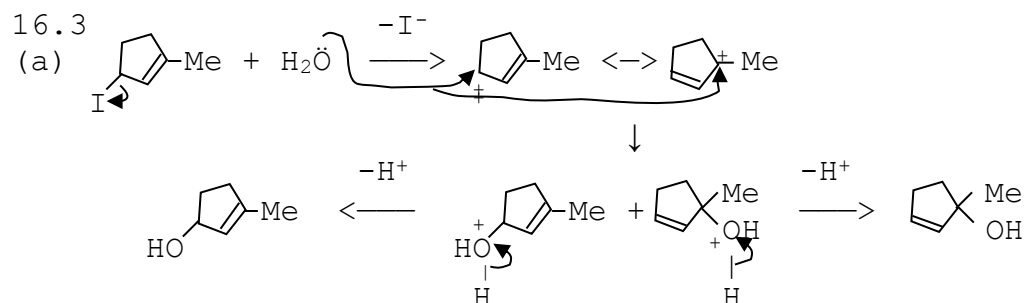
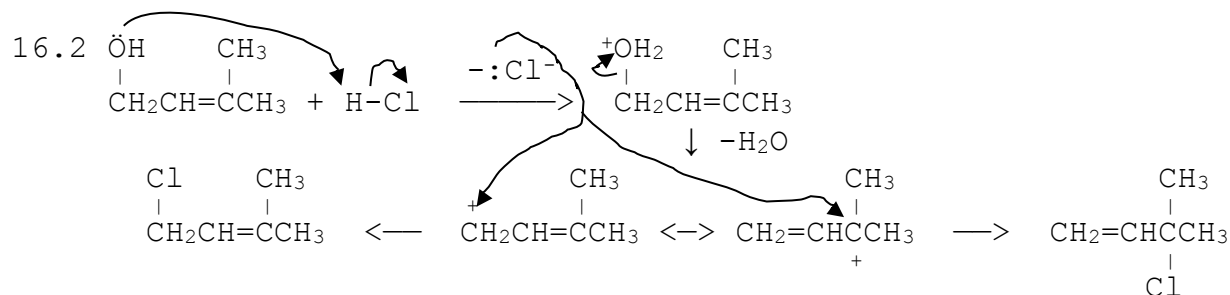
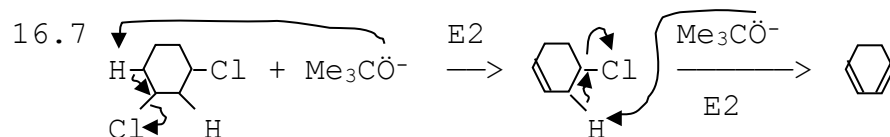
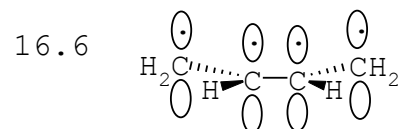
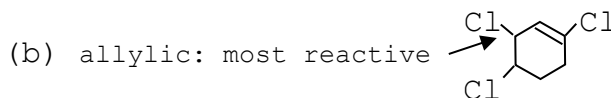
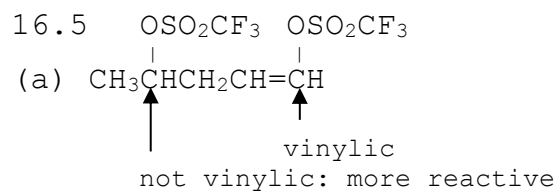
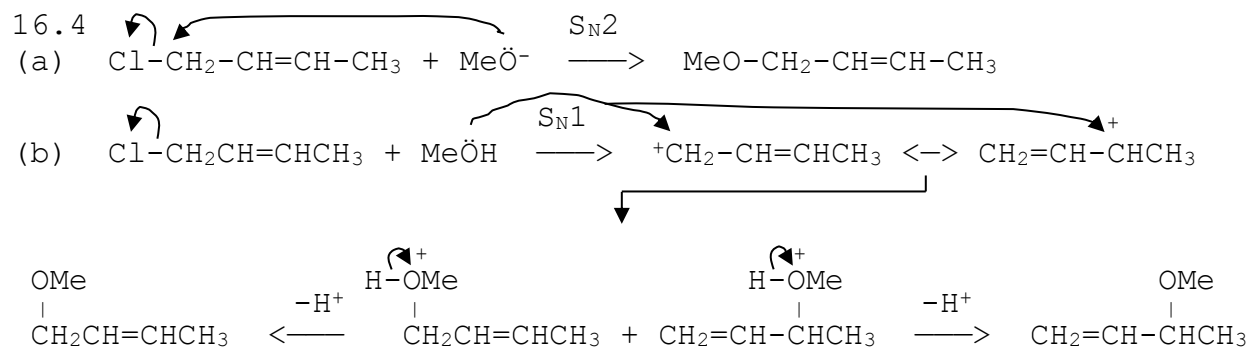


