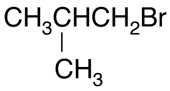
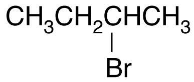
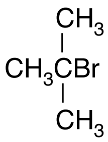
Chemguide – answers

NUCLEOPHILIC SUBSTITUTION

1. a) $CH_3CH_2CH_2CH_2Br$ or 

b) 

It doesn't matter which of the two middle carbon atoms you attach the bromine to. If you think you have another possibility, it is probably because you haven't drawn the longest chain horizontally. Try bending your structure. To be a secondary halogenoalkane, the halogen must be attached to a CH group.

c) 

However you have drawn this structure in space, there will be a carbon atom with three CH_3 groups and a bromine attached.

2. a) A nucleophile is a species (an ion or a molecule) which is strongly attracted to a region of positive charge in something else.

b) Each of these has an atom carrying at least one lone pair of electrons. In the case of hydroxide ions and cyanide ions, that atom also has a full negative charge. In the case of ammonia, the electronegativity of the nitrogen gives it a fairly negative charge.

3. a) The bond between the carbon and the bromine is polar because bromine is more electronegative than carbon. A lone pair on the oxygen is attracted to the slight positive charge on the carbon, and moves to form a bond with it. In the process, the electrons in the carbon-bromine bond are pushed entirely on to the bromine producing a bromide ion. The net effect is that the bromine has been substituted by an -OH group.

b) The solid line between the carbon and the bottom hydrogen represents a bond in the plane of the paper (or screen).

The wedge-shaped bond represents a bond coming out towards you.

The big dotted line between the two carbon atoms is a bond going back into the paper (or screen) away from you.

The two fainter dotted lines represent bonds half-made and half-broken.

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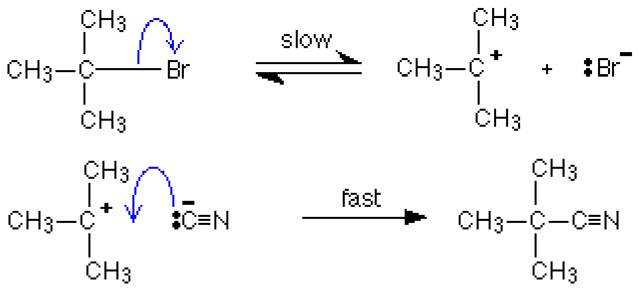
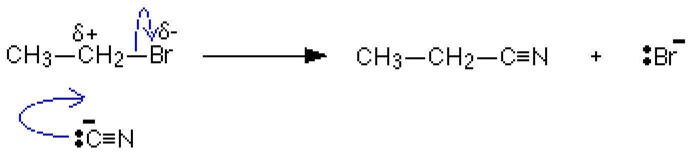
4. a) (i) With a primary halogenoalkane, the OH^- ion (or other nucleophile) approaches the halogenoalkane molecule from the back – the other side from the bromine atom. In a tertiary halogenoalkane, that other side is completely cluttered up by alkyl groups, and so the nucleophile can't get at the slightly positive carbon.

(ii) The tertiary halogenoalkane uses a mechanism involving the formation of a carbocation (carbonium ion). Because of the "electron pushing" effect of the three alkyl groups, a tertiary carbocation has the positive charge delocalised enough to stabilise the ion to an extent and allow its formation. The corresponding primary carbocation only has one alkyl group to help spread the charge, and the ion is too unstable to form in sufficient numbers.

b)

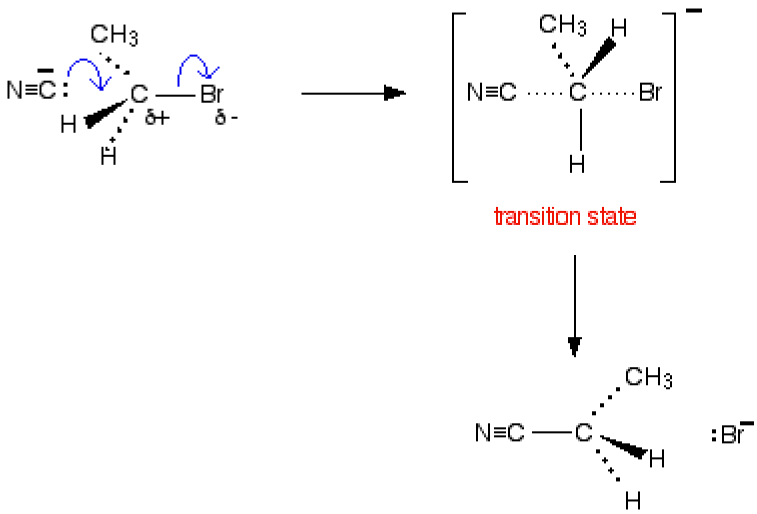


5.



