

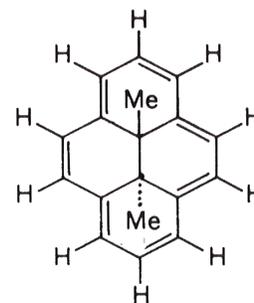
Chemistry 125 Seventh Examination
April 8, 2011

Name _____

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided. Question values correspond to allotted time. Don't waste too much time on cheap questions.

1. (3 min) Chemical shift and spin-spin splitting are important topics in chemical NMR spectroscopy. Explain whether these phenomena should be important in diagnostic MRI.

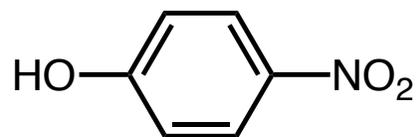
2. (4 min) Suppose you had two samples, one containing the hydrocarbon shown and another containing the same hydrocarbon after it had been treated with potassium metal in an inert solvent. Explain how you could tell which is which using NMR spectroscopy.



3. (5 min) **Explain** the **isomer distribution** in the product of mononitration of chlorobenzene **AND** explain whether you would need to be concerned about loss of this product due to its **further reaction** to give dinitrochlorobenzenes.

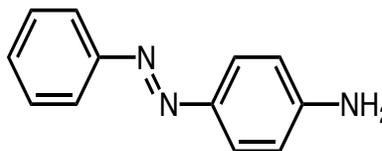
4. These pairs of numbers are relevant for distinguishing spectroscopically between (Z) and (E) disubstituted alkenes:
- 967 vs. 710 cm^{-1} 6-12 vs. 12-18 Hz
- A. (2 min) In each pair **CIRCLE** the member that indicates a (Z) alkene.
- B. (6 min) Choose **ONE** of the pairs of numbers and explain in detail **WHY** the isomers differ in this way.

5. (6 min) **Draw the multistep mechanism (curved arrows)** for forming the dimethylketal of 2-propanone (acetone), **AND explain** whether the equilibrium constant for formation of this ketal should be more or less favorable than that for forming the corresponding ketal of acetaldehyde ($\text{CH}_3\text{-CHO}$).



6. (5 min) p-Nitrophenol is a pH indicator changing from colorless to yellow (*i.e.* from absorbing only ultraviolet light to absorbing blue light) at pH 6. **Explain** which form (**acidic or basic**) should be colored **AND** which **orbitals** are mixed by the blue light.

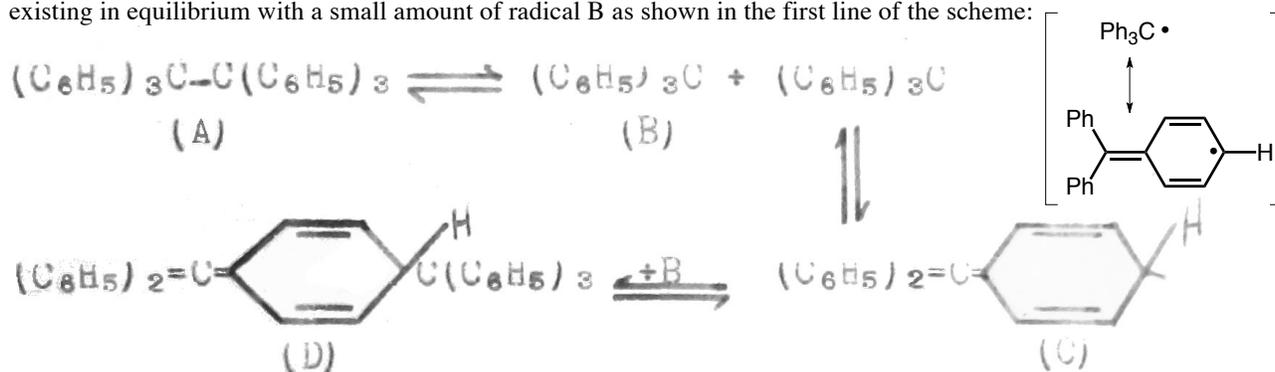
7. (5 min) Suggest a series of reactions that would allow preparing "aniline yellow" from benzene. Use any reagents you wish, but benzene must be the only source of carbon in the product. [HINT from Class of '98S]



Gomberg's Hydrocarbon

8. (2 min) What evidence suggested to Moses Gomberg in 1900 that the "hexaphenylethane" he had prepared was in fact the triphenylmethyl radical?

9. The scheme below is copied from the 1921 Ph.D. thesis of a Gomberg student at the University of Michigan. By this time Gomberg had decided that the "Gomberg Hydrocarbon" was mostly hexaphenylethane (A), a dimer existing in equilibrium with a small amount of radical B as shown in the first line of the scheme:



Structure C in the second line of the 1921 scheme is shown as if it were in equilibrium with the triphenylmethyl radical (B) in the top line. We would regard C as a resonance structure of B, drawing a vertical double-headed arrow and a dot instead of the short line at the far right of C. Note also that what appears to be the left-most double bond of C is in fact two single bonds between the carbon atom shown as =C= and the two C_6H_5 phenyl groups (see inset).

Gomberg's hexaphenylethane-triphenylmethyl equilibrium was accepted as gospel for more than half a century, until Dutch workers measured the 60 MHz **proton NMR** spectrum of Gomberg's hydrocarbon in 1968. They observed a complex pattern (integral 25 proton) at 6.8-7.4 ppm, a distorted pair of doublets ($J \sim 9\text{Hz}$, 4 protons) at 5.8-6.4 ppm, and a singlet proton signal at 5.0 ppm. [There may have been additional unreported splitting with very small J .]

Two years later a German group reported the ^{13}C NMR spectrum of a sample that had been prepared from $\text{Ph}_3^{13}\text{CCl}$. They observed two signals at 17 and 83 ppm from TMS, which is obviously inconsistent with the symmetrical $\text{Ph}_3\text{C}-\text{CPh}_3$ structure for the radical dimer..

- A. (6 min) Draw a structure for Gomberg hydrocarbon that is consistent with these two NMR spectra and label the atoms with the reported chemical shifts.

Question 9, cont.

- B.** (2 min) Explain how the proposed structures for Gomberg's hydrocarbon relate to Victor Meyer's thinking about Fischer esterification of dimethylbenzoic acid.
- C.** (2 min) Explain very briefly how the distorted pair of doublets at 5.8-6.4 ppm in the proton NMR spectrum might appear different if measured with a modern NMR spectrometer.
- D.** (2 min) What **reagents** would you use to prepare $\text{Ph}_3^{13}\text{CCl}$ from benzene and some simple molecule containing ^{13}C ?