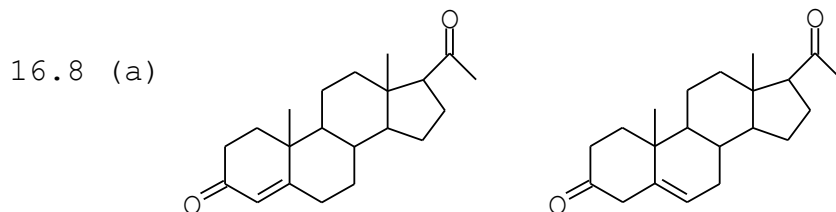
Answers to Puzzles of Chapter 16
Allylic and Conjugated Compounds

16.1 β -carotene & lycopene have many E & Z diastereomers.
Progesterone has many chiral atoms and stereoisomers.

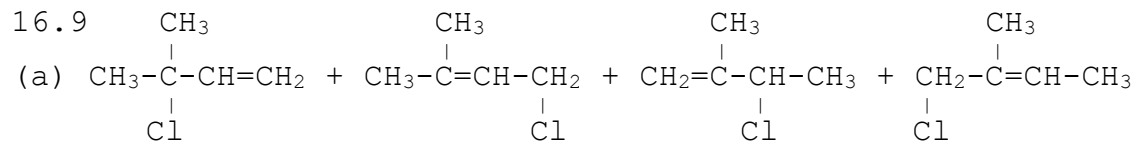


(b) This reaction would go faster because resonance stabilizes the C^+ product of the rls.

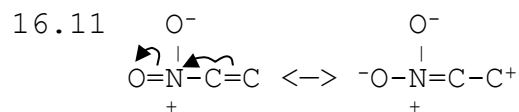
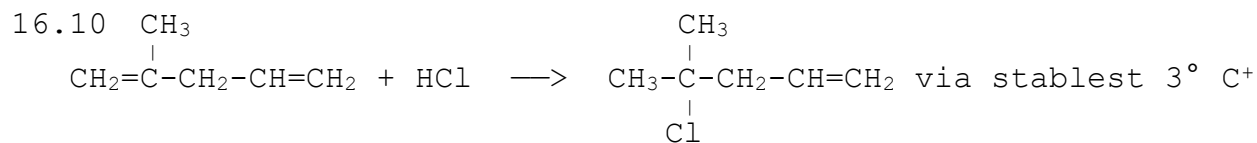
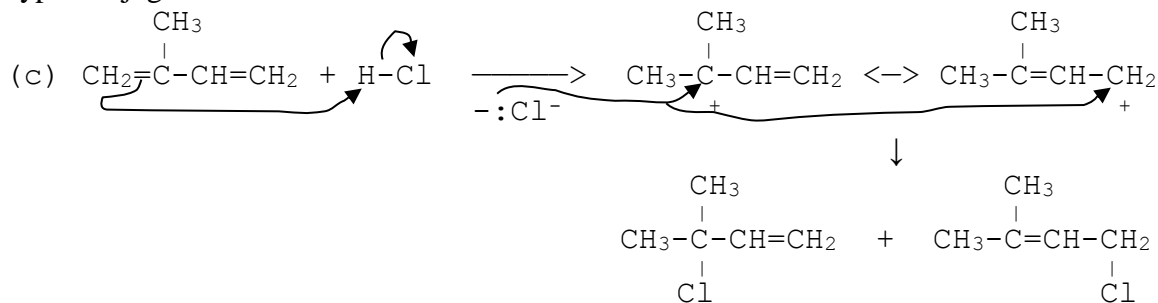




