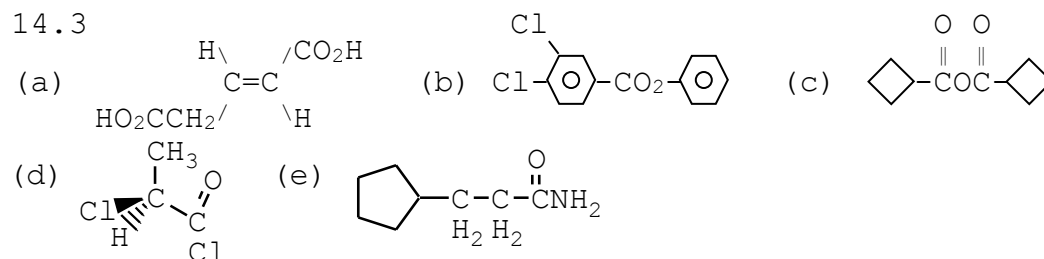


Answers to Puzzles of Chapter 14
Carboxylic Acid Derivatives

14.1 (a) aldehyde, ether, ketone (b) aldehyde, ester (c) acid anhydride (d) ketone, amine
(e) amide (f) ketone, alcohol (g) carboxylic acid (h) ketone, alkyl chloride (i) acid chloride

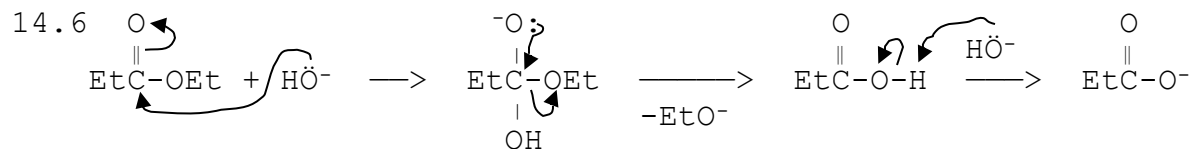
14.2 (a) 3-bromobutanoic acid (b) 2-methylpentanoyl chloride (c) propanoic anhydride
(d) *N*-phenylethanamide (e) sodium 2-propenoate (f) ethyl 4-hydroxybutanoate
(g) *N,N*-dimethylbenzamide (h) 4-chlorocyclohexanecarbonyl chloride

14.3

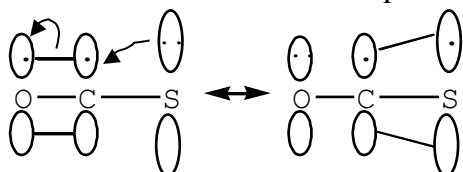


14.4 (a) propanoic acid: it has H "bonds" (b) *N*-methylethanamide: it has H "bonds"
(c) *N*-methylethanamide: it has H "bonds"

14.5 Insoluble in water because it has more than 5 C's per polar O functional group.



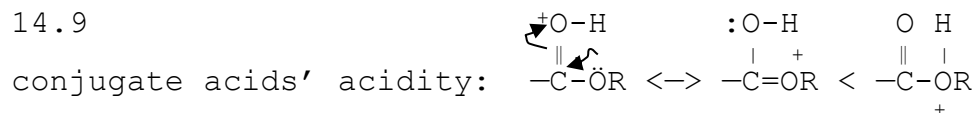
14.7 Thioesters are more electrophilic because S does not stabilize by resonance as much as O:



The *p* orbital of the 3rd-row S poorly overlaps the *p* orbital of the 2nd-row C.

