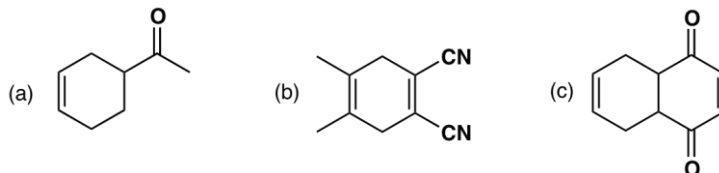


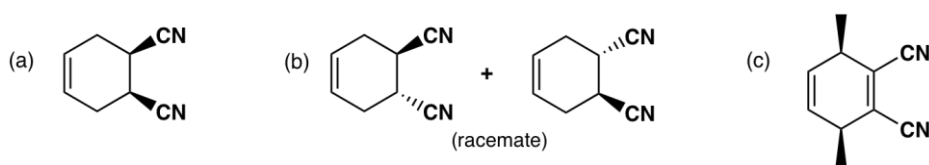
Solutions to Exercises, Chapter 21

21.1

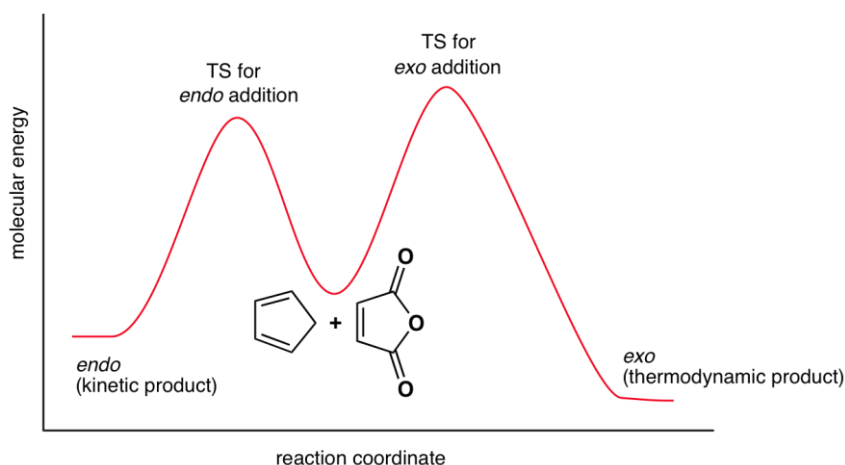


21.2 An electron-donating group raises the energy of MOs of the diene, so the energy level of its HOMO becomes higher and the interaction with the LUMO of the dienophile improves, resulting in higher reactivity.

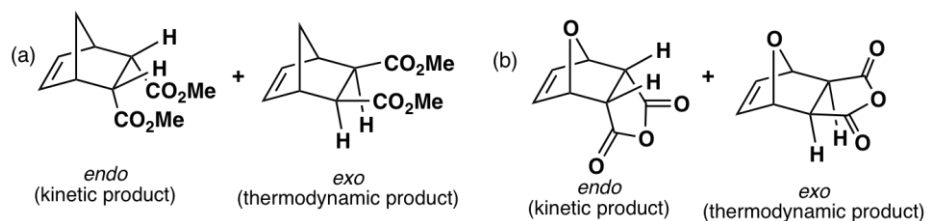
21.3



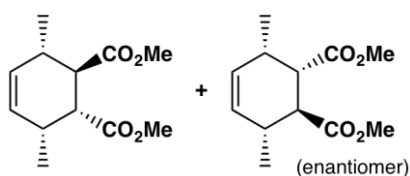
21.4 From the reactants in the middle, the transition structure (TS) for the formation of the *endo* isomer to the left is lower in energy than the TS for the formation of the *exo* isomer to the right. However, the *endo* isomer is less stable than the *exo* isomer. Consequently, the *endo* isomer is formed stereoselectively under kinetic control, but it isomerizes to the more stable *exo* isomer under thermodynamic control.



