Sample Problem 7.1

Will the following substitution reaction favor formation of the products?

Solution

Determine the basicity of the nucleophile ($^-$OH) and the leaving group (Cl^-) by comparing the pK_a values of their conjugate acids. **The stronger the conjugate acid, the weaker the base, and the better the leaving group.**

			conjugate acids	
nucleophile	$^-$OH	⟶	H_2O	pK_a = 15.7
leaving group	Cl^-	⟶	HCl	pK_a = −7
	weaker base		**stronger acid**	

Because Cl^-, the leaving group, is a weaker base than $^-$OH, the nucleophile, the reaction favors the products.

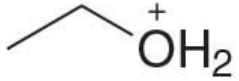
Compare the basicity of the leaving groups by comparing the pKa values of their conjugate acids.

a. 

pKa HBr = -9

b. 

pKa H_2O = 15.7

c. 

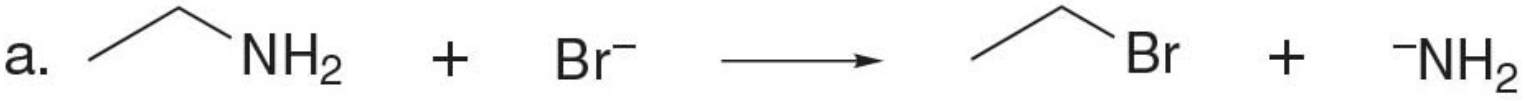
pKa H_3O+ = -1.7

d. 

pKa H_2 = 35

weaker base,
better leaving group

Will the following substitution reaction favor the formation of the products ?

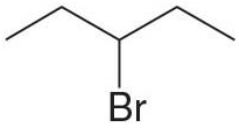
a. 

pKa HBr = -9

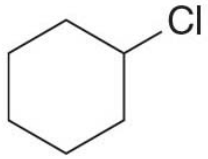
Because $-NH_2$, the leaving group, is a stronger base than Br-, the nucleophile, the reaction will not favor the products

pKa NH_3 = 38

Label the nucleophile and the leaving group, and draw the product of the substitution reaction.

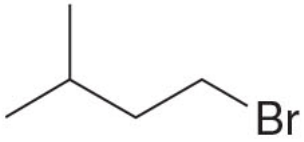
a. 

+ $^{-}OCH_2CH_3$ ⟶

b. 

+ NaOH ⟶

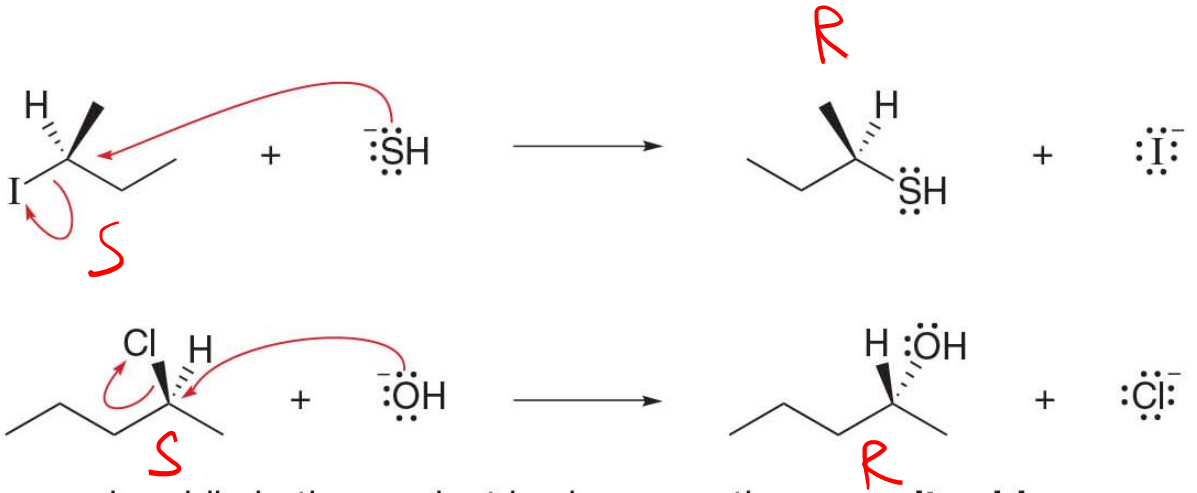
+ $CH_3\ddot{O}:^{-}$ ⟶

a. 

