

Exercise 12 - Controversial Chemicals: Syntheses and Issues

Because this exercise involves challenges that have multiple solutions, specific answers will not be provided here. One possible approach to these exercises is to have a class discussion. A group approach might also be worthwhile with each group critically evaluating the solutions of other groups.

- A. Di-2-ethylhexyl phthalate
 - 1. Should you be concerned that the mono ester will be formed and complicate the purification procedure?
 - 2. An alternative synthesis of phthalate esters involves the use of organic titanates. [see: <http://www.dupont.com/tyzor/pdf/plasticizer.pdf>]. Because of scale up and cost considerations, industrial organic syntheses often use techniques and catalysts that are not practical for the organic chemistry laboratory environment. For example, nylon 66 is easily prepared in the laboratory from 1,6-hexanediamine and adipoyl chloride. Industrially, the much cheaper adipic acid is used instead of adipoyl chloride. Because of the conditions required, adipic acid is not practical for use in the organic lab but is suitable for industrial conditions. Would the use of organic titanates be possible in your organic chemistry laboratory? Explain your answer.
- B. MTBE (methyl-t-butyl ether)
- C. Naproxen and Ibuprofen (comment on the structural relationship of these two chemicals)
- D. Aldrin or Chlordan(e)
- E. Chloroethene (vinyl chloride)
- F. Acrylamide
- G. Methyl methacrylate
- H. Bisphenol A
- I. Biacetyl
- J. BFR's (brominated fire retardants)
- K. Melamine

Exercise 13 - Material Selection

Material Selection Using the Internet. The very interesting and increasingly important field of material science involves determination of the properties of a material needed for an application and then selection and testing of possible materials. A very useful site for selecting polymers and metals for particular applications is:

<http://www.matweb.com/> <http://www.matweb.com/search/PropertySearch.aspx>

- | | | |
|--|---------------------------------|--|
| 1. aluminum. | density (g/cm ³) | 2.6989 |
| | electrical resistivity (ohm-cm) | 2.70x10 ⁻⁶ |
| | melting point (°C) | 660.37 |
| 2. Plexiglas VO52. | kind of polymer | <i>thermoplastic acrylic resin</i> |
| | water absorption (%) | 0.300 |
| | Vicat softening point (°C) | 97.2 |
| | transmission visible (%) | 92 |
| 3. Material selection - Polymers | | |
| a. 2 L bottle | desirable properties | <i>strength, transmission, water absorption, melting point, ability to be recycled, cost, toxicity</i> |
| | possible plastics | <i>PET, PE, polystyrene, polycarbonate, acrylic</i> |
| b. frying pan coating | desirable properties | <i>melting point, toxicity, cost</i> |
| | possible plastics | <i>PTFE (teflon)</i> |
| c. cell phone case | desirable properties | <i>strength, cost</i> |
| | possible plastics | <i>ABS, PBT</i> |
| d. food storage bags | desirable properties | <i>strength, transparency, water absorption, biodegradability, cost, inert</i> |
| | possible plastics | <i>PRT, PE, PVDC</i> |
| 4. Material selection - Metals and/or Metal Alloys | | |
| a. bicycle frame | desirable properties | <i>strength, cost, density, resistance to oxidation</i> |
| | possible metals | <i>titanium, aluminum, steel</i> |
| b. solder | desirable properties | <i>melting point electrical resistivity</i> |
| | possible metals | <i>silver solder</i> |
| c. electrical wire | desirable properties | <i>electrical resistivity, melting point, cost, malleability, strength</i> |
| | possible metals | <i>copper, aluminum</i> |
| d. nails | desirable properties | <i>strength, resistance to oxidation, cost</i> |
| | possible metals | <i>iron, steel</i> |

Exercise 14 - Thought Provoking Problems

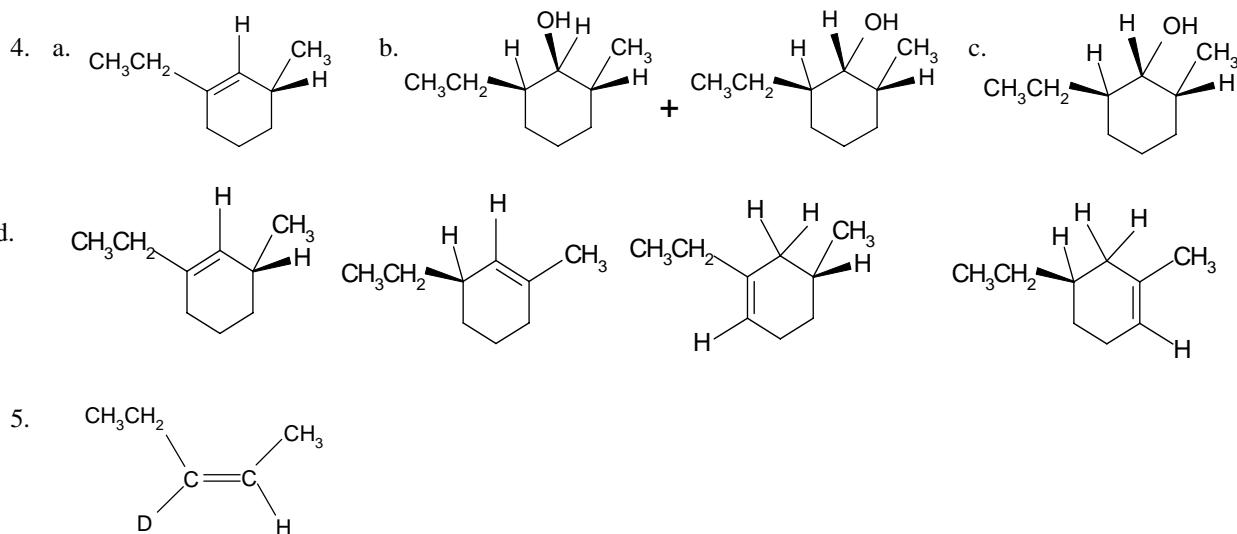
1. 1,2-Propadiene, also called allene, is the parent compound of a rare and here-to-fore rather neglected class of compounds that contain cumulated π bonds.
 - a. *The central carbon of allene is sp hybridized. As a result, the π bonds on either side of the central carbon are orthogonal. As a result the sp^2 orbitals on the 1 and 3 carbons must be in planes that are perpendicular to each other resulting in hydrogens on each end that are in perpendicular planes.*
 - b. *Hydrogenation of the three pentadienes is exothermic and results in the same product in all three cases. This means that the lower the heat of hydrogenation, the more stable the compound. Because of the interaction of the conjugated π bonds, 1,3-pentadiene is the most stable. 2,3-Pentadiene is the least stable for reasons that are difficult to describe.*
 - c. *Like a tetrahedral carbon, the CCC center has a 3 dimensional configuration around it and because of this, when the CCC has 4 different groups attached to it, there is no mirror plane in the molecule.*