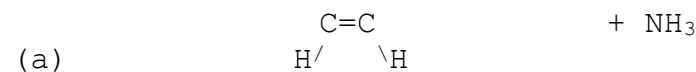
14.8 (a) ethanoyl chloride (b) ethanoic anhydride (c) methyl ethanoate (d) ethanamide

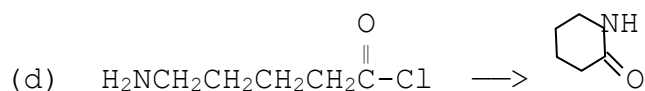
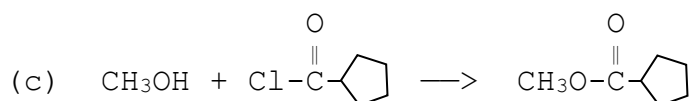
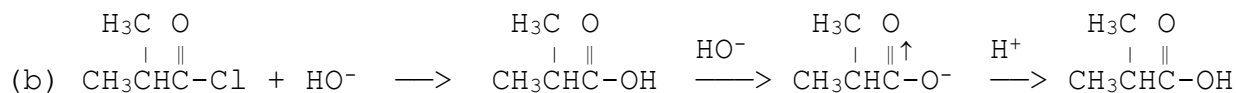
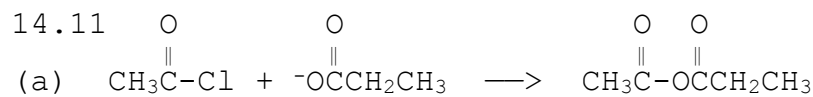
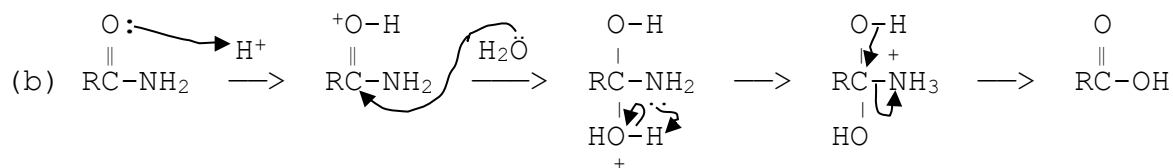
14.9



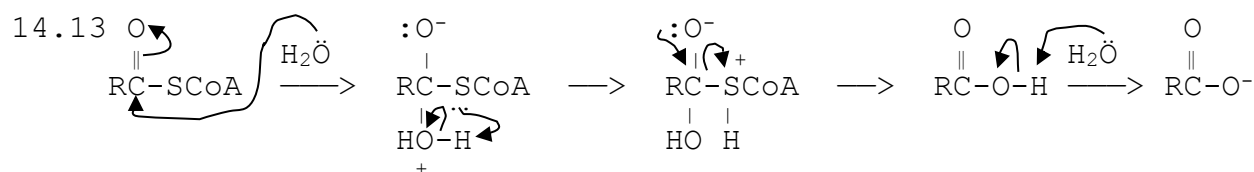
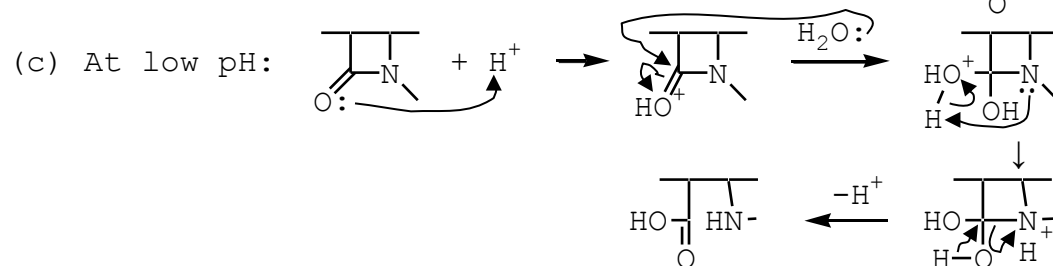
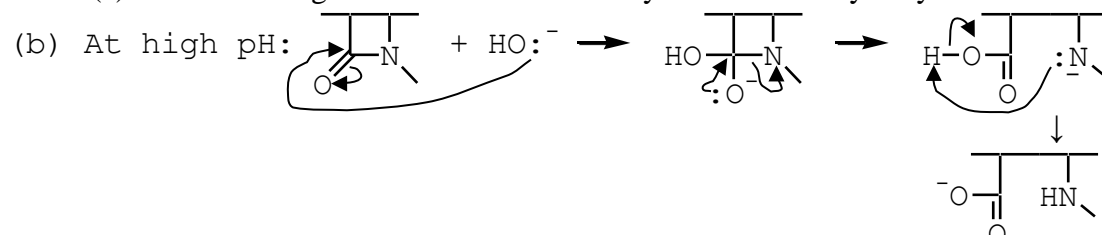
The 1st acid is easier to make because resonance stabilizes it.

