



Short Communication

Organocatalytic, rapid and facile cyclotrimerization of isocyanates using tetrabutylammonium phthalimide-*N*-oxyl and tetraethylammonium 2-(carbamoyl)benzoate under solvent-free conditions

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ABSTRACT

Tetrabutylammonium phthalimide-*N*-oxyl and tetraethylammonium 2-(carbamoyl)benzoate were found to be effective and easily accessible organocatalysts for selective cyclotrimerization of aryl and alkyl isocyanates under mild reaction conditions. The reaction proceeds smoothly using very low catalyst loadings of these metal-free organocatalysts (0.025 and 0.25 mol%, respectively) under solvent-free conditions at room temperature within a very short reaction time.

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1. Introduction

The most important reaction between isocyanates is cyclotrimerization to form the heteroaromatic isocyanurate (1,3,5-trisubstituted hexahydro-*s*-triazinetrione) ring. This heterocycle is thermally very stable and is used to enhance the physical properties of a wide variety of polyurethanes and other coating materials such as polyureas in commercial systems. Polymeric blends of isocyanurates demonstrate increased thermal resistance, flame retardation, chemical resistance, and film-forming characteristics [1–4]. Furthermore, different derivatives of isocyanurates have recently received considerable attention in other areas such as heterogeneous catalysis [5], periodic mesoporous organosilicas (PMOs) with uniformly distributed organic and organometallic groups within the silica framework [6,7], cross-linker and glass coating agent [8–10], drug delivery [11,12] selective ion bonding [13] and chiral discrimination [14].

The general route for the preparation of isocyanurates is the catalytic cyclotrimerization of the corresponding isocyanates. However, isocyanates are very active agents which produce different products such as trimer, dimer, carbodiimide, urethane or allophanate depending on the reaction conditions [3,15]. Therefore, developing of catalysts which promote cyclotrimerization selectively is of great importance due to wide application of isocyanurate structure in both industry and

academic studies [1–14]. Cyclotrimerization of isocyanates has been shown to be promoted by catalytic systems such as neutral trisamino-phosphines, trialkyl arsenic oxide, tertiary amines, and anions such as carboxylates, cyanate, phenoxide [3], fluoride [16], sulfite [17] or sulfate [18]. Catalysts containing metal species such as organotin compounds, arene manganese tricarbonyl, and nickel halides have also been reported [3]. Recently, metallic catalysts such as complexes of Yb, Eu, Sm, Nd, Yb [19], Sn, Ge [20,21], and Pd [22] or zirconacyclopentanes [23] have been employed. On the other hand, organocatalysis has received great attention due to the mildness of the reaction conditions, operational simplicity, the potential for the development of large scale versions of the reaction, the ready availability, and environmental friendliness in the recent years [24]. Along this line, organocatalysts such as *N*-heterocyclic carbenes (NHCs) [25], calcium carbene with chelating iminophosphorane substituents [26], an electron-rich trisaminophosphine [27], potassium or sodium salts of piperidinedithiocarbamate [28], *p*-toluenesulfinate [29], saccharin [30], phthalimide [31], and phthalimide-*N*-oxyl [32] have also been introduced.

In commercial systems, alkali metal carboxylates such as potassium acetate in combination with ethylene glycol or its oligomers and potassium 2-ethylhexanoate can be considered as standard catalysts. Furthermore, the quaternary ammonium carboxylates demonstrate high performance catalytic activity that can significantly assist in processing and/or physical property modification [33]. We have recently introduced tetrabutylammonium phthalimide-*N*-oxyl (TBAPINO) [34] and tetraethylammonium 2-(carbamoyl)benzoate (TEACB) [24] as efficient and metal-free organocatalysts for cyanosilylation of carbonyl

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