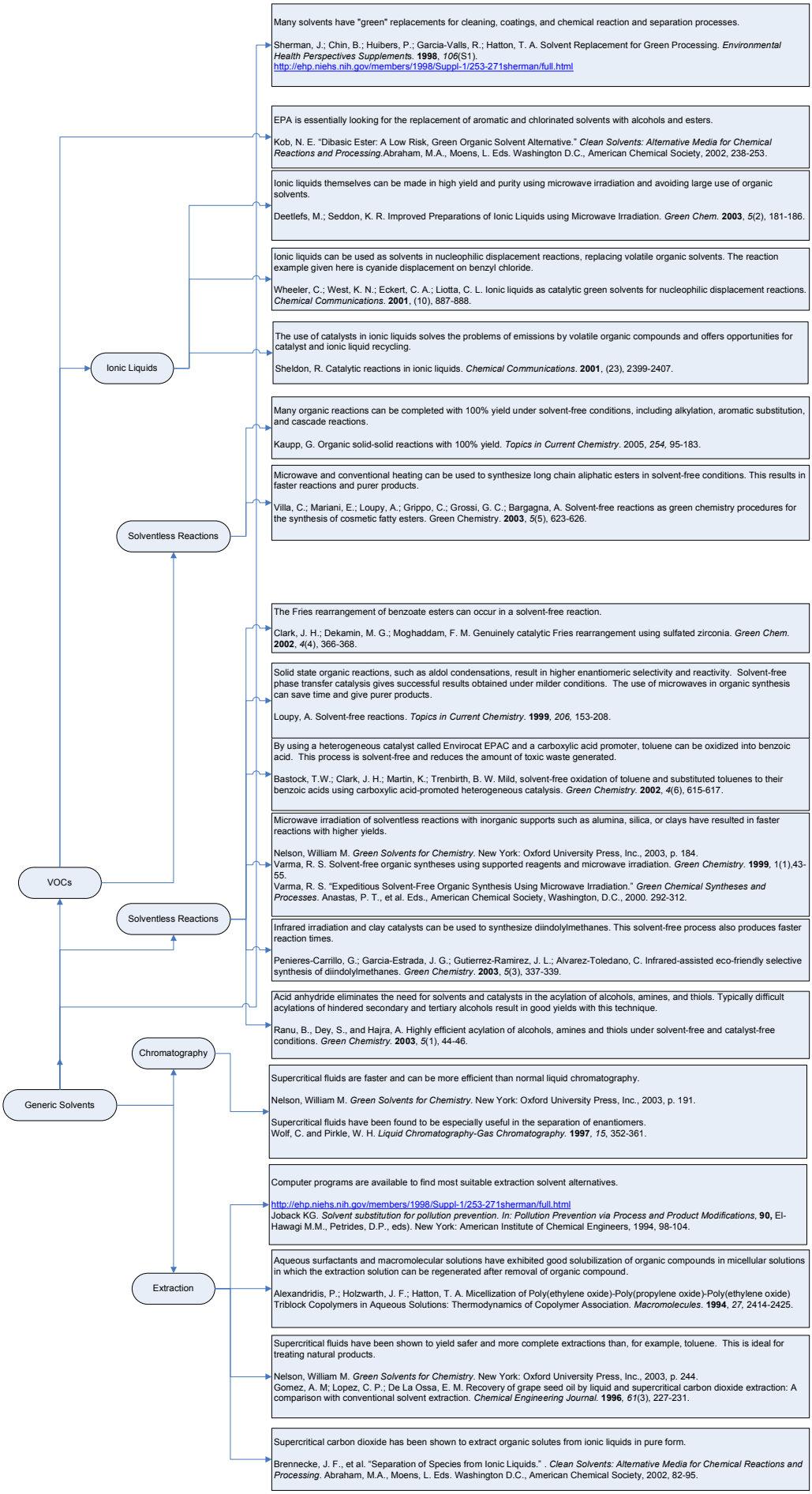
Many solvents have "green" replacements for cleaning, coatings, and chemical reaction and separation processes.
Sherman, J.; Chin, B.; Huibers, P.; Garcia-Valls, R.; Hatton, T. A. Solvent Replacement for Green Processing. Environmental Health Perspectives Supplements. 1998, 106(S1).
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EPA is essentially looking for the replacement of aromatic and chlorinated solvents with alcohols and esters.
Kob, N. E. "Dibasic Ester: A Low Risk, Green Organic Solvent Alternative." Clean Solvents: Alternative Media for Chemical Reactions and Processing.Abraham, M.A., Moens, L. Eds. Washington D.C., American Chemical Society, 2002, 238-253.
Ionic liquids themselves can be made in high yield and purity using microwave irradiation and avoiding large use of organic solvents.
Deetlefs, M.; Seddon, K. R. Improved Preparations of Ionic Liquids using Microwave Irradiation. Green Chem. 2003, 5(2), 181-186.
Ionic liquids can be used as solvents in nucleophilic displacement reactions, replacing volatile organic solvents. The reaction example given here is cyanide displacement on benzyl chloride.
Wheeler, C.; West, K. N.; Eckert, C. A.; Liotta, C. L. Ionic liquids as catalytic green solvents for nucleophilic displacement reactions. Chemical Communications. 2001, (10), 887-888.
The use of catalysts in ionic liquids solves the problems of emissions by volatile organic compounds and offers opportunities for catalyst and ionic liquid recycling.
