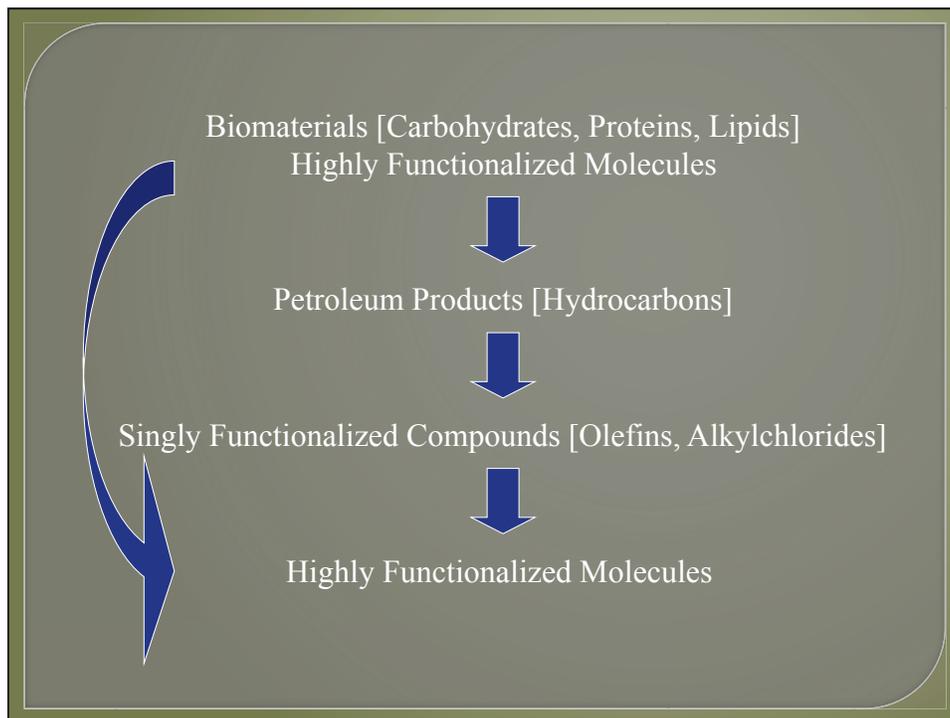


Energy usage

Chemicals and petroleum industries account for 50% of industrial energy usage.

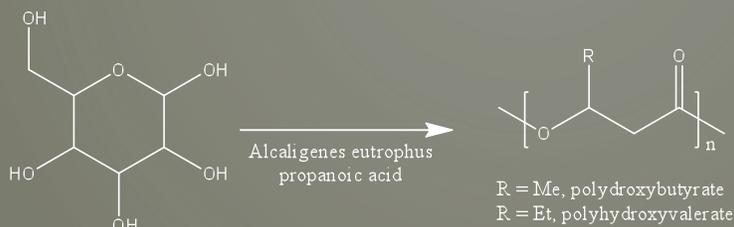
~1/4 of the energy used is consumed in distillation and drying processes.

7. Use of Renewable Feedstocks



Polymers from Renewable Resources: Polyhydroxyalkanoates (PHAs)

- Fermentation of glucose in the presence of bacteria and propanoic acid (product contains 5-20% polyhydroxyvalerate)
- Similar to polypropene and polyethene
- Biodegradable (credit card)



Polymers from Renewable Resources: Poly(lactic acid)



Beverages find a natural fit with NatureWorks® PLA packaging.

