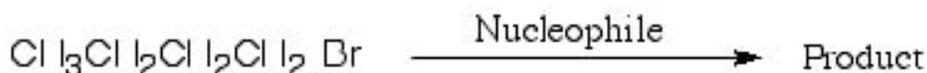


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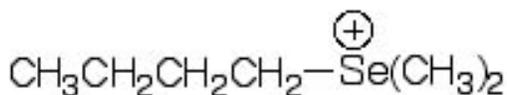
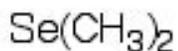
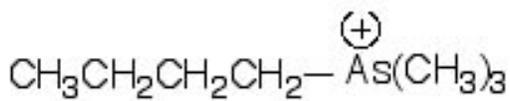
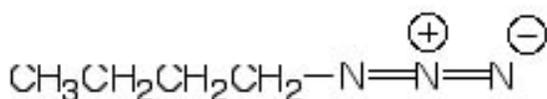
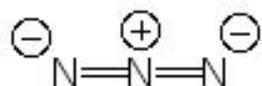
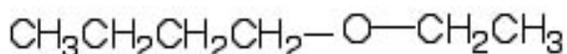
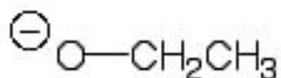
6-1 Although we can approach this exercise from a chemical perspective, one can also teach a non-chemist how to derive the answer once the name of the starting material is translated into a structure. Substitution reactions involve the replacement of an existing substituent with a new one that comes from the nucleophile. Because the electrons for the new bond to the nucleophile come from the nucleophile, if it starts with a negative charge, it becomes neutral as a substituent and if it is a neutral nucleophile, it becomes positively charged as a substituent (at least initially).



