

Phosgene

Synthesis

Several phosgene substitutes exist for the production of urea, including bis(4-nitrophenyl)carbonate, di-*tert*-butyl dicarbonate, 1,1-carbonylbisimidazole, 1,1-carbonylbisbenzotriazole, *S,S*-dimethyldithiocarbonate, and trihaloacetylchlorides, offer safer alternative synthesis pathways.

Bigi, F., Maggi, R., and Sartori, G. Selected syntheses of ureas through phosgene substitutes. *Green Chemistry*. **2000**, 2(4), 140-148.

A new phosgene-free and methylene chloride-free process of producing an aromatic polycarbonate satisfies most of the Articles for Green Chemistry. The process uses CO₂ as the starting material, and is also economically advantageous.

Fukuoka, S. et al. A novel non-phosgene polycarbonate production process using by-product CO₂ as starting material. *Green Chemistry*. **2003**, 5, 497-507.

Dimethyl carbonate (DMC) can replace phosgene and methyl halides in carbonylations and methylations. Using DMC produces less waste; DMC is made in a phosgene-free process, from methanol and oxygen.

Kirchhoff, M. Promoting Green Engineering through Green Chemistry. *Environmental Science & Technolog.* **2003**, 37(23), 5349-5353.

Tundo, P.; Selva, M. The Chemistry of Dimethyl Carbonate. *Acc. Chem. Res.* **2002**, 35(9), 706-716.

Titanosilicate molecular sieves serve as catalysts for the synthesis of polycarbonate precursors such as cyclic, dimethyl, and diphenyl carbonates, avoiding the need for phosgene and CO.

Srivastava, R., Srinivas, D., and Ratnasamy, P. Synthesis of polycarbonate precursors over titanosilicate molecular sieves. *Catalysis Letters*. **2003**, 91(1-2), 133-139.

In the synthesis of carbamates, the use of titanosilicate molecular sieves or metal phthalocyanine complexes enclosed in zeolite-Y as a recyclable catalyst eliminates the need for phosgene, isocyanate, and CO. This also avoids expensive separation of methanol-DMC in processes that use DMC. Carbamates are produced in yields greater than 80%.

Srivastava, R., Srinivas, D., and Ratnasamy, P. Phosgene-free synthesis of carbamates over zeolite-based catalysts. *Catalysis Letters*. **2004**, 97(1-2), 41-47.