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Solvent-free Efficient Synthesis of Symmetrical Isocyanurates by a Combination Catalyst: Sodium Saccharin and Tetrabutylammonium Iodide

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Summary. Combination of sodium saccharin and tetrabutylammonium iodide as a novel anionic catalyst system promotes selectively the trimerization of isocyanates to give symmetrical isocyanurates under solvent-free conditions.

Keywords. Sodium saccharin; Phase transfer catalyst; Symmetrical triaryl isocyanurate; Solvent-free condition.

Introduction

1,3,5-Triazinane-2,4,6 trione, known as isocyanurate, modifies the properties of polyurethane foams and resins [1]. Triaryl isocyanurates are useful activators for the continuous anionic polymerization and postpolymerization of ε-caprolactam to nylon-6 and insecticides [1c, 2]. Recently, the rigid structure of isocyanurate has found interesting applications in the fields of chiral discrimination and low toxicity drug delivery [3].

The general method to synthetize isocyanurates is based on the catalytic trimerization of the corresponding isocyanates. Many catalysts have been introduced for the reaction after the pioneering works in the last decades of the 19th century [1d] and the search for new catalysts continued to satisfy problems such as severe

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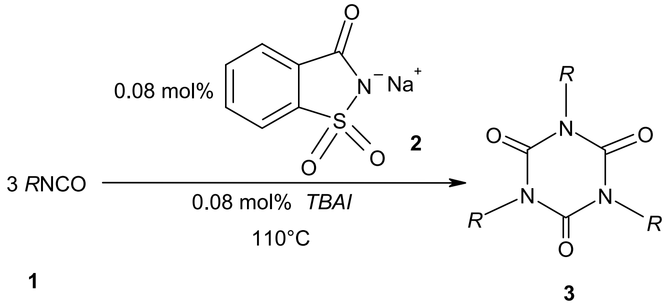
conditions, formation of byproducts such as dimer or carbodiimides, lengthy reactions, separation of the catalyst from products, and use of catalysts which are not readily available or even toxic [1]. With growing environmental concerns in recent years, finding new conditions which don't need hazardous solvents has been intensified [4]. In continuation of our interest to new safe anionic isocyanate cyclotrimerization catalysts [5] we now report a clean preparation of symmetrical aryl isocyanurates catalyzed by a combination of sodium saccharin (*SS*, **2**) and tetrabutylammonium iodide (*TBAI*).

Results and Discussion

Treatment of aryl isocyanates **1** with a mixture of **2** (0.08 mol%) and *TBAI* (0.08 mol%) at 110°C, affords the corresponding triaryl isocyanurates **3** as exclusive products, in excellent to moderate yields (Table 1). The combination system has a good activity even for cyclotrimerization of **1d**, which most of the previous catalysts failed to trimerize [1c]. The low yield of **3e** could be interpreted based on the steric hindrance around the isocyanate group in the substrate, which render the reaction less satisfactorily [6].

In conclusion, a new anionic catalyst has been found for the efficient trimerization of isocyanates under solvent-free and eco-friendly conditions. The catalytic activity of sodium saccharin even for trimerizing aryl isocyanates containing electron-donating substituents and under steric hindrance is notable.



Scheme 1

Table 1. Trimerization of isocyanates **1a–1c** by **2** to symmetrical isocyanurates under solvent-free condition

Substrate	*R*	Time/h	Yield/%
1a	Phenyl	0.75	79
1b	4-Chlorophenyl	0.3	90
1c	3,4-Dichlorophenyl	0.25	80
1d	4-Methoxyphenyl	3	85
1e	1-Naphthyl	24	20

Experimental

All yields refer to isolated products. All products were characterized by comparison of the spectral and physical data with those of authentic samples. FT IR Spectra were recorded as KBr pellets on a Nicolet spectrometer (Magna 550). A Bruker (DRX-500 Avance) NMR was used to record the ^{1}H NMR spectra. All NMR spectra were determined in $CDCl_3$ and acetone-d_6 at ambient temperature. GC-MS were recorded on a HP 6890-HP 5973 instrument. Melting points were determined on a Büchi B540 apparatus.

*Synthesis of Triaryl Isocyanurates (General Procedure Illustrated with **3d**)*

In a flame-dried 20 cm^3 flask equipped with a condenser attached to a $CaCl_2$ guard, 3.3 mg of **2** (0.016 mmol) and 2.58 cm^3 of **1d** (20 mmol) were added. The mixture was vigorously stirred and heated at 110°C. The termination of the reaction was found by appearance of a brownish white solid mass. After 3 h, the mixture was heated for additional 5 min. After cooling to room temperature, 25 cm^3 of diethyl ether were added and the solid was crushed. The mixture was stirred for further 10 min and filtered. Triturating the crude product with H_2O and recrystallization from ethanol afforded **3d** in 85% yield. Mp 259–61°C (Ref. [1c] 261–262°C); IR (KBr): $\bar{\nu} = 1725\,\mathrm{cm}^{-1}$ (C=O); ^{1}H NMR (acetone-d_6): $\delta = 3.834$ (s, 3OCH_3), 7.003–7.021 (d, 6H aromatic, $J = 8.96$ Hz), 7.331–7.348 (d, 6H aromatic, $J = 8.96$ Hz) ppm.

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