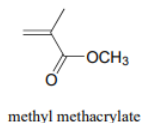
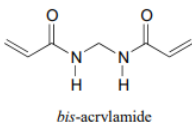


## 16.E: Radical Reactions (Exercises)

**P16.1:** Plexiglass is a polymer of methyl methacrylate. Show a mechanism for the first two propagation steps of polymerization (use  $X\cdot$  to denote the radical initiator), and show a structure for the plexiglass polymer. Assume an alkene addition process similar to that shown in the text for polyethylene.



**P16.2:** In section 16.3 we saw how acrylamide polymerizes to form the polyacrylamide used in PAGE protein gels. Polyacrylamide by itself is not sufficient by itself to form the gel - the long polyacrylamide chains simply slip against each other, like boiled spaghetti. To make a PAGE gel, with pores for the proteins to slip through, we need a crosslinker - something to tie the chains together, forming a three-dimensional web-like structure. Usually, a small amount of bis-acrylamide is added to the acrylamide in the polymerization mixture for this purpose.

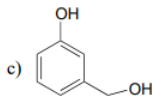
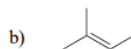
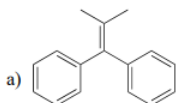


Propose a radical mechanism showing how bis-acrylamide might form crosslinks between two polyacrylamide chains.

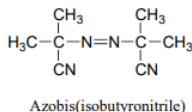
**P16.3:** Resveratrol is a natural antioxidant found in red wine (see section 16.5 for the structure).

- Draw one resonance structure to illustrate how the resveratrol radical is delocalized by resonance.
- Indicate all of the carbons on your structure to which the radical can be delocalized.
- Draw an alternate resveratrol radical (one in which a hydrogen atom from one of the other two phenolic groups has been abstracted). To how many carbons can this radical be delocalized?
- The curcumin structure is shown in the same figure as that of resveratrol, in section 16.5. Draw two resonance contributors of a curcumin radical, one in which the unpaired electron is on a phenolic oxygen, and one in which the unpaired electron is on a ketone oxygen.

**P16.4:** Draw the radical intermediate species that you would expect to form when each of the compounds below reacts with a radical initiator.



**P16.5:** Azobis(isobutyronitrile) is a widely used radical initiator which rapidly undergoes homolytic decomposition when heated.



Predict the products of this decomposition reaction, and show a likely mechanism. What is the thermodynamic driving force for homolytic cleavage?

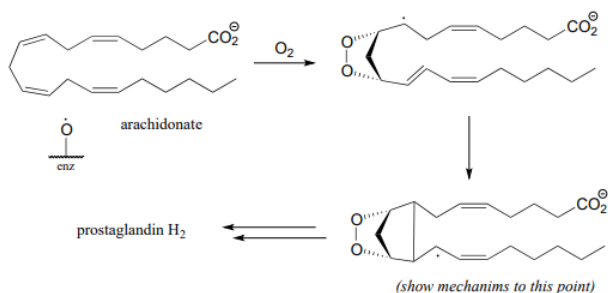
**P16.6:**

- When 2-methylbutane is subjected to chlorine gas and heat, a number of isomeric chloroalkanes with the formula  $C_5H_{11}Cl$  can form. Draw structures for these isomers, and for each draw the alkyl radical intermediate that led to its formation.
- In part a), which is the most stable radical intermediate?
- In the reaction in part a), the relative abundance of different isomers in the product is not exclusively a reflection of the relative stability of radical intermediates. Explain.

**P16.7:** We learned in chapter 14 that  $HBr$  will react with alkenes in electrophilic addition reactions with 'Markovnikov' regioselectivity. However, when the starting alkene contains even a small amount of contaminating peroxide (which happens when it is allowed to come into contact with air), a significant amount of 'anti-Markovnikov' product is often observed.

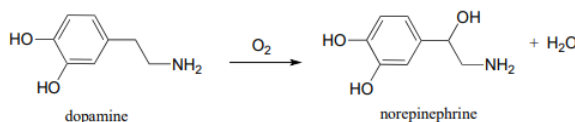
- Propose a mechanism for formation of the anti-Markovnikov addition product when 1-butene reacts with  $HBr$  containing a small amount of benzoyl peroxide
- Predict the product and propose a mechanism for the addition of ethanethiol to 1-butene in the presence of peroxide.

**P16.8:** In section 11.5 we learned that aspirin works by blocking the action of an enzyme that catalyzes a key step in the biosynthesis of prostaglandins, a class of biochemical signaling molecules. The enzyme in question, prostaglandin  $H$  synthase (EC 1.14.99.1) catalyzes the reaction via several single-electron steps. First, an iron-bound oxygen radical in the enzyme abstracts a hydrogen atom from arachidonate. The arachidonate radical intermediate then reacts with molecular oxygen to form a five-membered oxygen-containing ring, followed by closure of a cyclopentane ring to yield yet another radical intermediate. (Biochemistry 2002, 41, 15451.)

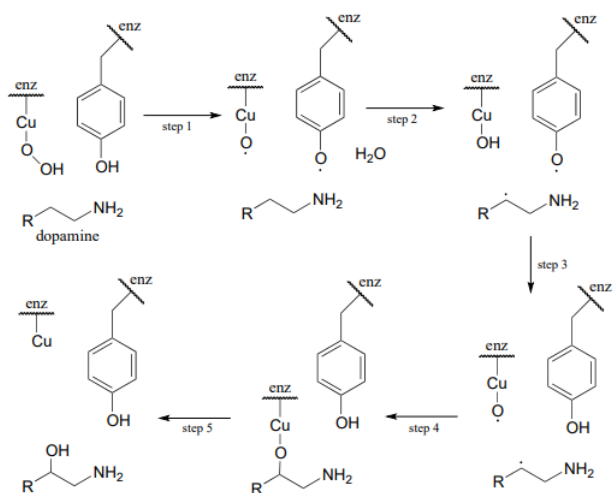


Propose a mechanism for the steps of the reaction that are shown in this figure.

**P16.9:** Some redox enzymes use copper to assist in electron transfer steps. One important example is dopamine  $\beta$ -monooxygenase (EC 1.14.1.1), which catalyzes the following reaction:



The following intermediates have been proposed: (see Biochemistry 1994, 33, 226) Silverman p. 222



Draw mechanistic arrows for steps 1-4.

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