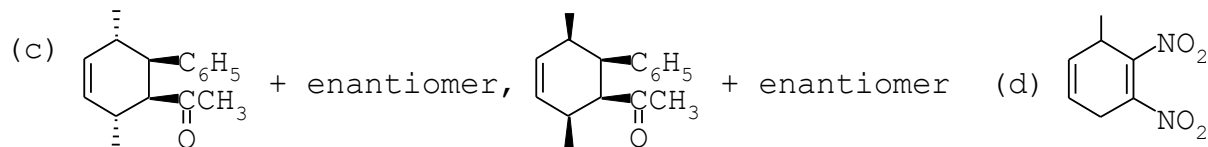
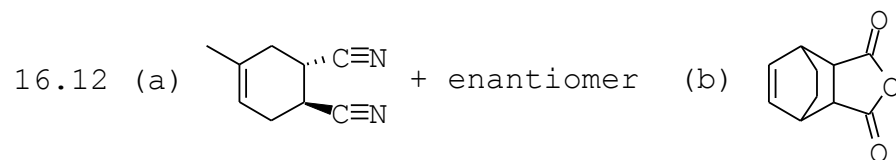
(b) The 1st steroid above because conjugation with the C=O stabilizes its C=C.



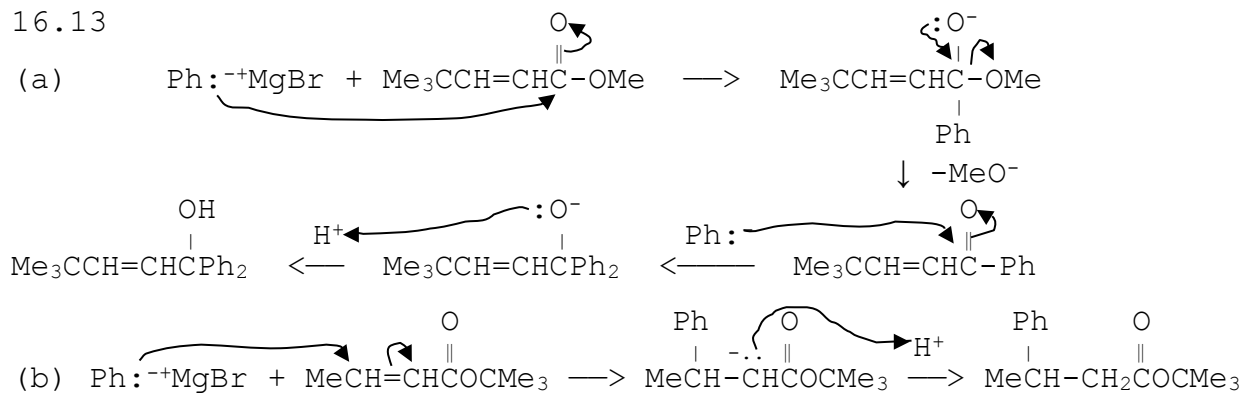
(b) The 1st 2 isomers are major: they form from the stabler allylic C⁺ with more hyperconjugation:



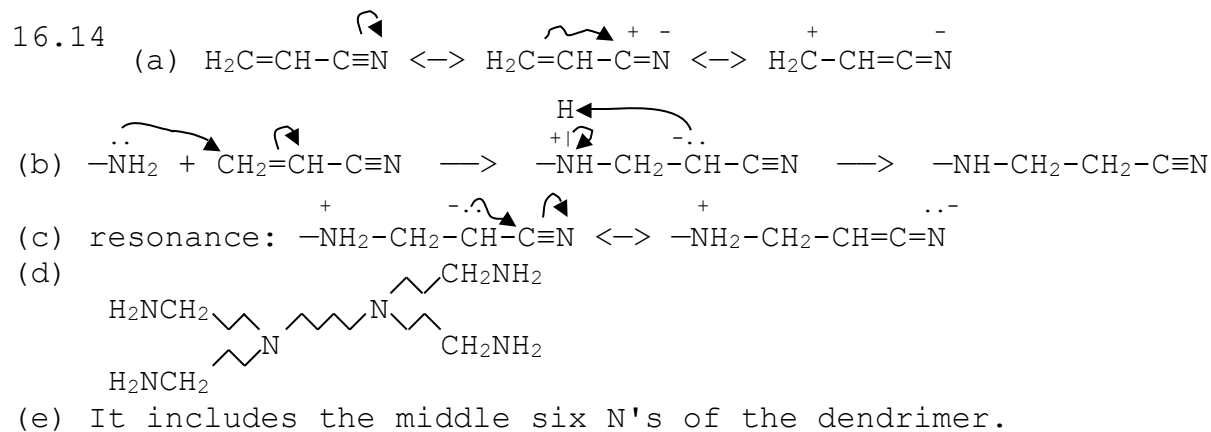
Also the ⁺N attracts & withdraws e⁻'s inductively.