Nucleophile



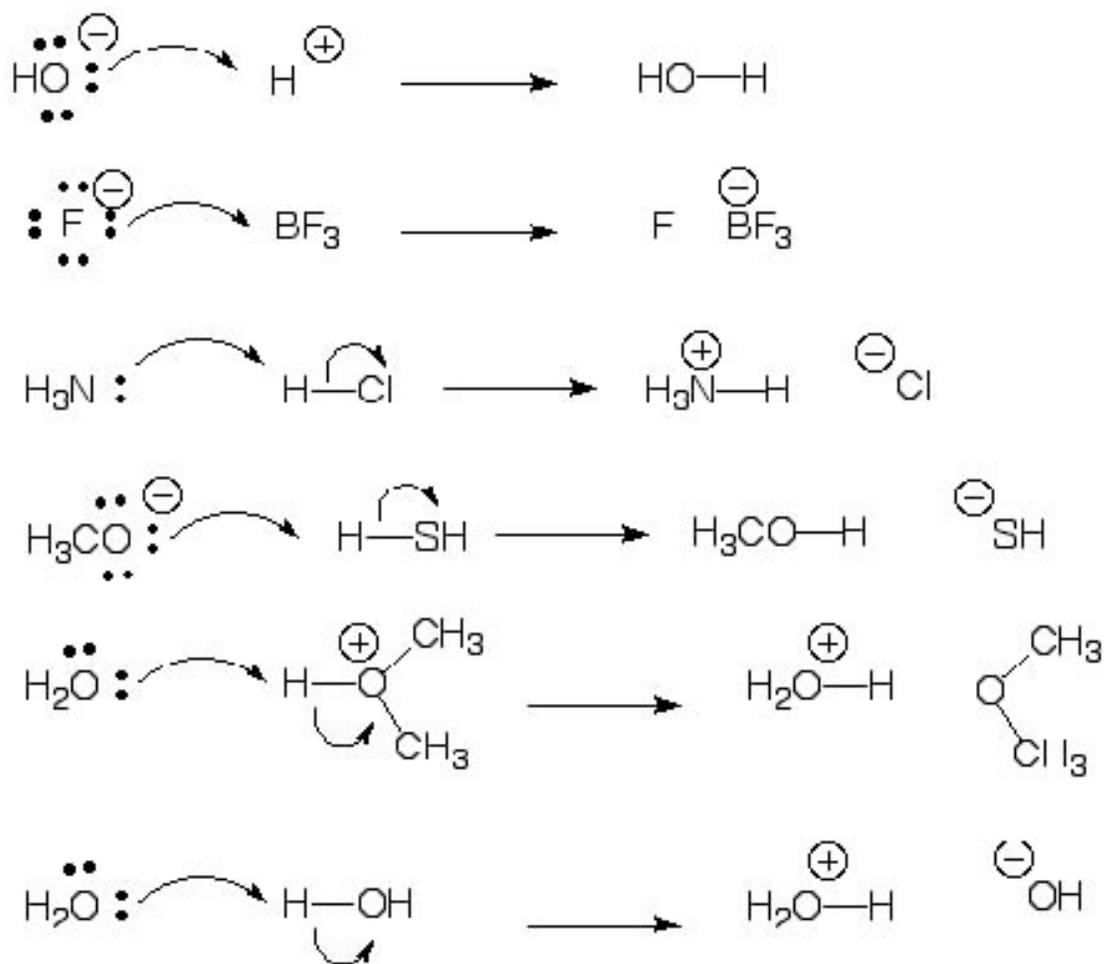
Product



6-2 This exercise is worked out on page 220 as "Working with Concepts".

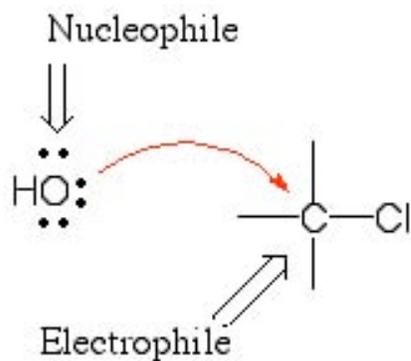
6-3

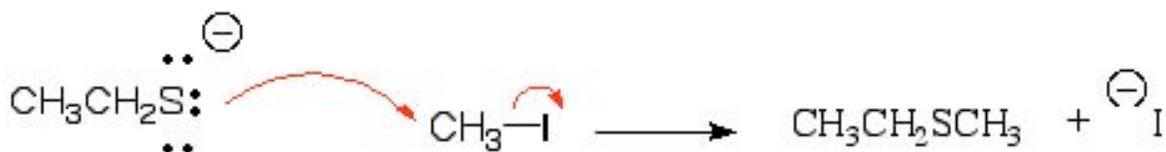
6-4



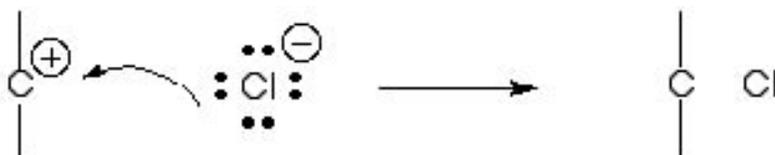
6-3

6-7 We can easily identify the nucleophile and electrophile in a substitution reaction once the mechanism is depicted with curved arrows. The head of the arrow points to the electrophile and the nucleophile can be found at the tail of the arrow. One example is shown below.





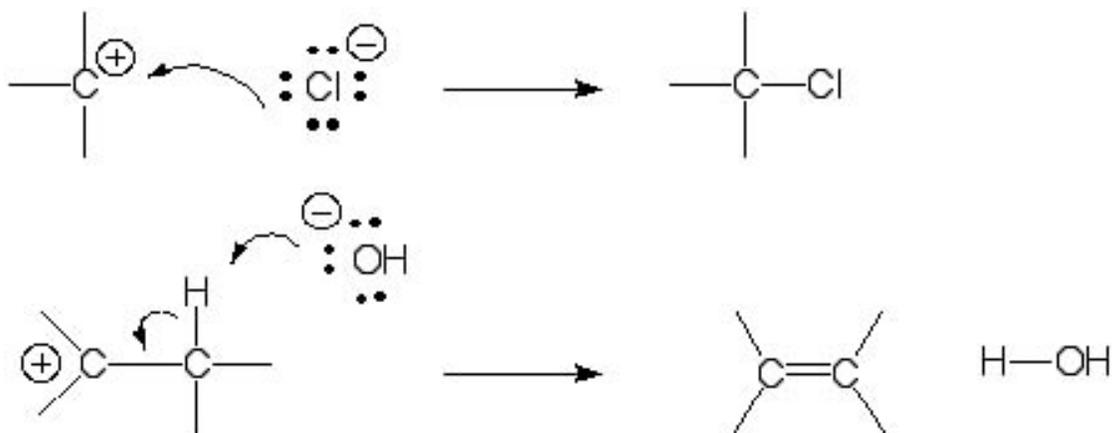
6-8 (a) Remember that we use curved arrows to indicate the change in position of electrons. Key here is that there is a pair of electrons in the product between C and Cl that is not present in the starting materials. All of the electrons about the carbon in the starting material are involved in bonds that are still present in the product so the electrons for the new C—Cl bond must come from the chloride ion. As the chloride ion has four lone-pairs of electrons, it is a rich source of electrons for the new bond.