14.10 $\text{CH}_3(\text{CH}_2)_7 \backslash / (\text{CH}_2)_7 \text{CO}_2\text{H}$



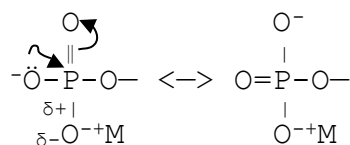


14.12 (a) Release of ring strain would cause the cyclic amide to hydrolyze more readily.



14.14 (a) The metal neutralizes a negative charge, which otherwise would destabilize the base e's of the leaving group.

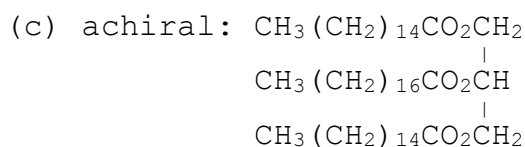
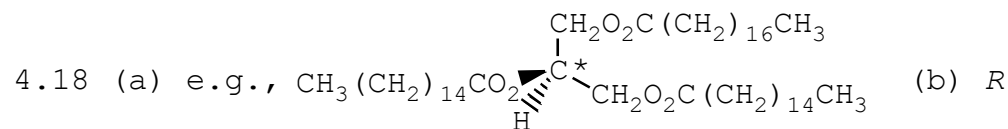
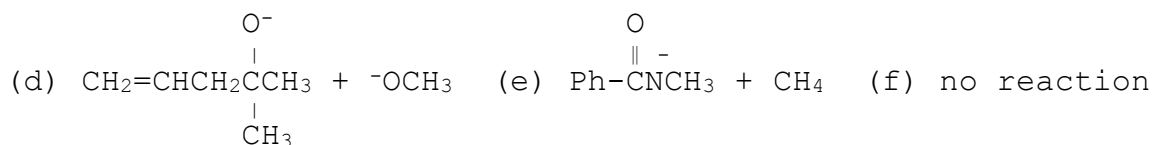
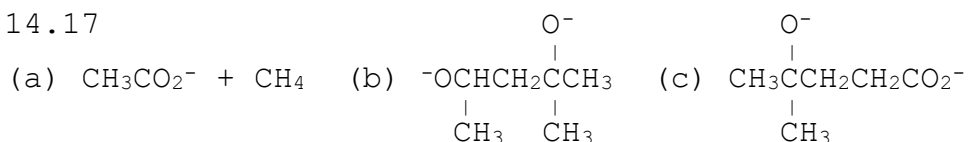
(b) Resonance & the δ^+ on the P from the EN O's stabilize the base e's:



14.15 The - charges on the O's repel nucleophiles, and the more EN P's have less δ^+ than the less EN carbonyl C's of an ordinary acid anhydride.

14.16 (a) $\text{CH}_3\text{CH}_2\text{O}^-$ (b) $^-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}^-$ (c) $^-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}^-$
 (d) $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{O}^- + ^-\text{OCH}_3$ (e) $\text{Ph}-\text{CH}_2\text{NHCH}_3$ (f) $\text{CH}_3\text{CH}_2\text{O}^-$

14.17

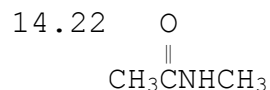


14.19 The polar ends in the water and the nonpolar ends sticking out of the water.

14.20 (a) 2 soap monoanions

(b) There are so many (> 30) C's surrounding the one ionic group that the total complex has too little polarity to dissolve in very polar H_2O .

14.21 Phosphatidylcholine molecules entrap an oil drop in a micelle with their nonpolar chains surrounding the oil and their polar groups sticking outward into the aqueous medium.

