

Chemistry 210

Exam III

University of Missouri-Columbia
Dr. Rainer Glaser
November 20, 1992

Name:

Answer Key

	Max.	Yours
Question 1	20	
Question 2	20	
Question 3	15	
Question 4	30	
Question 5	15	
Total	100	

Do not turn the page until advised to do so.

Question 1. Preparation of Alkynes. (20 points)

For each of the following preparations, clearly show every step of the reaction and show all of the reagents required for each step. It is not necessary to give the mechanism of these steps; just give starting materials, reagents and products for each step.

(a) Suggest a synthesis of the terminal alkyne butyne, $\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$, starting from the terminal butene, $\text{H}_3\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$. (8 points).

- (1) Bromination of the alkene yields the 1,2-dibromobutane. (2.5 p.)
- (2) Dibromide + 2 NaNH_2 , - 2 NaBr , - 2 NH_3 gives the butyne. (2.5 p.)
- (3) Butyne formed is deprotonated by the base present; + NaNH_2 , - NH_3 . (1.5 p.)
- (4) Reaction of the sodium acetylide with aqueous acid gives butyne. (1.5 p.)

Show all this in structural formulae.

(b) Now that we have made the terminal alkyne butyne, $\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$, let's use it to prepare the much larger, nonterminal, symmetric alkyne, $\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}_3$. Show how. The name of this alkyne is of course hexyne-3. (4 points for synthesis, 2 points for name)

- (1) Deprotonate with NaNH_2 ; $+\text{NaNH}_2$, $-\text{NH}_3$. (2 points)
- (2) Sodium acetylide reacts with *ethylchloride* to form product and NaCl . (2 points)

Show all this in structural formulae.

(c) With the terminal alkyne butyne, $\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$, we can also make the alcohol 3-hexyne-2-ol, $\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}(\text{OH})-\text{CH}_3$. Show how. (6 points for synthesis)

- (1) Deprotonate with a Grignard Reagent such as MeMgBr ; eliminates CH_4 . (2 points)
- (2) Magnesiumbromide acetylide reacts with *acetaldehyde* \rightarrow alcoholate of product. (2 p.)
- (3) Aqueous acid makes alcohol from alcoholate. (2 points)

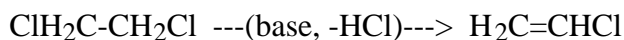
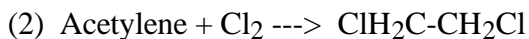
Show all this in structural formulae. Will accept any Grignard reagent. Will also accept other reasonable organometallic compounds.

Question 2. Reactions of Acetylenes. (20 points)

(a) Give a preparation of vinylchloride from acetylene. (Can be done in several ways, show one). (4 p)



or



(b) Let's take the symmetrical alkyne H₃C-CH₂-C≡C-CH₂-CH₃ and hydrate it. For this hydration, we use a dilute acid such as aqueous H₂SO₄. In addition, it is important to add a catalyst. Show all steps of the reaction and give the catalyst. Name the final product. What type of reaction occurs in the last step of the reaction? (8 points)

Catalyst is a "small metal cation" catalyst, strong Lewis acid: HgSO₄. (1.5 point)

The product is ethyl propyl ketone. (1 point)

The last step is a "tautomerization". (1.5 point)

(1) Add water to get the vinyl alcohol. (2 points)

(2) Tautomerize to ketone. (2 points)

Structural formulae need to be shown for all steps.