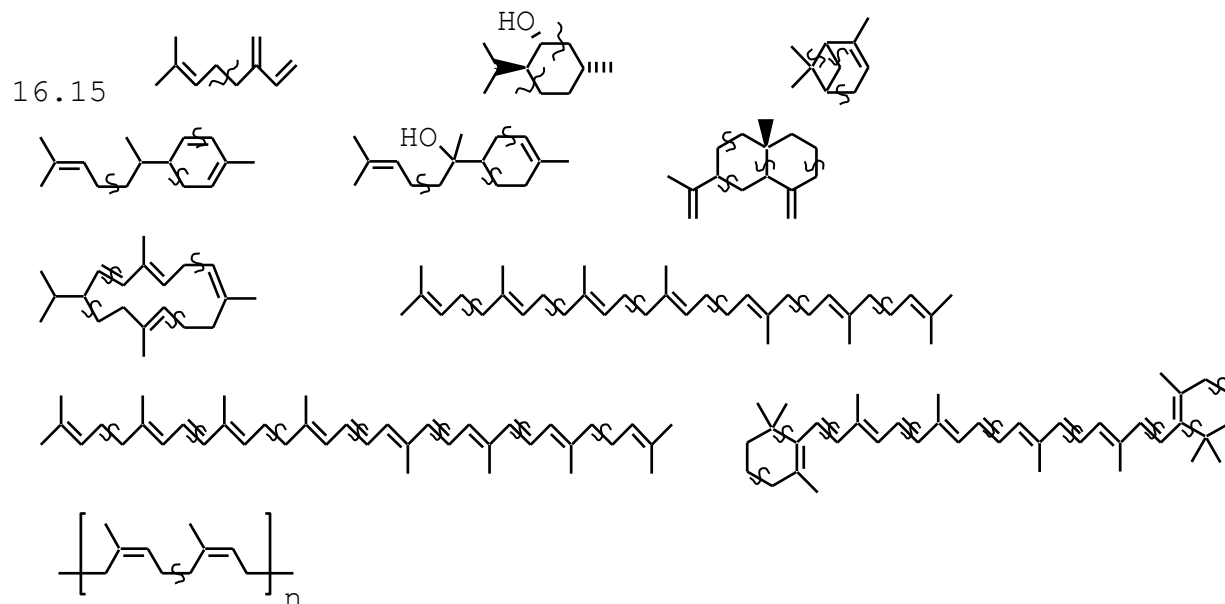
16.13



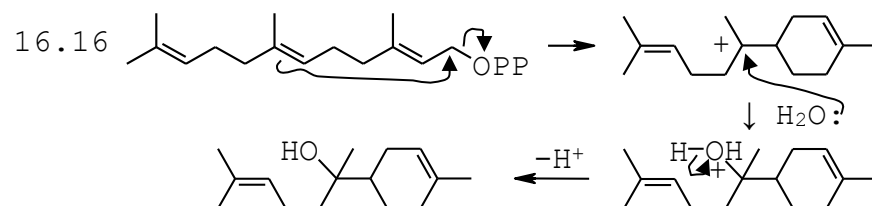
16.14

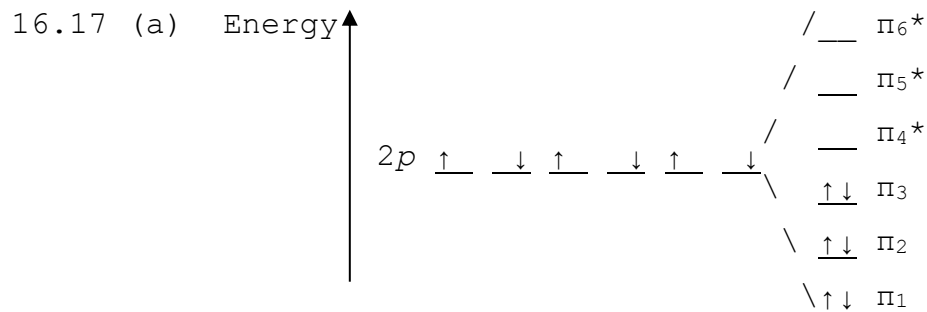


16.15



16.16





(b) This energy gap is smaller than that for a conjugated diene.

