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Glycerol-Based Bio-Solvents for Organic Synthesis

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Abstract : In the past two decades a variety of green solvents have been proposed, including water, ionic liquids, fluorous solvents, and supercritical fluids. However, their implementation in industrial processes is still limited due to their tedious and non-sustainable synthesis, lack of experimental data and familiarity, as well as operational restrictions and high cost. Several years ago we presented, for the first time, the use of glycerol-based solvents as alternative sustainable reaction mediums in both catalytic and non-catalytic organic synthesis. Glycerol is the main by-product from the conversion of oils and fats in oleochemical production. Moreover, in the past decade, its price has substantially decreased due to an increase in supply from the production and use of fatty acid derivatives in the food, cosmetics, and drugs industries and in biofuel synthesis, i.e., biodiesel. The renewable origin, beneficial physicochemical properties and reusability of glycerol-based solvents, enabled improved product yield and selectivity as well as easy product separation and catalyst recycling. Furthermore, their high boiling point and polarity make them perfect candidates for non-conventional heating and mixing techniques such as ultrasound- and microwave-assisted reactions. Finally, in some reactions, such as catalytic transfer-hydrogenation or transesterification, they can also be used simultaneously as both solvent and reactant. In our ongoing efforts to design a viable protocol that will facilitate the acceptance of glycerol and its derivatives as sustainable solvents, pure glycerol and glycerol triacetate (triacetin) as well as various glycerol-triacetin mixtures were tested as sustainable solvents in several representative organic reactions, such as nucleophilic substitution of benzyl chloride to benzyl acetate, Suzuki-Miyaura cross-coupling of iodobenzene and phenylboronic acid, baker's yeast reduction of ketones, and transfer hydrogenation of olefins. It was found that reaction performance was affected by the glycerol to triacetin ratio, as the solubility of the substrates in the solvent determined product yield. Thereby, employing optimal glycerol to triacetin ratio resulted in maximum product yield. In addition, using glycerol-based solvents enabled easy and successful separation of the products and recycling of the catalysts.

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