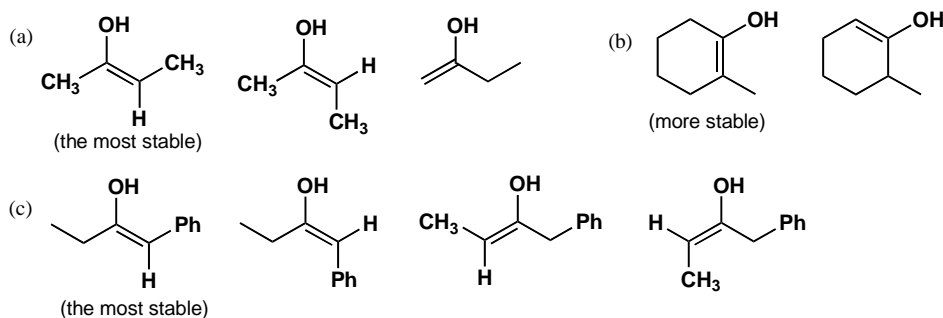
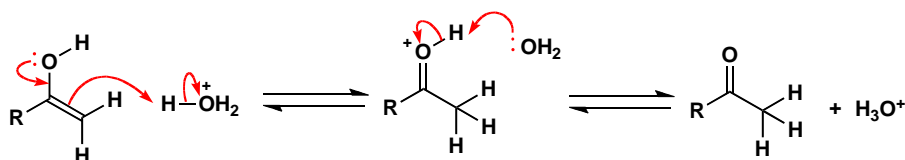


## Solutions to Exercises, Chapter 17

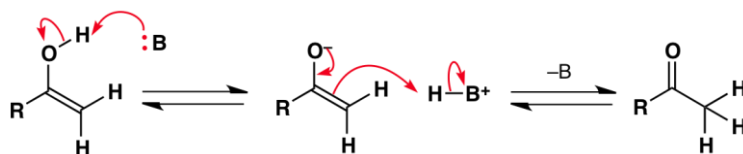
**17.1** The more substituted of a pair of isomeric enols is usually the more stable. In (c), the two enols with the Ph and the double bond conjugated will be more stable than the other two; regarding the pair of conjugated *E/Z* isomers, the one with the Ph and Et groups further away from each other will be the more stable and, consequently, the most stable of the four.



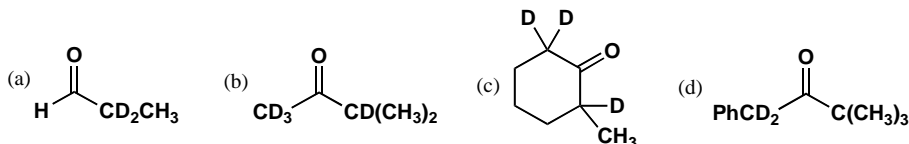
**17.2**



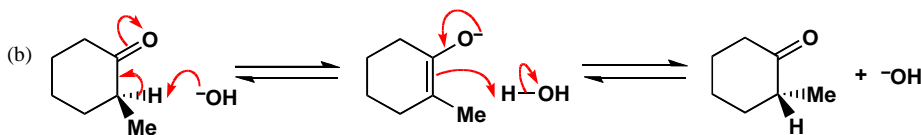
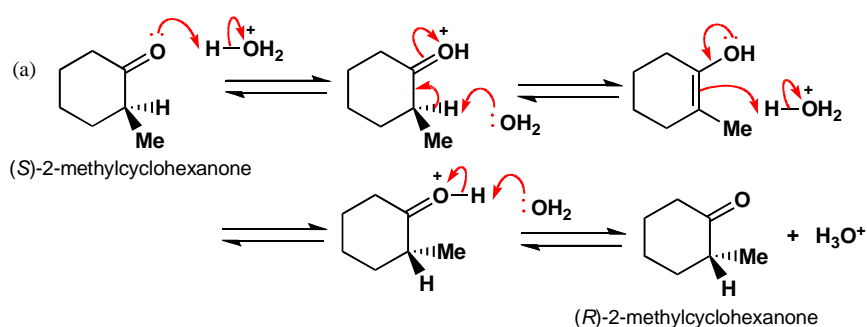
**17.3**