+ $:N(CH_2CH_3)_3$ ⟶

b. 

+ $H_2\ddot{O}:$ ⟶



- The bond to the nucleophile in the product is always on the **opposite side** compared to the bond to the leaving group in the starting material. If the leaving group is drawn to the left, the nucleophile approaches from the right. If the leaving group is drawn in front of the plane (on a wedge), the nucleophile approaches from the back and ends up on a dashed wedge.

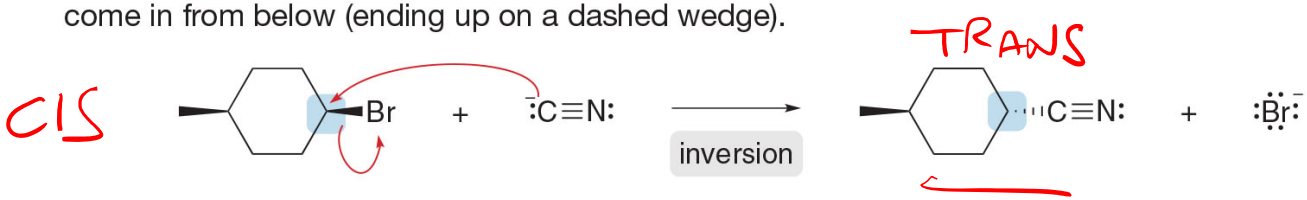
A

Sample Problem 7.2

Label the nucleophile and leaving group, and draw the product (including stereochemistry) of the following S_N2 reaction.

Solution

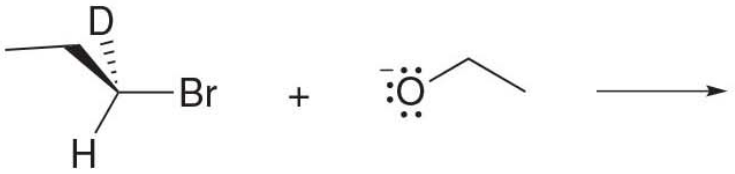
Br^- is the leaving group and ^-CN is the nucleophile. Because S_N2 reactions proceed with **inversion** of configuration and the leaving group is drawn above the ring (on a wedge), the nucleophile must come in from below (ending up on a dashed wedge).

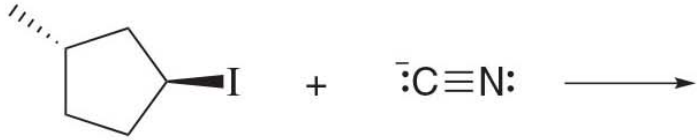


- **Inversion** of configuration occurs at the C – Br bond.
- Backside attack converts the **cis** starting material to a **trans** product because the nucleophile (^-CN) attacks from below the plane of the ring.

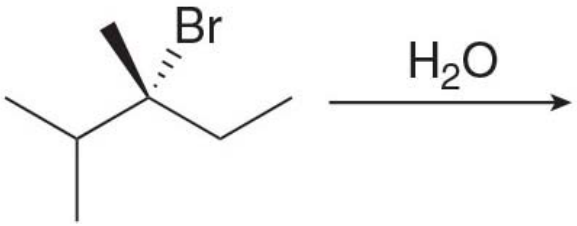
Hydrogen cyanide is weakly acidic with a pK_a of 9.2. It partially ionizes in water solution to give the cyanide anion, CN^-. A solution of hydrogen cyanide in water, represented as HCN, is called *hydrocyanic acid*.

Label the nucleophile and the leaving group, and draw the product of the following S_N2 reactions.

a. 

b. 

Label the nucleophile and the leaving group, and draw the product of the following S_N1 reactions.

a. 

b.