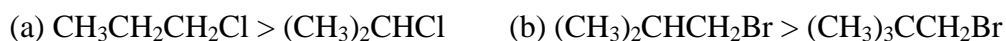


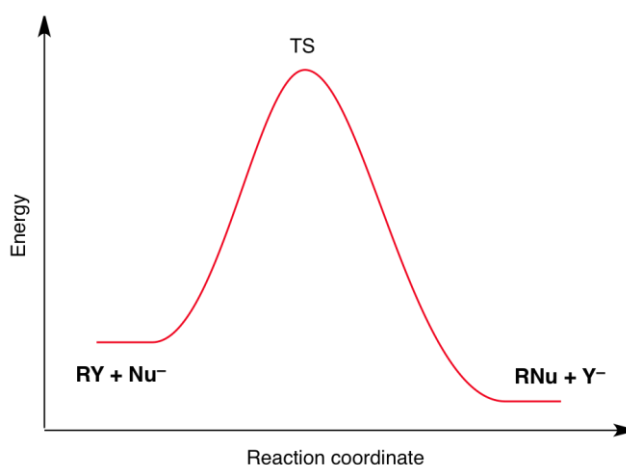
## Solutions to Exercises, Chapter 12

## 12.1

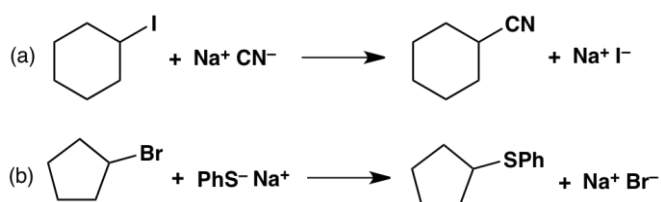


12.2 Both substitution reactions take place with inversion of configuration; consequently, *cis*- and *trans*-1-bromo-4-methylcyclohexanes give *trans*- and *cis*-4-methylcyclohexanols, respectively.

## 12.3



## 12.4



## 12.5

- (a) Reaction (2) is faster because the thiolate ( $\text{EtS}^-$ ) is a better nucleophile than the alkoxide ( $\text{EtO}^-$ ).
- (b) Reaction (2) is faster because iodide is a better nucleofuge than bromide.

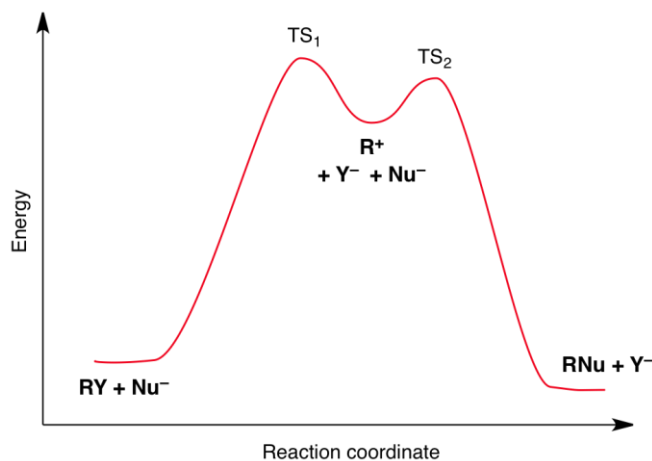
## 12.6

- (a) In both solvents, charge separation decreases as ionic reactants form transition structures, so the initial state is stabilized more strongly by solvation than the TS, and the effect is greater in the more polar solvent. It follows that the activation energy is larger and the rate constant correspondingly smaller in the more polar solvent ( $\text{H}_2\text{O}$ ).
- (b) The negative charge is conserved in both reactions, but becomes slightly more dispersed in each as reactants form the TS. As a result, the stabilizing effects of a polar solvent are larger in the initial state than in the TS, but only slightly, and the rate constant is only slightly smaller in the more polar solvent.

**12.7** Both reactions proceed by  $\text{S}_{\text{N}}2$  mechanisms and the anionic nucleophiles will be more strongly solvated in protic solvents; consequently, both reactions will be faster in a polar aprotic solvent than in a protic solvent.