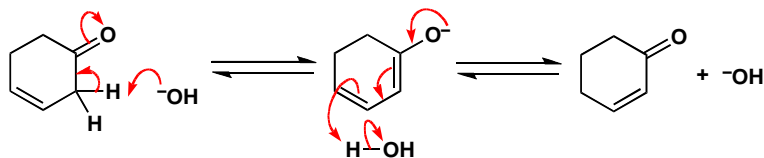
**17.4** The deuterium atoms in the following indicate where exchange can take place.



## 17.5

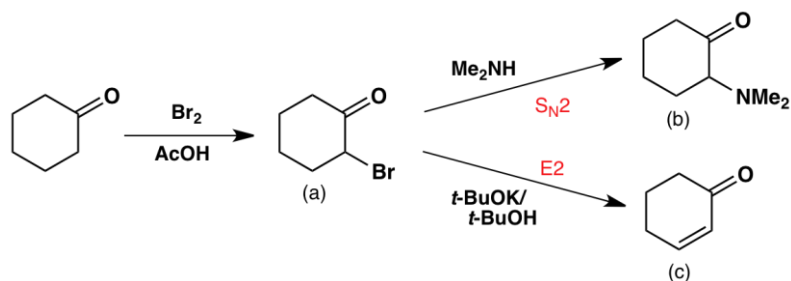


## 17.6

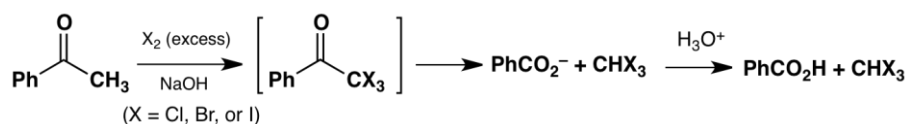
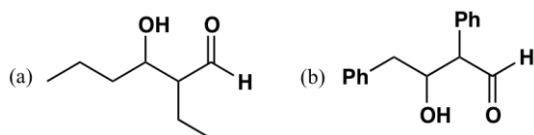
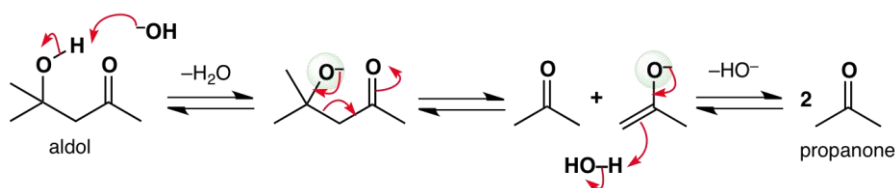
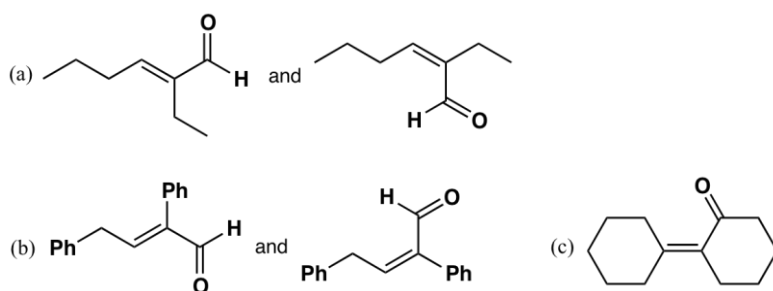


**17.7** Enolisation is usually the rate-determining step in the catalysed  $\alpha$ -halogenation of a carbonyl compound, and this is independent of the halogen. Consequently, the rate constant for the overall reaction is not affected by the identity of the halogen or its concentration.

