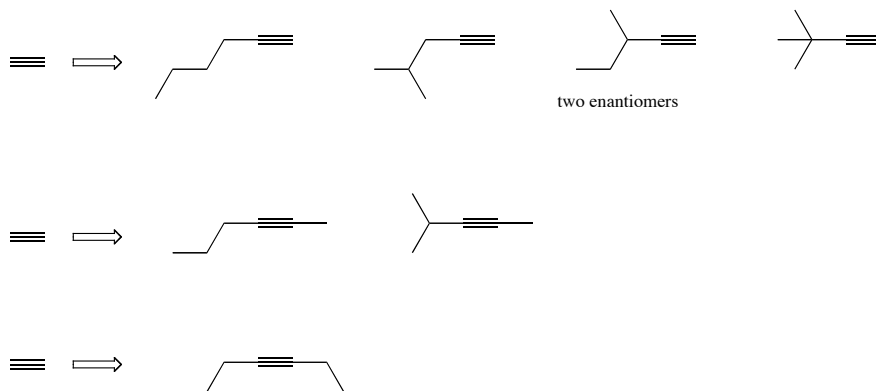


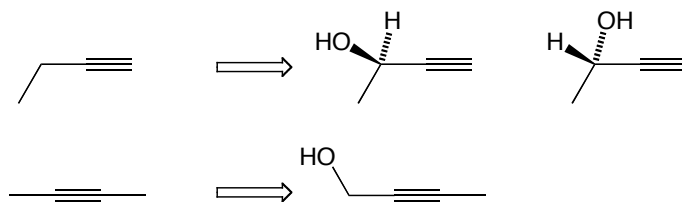
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13-1 a) You have worked exercises of this kind much earlier in the book. To find all of the isomers of a given formula, it is best to work in a systematic fashion. Here we know that the compounds are all alkynes and that from the formula we can conclude that there are no other double or triple bonds and no rings. Start with the triple bond and then systematically add the remaining four carbon atoms. See the answer in the back of the book for the IUPAC names.



b) See the answer in the back of the book for the IUPAC names.

c) Start by drawing all possible butynes and then add the OH functional group.



13-2 There are several ways to look at the bonding in alkynes. Perhaps the easiest to grasp is to compare the heat of hydrogenation of 2-butyne (−65.1) with that of *trans*-2-butene (−27.6). Clearly, reduction of the two  $\pi$  bonds in the alkyne release significantly more energy than twice the  $\pi$  bond in the alkene (65.1 versus 55.2, a difference of 10 kcal/mole).

13-3 This exercise is worked out in the book as "Working with Concepts".

13.4 The answer in the back of the book is adequate.

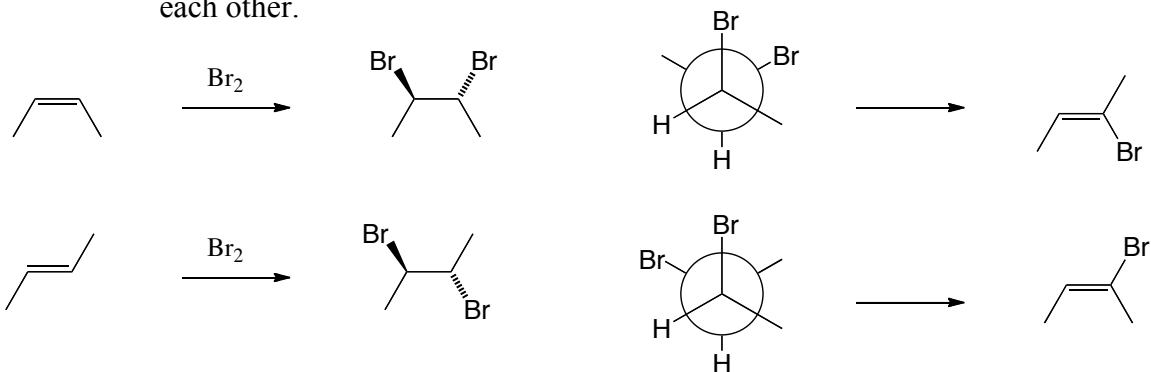
13-5 This exercise is worked out in the book as "Working with Concepts".

13-6 There is no special coupling in 2-pentyne as a result of the presence of the triple bond. Thus, the methyl group appears as a singlet and the ethyl group appears as a triplet and a quartet.