Beverages are enhanced with containers and labels made from NatureWorks PLA. Showcase your brand while allowing consumers to see and taste pure product. Even more refreshing is consumer reaction to the NatureWorks brand story. Market research clearly shows that consumers believe that beverages packaged in containers made from nature are fresher and more wholesome. Performance and the environmental attributes of bottles and labels made from PLA can provide you with a strong point of differentiation.



http://www.natureworkslc.com/corporate/nw_pack_home.asp

Raw Materials from Renewable Resources: The BioFine Process



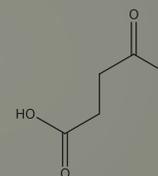
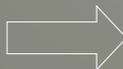
Paper mill
sludge



Agricultural
residues,
Waste wood



Municipal solid waste
and waste paper

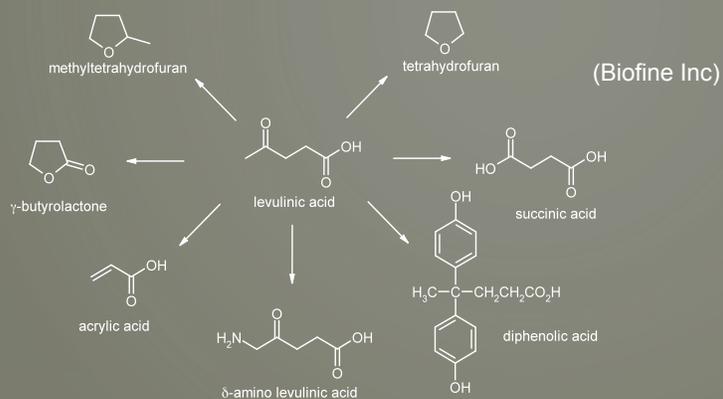


Levulinic acid

Green Chemistry Challenge Award
1999 Small Business Award

Levulinic acid as a platform chemical

- Conversion of waste biomass to levulinic acid
 - paper mill sludge, municipal solid waste,
 - unrecyclable waste paper, agricultural residues



8. Reduce Derivatives

Protecting Groups

2 synthetic steps are added each time one is used
Overall yield and atom economy will decrease

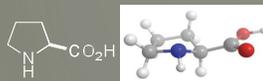
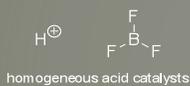
“Protecting groups are used because there is no direct way to solve the problem without them.”

9. Catalysis

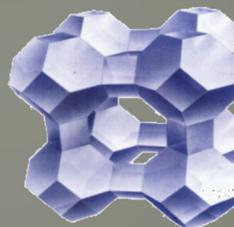
Different types of catalysts



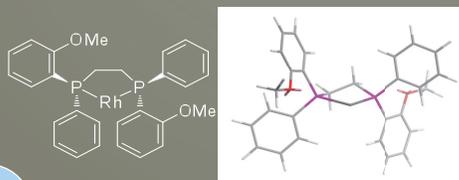
enzyme (biocatalyst)



L-proline (organocatalyst)



zeolite (crystalline aluminosilicate)



(R,R)-DIPAMP-Rh (organometallic complex)



copper-zinc crystallites on silica

Heterogeneous vs Homogenous

Heterogeneous

- Readily separated ✓
- Readily recycled / regenerated ✓
- Long-lived ✓
- Cheap ✓
- Lower rates (diffusion limited) ✗
- Sensitive to poisons ✗
- Lower selectivity ✗
- High energy process ✗
- Poor mechanistic understanding ✗

Homogeneous

- Difficult to separate ✗
- Difficult to recover ✗
- Short service life ✗
- Expensive ✗
- Very high rates ✓
- Robust to poisons ✓
- Highly selective ✓
- Mild conditions ✓
- Mechanisms often known ✓

Ultimate goal: to combine the fast rates and high selectivities of homogeneous catalysts with the ease of recovery / recycle of heterogeneous catalysts

10. Design for Degradation

Persistence

Early examples

- Sulfonated detergents
 - Alkylbenzene sulfonates – 1950's & 60's
 - Foam in sewage plants, rivers and streams
 - Persistence was due to long alkyl chain
 - Introduction of alkene group into the chain increased degradation
- Chlorofluorocarbons (CFCs)
 - Do not break down, persist in atmosphere and contribute to destruction of ozone layer
- DDT
 - Bioaccumulate and cause thinning of egg shells