16.18 (a) $E = 548 \text{ kJ/mol} = \nu \cdot 3.98 \times 10^{-13} \text{ s} \cdot \text{kJ/mol}$

$\nu = 1.38 \times 10^{15} \text{ s}^{-1}$

$\lambda = c/\nu = 3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1} / 1.38 \times 10^{15} \text{ s}^{-1} = 2.17 \times 10^{-7} \text{ m} = 217 \text{ nm}$

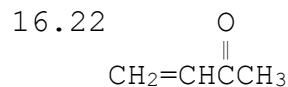
(b) Light of 217 nm λ is ultraviolet.

16.19 Compounds (a), (c), (d), (f), and (g) absorb strongly in UV-VIS spectroscopy.

16.20 (a) It has many conjugated double bonds which absorb much uv light.

(b) No. Because it has 18 C's per 2 polar O functional groups, it is only slightly polar.

16.21 (a) O_3 ; then Zn; then NaBH_4 ; then H^+ (b) anhyd. Cr(VI)



IR: 3100-3000 cm^{-1} (m): sp^2 C-H; 2950-2850 cm^{-1} (w): sp^3 C-H;

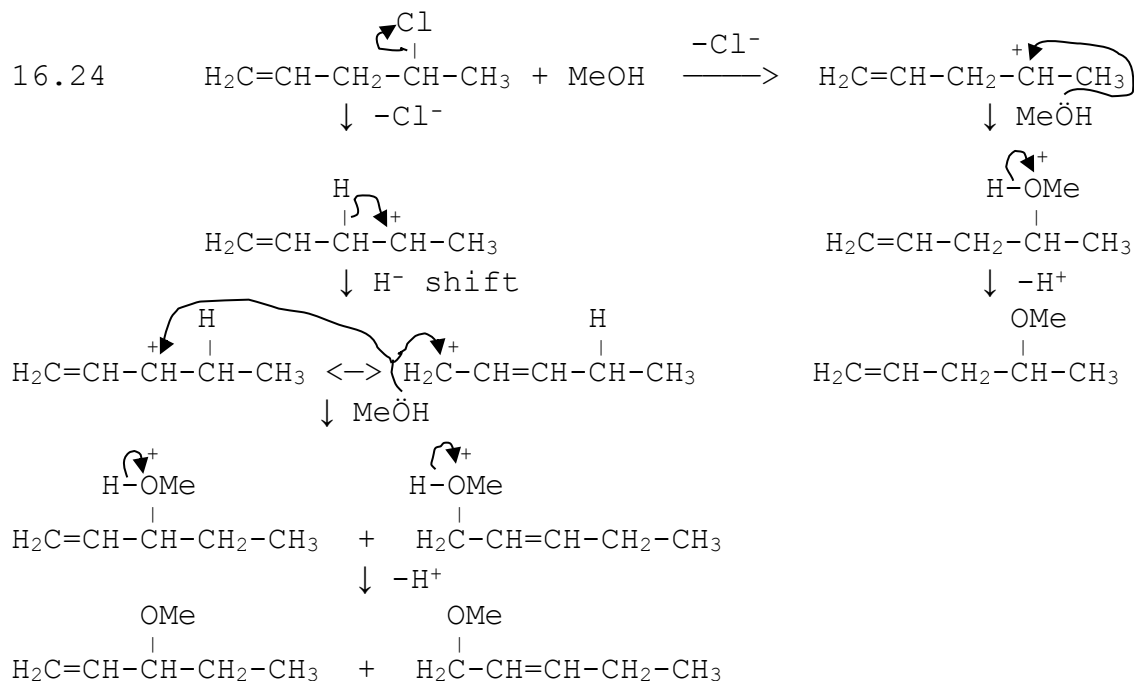
1680 cm^{-1} (s): conjugated C=O; 1620 cm^{-1} (s): conjugated C=C; 960 cm^{-1} (s): sp^2 C-H bend