2. Answer the questions below for each of the addition reactions listed:

a. reagent	# of products that can be separated	optically active fractions
HBr	2	1
HCl	2	2
Br ₂	2	2
Br ₂ /peroxide	1	1

b. How many of the fractions are optically active?

3. a. 3-bromo-3-methyl-1-butene at low temp.
1-bromo-3-methyl-2-butene at high temp.
b. Protonation in the 2 position yields the most highly resonance stabilized carbocation.



6. *The first step in S_N1 and $E1$ reactions is the cleavage of the carbon to leaving group bond to form a carbocation. Carbocation carbons are sp^2 hybridized. A planar carbocation cannot be achieved in this structure thus the intermediate would be very high in energy and could only go at very high temperature. In addition, the elimination would yield an extremely strained ring system. S_N2 reactions proceed through back side attack and inversion at the reaction center. Approach from the backside is not possible and inversion is not possible with this tied back carbon. Among other problems for the $E2$ like an $E1$ is the extremely strained ring system that would result (a violation of Bredt's law).*

7. a. cyclohexane (and other rings), 2,2-dimethylpropane
b. 5 isomers with 3 active.
8. (R)-1-Fluoro-2-cyanopropane (The reaction goes with inversion but there is a priority change for determining configuration)
9. In both cases, the 5 membered rings achieve a $4n + 2 \pi$ system by “borrowing” a pair of electrons from the rest of the molecule. The higher electron density in the 5 membered ring results in a dipole from the positive end to the high electron density 5 membered ring.
10. For the resonance structure of the intermediate with the positive charge on the carbon bearing the vinyl (happens for ortho or para attack) an additional resonance structure is possible. Inductively, the vinyl group should be fairly neutral as it has an sp^2 carbon bonded to the sp^2 carbon in the ring. The Hammett σ values for meta and para are 0.05 and -0.02 consistent with the resonance stabilization prediction.
11. This is evidence that the breaking of the C-H (or C-D) bond is not part of the rate determining step. This observation is consistent with the accepted mechanism in which the electrophile attacks and forms a resonance stabilized intermediate in the rate determining step of electrophilic aromatic substitutions. The change to the C-H bond is primarily a change in hybridization and does not cause a significant isotope effect.
12. $CH_3CDOHCH_2CH_3$
13. A = (3R)-3-methyl-1-pentene B = 3-methylpentane C = 2-methylbutanal
14. a. This evidence supports attack of the ethanolic oxygen on the carboxyl carbon rather than displacement of the ethanolic OH by the ethanol.
b. This evidence supports reversible formation of a tetrahedral intermediate that results from attack of the water on the carboxyl carbon.
15. c, e, g, h, j, k, n, o all have $4n + 2 \pi$ electrons in a planar cyclic system. i appears to meet this requirement but the hydrogens inside the ring sterically interact and force the ring far enough out of planar to prevent aromaticity. k has 16 electrons but the two central electrons act like a localized π bond leaving a 14 π electron system.
16. One of the enantiomers of 2,4-dimethyl-2-hexene.
17. Since the hydrogenation eliminates the chirality, there must be a central carbon bonded to either a vinyl and an ethyl with the remaining alkyl group a propyl or isopropyl or a propenyl (cis or trans) and propyl or an allyl and propyl. Since each could be R or S there are 10 possibilities. While nmr could probably limit the number of possibilities, distinguishing them will probably require matching ir or nmr spectra.
18. C could be ethylbenzene or 1,3-dimethylbenzene.
19. Visible spectrophotometers measure the amount of absorption and the wavelength much more precisely than the eye. While the gas chromatograph does depend on volatility and absorptivity, the mechanism of smell has not been duplicated by an instrument. Until the mechanism of smell is understood it will not be possible to attempt to make an instrument that measures the same parameters.
20. Since the visible reason involves electron transitions, it was possible for life to evolve with a mechanism for distinguishing transitions of different wavelengths. Ultraviolet is more challenging as there is enough energy to break bonds and destroy molecules. Humans do detect infrared in the form of heat by touch but distinguishing wavelengths in the ir is a challenge even for instrument makers.
21. This will be left for class discussion but there are limitations to size and necessary physical features for manipulation, movement, sensing, communicating, reproducing and energy consumption. Notice that despite the diversity of life on earth, there are many common features to nature's creatures.