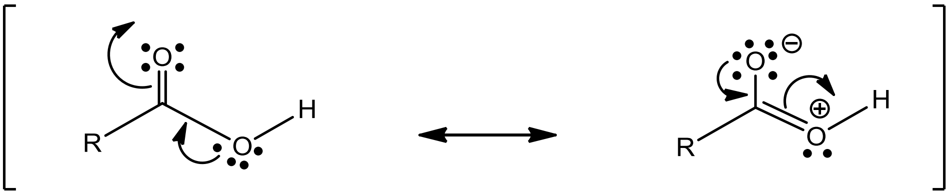


D

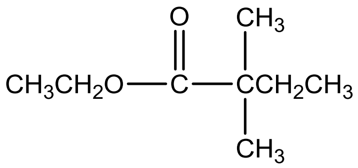
We now have to compare the stability of the carboxylate ions formed in each acid. The carboxylate ion formed from **B**, has a Cl atom on the C atom adjacent to the COO^- group. The electronegative Cl atom withdraws electron density from the carboxylate ion, thereby stabilizing the carboxylate ion and increasing the strength of the acid. Carboxylic acid, **B**, is therefore the stronger acid than **C** (no Cl atoms). In **A** the electron-withdrawing Cl is further away from the COO^- group than the Cl group in **B** - the Cl group in **B** has a stronger electron-withdrawing effect on the COO^- group than in **A**. Carboxylic acid, **B**, is thus a stronger acid and **A.** In going from **B** to **D,** there is an additional electron-withdrawing Cl on the C adjacent to the COO^- group (in **D**) - the two Cl groups have a stronger electron-withdrawing effect on the COO^- group than one Cl group (in **B**). The carboxylate ion formed for **D** is therefore more stable than the carboxylate ion formed for **B** and **D** is thus a stronger acid than **B.**

29. Correct answer: **(4)** **One of the unshared electron pairs on the hydroxyl oxygen is delocalized into the electrophilic pi system of the carboxyl group.**

The above statement is correct. The carboxyl group is the functional group of carboxylic acids and resonance delocalization takes place:



30. Correct answer: **(1)**

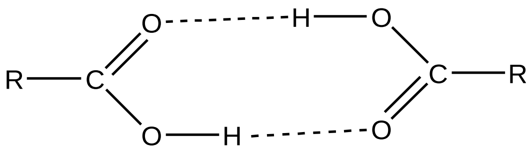


$$CH_3CH_2O{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_3$$

The above is the correct structure of ethyl 2,2-dimethylbutanoate.

‘butan’ → carbon chain of 4 C’s – all with C-C single bonds; ‘oate’ → this is an ester and has a –(C=O)OR functional group with C=O designated as C-1; ‘2,2-dimethyl’ → there are two CH_3 groups on C-2. The ‘ethyl’ indicates that this is an ethyl ester i.e. the OR group is OCH_2CH_3.

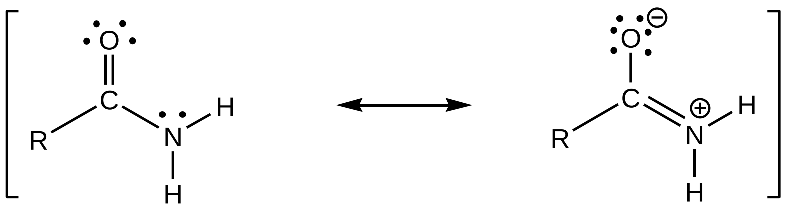
31. Correct answer: **(2)**



Carboxylic acids boil at much higher temperatures than ketones or alcohols of similar molecular weights due to hydrogen bond formation. This interaction is a very strong intermolecular hydrogen bond formation. The above shows hydrogen bonding that exists between 2 acid molecules – dimer formation. [Show the hydrogen bonding between alcohol molecules].

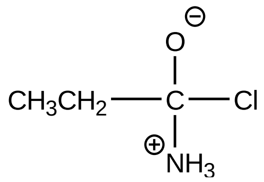
(4) Shows the hydrogen bonding between an acid molecule and water.

32. Correct answer: **(4)**



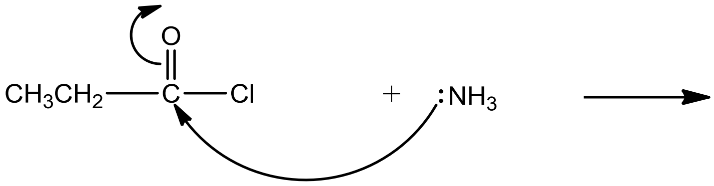
In the reaction of an amide with a strong acid, protonation takes place at the oxygen instead of the nitrogen atom because in the resonance structure the O has a partial negative charge and N a partial positive charge – electrons on O are available for donation to the proton.

33. Correct answer: **(3)**



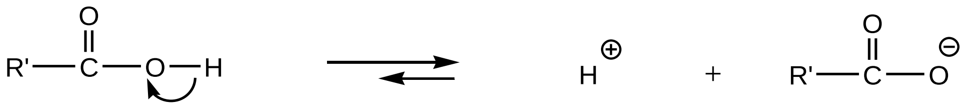
$CH_3CH_2C(O^-)(Cl)NH_3^+$

The above intermediate is formed in the step shown below:

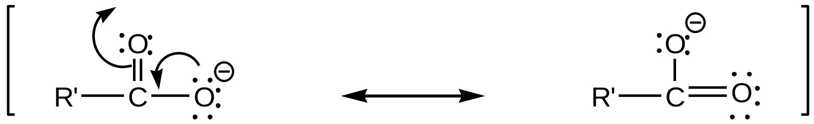


34. Correct answer: **(1)** **resonance stabilization of the carboxylate ion**

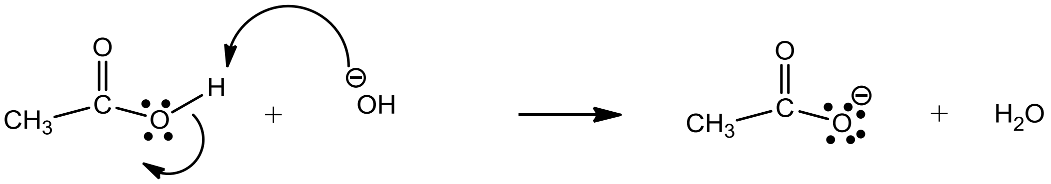
The OH groups of carboxylic acids are more acidic than alcohols because of resonance stabilization of the carboxylate ion. In solution, the carboxylic acid ionizes as follows:



The resultant carboxylate ion is stabilized by resonance:



35. Correct answer: **(2)**



The above mechanistic step represents the reactivity of carboxylic acids. The base abstracts the acidic proton in an acid-base reaction.