Here the bond changes for which we must account are: breaking C—H making O—H and C—C

Again, the carbon with the positive charge has no electrons to use for the new (and second) C—C bond to its neighboring carbon. Likewise, we see that the oxygen in the products is neutral whereas it has a negative charge in the starting materials, from which we can conclude that it must be giving up electrons in the reaction. Thus, the new O—H bond is formed using a lone-pair of electrons from oxygen, and the new C—C bond is formed from the C—H that is lost.

6-9 This exercise is worked out on page 224 as "Working with Concepts".



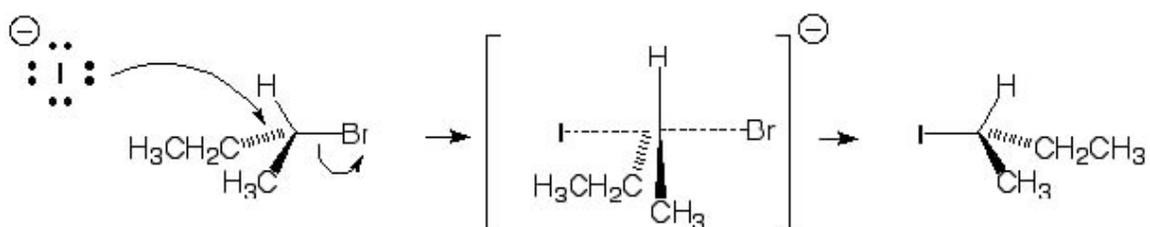
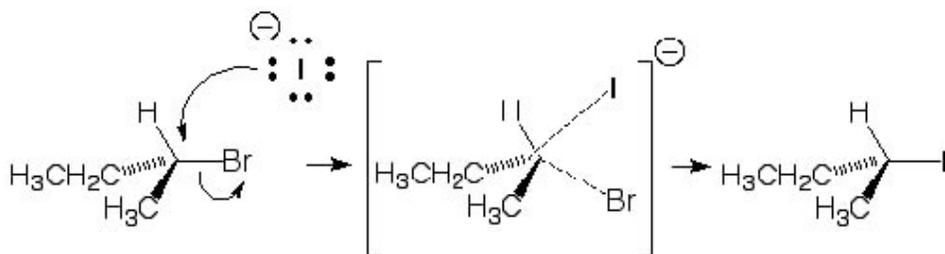
6-10 This is an example of a substitution reaction where the azide ion displaces iodide ion resulting in methyl azide (CH_3N_3). Keep in mind that as written, the rate equation above this exercise on page 224 of the textbook has concentration values ($[\text{A}]$) that are to be entered without units. The exercise is asking us to solve for k given that we know both concentrations of reagents in a bimolecular reaction as well as value of the rate. We can rearrange the equation to solve for k :

$$k = \text{Rate}/([\text{CH}_3\text{I}][\text{NaN}_3]) = 3.0 \times 10^{-10}/(0.01 \times 0.01) = 3.0 \times 10^{-6}$$

