

## Chapter 12. Ouellette, 2/e. Chemistry X402.

Ch 12. Carboxylic acids and esters.

**Skip:** Sect 7, 10.

**Also read:** Review background sections such as Ch 2 Sections 3, 7, 8.

### Essays

- *Required:* p 352 (Polyesters). Condensation polymers are important in biology.

The following two essays are not required for now, but they will be required for our Metabolism section, which follows Ch 15. You might glance at them now, as a preview.

- p 348 (thioesters);
- p 354 (phosphate derivatives).
- The Essay on p 337 gives some insight into the chemical industry, with some interesting history. Not required.

⇒ **Practice quizzes**, at web site: One, mentioned before, is on Oxidation and reduction, and relates material from Ch 4-12. One, labeled for Ch 12, also includes considerable review.

### Notes

Sect 1. The big perspective is that this chapter discusses more complex carbonyl compounds, compared to those of Ch 10. They all have a carbonyl group, plus something else of interest attached to the carbonyl C. The carboxylic acids and esters are the major stable compounds of this type. The amides also fit, but we focus on them later (Ch 14). Acyl chlorides, acid anhydrides, and thioesters are more of interest as unstable intermediates than in their own right. But they are very useful, and some are important in biochemistry.

Sect 2. Naming of acids and esters is important, but don't worry about trying to name the others. (We will deal with naming of amides in Ch 14.)

I will not assume that you know the common names of the organic acids (e.g., Tables 12.1 & 2). You can always use systematic names when providing names; I will give both common and systematic names. But I should stress that some of these names really are quite common. Be guided by your own work and requirements; you probably want to know at least some of them.

Sect 3. Table 12.3 lacks the MP for several compounds. The MP of the first eight carboxylic acids (C<sub>1</sub> to C<sub>8</sub>) are (in °C): 5, 17, -21, -8, -35, -2, -8, 17. Your comments? (Advanced. Recall a note in Ch 3 handout that BP trends tend to be simpler than MP trends.)

Sect 4. Careful about getting bogged down in all the numbers. The big story is that carboxylic acids are acids -- generally rather weak. Resonance stabilization of the carboxylate ion is one

reason for the acidity. Table 12.6 shows that all alkanolic acids have similar acidity; electron-withdrawing groups nearby enhance the acidity.

Sect 5. The first three reactions shown are review. You can treat the rest of this section (from mid p 343) as “advanced”.

Sect 6. The terminology here is very organic. The big story is that a variety of substitutions can let you make one of these acyl compounds from another. There is a general order of reactivity, which is useful (Fig 12.3). These reactions are important in organic chem -- and in biochem. We will follow up on these ideas. It is probably a good first step to take Fig 12.3 as a conceptual point (order of reactivity), with the specific details to follow (you can write them on your note sheet).

Sect 8. Note that the simple interconversion of acids and esters is not very efficient. “Activating” the acid (making the chloride or anhydride) is a big help; this is an application of Sect 6. The Essay on p 352, which is assigned, goes with this section.

General. The special properties of the carboxyl group show how two groups can interact, especially when very close. Other examples we have seen include the aromatic system of benzene, and  $\alpha$ -hydrogen effects.

### **Errata**

p 354, Essay, last paragraph on left. First sentence is not quite correct; it is not true for the esters of mono-phosphoric acid. All subsequent discussion is fine, and should make this clear.

p 361, # 5c. Answer says trans; should be cis.

**Suggested problems.** Models exercises are good. For the regular exercises, 1-30 & 45-48 are good. 33-44 deal with reactions, including some we skipped; some of the questions are fairly challenging. I encourage you to at least sample these. 31-32 & 49-52 are on skipped sections.

*⇒ Are there topics for this or other recent chapters where a supplementary set of more focused problems would be good? Please let me know.*

### **Overview of skipped sections**

Sect 7. Reduction of acyl derivatives requires a very strong reducing agent -- and inevitably goes all the way to the alcohol.

Sect 10. This follows from Ch 10 Sect 11, on aldol condensations. The Claisen condensation discussed here is similar, but with acyl compounds. Both involve an  $\alpha$ -H as the key to giving a nucleophile, and both make new C-C bonds. The aldol condensation is an addition reaction; the Claisen condensation is a substitution. There is some biochem here, but you can read this later, with Metabolism.

**Further reading**

L E L Rasmussen et al, Mellifluous matures to malodorous in musth. *Nature* 415:975, 2/28/02. It has long been recognized that the younger mature male elephants smell like honey during mating season. Here, they confirm that at the chemical level. The older males have more offensive odors. The authors argue that the odors help to maintain social structure. Many of the odor constituents are fairly simple O-compounds from Ch 8-12.

R A Gross & B Kalra, Biodegradable polymers for the environment. *Science* 297:803, 8/2/02. Part of a feature section on Green Chemistry. All of the polymers are condensation polymers, which are susceptible -- at least in principle -- to chemical or enzymatic hydrolysis. For an exchange of letters about this paper see: *Science* 299:822, 2/7/03, under the heading "Biopolymers and the Environment". This exchange shows the complexity of predicting the economic merit of new developments. There is also a specialty application of biodegradable polymers in medicine; see Yoshimoto et al (2003), below, as an example. Also see Computer Resources, below.