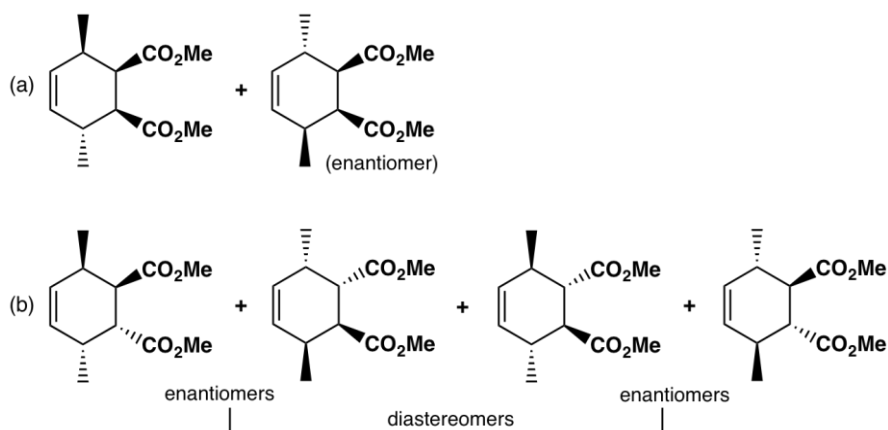
21.5



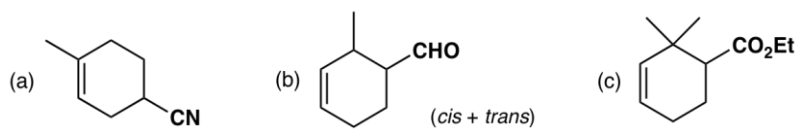
21.6



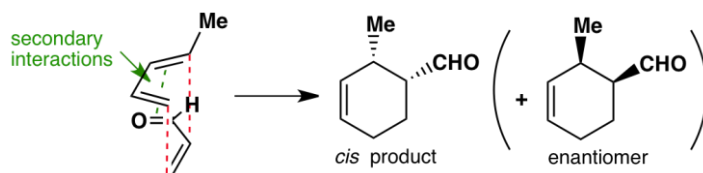
21.7



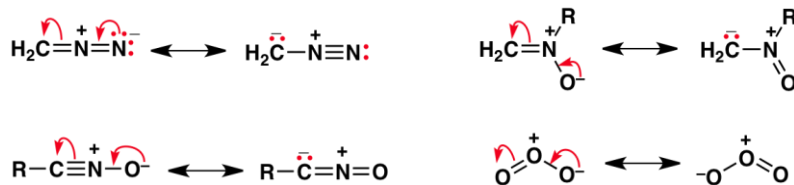
21.8



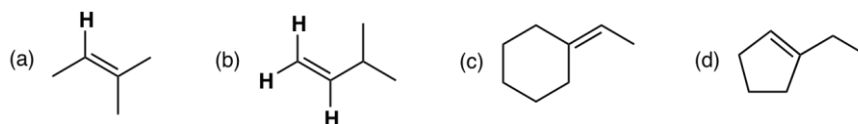
In reaction (b), the *cis* isomer is formed preferentially because of the secondary orbital interactions as illustrated; although this product is chiral, it will be racemic.



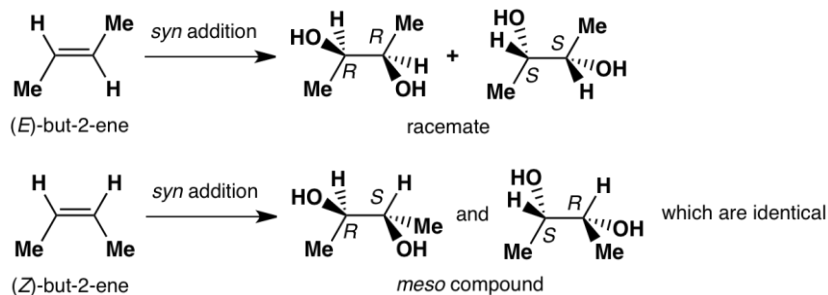
21.9



21.10

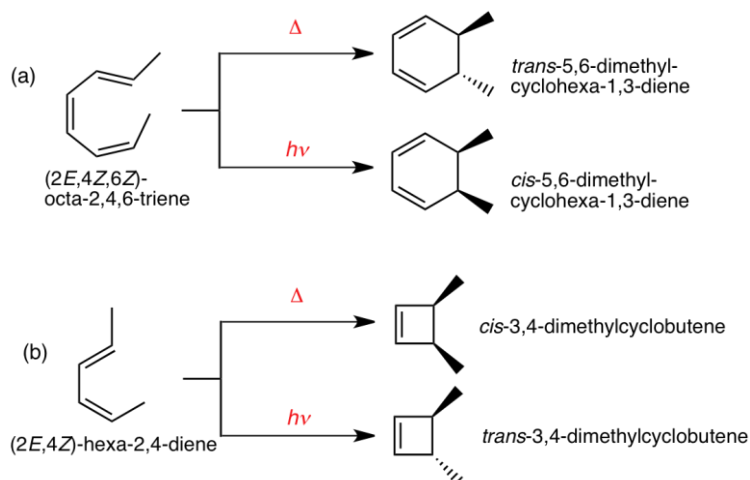


21.11 The (*E*) isomer gives racemic butane-2,3-diol by *syn* addition, while the (*Z*) isomer gives the single *meso* compound (*syn* addition from above and below the plane of the double bond gives the same compound).

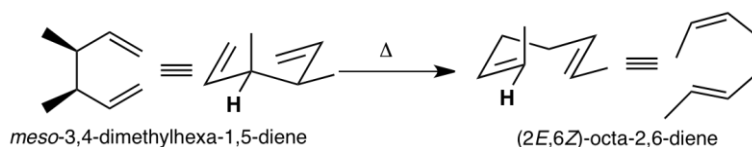


21.12 Reaction (a) is a [2+2] cycloaddition and occurs photochemically. Reaction (b) is [4+6] cycloaddition and is thermally allowed.

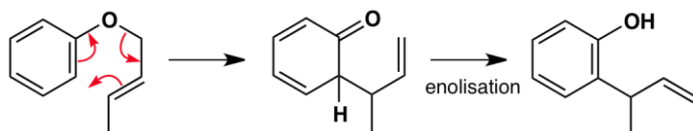
21.13



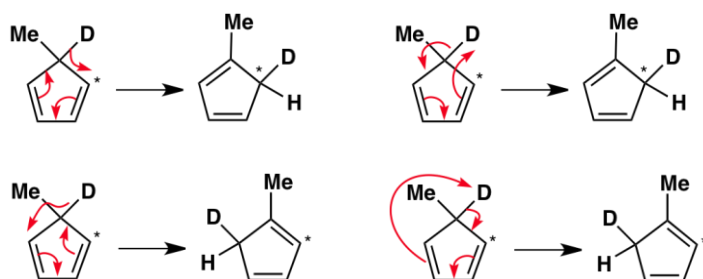
21.14



21.15 The product is *o*-(1-methylallyl)phenol. This result is compatible with a concerted reaction *via* a cyclic transition structure; the new bond is formed at the other end of the allylic part of the butenyl group.



21.16



The asterisk * indicates ^{13}C . Two differently labeled 1-methylcyclopenta-1,3-diene products are possible in this single-step rearrangement.