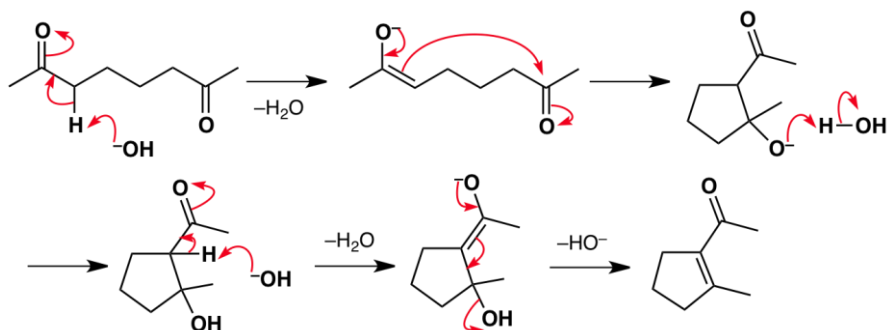
**17.8** Like simpler haloalkanes,  $\alpha$ -halo ketones undergo bimolecular nucleophilic substitution and elimination (see Chapters 12 and 13), and often more readily.



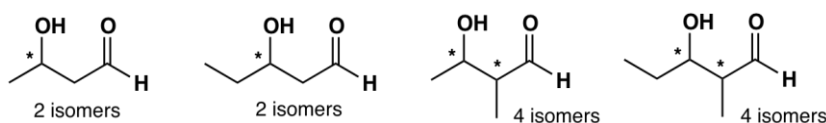
**17.9** The first bromine substituent is an electron-withdrawing group so, as explained under Scheme 17.8, the second bromination under basic conditions will occur at the C already bearing a bromine to give the 2,2-dibromo compound. With acid catalysis, however, as explained under Scheme 17.7, the first Br causes a second bromination at the same C to be appreciably slower than the first bromination. The effect of the  $\alpha$ -C-Br carbon on bromination at the alternative ( $\alpha'$ ) carbon is much smaller so, with two equivalents of Br<sub>2</sub>, the second bromination occurs at the  $\alpha'$  C to give the 2,6-dibromo compound.

**17.10****17.11****17.12****17.13**

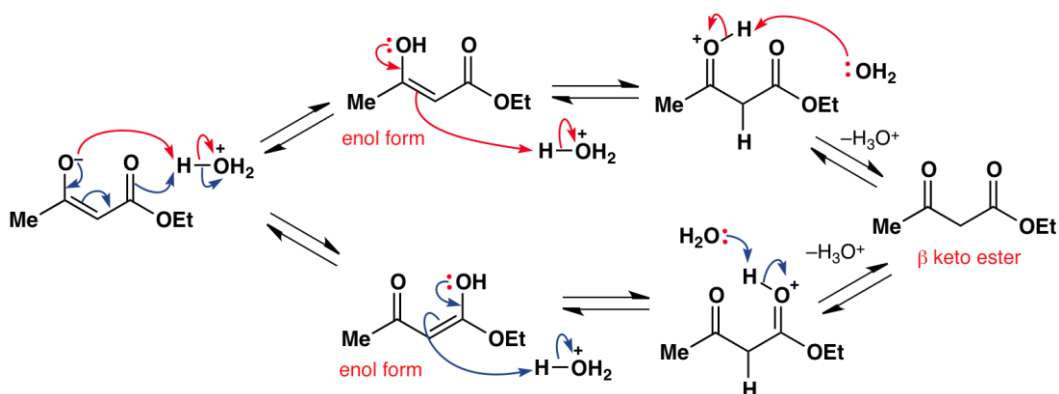
## 17.14



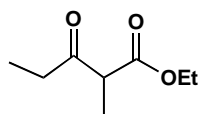
**17.15** Chirality centres are shown by \*: each of the first two products has one chirality centre and, therefore, two enantiomers; each of the other two has two chirality centres and, therefore, four stereoisomers (see Chapter 11 for relationships between stereoisomers with more than one chirality centre).