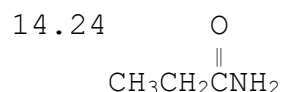


IR: 3300 cm^{-1} (s): 2° amide N-H (only 1 strong band above 3160); 2950 cm^{-1} (m): sp^3 C-H; 1670 cm^{-1} (s): C=O of amide; 1560 cm^{-1} (s): N-H bend of 2° amide

Because there is no aldehyde and there there are only 3 C's in the molecule, both the carbonyl C and the amide N must have methyl groups.

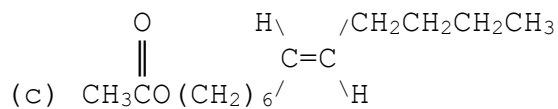
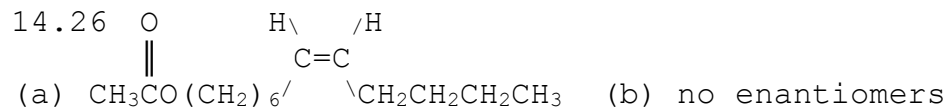
14.23 (a) $2950\text{--}2800\text{ cm}^{-1}$ (s): sp^3 C-H; $2700\text{--}2550\text{ cm}^{-1}$ (m): O-H of carboxylic acid; 1750 cm^{-1} (s): ester C=O; 1690 cm^{-1} (s): carboxylic acid C=O; 1600 cm^{-1} (s): phenyl $\text{C}=\text{C}$; $1300, 1180\text{ cm}^{-1}$ (s): C-O; 920 cm^{-1} (s): sp^2 C-H bend

(b) The carboxylic acid C=O in resonance with the benzene ring absorbs at $1690 < 1700\text{ cm}^{-1}$.

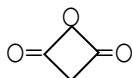


NH_2 : δ 6.5 (s) & 6.2 (s); CH_2 : δ 2.2 (q); CH_3 : δ 1.2 (t)

14.25 (a) 3-chlorobenzoyl chloride (b) 2-hydroxypropanamide
 (c) cyclobutyl 4,4,4-trichlorobutanoate (d) pentanedioic anhydride
 (e) lithium 2-bromopropanoate (f) methyl (*E*)-2,4-pentadienoate



14.27 (a) propanedioic anhydride:

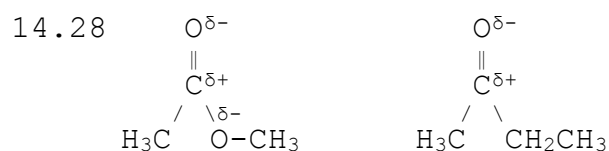


(b) e.g., 2-chlorobutanoyl chloride: $\text{CH}_3\text{CH}_2\text{-CHCl-COCl}$

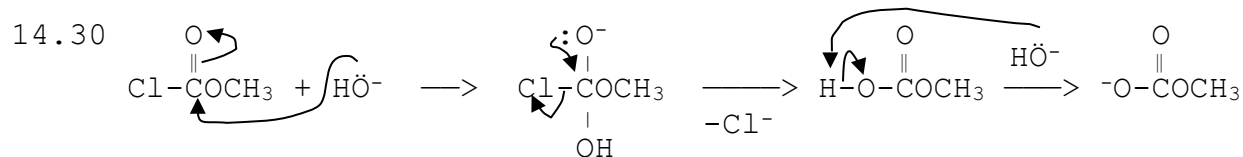
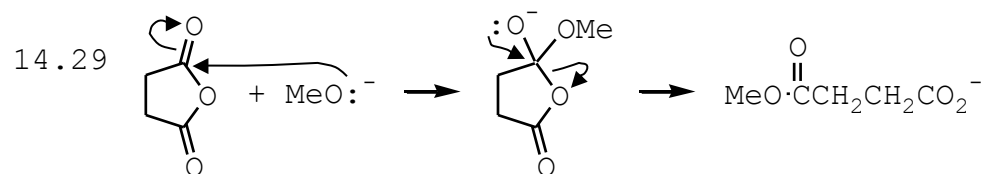
(c) *N,N*-diethylcyclopentanecarboxamide: -CONEt_2

