Efficient and Selective Trimerization of Aryl and Alkyl Isocyanates Catalyzed by Sodium *p*-Toluenesulfinate in the Presence of TBAI in a Solvent-Free Condition

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(Received April 20, 2001)

Aryl and alkyl isocyanates have been efficiently converted into symmetrical trisubstituted aryl and alkyl isocyanurates, catalyzed by sodium *p*-toluenesulfinate on its own or in the presence of tetrabutylammonium iodide (TBAI), in a solvent-free condition. The latter has been shown to have a higher catalytic activity.

The aromatic heterocyclic structure of 1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)trione, known as isocyanurate, modifies polyurethanes and coating materials regarding various properties, such as enhanced thermal and chemical resistance, flame retardation, and film-forming characteristics.[1–6]

The general route to construct the isocyanurate ring and to prepare symmetrical derivatives is catalytic trimerization of the corresponding isocyanates. Owing to the industrial importance of the reaction, therefore, the search for new catalysts continues to draw the attention of numerous industrial research groups.[6–9]

We have recently introduced sodium or potassium piperidinedithiocarbamate and nitrite for the efficient and rapid trimerization of aryl and alkyl isocyanates in a solvent-free condition.[10] In continuation of our interest in this field, we wish to report here on a new anionic and efficient catalyst for the trimerization of isocyanates, namely sodium *p*-toluenesulfinate.

Sodium *p*-toluenesulfinate is mostly used for the preparation of chiral sulfoxides to induce asymmetric induction.[11] Thus, it was found that when phenyl isocyanate is heated with 2 mole% of sulfinate salt at 140 °C, 1,3,5-triphenyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (triphenyl isocyanurate) (Table 1, entry 1) appears as a white precipitate after 12 min at 90% yield.[12] A TLC comparison of the crude product with an authentic sample reveals that the trimer is the only product of the reaction. The reaction conditions were optimized with respect to mol% of the catalyst as well as its efficiency, reaction time and temperature. The results are summarized in Table 1. As it shows 1.25 mol% of the catalyst and a temperature of 140 °C are conditions of choice. The optimal condition was applied for a number of aryl isocyanates, the excellent results are summarized in Table 2. 1-Naphthyl isocyanate gives low yield (Table 2, entry 7) in accordance with literature results.[7c]

Table 1. Trimerization of Phenyl Isocyanate at Various Concentrations of (1), Tetrabutylammonium Iodide, and Temperatures

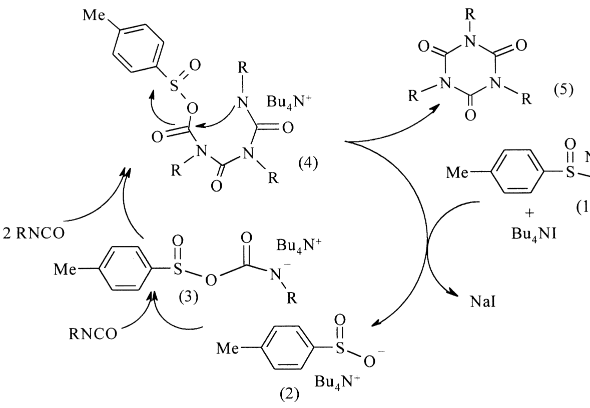
Entry	1	TBAI	Temperature	Time	Yield
	mol%	mol%	°C	min	%
1	2	0.0	140	9	90
2	1.5	0.0	140	12	89
3	1.25	0.0	140	14	94
4	1	0.0	140	18	85
5	0.5	0.0	140	25	77
6	1.25	0.0	120	30	78
7	1.25	0.0	100	40	73
8	1.25	0.0	r.t.	48h	trace
9	1.25	0.5	140	3.5	97
10	0.333	0.3	140	2.5	95
11	0.2	0.1	140	3.5	93
12	0.2	0.1	70	5	98
13	0.2	0.1	r.t.	15	91

The trimerization of isocyanates, catalyzed by (1), proceeds in a heterogeneous system, in contrast to our previous observation for sodium or potassium piperidinedithiocarbamate, which dissolve in isocyanates at elevated temperatures. Sodium *p*-toluenesulfinate forms a colloidal state with isocyanates at 140 °C, which is probably due to its greater polarity compared with piperidinedithiocarbamate, and therefore, induces catalytic activity at higher concentrations. The catalytic-activity induction could be explained by the presence of a negative charge on the oxygen atoms of sodium *p*-toluenesulfinate which acts as a hard nucleophile. This phenomenon is intensi-