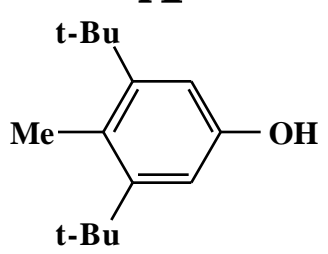
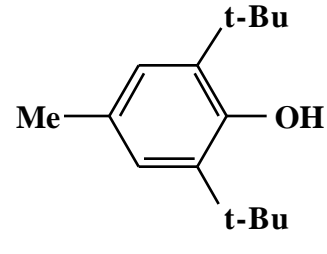
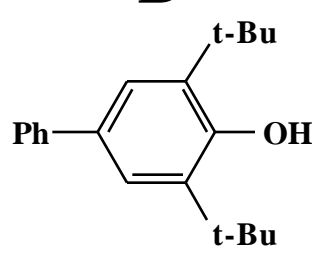
(c) A nice way to reduce alkynes to alkenes consists in the reduction with lithium metal in liquid ammonia. Show this reaction for H₃C-CH₂-C≡C-CH₂-CH₃ and fully name the product. (4 points for filling the gaps, 4 points for the synthesis and name)

Easy, but you need to remember that this gives the *trans* product.

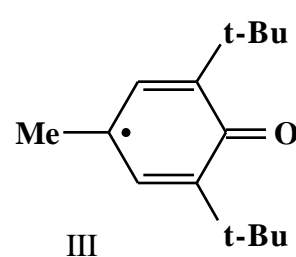
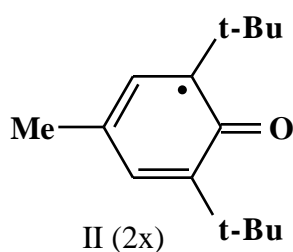
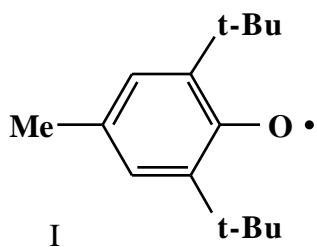
Name: *trans* hexene-3 or (E) hexene-3 (number can be in front)

Question 3. Inhibitors. (15 points)

BHT is a powerful radical inhibitor which is widely used as a preservative. Examine the slightly modified compounds **A** and **B**. Indicate for each whether it would be a better or worse inhibitor. Explain your answers carefully using resonance forms. (15 points)

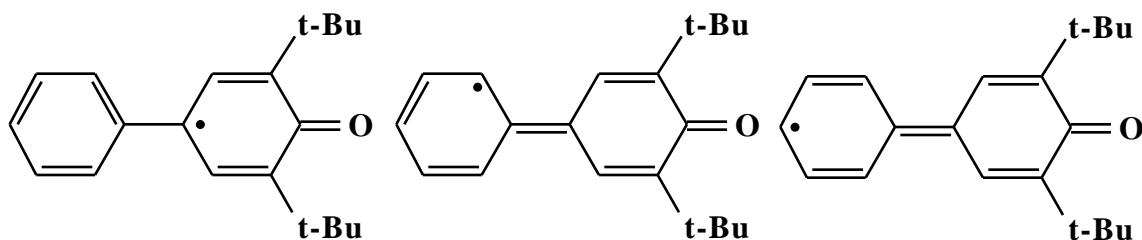
<p>A</p> 	<p>BHT</p> 	<p>B</p> 
<p>Better/Worse? (1.5 p)</p> <p>WORSE</p>		<p>Better/Worse? (1.5 p.)</p> <p>BETTER</p>

Explain your answers regarding **A** and **B** (6 p. each)

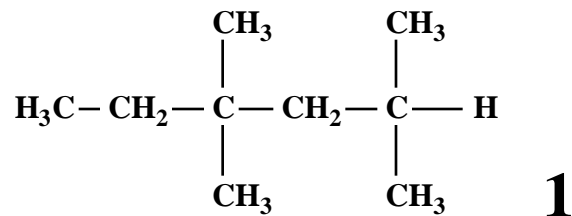


A is worse because the t-Bu groups are no longer at a place with spin density (as in II); thus they don't help stabilizing the radical.

B is much better because it allows for a delocalization of the spin density into the other ring. For example, the following resonance forms also are important.