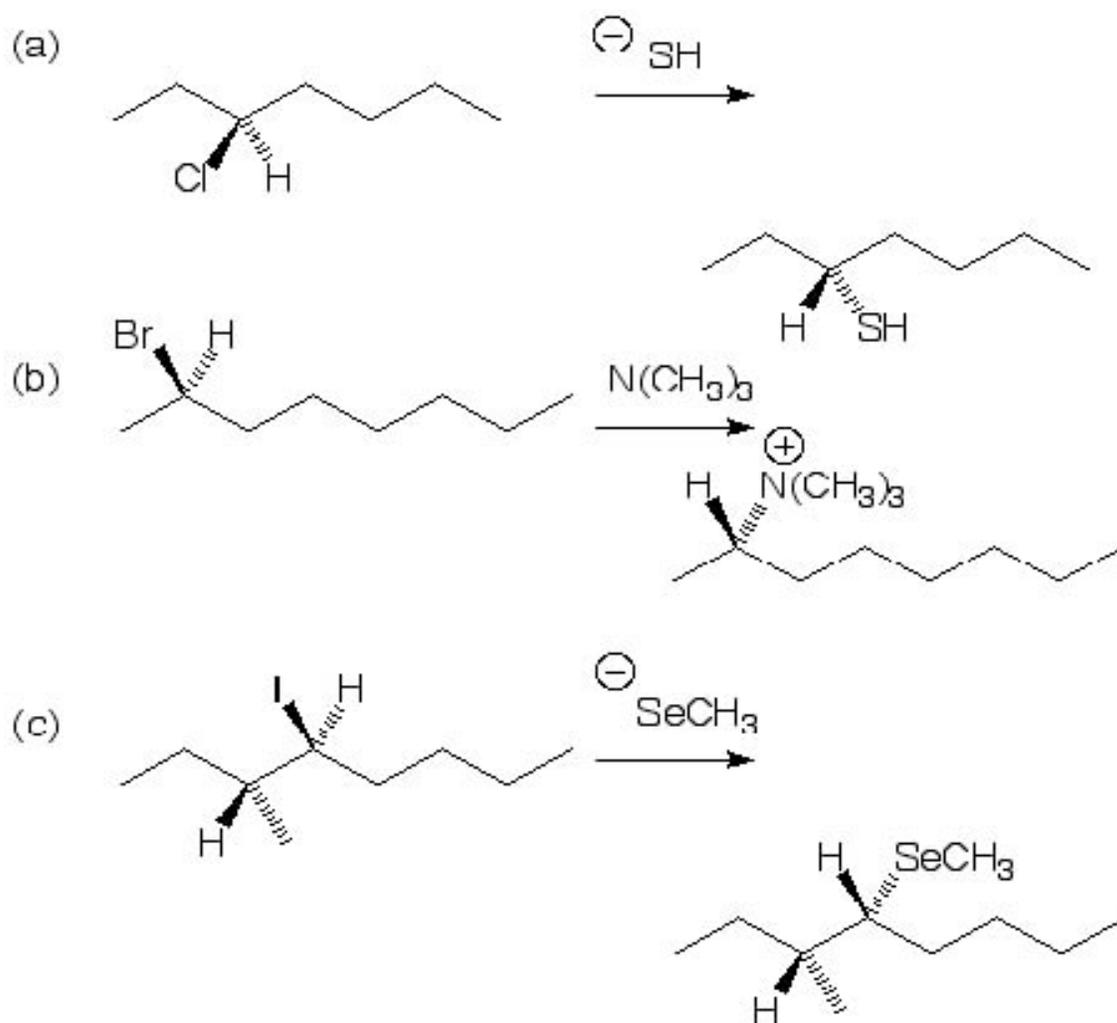
Because the product is produced in equimolar amounts as the iodide ion, the rate of appearance of the product is the same as iodide ion.

The remaining numerical answers are obtained by replacing the concentrations in the equation above for k with those given in the exercise.

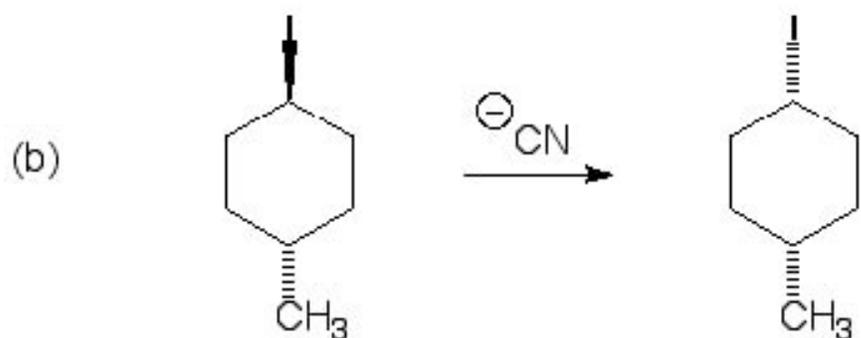
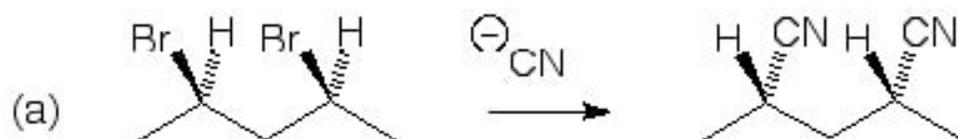
6-11