Make sure that you have shown the structure of the cyanide ion correctly in both this and the previous question.

If you have used the more complete version showing the structure of the transition state, it should look like this:



How do you know which version to use? You need to check past exam papers and their mark schemes from your examiners.

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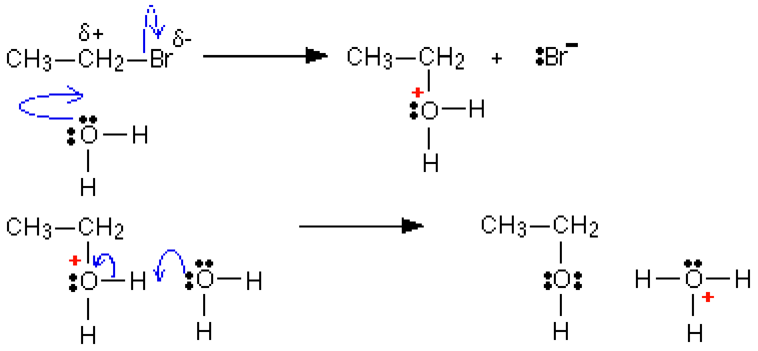
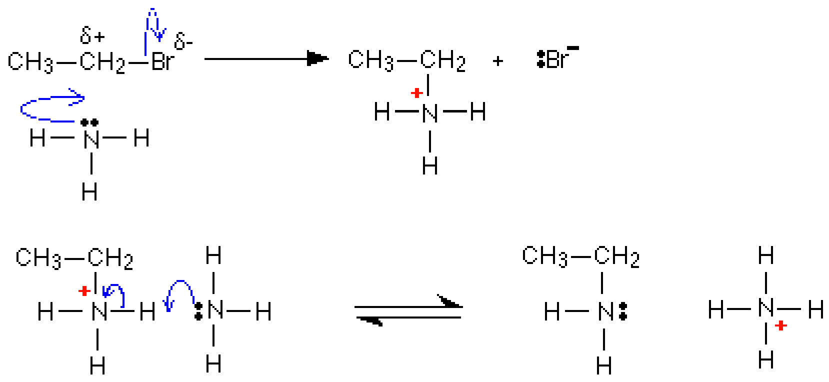
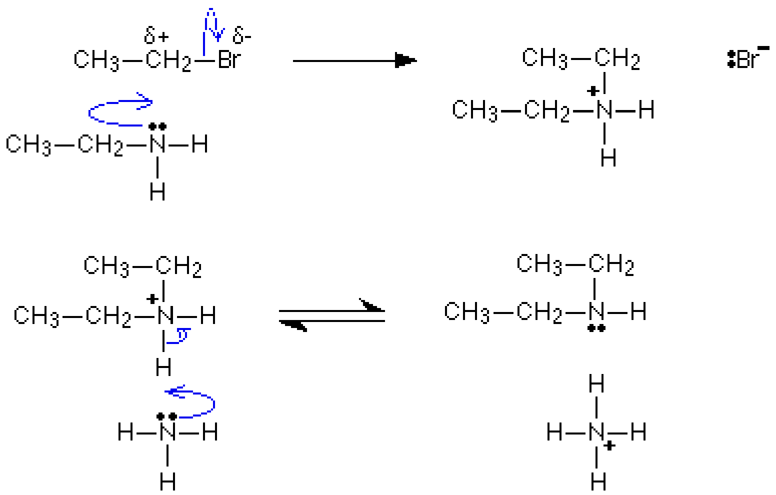
6. a) 

You must show the second stage involving the removal of the extra hydrogen on the oxygen.

b) OH^- ions are much better nucleophiles than water molecules because there is a full negative charge on the ion, but only a strong polarity on a water molecule.

7. a) 

b) 

c) Triethylamine is $(CH_3CH_2)_3N$. You just need to draw a structure showing 3 CH_3CH_2 groups attached (via the CH_2 – careful!) to the nitrogen atom. The question just asks for the structures, although in the context, it wouldn't hurt to include the lone pair on the nitrogen as well.

Tetraethylammonium bromide is $(CH_3CH_2)_4N^+ Br^-$. Draw the structure showing 4 CH_3CH_2 groups attached (via the CH_2 – again be careful!) to a nitrogen atom carrying a positive charge. *Don't* draw a line between the N and the Br. This is an ionic, not a covalent, bond.