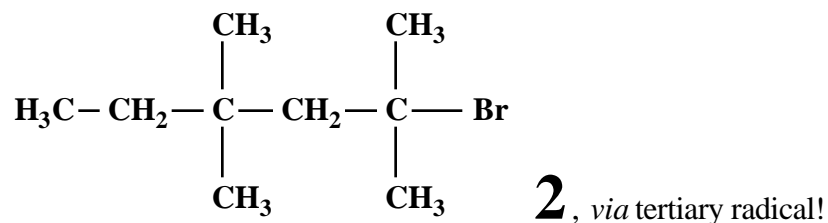


Question 4. Radical Chain Reactions. (30 points)

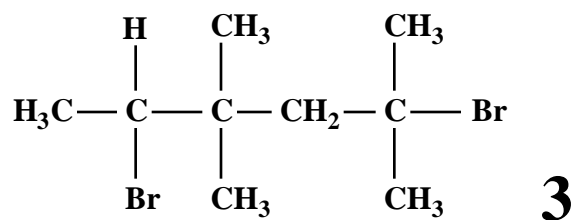


There are 20 hydrogen atoms in **1**. In case it matters, note that 100/20 is a nice and even 5.

(a) Show the most likely product **2** resulting from single bromination of **1**. Explain. (5 points)



(b) Show the most likely product **3** resulting from a second bromination of **2**. Give the two propagation steps for the preparation of **3** from **2**. (7 points)



second bromination at *less hindered & secondary* C. (3 points)

- (1) H abstraction from **2** yields secondary C radical. (2 points)
- (2) Reaction of C radical with Br₂. (2 points)

These steps should be shown with structural formulae.

Question 5. Polymers. (15 points)

Polyvinylchloride, or PVC for short, is widely in use for floor coverings and the like. PVC is prepared by radical chain polymerization of the monomer vinylchloride (give the name). We made this monomer above from acetylene. This polymerization starts with an initiation reaction, continues with a reaction between the starter radical and a monomer, and then propagates with a radical chain step and head-tail (head-tail, head-head, tail-tail) regiochemistry. (1 p. each blank)

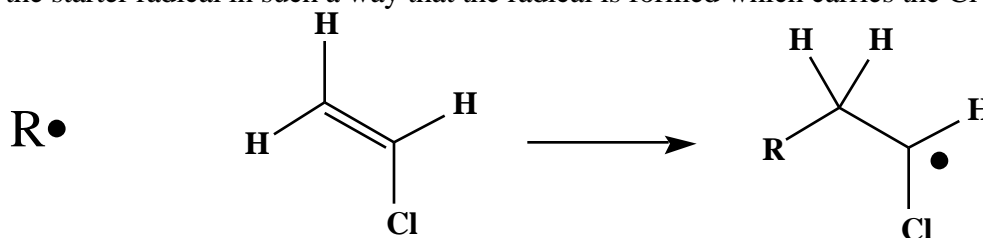
Give a typical initiator and its initiation reaction: (3 points)

Show any one of the three initiators discussed in the lecture.

In the following, the starter radical will be abbreviated R•

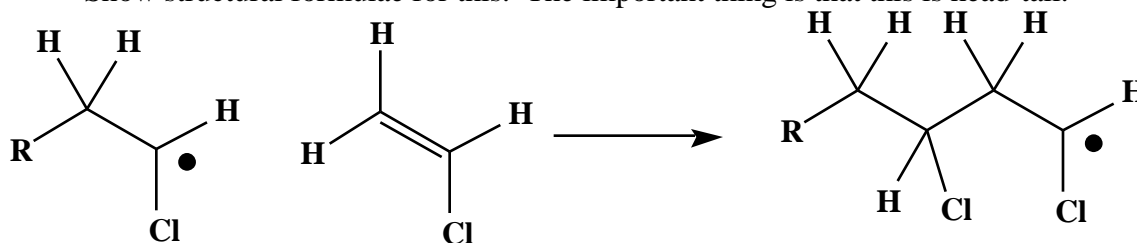
Show the reaction between the starter radical and the alkene. Pay attention to regiochemistry. (5. p)

Add the starter radical in such a way that the radical is formed which carries the Cl atom.



Show the radical chain propagation step. Pay attention to regiochemistry. (5. p)

Show structural formulae for this. The important thing is that this is head-tail.



/ The End /