6-12 Be careful when assigning stereochemistry to the product of an $\text{S}_{\text{N}}2$ reaction. Although physical inversion of configuration occurs in these reactions, this does not guarantee that the *R,S* configuration of the product will be opposite that of the starting material. Remember that the Cahn, Ingold, Prelog rules assign priorities based upon atomic weight of substituents and **ONLY** if the nucleophile occupies the same place in the order of substituents is a change from *R* to *S* a given. As most of our nucleophiles have nitrogen or oxygen as the center of nucleophilicity, it will be the exception that the configure designator does not change.



6-13 This is basically the same exercise as 6-10 with the twist that the first examples involve *two* S_N2 reactions on the same molecule.



6-14 The key to this exercise is understanding that the S_N2 reaction involves back side attack with the result that the product has the nucleophile attached on the side opposite to that from which the leaving group departed. Note that this process will result in an inversion of configuration (e.g., *S* to *R*) so long as the nucleophile the same position in the order of priorities of substituents as the leaving group. In this reaction, the stereocenter of the starting alkyl iodide has iodine as the substituent of highest priority and the product has the oxygen as highest priority so the reaction will result in a change of handedness as assigned by the Cahn, Ingold, Prelog Rules. To obtain the opposite configuration from (*S*)-2-iodooxane, we need to have a single S_N2 reaction. We can use the sequence of displacement with acetate ion followed by the conversion of the acetate to the alcohol. To obtain (*R*)-2-iodooxane we must perform to inversion reactions. We can start by displacing iodide with bromide and then follow, as above, using acetate followed by conversion of the ester to the alcohol.

6-15 This exercise is worked out on page 229-30 as "Working with Concepts".

6-16

6-17 The key to the rule that "diastereomers produce diastereomers" is that diastereomers must differ in some but not all stereocenters

(else they would be enantiomers). As an example, let's take to diastereomers:

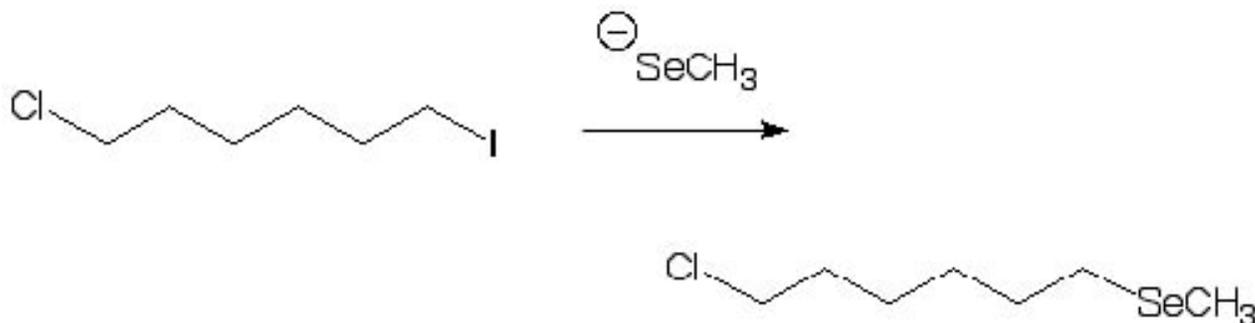
R—*S* and *S*—*S*. Changing the stereo center on the left leads to:

S—*R* and *R*—*R* which are diastereomers (so long as the two centers are different, that is we do not have the possibility of a meso). Changing the right center leads to:

R—*R* and *S*—*R* which again are diastereomers and finally, changing both leads to:

S—*R* and *R*—*R*, diastereomers again.