Table 2. Trimerization of Aryl and Alkyl Isocyanates at Optimized Condition

Entry	Isocyanate	1	TBAI	Temperature	Time	Yield
		mol%	mol%	°C	min	%
1	Phenyl	1.25	0.0	140	14	94
2	Phenyl	0.2	0.1	70	5	98
3	4-Chlorophenyl	1.25	0.0	140	10	93
4	4-Chlorophenyl	0.2	0.1	70	3.5	89
5	3,4-Dichloro-phenyl	1.25	0.0	140	7	91
6	3,4-Dichloro-phenyl	0.2	0.1	70	3	93
7	1-Naphthyl	1.25	0.0	140	24h	39
8	1-Naphthyl	0.2	0.1	70	12h	80
9	Ethyl	0.2	0.1	60	15h	72
10	Butyl	0.2	0.1	70	12h	80
11	Butyl	0.2	0.1	110	8h	86

a) All yields refer to isolated products which were characterized by mp, IR, ^{1}H NMR, and their spectroscopic data were similar to those reported in Ref. 7.



Scheme 1.

fied by the *alpha effect* from the sulfur atom, having a pair of nonbonding electrons, which can attack isocyanates as hard heterophiles.[13b] A similar behavior has been observed in the nitrite ion[13a] as well. The trimerization process is, therefore, proceeded by an initial attack of (1) on the first isocyanate molecule, followed by attacks of the resulting intermediates on two isocyanate molecules, leading to an isocyanurate as (1) leaves (Scheme 1).

In order to enhance the solubility of sodium *p*-toluenesulfinate and to increase its nucleophilicity, a catalytic amount of a quaternary ammonium halide was added as a phase-transfer catalyst. The synthesis of isocyanurates, catalyzed by tetrabutylammonium flouride, was previously reported, while no catalytic activity was observed when using quaternary ammonium salts of other halides.[1,9b] Based on these data, the efficiency of sulfinate salt in the presence of tetrabutylammonium iodide was investigated. Among quaternary ammonium salts of halides the iodide salt has the softest anion; interestingly, it was found that the catalyst–tetrabutylammonium iodide system has a better catalytic activity than sulfinate salt. Table 1 gives the optimized conditions in the presence of ammonium salt (Table 1, entry 12). It can be deduced that when ammonium salt is added to the reaction medium, the amount of sulfinate salt, time, and temperature are reduced by a factor of 1/6, 1/2, and 1/3, respectively. The optimal conditions were also applied for a number of aryl and alkyl isocyanates except for ethyl isocyanate, in which the reaction was performed near its boiling point. The results are summarized in Table 2. To the best of our knowledge, a few catalysts are able to catalyse the trimerization of alkyl isocyanates.[2,9b] Interestingly, it was found that alkyl isocyanurates can also be prepared under our reaction conditions (Table 2, entries 9–11).

In conclusion, sodium *p*-toluenesulfinate, either alone or in the presence of tetrabutylammonium iodide, is an efficient catalyst for the selective and convenient trimerization of aryl and alkyl isocyanates under solvent-free and environmentally friendly conditions. Further applications of this methodology will be presented in due course.

Experimental

The experiments were caried out under a dry-nitrogen atmosphere. The isocyanates were purchsed from Merck and Aldrich companies. ^{1}H-NMR spectra were recorded on a Bruker FT-80 AC spectrometer. IR spectra were performed on a Mattson 1000 spectrometer. Melting points were determined on a Mettler FPS, and are uncorrected. All products were known, and their spectroscopic data were simillar to those reported in the litrature.[7]

General Procedure for Trimerization of Isocyanates: In a 20 mL flask equipped with a condenser was placed isocyanate (15 mmol), sodium *p*-toluenesulfinate 0.0053 g (0.2 mol%), and tetrabutylammonium iodide 0.0054 g (0.1 mol%) under dry conditions. The reaction mixture was stirred and heated in an oil bath at 70 °C. After the required times (see Table 2) dry diethyl ether (5 mL) was added and filtered. Further isolation of the product was carried out as previously reported.[1,10] The sodium *p*-toluenesulfinate used in this work was supplied as a monohydrate from Lancaster, England, and was dried after powdering in vacuum at 130 °C for 2 h.

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