(d) ethyl hexanoate: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$

(e) methyl propanoate: $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$



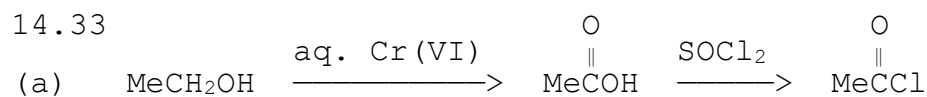
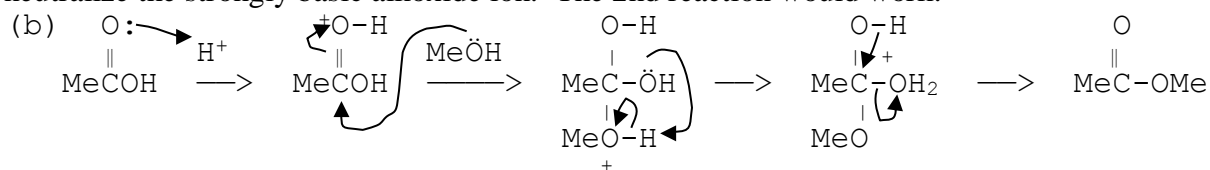
Unlike the ketone, the ester has a polar C-O single bond, which partially opposes the polar carbonyl C=O. So the less polar ester has smaller dipole-dipole forces & bp.

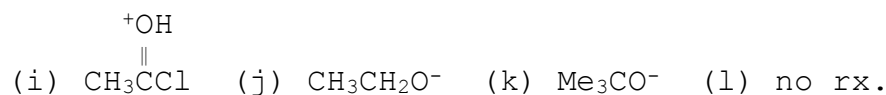
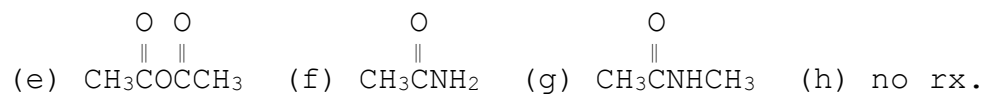
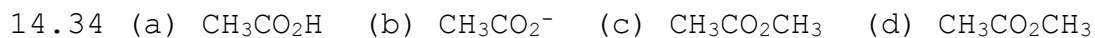
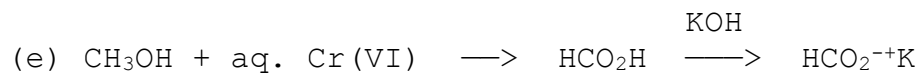
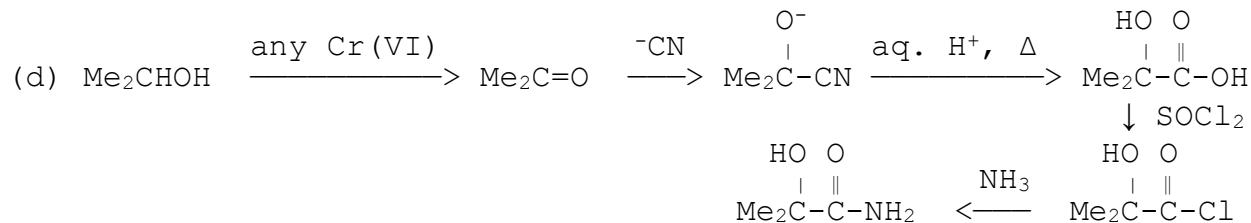
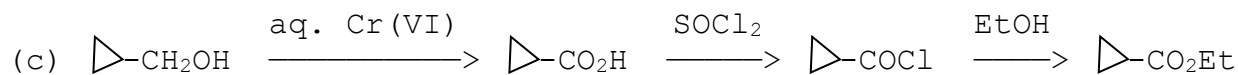
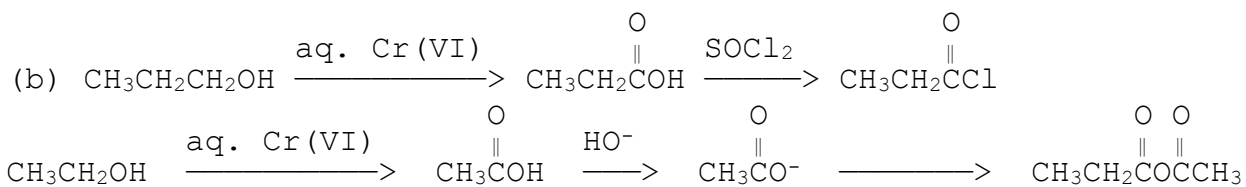


