Exercise 12

Controversial Chemicals: Syntheses and Issues

Fig. X12-1

Rachel Carson (1907 - 1964)
Author of the world awakening environmental book *Silent Spring*.

"The more clearly we can focus our attention on
the wonders and realities of the universe about us,
the less taste we shall have for destruction."
Rachel Carson ©1954

Discussion

From medicines to plastics and food preservatives to pesticides, we live in a world of synthetic organic chemicals that help to enhance life and make it more enjoyable. However, chemistry often gets a bad rap as people tend to focus on the negative aspects of chemistry while ignoring the many benefits. As an example, DDT has been banned because it is persistent in the environment (about a 20 year half life) and is very harmful to wildlife. Birds are especially susceptible to its effects as DDT causes thinning and breaking of egg shells. On the other side of the coin, however, DDT saved millions of lives by helping to control the mosquito population that is responsible for the spread of malaria. However, the toxicity of DDT to mosquitos considerably decreased with usage as mosquitos developed resistance to DDT. Fortunately, the use of DDT has substantially decreased and better alternatives have been developed. One of the lessons here is that we need to thoroughly test chemicals for potential negative side effects before putting the chemical into widespread use.

This exercise will focus on some chemicals that have caused some controversy regarding their use. These chemicals have been selected because they probably could be synthesized in a few steps in an undergraduate organic chemistry laboratory from commercially available chemicals. You should suggest a possible synthetic pathway (appropriate for your organic chemistry course) to the chemical from commercially available chemicals. To determine the availability and cost of chemicals, you should refer to a hard copy of a chemical catalog (such as Aldrich) or to one of the online chemical catalogs.

Chemical catalogs (contain some properties and/or MSDS) -

a. Aldrich, Sigma, Fluka (now with MSDS) - http://www.sigmaaldrich.com/
b. Alfa - http://www.alfa.com/alf/laboratory_chemical_suppliers.htm
c. Arcos and Fisher - http://www.fishersci.com/
d. JT Baker (&Mallinckrodt) - http://www.mallbaker.com/changecountry.asp?back=/Default.asp
e. Acros - http://www.acros.com/portal/alias__Rainbow/lang__en/tabID__21/DesktopDefault.aspx
f. Chemicalland - http://www.chemicalland21.com/listaz01.htm

In addition, you should perform an Internet search on the chemical to determine the applications and problems with the chemical. Answer the questions about each chemical, write a paragraph on the issues surrounding the chemical and make a recommendation regarding its future use.

The following sites are good starting points for online syntheses:

Organic Synthesis - http://www.orgsyn.org/ (requires plug-in)
http://webreactions.net/
http://www.chempensoftware.com/organicreactions.htm
http://www.monomerchem.com/display4.html
http://www.alsnotebook.com/exp.proc.intro..html
http://cmldprotocols.bu.edu/cmld/index.jsp
http://www.chemthes.com/rxn-type.php
http://cssp.chemspider.com/About.aspx
http://www.organic-chemistry.org/reactions.htm
http://synthesisexplorer.rsc.org/

For health and environmental effects of chemicals, the sites below could be useful. It is also possible to obtain information by googling the name of the compound.

http://ull.chemistry.uakron.edu/erd/
http://www.syrres.com/esc/chemfate.htm
http://chem.sis.nlm.nih.gov/chemidplus/ or http://chem.sis.nlm.nih.gov/chemidplus/chemidlite.jsp
http://pubchem.ncbi.nlm.nih.gov/
http://www.nlm.nih.gov/pubs/factsheets/toxnetfs.html
http://www.cdc.gov/niosh/npg/npgsyn-a.html
http://www.epa.gov/chemfact/
http://www.ilo.org/safework/info/databases/lang--en/WCMS_113134/index.htm

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