16.23 (a) 3020 cm^{-1} (w): sp^2 C-H; 2950-2850 cm^{-1} (s): sp^3 C-H;

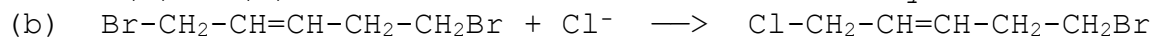
1700 cm^{-1} (s): unconjugated C=O; 1660 cm^{-1} (s): conjugated C=O; 1615 cm^{-1} (m): C=C;

870 cm^{-1} (m): sp^2 C-H bend

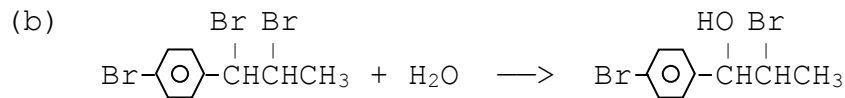
(b) It is at lower frequency than normal because it is conjugated.



16.25 (a) C(1) reacts faster because it is allylic.

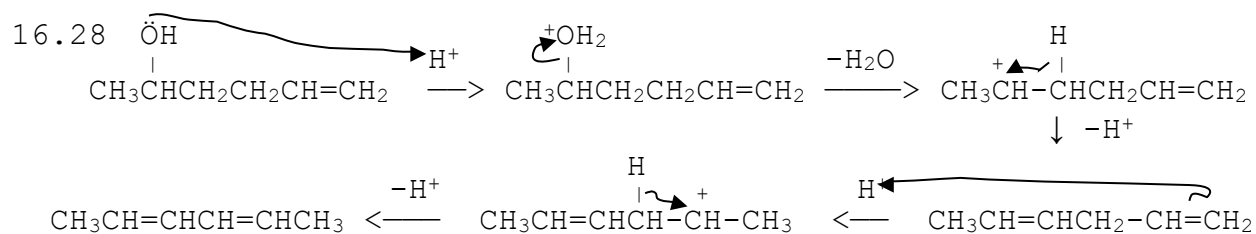


16.26 (a) The benzylic carbon reacts fastest.

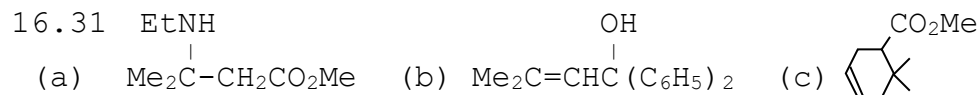
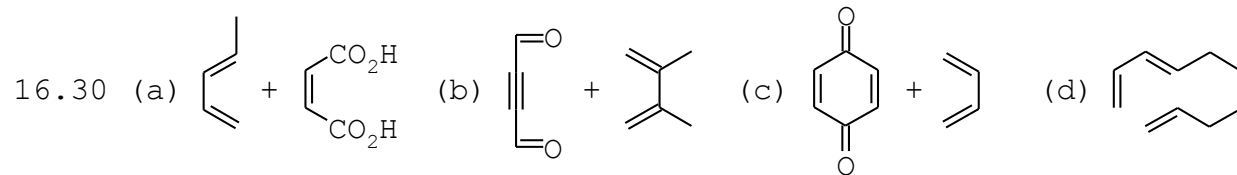


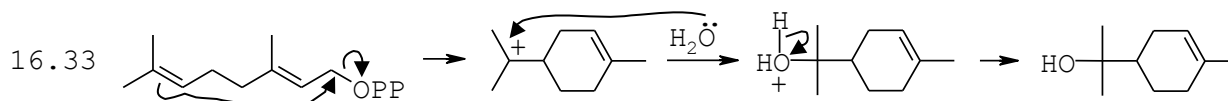
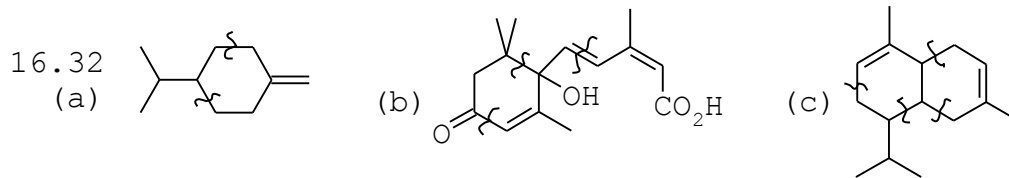
16.27 (a) 1,2-hexadiene evolves the most heat: this cumulated diene is the least stable diene.