14.31 (a) No, because I^- is a weak, soft base and a weak nucleophile for the hard electrophile.

(b) No, because esters do not normally react by $\text{S}_{\text{N}}2$.

14.32 (a) The 1st reaction would not work because the carboxylic acid would immediately neutralize the strongly basic alkoxide ion. The 2nd reaction would work:





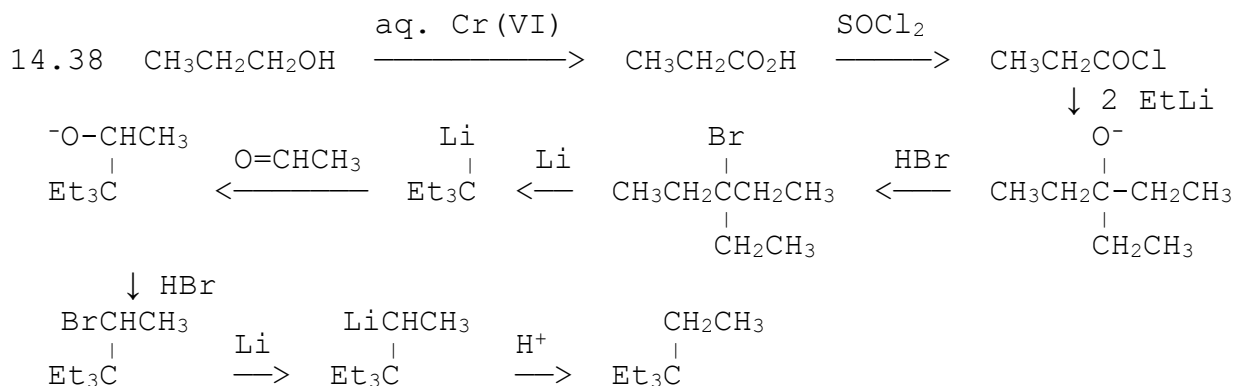
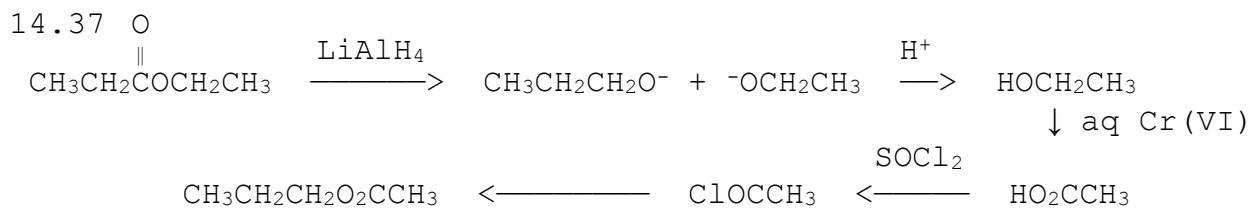
14.35 (a) propanedioic anhydride, because hydrolysis relieves ring strain.

(b) ethanoic anhydride, because its hydrolysis forms more (2) products favored by entropy.

