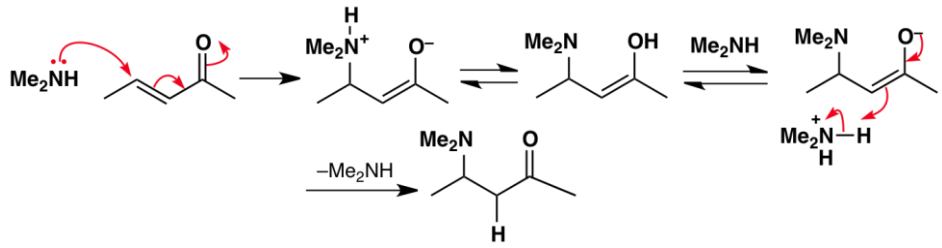
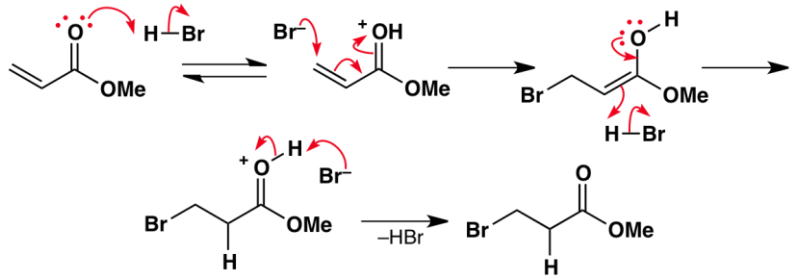
Solutions to Exercises, Chapter 18

18.1



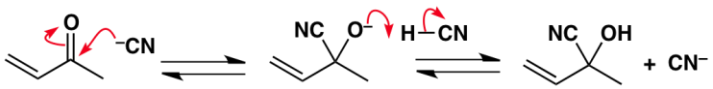
18.2

18.3

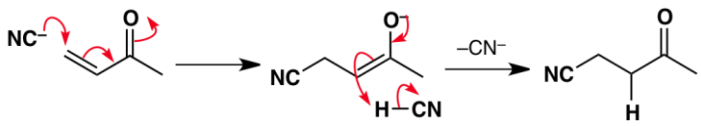


18.4 The acid (AH) will protonate the CN^- to an extent determined by its strength (see Chapter 6): AH + CN^- ⇄ A^- + HCN, then either HCN or AH will participate as the proton donor in the second steps of the following reactions.

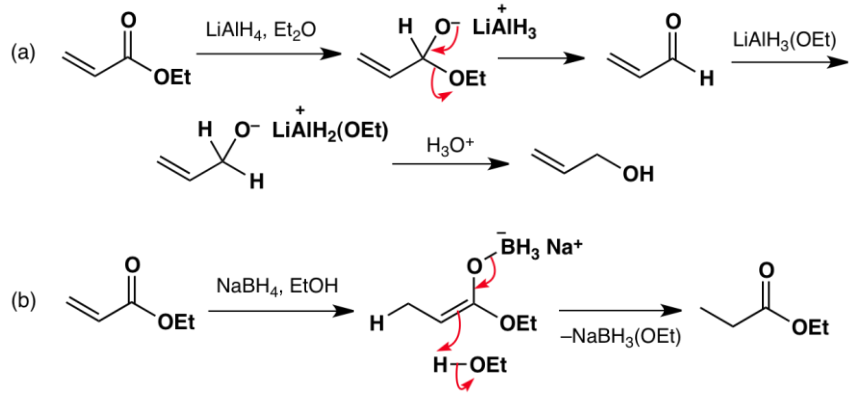
Carbonyl addition:



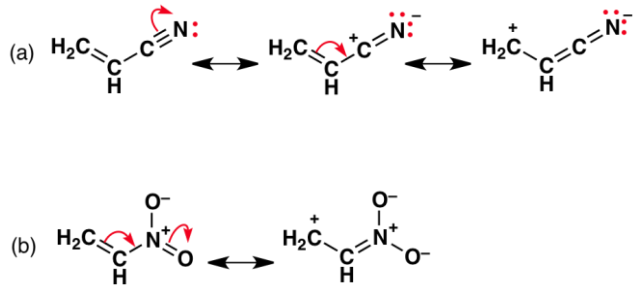
Conjugate addition:



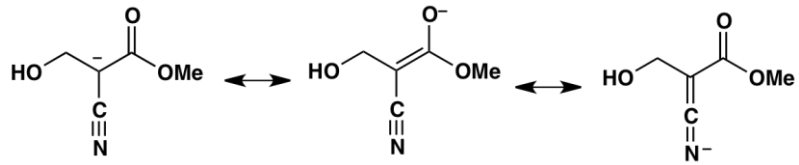
18.5



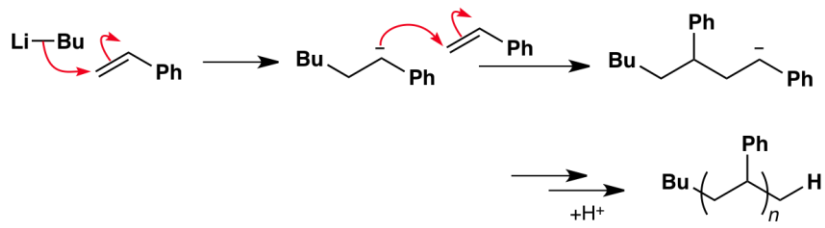
18.6



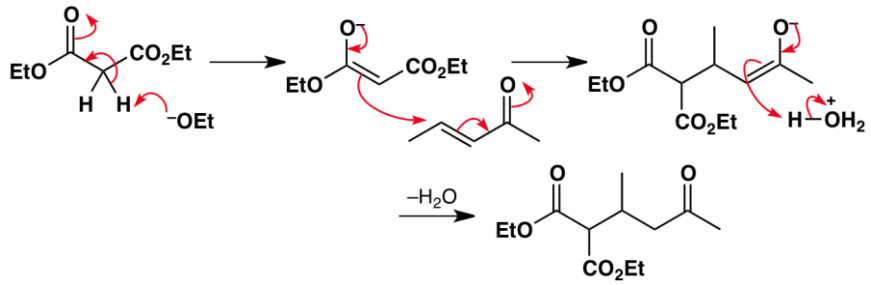
18.7



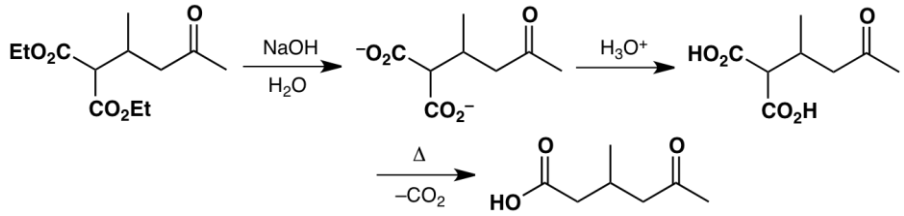
18.8



18.9

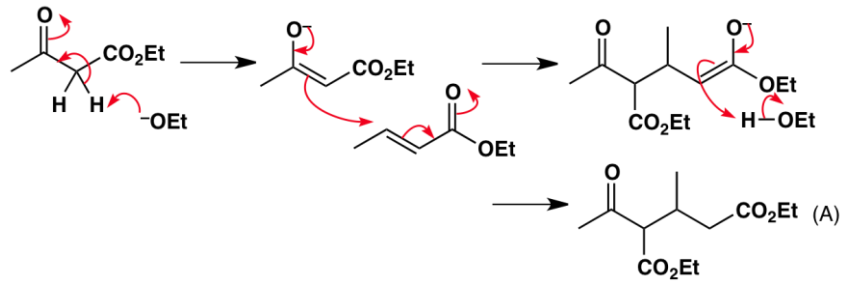


18.10

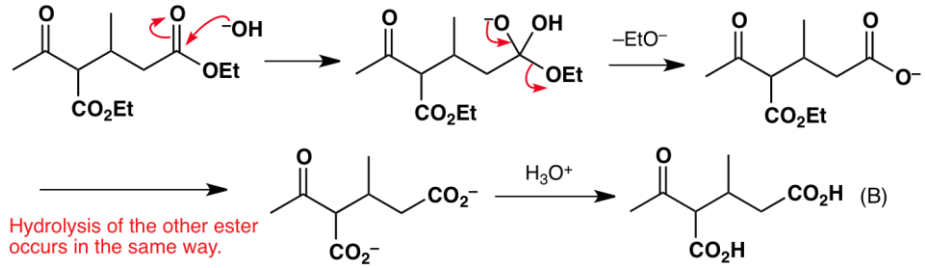


18.11

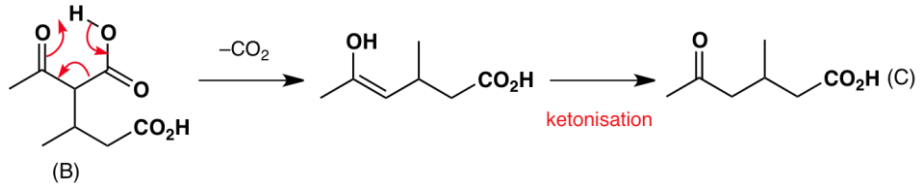
Michael addition:



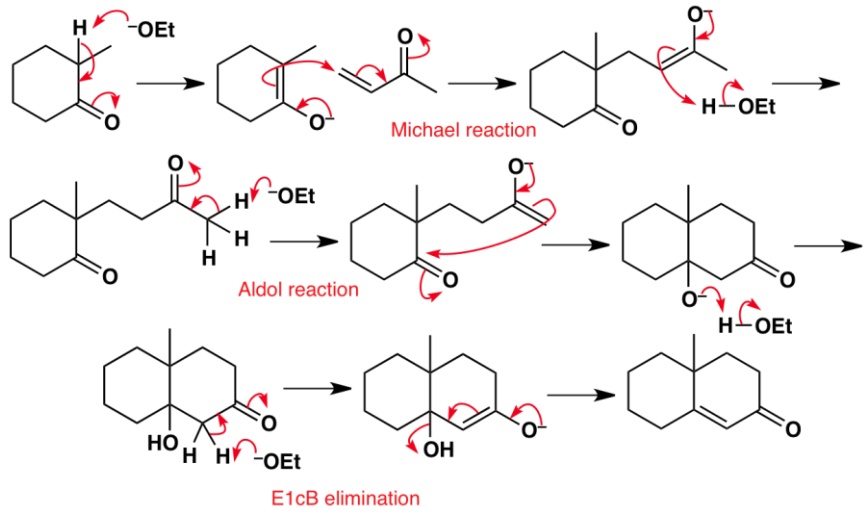
Ester hydrolysis:



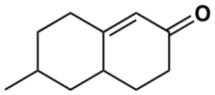
Decarboxylation:



18.12

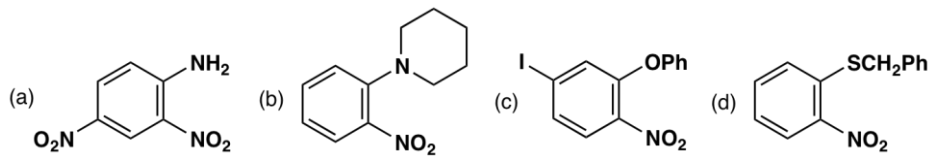


18.13



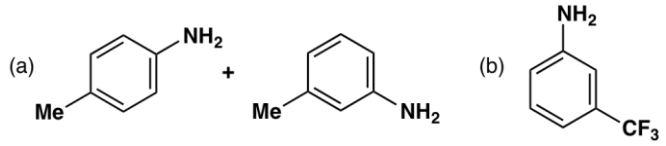
18.14 The intermediate carbanion (Meisenheimer complex) formed by addition of methoxide is resonance-stabilized by nitro groups in *o*- and *p*-positions, as shown in Scheme 18.12, and the effect is cumulative. In contrast, the *m*-nitro group cannot participate in the conjugative stabilization of the carbanion (see Sub-section 16.4.2 to compare the effects of substituents upon the stability of benzenium ions). Consequently, the order of reactivity is as shown.

18.15



18.16 A non-activated halobenzene can undergo nucleophilic substitution only by the benzyne mechanism, but this substrate cannot form a benzyne intermediate because both the *ortho* positions are blocked by methyl groups.

18.17



18.18