Sheldon, R. Catalytic reactions in ionic liquids. Chemical Communications. 2001, (23), 2399-2407.
Ionic Liquids
Many organic reactions can be completed with 100% yield under solvent-free conditions, including alkylation, aromatic substitution, and cascade reactions.
Kaupp, G. Organic solid-solid reactions with 100% yield. Topics in Current Chemistry. 2005, 254, 95-183.
Microwave and conventional heating can be used to synthesize long chain aliphatic esters in solvent-free conditions. This results in faster reactions and purer products.
Villa, C.; Mariani, E.; Loupy, A.; Grippo, C.; Grossi, G. C.; Bargagna, A. Solvent-free reactions as green chemistry procedures for the synthesis of cosmetic fatty esters. Green Chemistry. 2003, 5(5), 623-626.
Solventless Reactions
The Fries rearrangement of benzoate esters can occur in a solvent-free reaction.
Clark, J. H.; Dekamin, M. G.; Moghaddam, F. M. Genuinely catalytic Fries rearrangement using sulfated zirconia. Green Chem. 2002, 4(4), 366-368.
Solid state organic reactions, such as aldol condensations, result in higher enantiomeric selectivity and reactivity. Solvent-free phase transfer catalysis gives successful results obtained under milder conditions. The use of microwaves in organic synthesis can save time and give purer products.
Loupy, A. Solvent-free reactions. Topics in Current Chemistry. 1999, 206, 153-208.
By using a heterogeneous catalyst called Envirocat EPAC and a carboxylic acid promoter, toluene can be oxidized into benzoic acid. This process is solvent-free and reduces the amount of toxic waste generated.
Bastock, T.W.; Clark, J. H.; Martin, K.; Trenbirth, B. W. Mild, solvent-free oxidation of toluene and substituted toluenes to their benzoic acids using carboxylic acid-promoted heterogeneous catalysis. Green Chemistry. 2002, 4(6), 615-617.
Microwave irradiation of solventless reactions with inorganic supports such as alumina, silica, or clays have resulted in faster reactions with higher yields.
Nelson, William M. Green Solvents for Chemistry. New York: Oxford University Press, Inc., 2003, p. 184.
Varma, R. S. Solvent-free organic syntheses using supported reagents and microwave irradiation. Green Chemistry. 1999, 1(1),43-55.
Varma, R. S. "Expeditious Solvent-Free Organic Synthesis Using Microwave Irradiation." Green Chemical Syntheses and Processes. Anastas, P. T., et al. Eds., American Chemical Society, Washington, D.C., 2000. 292-312.
VOCs
Solventless Reactions
Infrared irradiation and clay catalysts can be used to synthesize diindolylmethanes. This solvent-free process also produces faster reaction times.
Penieres-Carrillo, G.; Garcia-Estrada, J. G.; Gutierrez-Ramirez, J. L.; Alvarez-Toledano, C. Infrared-assisted eco-friendly selective synthesis of diindolylmethanes. Green Chemistry. 2003, 5(3), 337-339.
Acid anhydride eliminates the need for solvents and catalysts in the acylation of alcohols, amines, and thiols. Typically difficult acylations of hindered secondary and tertiary alcohols result in good yields with this technique.
Ranu, B., Dey, S., and Hajra, A. Highly efficient acylation of alcohols, amines and thiols under solvent-free and catalyst-free conditions. Green Chemistry. 2003, 5(1), 44-46.
Chromatography
Generic Solvents
Supercritical fluids are faster and can be more efficient than normal liquid chromatography.
Nelson, William M. Green Solvents for Chemistry. New York: Oxford University Press, Inc., 2003, p. 191.
Supercritical fluids have been found to be especially useful in the separation of enantiomers.
Wolf, C. and Pirkle, W. H. Liquid Chromatography-Gas Chromatography. 1997, 15, 352-361.
Computer programs are available to find most suitable extraction solvent alternatives.
http://ehp.niehs.nih.gov/members/1998/Suppl-1/253-271sherman/full.html
Joback KG. Solvent substitution for pollution prevention. In: Pollution Prevention via Process and Product Modifications, 90, El-Hawagi M.M., Petrides, D.P., eds). New York: American Institute of Chemical Engineers, 1994, 98-104.
Aqueous surfactants and macromolecular solutions have exhibited good solubilization of organic compounds in micellular solutions in which the extraction solution can be regenerated after removal of organic compound.
Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. Micellization of Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) Triblock Copolymers in Aqueous Solutions: Thermodynamics of Copolymer Association. Macromolecules. 1994, 27, 2414-2425.
Extraction
Supercritical fluids have been shown to yield safer and more complete extractions than, for example, toluene. This is ideal for treating natural products.
Nelson, William M. Green Solvents for Chemistry. New York: Oxford University Press, Inc., 2003, p. 244.
Gomez, A. M; Lopez, C. P.; De La Ossa, E. M. Recovery of grape seed oil by liquid and supercritical carbon dioxide extraction: A comparison with conventional solvent extraction. Chemical Engineering Journal. 1996, 61(3), 227-231.
Supercritical carbon dioxide has been shown to extract organic solutes from ionic liquids in pure form.
Brennecke, J. F., et al. "Separation of Species from Ionic Liquids." . Clean Solvents: Alternative Media for Chemical Reactions and Processing. Abraham, M.A., Moens, L. Eds. Washington D.C., American Chemical Society, 2002, 82-95.