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N-Heterocyclic Carbenes as Highly Efficient Catalysts for the Cyclotrimerization of Isocyanates

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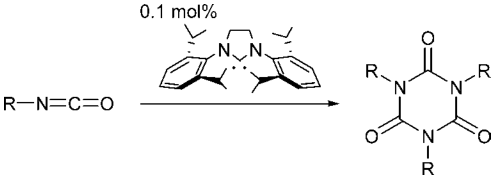
ABSTRACT



A series of N-heterocyclic carbenes (NHCs) were evaluated as potential catalysts for the cyclotrimerization of isocyanates to afford isocyanurates. 1,3-Bis-(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr) was found to be a highly efficient catalyst for the cyclotrimerization of a variety of isocyanates.

Isocyanurates, the aromatic products arising from cyclotrimerizing isocyanates, are used to enhance the physical properties of a wide variety of polyurethanes and coating materials.[1] Polymeric blends of isocyanurates show increased thermal resistance, flame retardation, chemical resistance, and film-forming characteristics.[2] For example, triaryl isocyanurates are often used as activators for the polymerization and postpolymerization of ϵ-caprolactam in the production of nylons with high melt viscosities.[3] Triallyl isocyanurate has been used in the preparation of flame-retardant laminating materials for electrical devices as well as in the preparation of copolymer resins that are water-resistant, transparent, and impact-resistant.[4]

The commercial importance of isocyanurates has led to considerable effort in developing effective methods for their synthesis through isocyanate cyclotrimerization. Numerous catalysts have been discovered that facilitate this reaction.[5] Lewis base catalysts include phosphines,[6] amines,[7] NO,[8] and alkoxyalkenes,[9] as well as salts containing *p*-toluenesulfinate,[10] cyanate,[11] fluoride,[12] or carbamate anions.[13] Organometallic compounds, which in some cases may proceed

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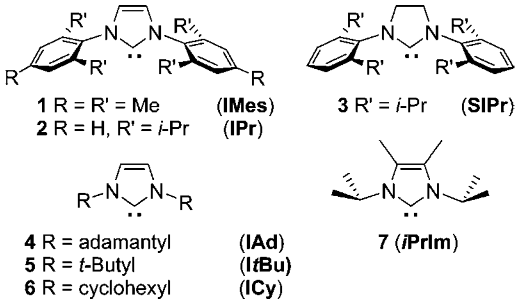
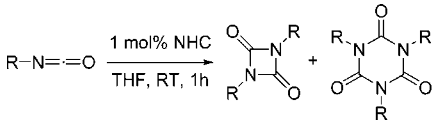


Figure 1. N-Heterocyclic carbenes (NHC).

through Lewis acid-catalyzed pathways, include organotin compounds,[14] alkylzinc amides, and alkoxides,[15] and copper(II) and nickel(II) halides.[8] Unfortunately, many of these systems suffer from (1) severe reaction conditions, (2) poor selectivity and a high formation of byproducts, (3) functional group incompatibility, and/or (4) difficulty in the removal of the catalysts. To date, the most effective catalyst for the cyclotrimerization of both aryl and alkyl isocyanates is an extremely basic, tethered proazaphosphatrane.[6a] During our investigation of Ni-catalyzed cycloadditions of diynes and isocyanates,[16] we discovered that N-heterocyclic carbenes (NHCs)[17] also cyclotrimerize isocyanates to their respective isocyanurates. Herein, we disclose further details on this discovery.[18]

A variety of NHCs were screened as potential catalysts (see Figure 1). Both phenyl isocyanate and cyclohexyl isocyanate were used as model substrates (eq 1), and the results are summarized in Table 1. Unsaturated NHCs bearing aryl rings (entries 2 and 3) were ineffective for the cyclotrimerization of phenyl isocyanate, whereas a saturated analogue, SIPr, displayed high catalytic activity (entry 4). NHCs bearing alkyl substituents were also active phenyl isocyanate cyclotrimerization catalysts, but only ICy afforded a high yield (entries 5−8). Interestingly, analogous reactions run with cyclohexyl isocyanate did not follow the same pattern of reactivity. The predominant product obtained with most of the NHC catalysts was a cyclodimer rather than the isocyanurate. One exception was IMes, which afforded a 3:1 mixture of dimer:trimer (entry 10). The only catalyst found to successsfully cyclotrimerize cyclohexyl isocyanate in high yield was SIPr (entry 12), which, as described above, also afforded a high yield of isocyanurate (**8**)[6a] with phenyl isocyanate. As expected, no reaction was observed in the absence of catalyst for either isocyanate.