6-18 With only one equivalent of the nucleophile present, the reaction will be dominated by displacement of the better leaving group. In this example, iodide is a much better leaving group than is chloride so the product will be:



6-19 The key to understanding this exercise is the simple concept that, other factors being equal, acidity increases from left to right in a row of the periodic table and increases down a column. The exception is part (c) which asks for a comparison of HClO_2 and HClO_3 . The greater acidity of the latter stems from the additional oxygen substituent on chlorine that further withdraws electron density and helps disperse the negative charge in the conjugate base. The conjugate bases are derived simply by removing a proton from the acid.

The last part of this question is very poor, indeed. Of all of the conjugated bases, only Br^- is a common leaving group.

6-20 We know that basicity is related to acidity and the stronger the

acid, the weaker is its conjugate base as a base. You can derive the answers to this exercise by converting all of the bases into their conjugated acids and then use the concepts in the answer to exercise 616 to rank the acids.

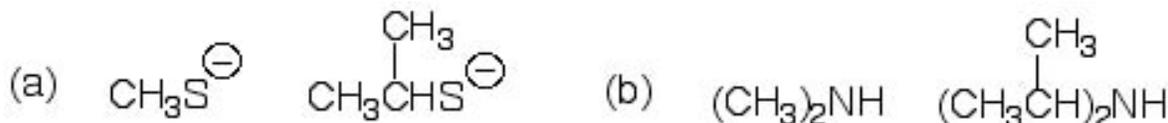
6-21 So long as all other factors are the same (or nearly the same), a nucleophile with a negative charge will be more reactive than one that is neutral.

6-22 As the number of protons in the nucleus increases from left to right in the periodic table, the more tightly the atom holds onto electrons. One example is a decrease in basicity from left to right (e.g., NH_3 is more basic than is H_2O). Further, nucleophilicity decreases proceeding to the right in the periodic table. Thus:

- (a) sulfur is more nucleophilic than is chlorine;
- (b) phosphorus is more nucleophilic than is sulfur;
- (c) selenium is more nucleophilic than is bromine;
- (d) oxygen is more nucleophilic than is fluorine

6-23 The degree of nucleophilicity increases going down the periodic table (so long as all other factors are equal). As a result, selenium is more nucleophilic than is sulfur and phosphorous is more nucleophilic than is nitrogen.

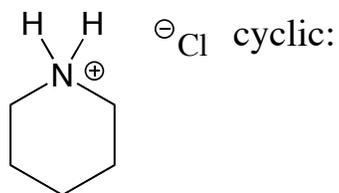
6-24 Bulk resulting from additional substituents near the nucleophilic atom in the nucleophile raises the transition state energy in a second order substitution reaction and, as a result, the rate is reduced. For both parts of this exercise, the second nucleophile is the more hindered by additional substituents near the nucleophile.



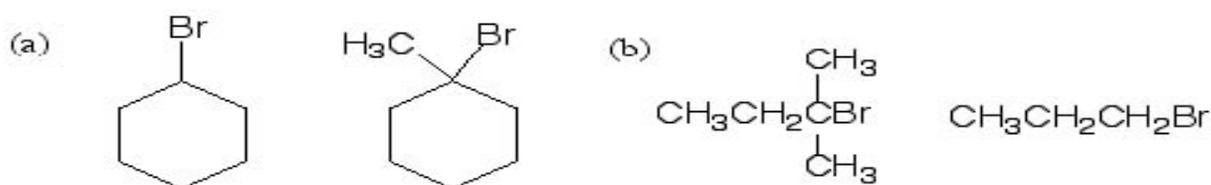
6-25 This exercise is worked out on page 238 as "Working with Concepts".

6-26 Here we have an example where the nucleophile (nitrogen) is part of the structure that contains the carbon bearing the leaving group. The

product will be



6-27 All that is required here is to determine the degree of substitution of the carbon bearing the leaving group. For (a) the comparison is between secondary and tertiary---the secondary will react more rapidly. In (b), the first alkyl bromide is tertiary and the second is primary--primary reacts faster.



6-28 The key here is that although both of these alkyl bromides are primary, the degree of substitution on the carbon adjacent to that bearing bromine differs. For the left-hand alkyl bromide this carbon is tertiary whereas that on the right is quaternary. The additional substitution near the carbon undergoing substitution will reduce the rate. Table 5-9 provides a quantitative comparison as the difference between these alkyl bromides is the same as the last two entries in the Table where we can see there is more than a 100 fold difference in rate.