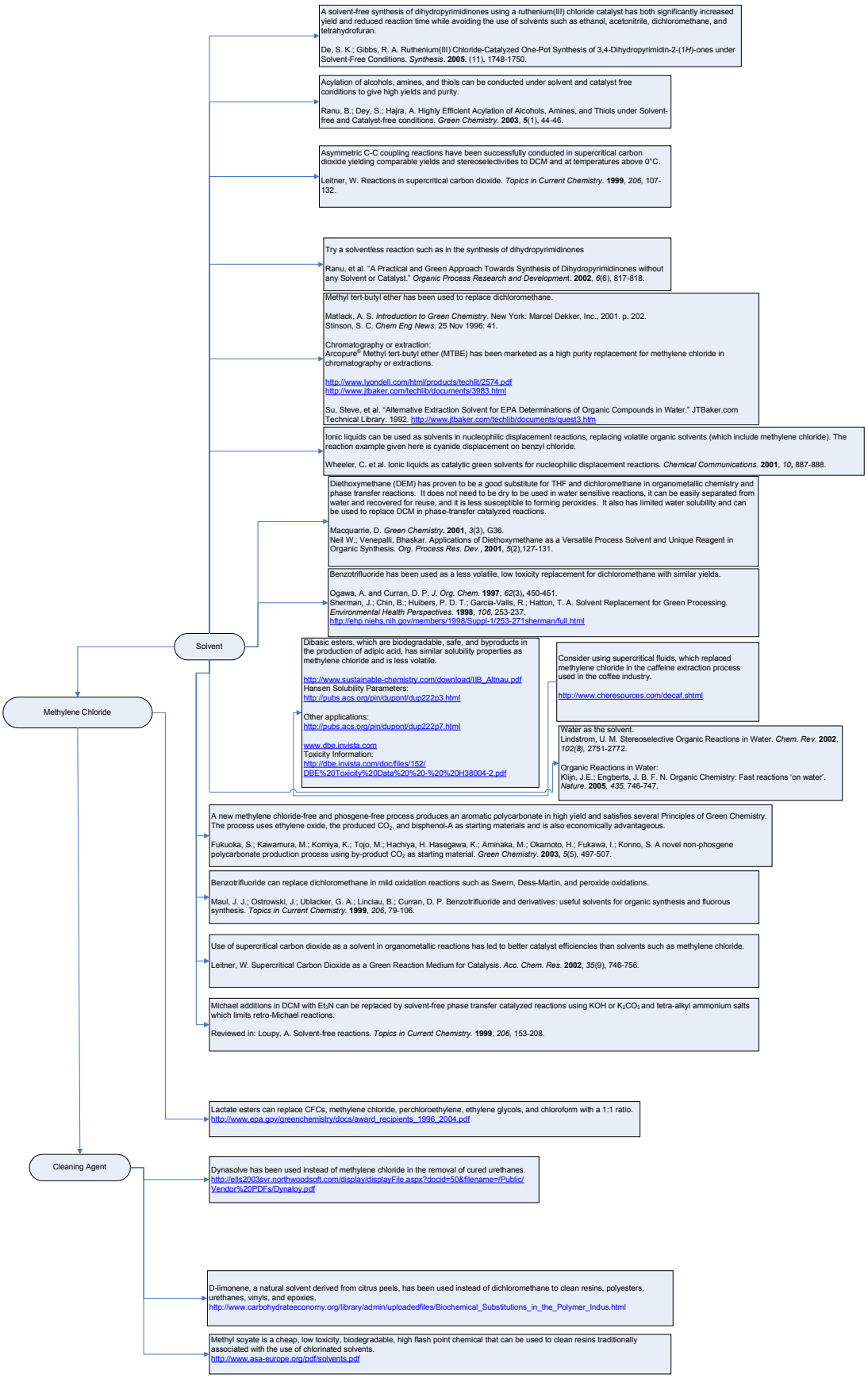
Methylene Chloride
Solvent
A solvent-free synthesis of dihydropyrimidinones using a ruthenium(III) chloride catalyst has both significantly increased yield and reduced reaction time while avoiding the use of solvents such as ethanol, acetonitrile, dichloromethane, and tetrahydrofuran.
De, S. K.; Gibbs, R. A. Ruthenium(III) Chloride-Catalyzed One-Pot Synthesis of 3,4-Dihydropyrimidin-2-(1*H*)-ones under Solvent-Free Conditions. *Synthesis*. **2005**, (11), 1748-1750.
Acylation of alcohols, amines, and thiols can be conducted under solvent and catalyst free conditions to give high yields and purity.
Ranu, B.; Dey, S.; Hajra, A. Highly Efficient Acylation of Alcohols, Amines, and Thiols under Solvent-free and Catalyst-free conditions. *Green Chemistry*. **2003**, *5*(1), 44-46.
Asymmetric C-C coupling reactions have been successfully conducted in supercritical carbon dioxide yielding comparable yields and stereoselectivities to DCM and at temperatures above 0°C.
Leitner, W. Reactions in supercritical carbon dioxide. *Topics in Current Chemistry*. **1999**, *206*, 107-132.
Try a solventless reaction such as in the synthesis of dihydropyrimidinones
Ranu, et al. "A Practical and Green Approach Towards Synthesis of Dihydropyrimidinones without any Solvent or Catalyst." *Organic Process Research and Development*. **2002**, *6*(6), 817-818.
Methyl tert-butyl ether has been used to replace dichloromethane.
Matlack, A. S. *Introduction to Green Chemistry*. New York: Marcel Dekker, Inc., 2001. p. 202.
Stinson, S. C. *Chem Eng News*. 25 Nov 1996: 41.