T Lütke-Eversloh et al, Biosynthesis of novel thermoplastic polythioesters by engineered *Escherichia coli*. *Nature Materials* 1:236, 12/02. We briefly note thioesters, which are important in biology (Metabolism chapter). Recently, these workers found that some bacteria accumulate polymers with a mix of thioester and ester linkages. They explore that further here, with strains engineered to produce polymers with entirely thioester linkages. It would seem that this work opens up a new class of polymer for study. Also see Dias et al (2006) and Computer resources.

H Yoshimoto et al, A biodegradable nanofiber scaffold by electrospinning and its potential for bone tissue engineering. *Biomaterials* 24:2077-2082, 5/03. The polymer being tested is a polyester.

M Ono et al, Insect signalling: Components of giant hornet alarm pheromone. *Nature* 424:637, 8/7/03. Analysis shows that the alarm pheromone contains a variety of alcohols and esters. Of particular concern is that one of the esters is commonly used in products for human use, such as perfumes. Thus they wonder whether this use might promote hornet attacks.

T Clarke, Music and Chemistry: Organ failure. *Nature* 427:8, 1/1/04. News feature. Pipe organs in Europe (except in Britain) are corroding. One contributing factor seems to be the acetic acid fumes given off by the oak wood used in restoration.

A-D Fortineau, Chemistry perfumes your daily life. *J Chem Educ* 81:45, 1/04. Discussion of natural and synthetic perfume ingredients, many of which are O-compounds.

R Renner, Environmental chemistry: Tracking the dirty byproducts of a world trying to stay clean. *Science* 306:1887, 12/10/04. News. Discussion of the problem of fluorinated chemicals as environmental contaminants. Fluorinated compounds are used as stain removers; they are made from volatile smaller molecules. Teflon is a fluorinated polymer which can yield mobile (small molecule) products upon combustion. Fluorinated compounds are quite resistant to

degradation. They are being found in animals, though whether there is any significant problem remains an open question.

J Zhang et al, Facile conversion of alcohols into esters and dihydrogen catalyzed by new ruthenium complexes. *J Am Chem Soc* 127:10840-1, 8/10/05. They work on the production of esters by oxidative coupling of two alcohols. In this process, the production of H<sub>2</sub> serves to drive the reaction toward ester formation. They suggest that the reaction proceeds through a hemiacetal intermediate, which is then dehydrogenated.

M E Frederickson et al, Ecology: 'Devil's gardens' bedevilled by ants. *Nature* 437:495, 9/22/05. "An ant species uses herbicidal weaponry to secure its own niche in the Amazonian rainforest." This ant kills plants other than its host -- with formic acid.

A L Huang et al, The cells and logic for mammalian sour taste detection. *Nature* 442:934, 8/24/06. Sour taste is due to acids. Its "purpose" might be to warn us of spoiled or unripe food. Here they develop information on the taste receptors for "sour". Interestingly, the same receptor is found in the nervous system, where it may serve to monitor the pH of the brain fluids. For more, see Chandrashekar et al (2006).

M R Guasch-Jané et al, First evidence of white wine in ancient Egypt from Tutankhamun's tomb. *Journal of Archaeological Science* 33:1075-1080, 8/06. They analyze dry residues from wine amphorae found in King Tut's tomb. As markers, they use tartaric acid as a general marker for grapes, and syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid, a part of the red pigment) as a marker for red wine. Some samples contained tartaric acid but not syringic acid; they conclude that these likely contained white wine. An interesting article at several levels.

C Huber & G Wächtershäuser,  $\alpha$ -Hydroxy and  $\alpha$ -amino acids under possible Hadean, volcanic origin-of-life conditions. *Science* 314:630, 10/27/06. In the tradition of Miller & Urey, they try to see whether interesting organic molecules can be made under conditions they think might mimic those involved with the origin of life. Such work explores interesting chemistry, and certainly gives us some ideas to chew on. However, the relevance of any particular piece of such work is speculative. There was a lively follow-up exchange of letters: 315:937, 2/16/07.

M Carroll, Immunology: Exposure of an executioner. *Nature* 444:159, 11/9/06. News. "The complement C3 protein binds to pathogens, singling them out for execution by the immune system. Structural studies show how the chemical group responsible for this binding is exposed on activation." A thioester is a key component of the vertebrate complement system. This news story discusses recent work revealing how the system keeps that reactive group "hidden" until needed. But there is at least suspicion that unwanted accidental exposure of the reactive thioester is behind some inflammatory diseases.

J Chandrashekar et al, The receptors and cells for mammalian taste. *Nature* 444:288, 11/16/06. Review. A good overview of the whole field of taste receptors. Also see Huang et al (2006). (This is the first of a series of reviews in this issue on chemical sensing.)

R L Hudson, Astrochemistry examples in the classroom. *J Chem Educ* 83:1611, 11/06. The general spirit of the article is to explore some non-earth chemistry. The principles are often the

same, but with “unusual” chemicals. On the Intro Chem practice quiz for Acids and Bases, there is a question that was stimulated by this article.

J M L Dias et al, Recent advances in polyhydroxyalkanoate production by mixed aerobic cultures: From the substrate to the final product. *Macromolecular Bioscience* 6:885, 11/06. A good overview of bacterial PHAs (polyhydroxyalkanoates), with a focus on a novel approach to lowering the cost, by using mixed cultures. Also see Lütke-Eversloh et al (2002) and Computer resources.

**Computer resources** (See web page for details and links.)

For more about polymers, see the Macrogalleria site, listed for Ch 4.