



John W. Frost

Green Chemistry

UNIVERSITY
DISTINGUISHED PROFESSOR

(b. 1955)

B.S., 1977,
Purdue Univ.;

Ph.D., 1981,
Massachusetts Institute of Technology.

517-353-0502

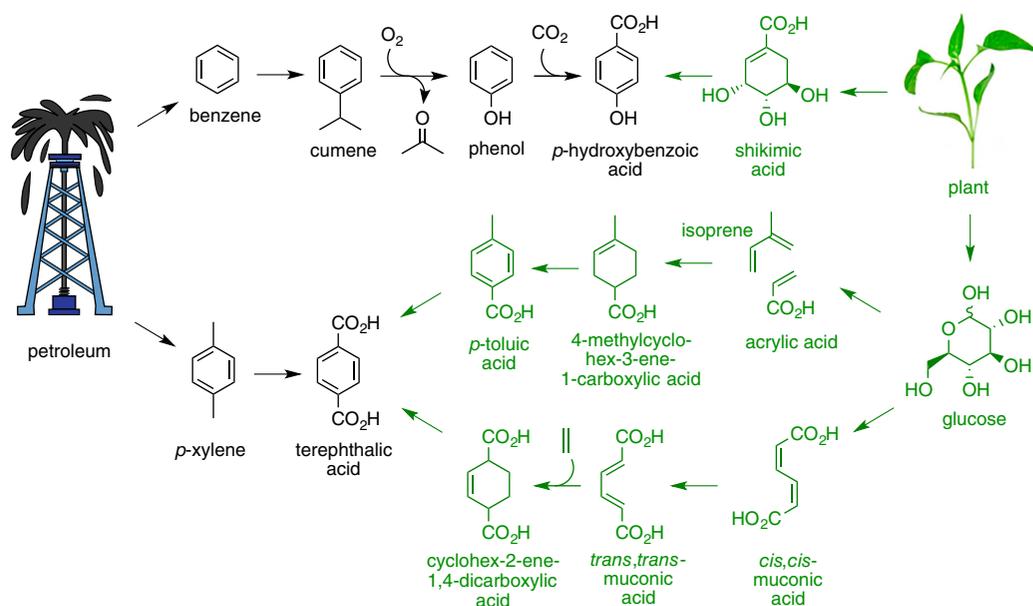


Green chemistry is being elaborated that enables CO₂ fixed by plants to be converted into chemicals currently derived from the BTX (benzene toluene xylene) fraction of petroleum refining. Nonrenewable fossil fuel feedstocks, carcinogenic starting materials and toxic intermediates are avoided. In addition, an array of new monomers is being synthesized to identify structures that are: (a) free of endocrine disruption activity, and (b) lead to polymers and plasticizers characterized by novel materials properties.

Current commercial synthesis of *p*-hydroxybenzoic acid begins with BTX-derived benzene and proceeds through cumene and phenol as intermediates. Carboxylation of potassium phenolate affords *p*-hydroxybenzoic acid monomer, which typically constitutes 50% of the mass of liquid crystalline polymers. A green synthetic alternative has been elaborated whereby *p*-hydroxybenzoic acid is synthesized in a single step in high conversion and good selectivity from nontoxic shikimic acid. Shikimic acid, in turn, is microbially synthesized from plant-derived glucose or isolated directly from plants such as *Ginkgo biloba*. Shikimic acid's solubility in *n*-butanol and propensity to crystallize from *n*-butanol facilitate its isolation from fermentation broth or plant tissue. Green synthesis of

p-hydroxybenzoic acid eliminates the need for using carcinogenic benzene as a starting material and toxic phenol as an intermediate.

BTX-derived xylene is industrially oxidized to terephthalic acid, which is polymerized with ethylene glycol to produce poly(ethylene terephthalate) PET. Over 50 × 10⁹ kg of terephthalic acid are globally produced each year. Two green synthetic alternative routes have been developed. Isoprene and acrylic acid microbially synthesized from glucose undergo a cycloaddition to form 4-methylcyclohex-3-ene-1-carboxylic acid. Dehydrogenation affords terephthalic acid. Alternatively, *cis,cis*-muconic acid microbially synthesized from glucose is isomerized and the resulting *trans,trans*-muconic acid reacted in a cycloaddition with bioethanol-derived ethene to yield cyclohex-2-ene-1,4-dicarboxylic acid. Dehydrogenation affords terephthalic acid. In addition to use of renewable feedstocks, the new routes enable the first practical synthesis of substituted terephthalates when substituted acrylic acids and substituted ethenes are employed. Furthermore, a parallel world of 1,4-cyclohexane and 1,4-cyclohexene 1,4-dicarboxylic acids has been created, which affords unique opportunities to avoid aromatic-associated, endocrine disruption activity while enabling the fabrication of novel materials. ♻️



SELECTED PUBLICATIONS

B-O-B catalyzed cycloadditions of acrylic acids, Zhang, P.; Kriegel, R. M.; Frost, J. W. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6991-6995.

Synthesis of Terephthalic Acid from Methane, Zhang, P.; Nguyen, V.; Frost, J. W., *ACS Sustainable Chem. Eng.* **2016**, *4*, 5998-6001.

Synthesis of Biobased Terephthalic Acid from Cycloaddition of Isoprene with Acrylic Acid, K.K. Miller, P. Zhang, Y. Nishizawa-Brennen, and J. W. Frost, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2053-2056.