Degradation of Polymers: Polylactic Acid

- ◆ Manufactured from renewable resources
 - Corn or wheat; agricultural waste in future
- ◆ Uses 20-50% fewer fossil fuels than conventional plastics
- ◆ PLA products can be recycled or composted

Cargill Dow

11. Real-time Analysis for Pollution Prevention

12. Inherently Safer Chemistry for Accident Prevention

Inherently Safer Chemistry for Accident Prevention

Tragedy in Bhopal, India - 1984

In arguably the worst industrial accident in history, 40 tons of methyl isocyanate (MIC) were accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 15,000 people died and hundreds of thousands more were injured.

Chemists try to avoid things that explode, light on fire, are air-sensitive, etc.

In the "real world" when these things happen, lives are lost.

Minimize hazard

- ◆ Catalytically synthesize methylisocyanate to reduce risk of exposure
 - eliminates use of phosgene

Manzer, DuPont

OLD SYNTHESIS OF METHYLISOCYANATE



NEW SYNTHESIS OF METHYLISOCYANATE



PROTECT YOUR CHILDREN Against Disease-Carrying Insects!



TRIMZ DDT
CHILDREN'S ROOM
WALLPAPER and Ceiling
Paper

KILLS FLIES, MOSQUITOS, ANTS
... as well as moths, bedbugs, silverfish and other household pests after contact!

MEDICAL SCIENCE KNOWS many common insects breed in filth, live in filth and carry disease. Science also recognizes the dangers that are present when these disease-carrying insects invade the home. Actual tests have proved that one fly can carry as many as 6,000,000 bacteria! Imagine the health hazard—especially to children—from flies seriously suspected of transmitting such diseases as scarlet fever, measles, typhoid, diarrhea... even dread polio! Some types of mosquitos carry malaria and yellow fever. And any mosquito bite is painful and easily infected when scratched.

NON-HAZARDOUS to children or adults, to pets or clothes. Certified to be absolutely safe for home use. Tested and commended by Parents' Magazine.

GUARANTEED effective against disease-carrying insects for 1 year. Actual tests have proven the insect-killing properties still effective after 2 years of use.

NO SPRAYS! NO LIQUIDS! NO POWDERS! So convenient, so safe because the DDT is fixed to the paper. It can't rub off!

BEAUTIFUL! "Jack and Jill" or "Disney Favorites"—any new patterns that protect as they beautify a child's room. **DDT CEILING PAPERS, TOO!** Extra protection for your child's room—for every other room in the house. Choice of two tints.



Just Dip in Water and Apply

READY-PASTED! Just Dip in Water and Hang!
Anyone can put Trimz Wallpaper up without help or previous experience. Millions have done it—proved it's quick, clean, easy! Nothing to get ready—no tools, paste or mess. Just cut strips to fit, dip in water and hang. It's dry in 20 minutes! Guaranteed to stick—guaranteed to please or money back. And so inexpensive! You can protect your child for \$8 to \$12—depending on size of room.

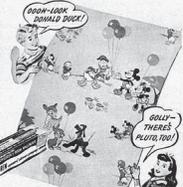
Trimz DDT Children's Room Wallpaper, Trimz DDT Cedar Closet Wallpaper now available at Department, Chain, Hardware, Paint, and Wallpaper stores everywhere.

Many beautiful new patterns also available in regular Trimz Ready-Pasted Wallpaper at \$1.98, \$2.49, \$2.99 per box.