(b) (*E*)-1,3-hexadiene evolves the least heat because this conjugated diene is the most stable diene.



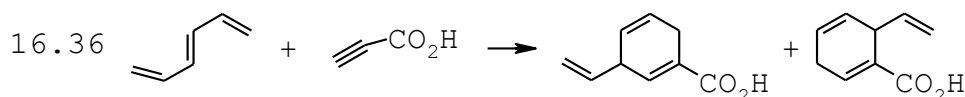
16.29 $\text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{HI} \longrightarrow \text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CH}=\text{CH}_2 \leftrightarrow \text{CH}_3-\text{CH}=\text{CH}-\overset{+}{\text{C}}\text{H}_2$
 Resonance stabilizes this allylic C⁺ more than the diene. The other C⁺ has no resonance.





16.35 (a) No, because $170 \text{ nm} < 200 \text{ nm}$, the normal limit.

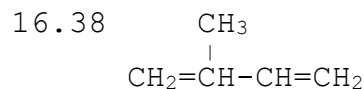
(b)
$$E = \frac{3.00 \times 10^8 \text{ m/s}}{170 \times 10^{-9} \text{ m}} \cdot 3.98 \times 10^{-13} \text{ s} \cdot \text{kJ/mol} = 700 \text{ kJ/mol}$$



(a) All 4 chemicals have conjugated π bonds & so absorb strongly.

(b) With 3 conjugated double bonds the hexatriene absorbs strongly at the longest λ .

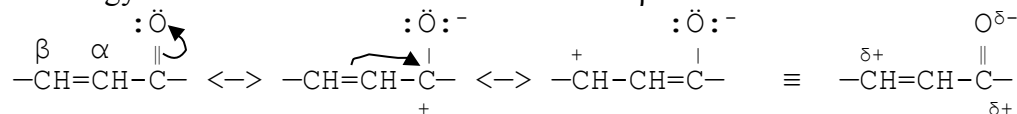
16.37 (a) β -carotene: more conjugated π bonds (b) β -carotene: more conjugated π bonds



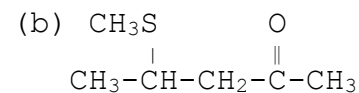
3080 cm^{-1} (m): sp^2 C-H; $3000\text{-}2850 \text{ cm}^{-1}$ (m): sp^3 C-H; 1600 cm^{-1} (s): conjugated C=C; $990, 890 \text{ cm}^{-1}$ (s): sp^2 C-H bend

16.39 No: the 2 planes of the pairs of bonding p orbitals are perpendicular to each other.

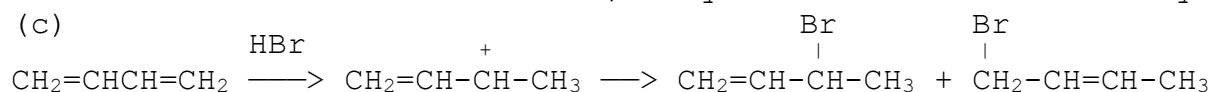
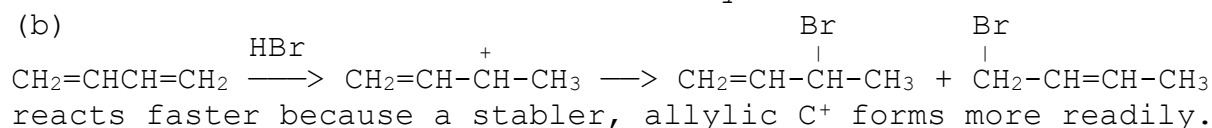
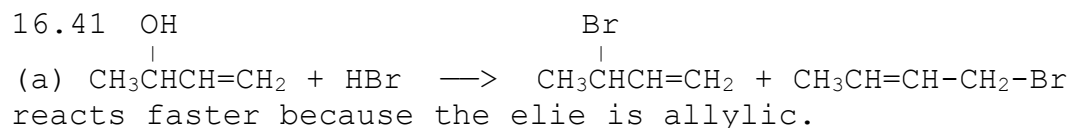
16.40 (a) With opposite charges closer together, the resonance form with + on the carbonyl C has less energy than the resonance form with + on the β C:



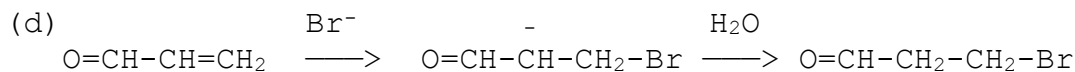
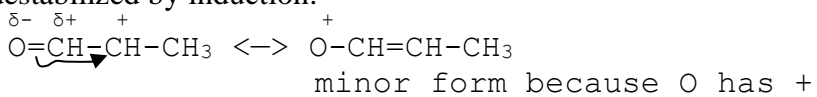
Therefore the carbonyl C has more δ^+ and is harder than the β C.



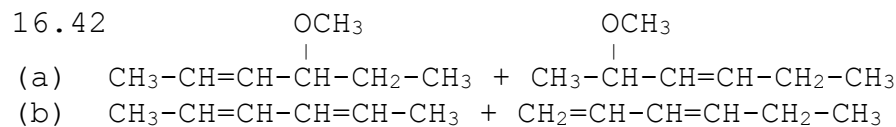
because the soft nucleophile prefers the softer electrophile.



reacts faster because the alternative cation is not allylic, not well stabilized by resonance, and destabilized by induction:

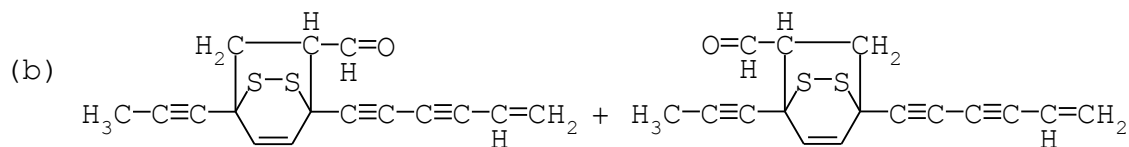


reacts faster because the α,β -unsaturated carbonyl's β carbon is an electrophile.

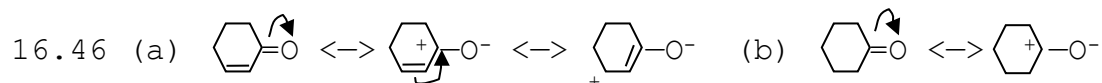


16.43 (a) It can't be done. (b) Me shift during a C^+ rearrangement.

16.44 (a) The π bonds in conjugated $\text{C}\equiv\text{C}$'s: their linear geometries prevent *s-cis* orientation.

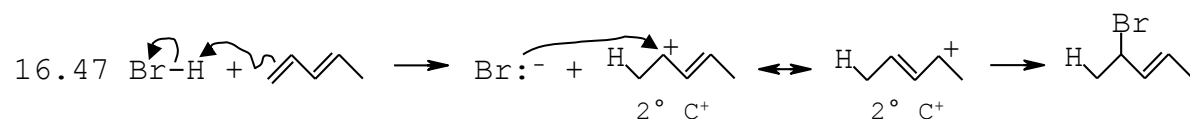


16.45 No, because without conjugated π bonds water does not absorb much UV light. So light clouds can let enough UV light through to tan skin.

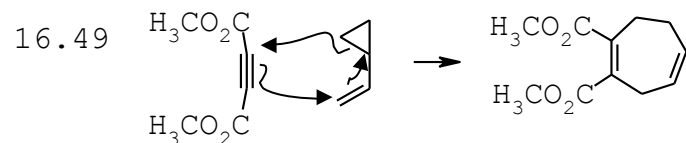
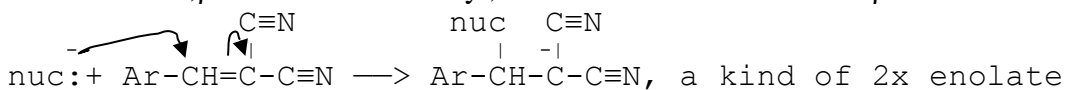


(c) because the 3rd resonance form gives the β C $\delta+$.

(d) because the 3rd resonance form \downarrow $\delta+$ on the carbonyl C.



16.48 Like an α,β unsaturated carbonyl, CS could add a nuc to the C β to the $\text{C}\equiv\text{N}$'s:



6/05