(c) propanedioic anhydride \longrightarrow $^- \text{O}_2\text{CCH}_2\text{CO}_2^-$

ethanoic anhydride \longrightarrow CH_3CO_2^-

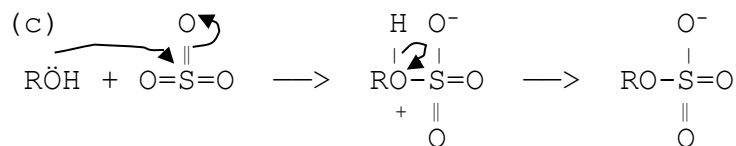
14.36 The simple glucose electrophile has no good leaving group.



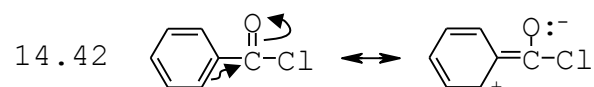
14.39 No, because it continues the regular, anti-staggered conformation of the C chain.

14.40 (a) The alcohol is the nuc and the SO₃ is the elie.

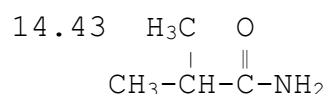
(b) With 6 bonds to EN O's, S has much δ⁺. Trigonal planar, S is also open to nucleophilic attack.



14.41 Being both hydrophilic & hydrophobic, detergent and the phosphoglycerides from membranes combine to form mixed micelles, which destroy the membrane.



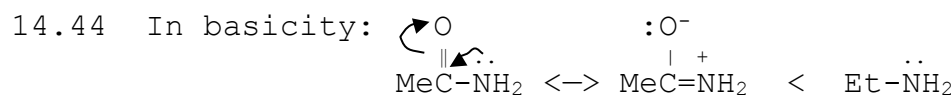
Resonance lowers the bond order of the carbonyl, so IR light of less energy is needed.



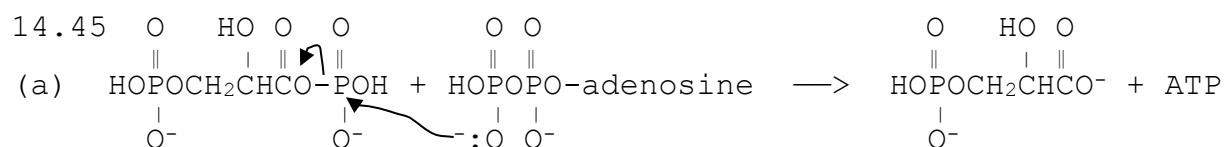
IR: 3340, 3170 cm⁻¹ (m): 2 N-H of 1° amide; 3000-2850 cm⁻¹ (s): sp³ C-H; 1650 cm⁻¹ (s): C=O;

1640 cm⁻¹ (s): N-H bend of 1° amide.

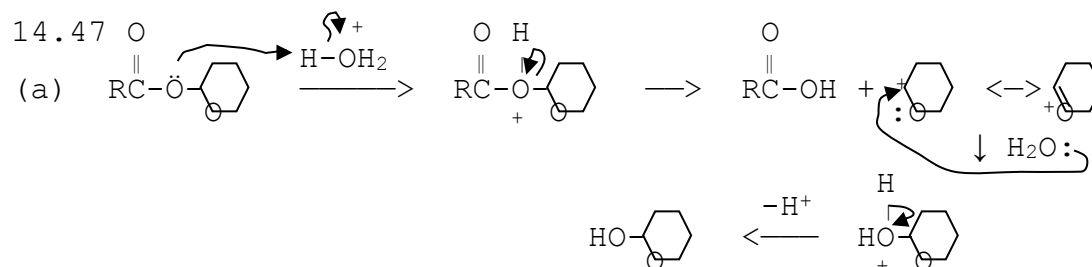
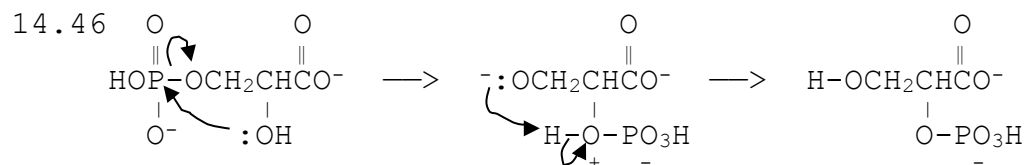
NMR: δ 7.1 (s), 6.6 (s): N-H; δ 2.4 (m): CH; δ 1.1 (d): CH₃