Table 1. NHC-Catalyzed Isocyanate Trimerization[a]



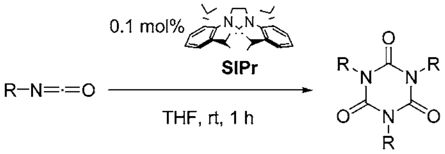
(1)

entry	NHC	RNCO	% yield[b] dimer	% yield[b] trimer
1	none	PhNCO	0	0
2	IMes	PhNCO	0	14
3	IPr	PhNCO	0	0
4	SIPr	PhNCO	0	>99
5	IAd	PhNCO	0	23
6	I*t*Bu	PhNCO	0	54
7	ICy	PhNCO	0	>99
8	*i*PrIm	PhNCO	0	60
9	none	CyNCO	0	0
10	IMes	CyNCO	55	18
11	IPr	CyNCO	14	0
12	SIPr	CyNCO	0	95
13	IAd	CyNCO	58	0
14	I*t*Bu	CyNCO	64	0
15	ICy	CyNCO	62	2
16	*i*PrIm	CyNCO	4	11

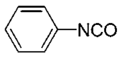
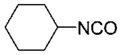
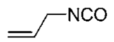
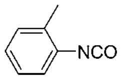
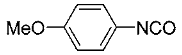
[a] Reactions conditions: 1 mol % NHC, 0.20 M RCNO in THF at room temperature, 1 h. [b] Determined by GC relative to naphthalene as an internal standard.

The high activity of SIPr prompted us to optimize the reaction further using this catalyst (Table 2). When the

Table 2. Isocyanate Trimerization Catalyzed by SIPr[a]



(2)

entry	RNCO[b]	product	% yield[c]
1		8	99
2			98[d,e]
3			97[f]
4		9	99[d]
5		10	98[d,g]
6		11	97[h]
7		12	85

[a] Reactions were run with 0.1 mol % catalyst in THF. [b] Isocyanates were degassed and dried prior to cyclotrimerization. [c] Isolated yields (average of at least two runs). [d] Reaction was run in neat isocyanate. [e] Performed with 0.001 mol % catalyst. [f] Degassed but nondried PhNCO was used. [g] Performed with 0.01 mol % catalyst. [h] Mixture of isomers were obtained.

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[18] An early report indicated that 1,3-diphenyl-4,5-dihydro-imidazol-2-ylidene reacts with 2-aryl or 2-vinyl isocyanates to form spirohydantoins. We see no evidence of spirohydantoin formation in our reactions. See: Schössler, W.; Regitz, M. *Chem. Ber.* **1974**, *107*, 1931.

starting materials were both dry and degassed, quantitative yields were obtained using only a 0.001 mol % catalyst loading (entry 2). Isocyanates that had been only degassed also readily underwent cyclotrimerization but required a higher catalyst loading (0.1 mol %, entry 3). Performing the cyclotrimerization in neat cyclohexyl isocyanate afforded a quantitative yield of product (**9**)[19] using only 1 mol % catalyst. The purification of these reactions was very straighforward: isocyanurates were obtained by simply filtering and washing the product from the reaction mixture at the conclusion of the reaction.[20]

The scope of isocyanate substrates was also investigated (eq 2, Table 2). Allyl isocyanate afforded a commercially important isocyanurate (**10**)[6a] in excellent yield (entry 5). (o-CH_3)C_6H_5−NCO was converted in 97% yield to the respective isocyanurate (**11**),[21] indicating that increasing the steric hindrance around the isocyanate does not hinder the reaction (entry 6).[22] Similarly, p-OMe-C_6H_4NCO was also successfully converted to its isocyanurate (**12**)[6a] in 85% yield (entry 7). Such electron-dense substrates have typically displayed low reactivities in isocyanate cyclotrimerization reactions when other catalyst systems have been employed.[9]

Imidazolylium carboxylates, formed by reacting an NHC with CO_2,[23] were also found to be effective catalysts for the cyclotrimerization of isocyanates. For example, air-stable *i*PrImCO_2 (**13**) readily cyclotrimerized phenyl isocyanate quantitatively.

Diisocyanate homopolymerization using NHCs was also examined. When SIPr (1 mol %) was added to a solution 1,6-diisocyanatohexane (0.5 M, THF) at room temperature, a translucent solid formed within minutes. Further characterization of this solid revealed that a polyamide was formed with an exclusive isocyanurate-linked backbone (as determined by FT-IR spectroscopy[24,25]).

In conclusion, a variety of N-heterocyclic carbenes and imidazolylidene carboxylates were found to cyclotrimerize isocyanates to their respective isocyanurates. The most active catalyst was found to be SIPr, which efficiently cyclotrimerized alkyl, aryl, and allyl isocyanates and also afforded a polyamide with isocyanurate linkages.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and IR data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] **Representative Procedure for Isocyanate Cyclotrimerization Using SIPr.** Under a nitrogen atmosphere, a solution of PhNCO (1:1 v:v in THF) was added to an oven-dried round-bottom flask containing SIPr (0.1 mol %) and equipped with a magnetic stir bar. The reaction was stirred at room temperature. The resulting precipitate was filtered, washed with pentane, and dried in vacuo to afford the isocyanurate as a white solid in 99% yield.

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[22] Isocyanurates are planar with hindered rotation about the $C-N_{\text{substituent}}$ bond. Thus, the methyl substituents on the aryl ring may be locked on the same side or on opposite sides (or a combination thereof) of the isocyanurate core. We obtained a statistical mixture of these possible isomers in the cyclotrimerization to isocyanurate **11**.

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