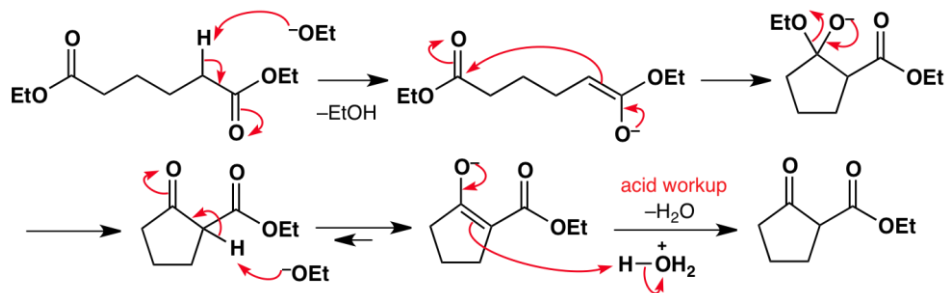
**17.16** Upon addition of an aqueous acid, the enolate is immediately protonated on oxygen to give the two enols as indicated below by red and blue curly arrows. Both enols then isomerize more slowly to give the equilibrium proportion of the more stable  $\beta$  keto ester.



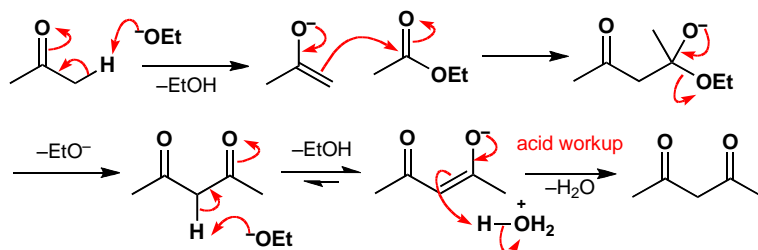
17.17



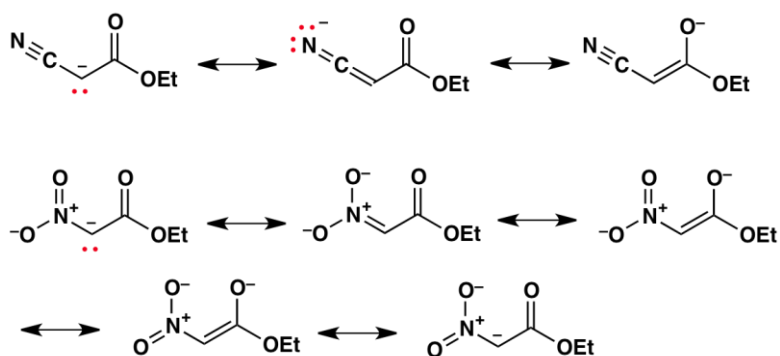
17.18



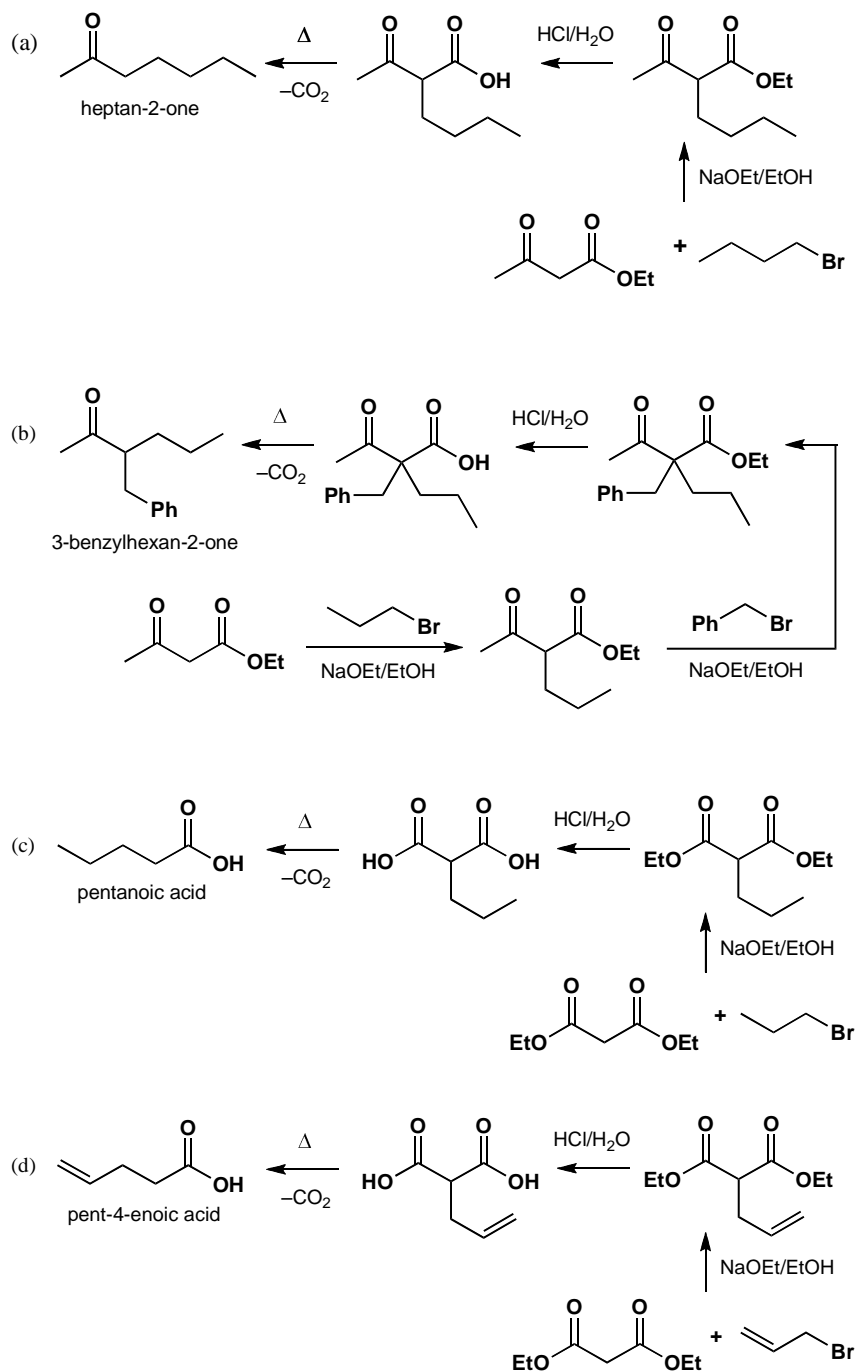
17.19



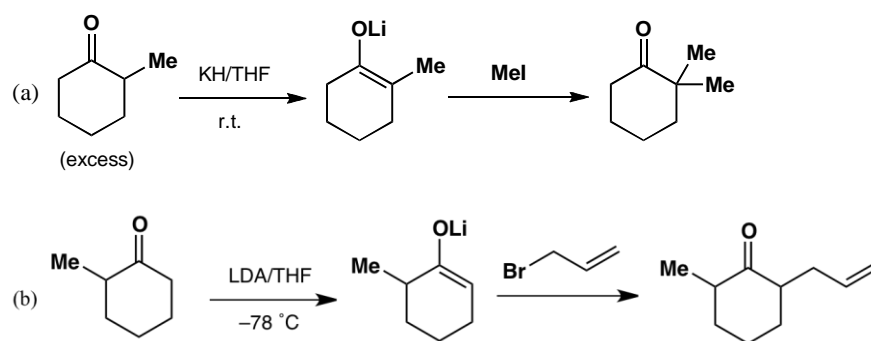
17.20



## 17.21



## 17.22



## 17.23

