

# Chem 221b

## Problem Set 7

### Chapters 20 & 21

#### Carboxylic Acids and Their Derivatives

Due: Monday, March 28, 2005

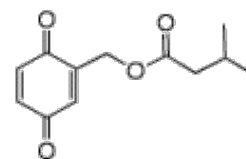
### Esters

Esters are pleasant smelling, volatile compounds. Isoamyl acetate (oil of banana), ethyl butyrate (pineapple), and methyl salicylate (wintergreen) to name a few. Apparently esters are pleasant to roaches.

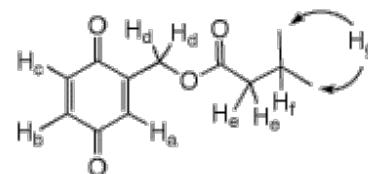
The February 18 issue of *Science* (2005, pg. 1104) reveals how [entomologists and chemists](#) unraveled the structure of the sex pheromone of the ubiquitous German cockroach, *Blattella germanica*. [HTML version](#). [PDF version](#).



*Blattella germanica*



*Blattellaquinone*



$$J_{fg} = J_{ef} = 8.6 \text{ Hz}$$

$$J_{ab} = J_{ad} = 2.0 \text{ Hz}$$

$$J_{bc} = 10.0 \text{ Hz}$$

1. Read the short paper cited above and see what issues apply to what you have learned in organic chemistry. The PDF version is better for general reading but the HTML permits blow-ups of the nmr spectrum if you need to measure coupling constants.

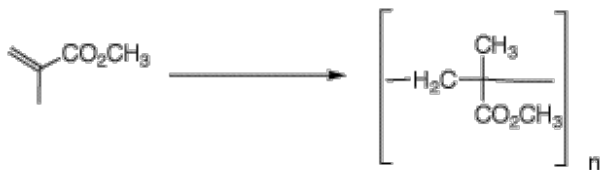
- What was the source of the pheromone?
- How was blattellaquinone detected by gas chromatography?
- Account for the peak  $m/z = 180$  in the EI mass spectrum.
- Given the  $^1\text{H}$  NMR data on the right, assign each of the hydrogens ( $\text{H}_a\text{-g}$ ) to a chemical shift and explain the multiplicity and coupling patterns.

Chemical Shift ( $\delta$ )
0.786
1.920
1.989
4.721
5.916
5.943
6.356

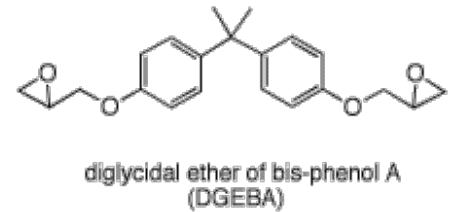
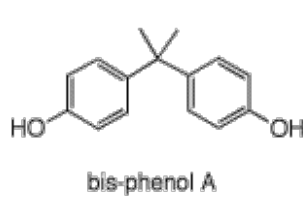
2. Consider the synthesis of blattellaquinone described in Fig. 2, pg. 1105.

- Design a synthesis of isovaleroyl chloride from isobutylene.
- Design a synthesis of dimethylgentisyl alcohol (2,5-dimethoxybenzyl alcohol) from benzene, methanol, and paraformaldehyde as the only sources of carbon.
- Why is the acid chloride preferable to the anhydride of isovaleric acid in the esterification?
- DMAP used in the esterification is an acronym for 4-(N,N)-**dimethylaminopyridine**. DMAP is a stronger base (~10-fold), and a better nucleophile, than pyridine. Explain the enhanced reactivity of DMAP. What is the  $\sim pK_b$  of DMAP?
- The cerium reagent is a one electron oxidant. How many equivalents of cerium reagent are required? What is the oxidation level change for cerium (ceric  $\rightarrow$  cerous)?
- During this oxidation two equivalents of methanol are lost. Write a mechanism for this process.

3. The polymerization of methyl methacrylate forms Plexiglass. In the formation of modern dental composites, the photo-initiator camphorquinone (PS2) causes cross-linked polymerization of a mixture of bis-GMA and TEGDMA.



Polymerization of Methyl Methacrylate



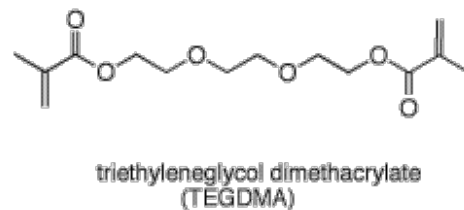
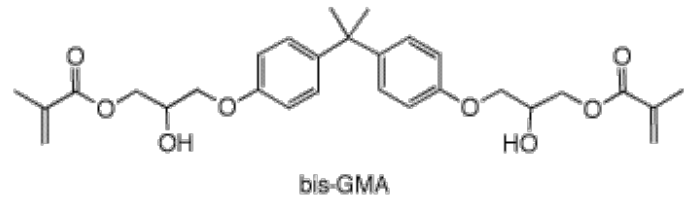
a) Show how bis-phenol A may be prepared from phenol and acetone. Provide a catalyst and mechanism.

Bis-phenol A is converted into DGEBA as shown on page 630.

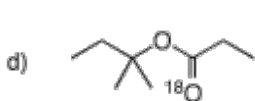
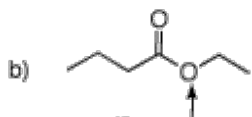
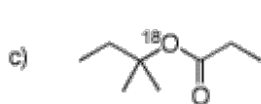
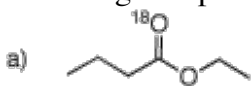
b) Is DGEBA a single compound? Explain.

c) What experiment could you design to demonstrate that this is the mechanism and not direct displacement on the carbon-chlorine bond?

d) Given methacrylic acid, how might you convert DGEBA into bis-GMA.



4. You have access to compounds with three or fewer carbon atoms,  $^{18}\text{O}$  water and all reagents. Prepare the following compounds.



What are the products formed in the aqueous acid hydrolysis of a-d? Account for the labeled oxygen.

5. Complete each of the following problems.