Chromatography or extraction:
Arcopure® Methyl tert-butyl ether (MTBE) has been marketed as a high purity replacement for methylene chloride in chromatography or extractions.
http://www.lyondell.com/html/products/techlit/2574.pdf
http://www.jtbaker.com/techlib/documents/3983.html
Su, Steve, et al. "Alternative Extraction Solvent for EPA Determinations of Organic Compounds in Water." JTBaker.com Technical Library. 1992. http://www.jtbaker.com/techlib/documents/guest3.htm
Ionic liquids can be used as solvents in nucleophilic displacement reactions, replacing volatile organic solvents (which include methylene chloride). The reaction example given here is cyanide displacement on benzyl chloride.
Wheeler, C. et al. Ionic liquids as catalytic green solvents for nucleophilic displacement reactions. *Chemical Communications*. **2001**, *10*, 887-888.
Diethoxymethane (DEM) has proven to be a good substitute for THF and dichloromethane in organometallic chemistry and phase transfer reactions. It does not need to be dry to be used in water sensitive reactions, it can be easily separated from water and recovered for reuse, and it is less susceptible to forming peroxides. It also has limited water solubility and can be used to replace DCM in phase-transfer catalyzed reactions.
Macquarrie, D. *Green Chemistry*. **2001**, 3(3), G36.
Neil W.; Venepalli, Bhaskar. Applications of Diethoxymethane as a Versatile Process Solvent and Unique Reagent in Organic Synthesis. *Org. Process Res. Dev.*, **2001**, *5*(2),127-131.
Benzotrifluoride has been used as a less volatile, low toxicity replacement for dichloromethane with similar yields.
Ogawa, A. and Curran, D. P. *J. Org. Chem.* **1997**, *62*(3), 450-451.
Sherman, J.; Chin, B.; Huibers, P. D. T.; Garcia-Valls, R.; Hatton, T. A. Solvent Replacement for Green Processing. *Environmental Health Perspectives*. **1998**, *106*, 253-237.
http://ehp.niehs.nih.gov/members/1998/Suppl-1/253-271sherman/full.html
Dibasic esters, which are biodegradable, safe, and byproducts in the production of adipic acid, has similar solubility properties as methylene chloride and is less volatile.
http://www.sustainable-chemistry.com/download/IIB_Altnau.pdf
Hansen Solubility Parameters:
http://pubs.acs.org/pin/dupont/dup222p3.html
Other applications:
http://pubs.acs.org/pin/dupont/dup222p7.html
www.dbe.invista.com
Toxicity Information:
http://dbe.invista.com/doc/files/152/DBE%20Toxicity%20Data%20%20-%20%20H38004-2.pdf
Consider using supercritical fluids, which replaced methylene chloride in the caffeine extraction process used in the coffee industry.
http://www.cheresources.com/decaf.shtml
Water as the solvent.
Lindstrom, U. M. Stereoselective Organic Reactions in Water. *Chem. Rev.* **2002**, *102(8)*, 2751-2772.
Organic Reactions in Water:
Klijn, J.E.; Engberts, J. B. F. N. Organic Chemistry: Fast reactions 'on water'. *Nature*. **2005**, *435*, 746-747.
A new methylene chloride-free and phosgene-free process produces an aromatic polycarbonate in high yield and satisfies several Principles of Green Chemistry. The process uses ethylene oxide, the produced CO_2, and bisphenol-A as starting materials and is also economically advantageous.
Fukuoka, S.; Kawamura, M.; Komiya, K.; Tojo, M.; Hachiya, H. Hasegawa, K.; Aminaka, M.; Okamoto, H.; Fukawa, I.; Konno, S. A novel non-phosgene polycarbonate production process using by-product CO_2 as starting material. *Green Chemistry*. **2003**, *5*(5), 497-507.
Benzotrifluoride can replace dichloromethane in mild oxidation reactions such as Swern, Dess-Martin, and peroxide oxidations.
Maul, J. J.; Ostrowski, J.; Ublacker, G. A.; Linclau, B.; Curran, D. P. Benzotrifluoride and derivatives: useful solvents for organic synthesis and fluorous synthesis. *Topics in Current Chemistry*. **1999**, *206*, 79-106.
Use of supercritical carbon dioxide as a solvent in organometallic reactions has led to better catalyst efficiencies than solvents such as methylene chloride.
Leitner, W. Supercritical Carbon Dioxide as a Green Reaction Medium for Catalysis. *Acc. Chem. Res.* **2002**, *35*(9), 746-756.
Michael additions in DCM with Et_3N can be replaced by solvent-free phase transfer catalyzed reactions using KOH or K_2CO_3 and tetra-alkyl ammonium salts which limits retro-Michael reactions.
Reviewed in: Loupy, A. Solvent-free reactions. *Topics in Current Chemistry*. **1999**, *206*, 153-208.
Lactate esters can replace CFCs, methylene chloride, perchloroethylene, ethylene glycols, and chloroform with a 1:1 ratio.
http://www.epa.gov/greenchemistry/docs/award_recipients_1996_2004.pdf
Cleaning Agent
Dynasolve has been used instead of methylene chloride in the removal of cured urethanes.
http://ells2003svr.northwoodsoft.com/display/displayFile.aspx?docid=50&filename=/Public/Vendor%20PDFs/Dynaloy.pdf
D-limonene, a natural solvent derived from citrus peels, has been used instead of dichloromethane to clean resins, polyesters, urethanes, vinyls, and epoxies.
http://www.carbohydrateeconomy.org/library/admin/uploadedfiles/Biochemical_Substitutions_in_the_Polymer_Indus.html
Methyl soyate is a cheap, low toxicity, biodegradable, high flash point chemical that can be used to clean resins traditionally associated with the use of chlorinated solvents.
http://www.asa-europe.org/pdf/solvents.pdf