TRIMZ READY-PASTED WALLPAPER

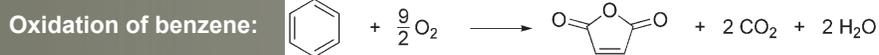
Another Product of TRIMZ CO., INC., Division of UNITED WALLPAPER

World's Leading Designer and Largest Manufacturer, Merchandise Mart, Chicago 54, Illinois



Case study

Maleic anhydride may be prepared using two routes:

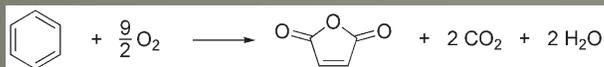


The benzene oxidation route typically occurs in 65 % yield and produces 35 g non-benign waste for every 100 g benzene used, while the but-1-ene route only gives yields of 55 %, and produces 45 g waste per 100 g but-1-ene.

- (a) Assuming that each reaction is performed in the gas phase only, and that no additional chemicals are required, calculate (i) the atom economy and (ii) the effective mass yield of both reactions. You should assume that O_2 , CO_2 and H_2O are benign chemicals.
- (b) Which route would you recommend to industry? Outline the factors which might influence your decision.

Case study

Benzene Oxidation



RMM of reactants = $78 + (4.5 \times 32) = 222$
 RMM of desired product = 98

\therefore Atom economy = 44 %

But-1-ene Oxidation



RMM of reactants = $56 + (3 \times 32) = 152$
 RMM of desired product = 98

\therefore Atom economy = 64 %

Case study

There are several ways of tackling this question - this is one way...

Benzene Oxidation

100 g benzene (1.28 mol) would give 81.5 g maleic anhydride (0.83 mol, 65 %).

$$\begin{aligned} \text{EMY} &= \frac{\text{mass of maleic anhydride}}{\text{mass of non-benign reagents}} \times 100 \% \\ &= [81.5 / 100] \times 100 \% \\ &= \mathbf{81.5 \%} \end{aligned}$$

But-1-ene Oxidation

100 g but-1-ene (1.79 mol) would give 96.3 g maleic anhydride (0.98 mol, 55 %).

$$\begin{aligned} \text{EMY} &= \frac{\text{mass of maleic anhydride}}{\text{mass of non-benign reagents}} \times 100 \% \\ &= [96.3 / 100] \times 100 \% \\ &= \mathbf{96.3 \%} \end{aligned}$$

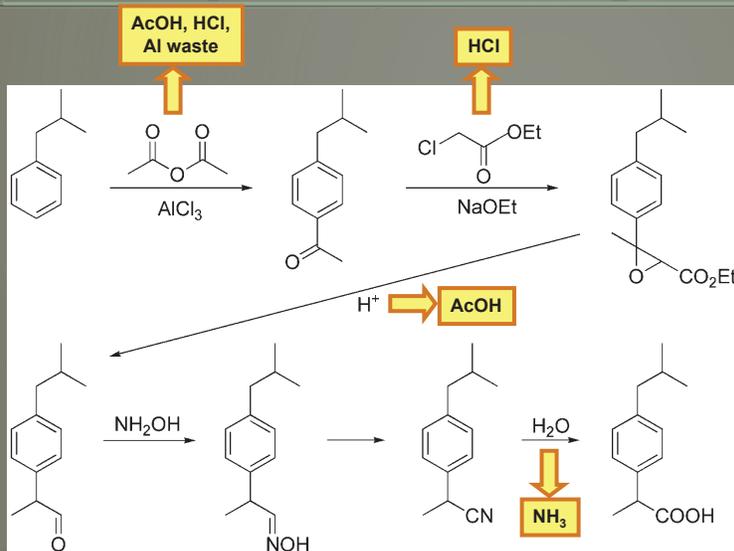
Recommendation?

The butene oxidation route would appear to be slightly greener (higher atom economy and a higher effective mass yield). It also avoids the use of the toxic reagent benzene (we would therefore expect its wastestream to be less hazardous). However, the percentage yield is higher for the benzene oxidation route.

However, without a full life cycle analysis (which would take into account the environmental impact of producing both benzene and butene) a definitive answer is clearly not possible.

Recommendation: Butene route is possibly better - but only if raw material costs are acceptable.

Boots synthesis of Ibuprofen



Hoechst synthesis of Ibuprofen