**13-7** Note that the stereochemistry of the starting alkene has no consequence for the sequence leading to the alkyne.

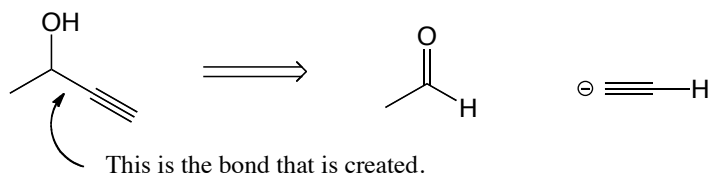
**13-8** Recall that:

- 1) Addition of bromine to an alkene occurs in a *trans* fashion;
- 2) E2 reactions proceed with the hydrogen and leaving group anti periplanar to each other.



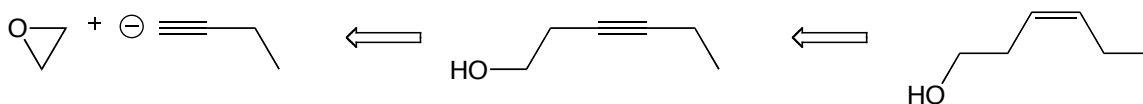
**13-9** The answer in the back of the book is adequate.

**13-10** The exercise only requires that you use “techniques outlined in this section”. As you learn your reactions it is good to focus on what happens (e.g., reduction with NaBH<sub>4</sub> can be used to convert an aldehyde to a primary alcohol). But it is also good to store the reaction by the functional group that it makes. Thus, primary alcohols can be synthesized by reduction of aldehydes with NaBH<sub>4</sub>. In this section, we learned of a reaction that specifically makes an alcohol with an adjacent triple bond: the addition of an alkyne anion to a ketone or aldehyde. This reaction makes a new C—C bond between the carbonyl carbon of the starting material and the Sp-hybridized carbon of the triple bond. To find the starting material, we simply look at the product and undo this reaction.



**13-11** Do not become distracted by all of the functional groups present. Lindlar reduction only affects the transformation of alkynes to *cis*-alkenes.

**13-12** To this point you have learned only one way to make a *cis* alkene: reduction of an alkyne with Lindlar catalyst. So working backwards (retrosynthetic analysis), we see that a precursor for the desired alkene could be the corresponding alkyne. Notice that this alkyne has two functional groups: the alkyne; and the primary alcohol. You have learned only a limited number of reactions that generate molecules with more than one functional group. One is the reaction the anion of a terminal alkyne with an epoxide.



**13-13** This exercise is worked out in the book as "Working with Concepts".

**13-14** The answer in the back of the book is adequate.

**13-15** The answer in the back of the book is adequate.

**13-16** Remember that only terminal and symmetrical alkynes lead to a single ketone. Unsymmetrical, non-terminal alkynes produce nearly equal amounts to two different ketones. See the answer in the back of the book for the structures of the expected products.

**13-17** The answer in the back of the book is adequate.

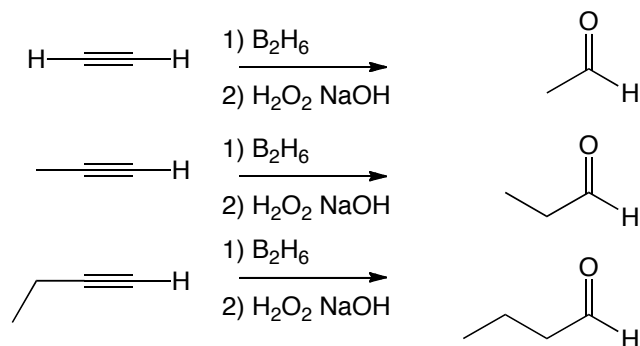
**13-18** Remember that only terminal and symmetrical alkynes lead to a single ketone. Unsymmetrical, non-terminal alkynes produce nearly equal amounts to two different ketones. See the answer in the back of the book for the structures of the expected products.

**13-19** This exercise is worked out in the book as "Working with Concepts".

**13-20** The answer in the back of the book is adequate.

**13-21** Alkyl boranes are formed by hydroboration of alkenes. Dicyclohexyl borane is prepared by the reaction of borane with two equivalents of cyclohexene.

**13-22** It is sometimes valuable to "verbalize" what a reaction does in terms of bond breaking/bond making. Hydroboration oxidation of a terminal alkyne results in removal of both  $\pi$  bonds between the carbons and the addition of an oxygen to the end carbon with both a  $\sigma$  and  $\pi$  bond (an aldehyde).



**13-23** Here, we simply need to “undo” what the hydroboration-oxidation reaction does (see Exercise **13-22**).

**13-24** The answer in the back of the book is adequate.