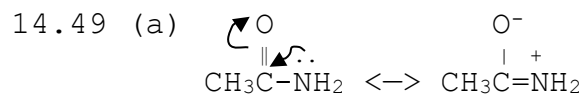
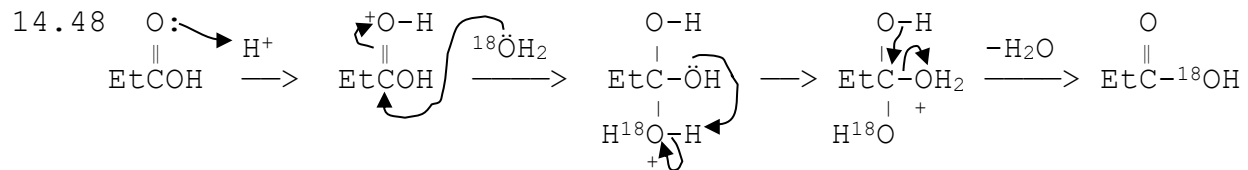
because resonance stabilizes the base e's in the amide.



(b) The preferred phosphate is part of a more reactive mixed acid anhydride.

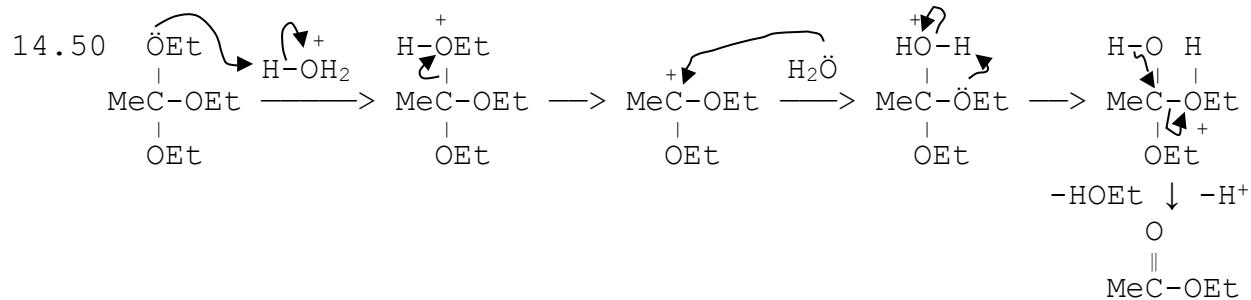


(b) resonance stabilizes the C⁺

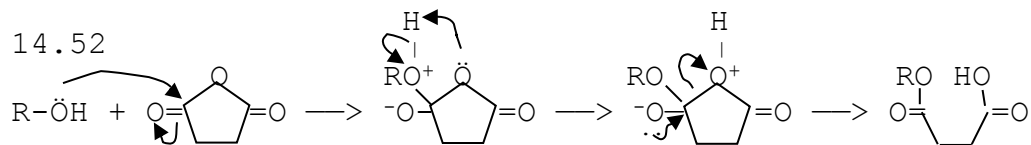


By providing double bond character, resonance shortens the C-N bond.

(b) Being less EN, N can delocalize its lone pair more in resonance than O can.



14.51 unsaturated fat with cis C=C \rightleftharpoons saturated fat \rightleftharpoons unsaturated fat with trans C=C
 A trans C=C is stabler than a cis C=C because of steric repulsion. So trans fats readily form.



14.53 unsaturated: these would have a lower mp and more needed flexibility at low temperatures.

14.54 (a) It has 24 C's with 4 polar functional groups. 24:4 > 5:1.

(b) The metal complex adds ionic polarity to the ring region; the long hydrocarbon tail is nonpolar. So like any detergent it has both hydrophilic and lipophilic part.