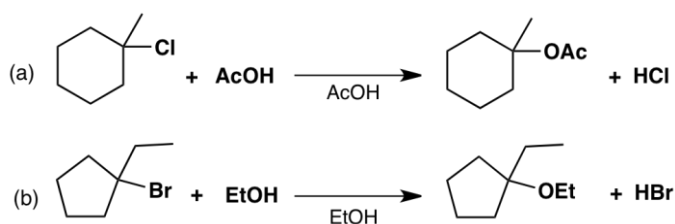
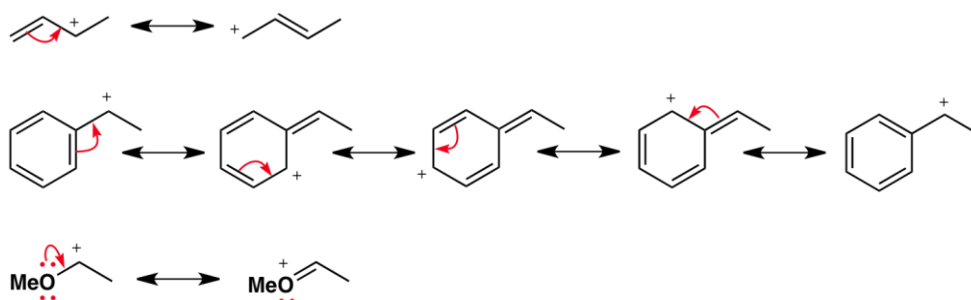
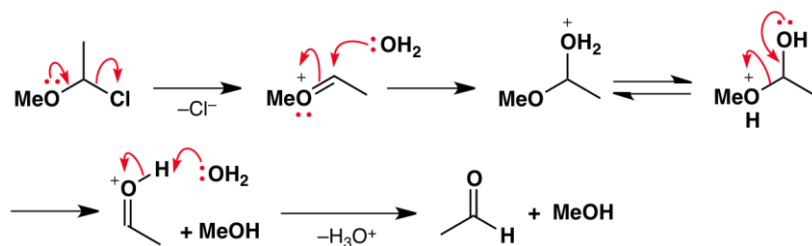
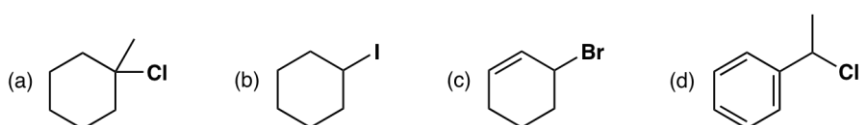
- (a) Faster in ethanenitrile (acetonitrile) than in methanol.
- (b) Faster in DMF than in NMF, NMF being a protic solvent.

## 12.8



**12.9** Hydrolysis of  $\text{Me}_3\text{CBr}$  in water,

leads to the formation of  $\text{H}_3\text{O}^+$  so the rate of the reaction can be related to the rate of change in  $[\text{H}_3\text{O}^+]$  which can be measured by pH measurements at known time intervals.

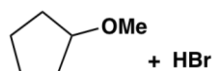
**12.10****12.11****12.12** The organic products are ethanal (acetaldehyde) and methanol.**12.13**

(a)  $3^\circ > 2^\circ$ . (b) Iodide is the better nucleofuge. (c) Conjugation between the carbenium ion centre and the double bond stabilizes the intermediate. (d) Conjugation between the carbenium ion centre and the phenyl group stabilizes the intermediate.

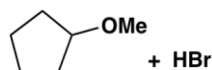
**12.14** Solvolysis of *cis*-1-acetoxy-2-bromocyclohexane occurs with inversion of configuration at one carbon, so the optical activity of the reactant would change to that of the product following the first-order kinetics. In contrast, the *trans* isomer gives racemic product, as explained by Scheme 12.8, so the optical activity would be lost following the first-order kinetics.

**12.15**

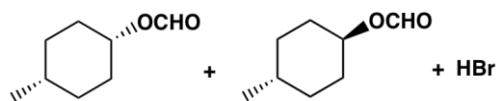
(a)  $S_N1$  of  $2^\circ$  alkyl bromide in a nucleophilic solvent (solvolysis).



(b)  $S_N2$  with a powerful nucleophile  $HS^-$  in a polar aprotic solvent.



(c)  $S_N1$  solvolysis in a weakly nucleophilic polar solvent to give products with both inversion and retention of configuration.



(d)  $S_N2$  with a good nucleophile  $CN^-$  in a polar aprotic solvent to give the product with inversion of configuration.

