Quaternary ammonium halides/2-tributylstannylpropanol: an efficient cyclotrimerization catalyst system for aromatic isocyanurate synthesis

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(Received 13 June 1994)

α-Organotin alcohols and quaternary ammonium salts, when used jointly, present a very high activity for the trimerization of aromatic isocyanates. If used separately, no catalytic activity is observed.

(Keywords: α-organotin alcohols; quaternary ammonium halides; cyclotrimerization)

Triisocyanurates are characterized by an outstanding thermal stability. This behaviour is of great significance in polymer manufacture and has been exploited to prepare many branched or crosslinked polymers of commercial relevance. Polyisocyanurate foams are at this time the most effective insulation materials, and no competitive product can match their combination of chemical and fire resistance, compressive strength, R-values and cost-effectiveness.

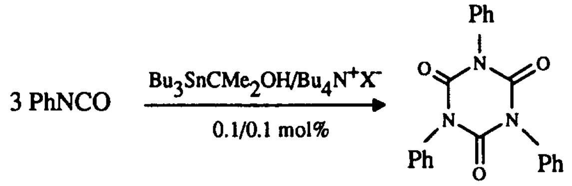
Cyclotrimerization of isocyanates has been shown to be strongly promoted by a broad spectrum of efficient acidic and basic catalysts[1,2]. Among the several families, various metal compounds exhibit a marked activity, which depends largely on the chemical structure of each specific metal derivative, and act as trimerization catalysts via further reaction of the resulting adduct with isocyanates. Tin chemicals, however, do not display the exceptional catalytic activity observed in urethane and polyurethane chemistry[3,4].

In this context, we recently demonstrated the pronounced efficiency of organotin α-substituted alcohols for urethane and polyurethane preparations[5]. Thus, starting from 2-tributylstannylpropanol (2-TBSP) as the model compound, we have investigated and optimized the catalysed addition of thermally sensitive tertiary alcohols to phenyl isocyanate. As a result, the reaction led to a nearly quantitative yield of trimer-free carbamate, whereas a favoured trimerization pathway has been shown to take place for alcohols bearing a nitrogen substituent.

Contrary to the classic synergistic effect observed in urethane and polyurethane field with many organotins (mainly organotin carboxylates) and tertiary amine combinations[1,2], which generally leads to a rate enhancement of the phenyl isocyanate–active hydrogen compound reaction, the 2-TBSP/aminoalcohol combination promotes the trimerization process.

Owing to the industrial importance of the catalytic aspects of the reaction, the search for new catalysts continues to draw the attention of numerous industrial research groups. With this aim, the synthesis of aromatic isocyanurates by fluoride salts such as tetrabutylammonium fluoride (TBAF) has been reported recently, while no catalytic activity could be observed with the chloride[6].

Based on these findings, and on our own observations that quaternary ammonium halides (Cl, Br, I) alone do not catalyse the trimerization reaction, we investigated the cocatalytic efficiency of 2-TBSP in organotin alcohol–quaternary ammonium halide systems:



The group of quaternary ammonium salts and isocyanates used in this study (*Table 1*) was obtained from Aldrich Chemical Company and reacted without further purification, except for the phenyl isocyanate which was purified by distilling under reduced pressure from P_2O_5. 2-TBSP [$Bu_3SnC(Me)_2OH$] was synthesized very easily according to a previous report[7]. Isocyanurates were characterized by comparison of their physicochemical properties with those of authentic samples prepared by standard procedures[8,9].

In a typical experiment, 55 mg (1.7×10^{-3} mol) tetrabutylammonium bromide and 60 mg (1.7×10^{-3} mol) 2-TBSP were added with stirring to 20.2 g (0.17 mol) phenyl isocyanate. The solid state was reached after 7 min at ambient temperature: yield 18.8 g (93%); m.p. 283–284°C (literature[6] 285°C).

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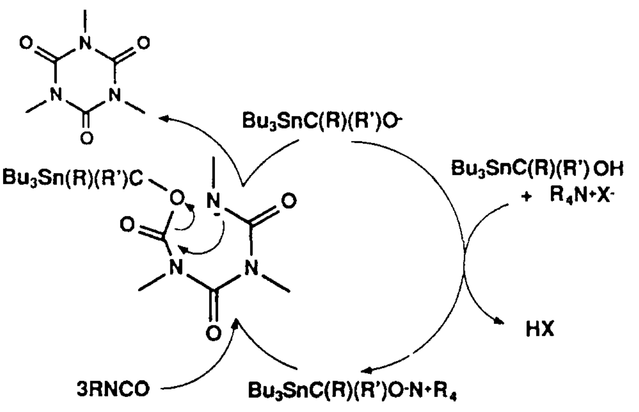
0032-3861/94/23/5146-02

Table 1 Trimerization of phenyl isocyanate with various $R_4N^+X^-$/2-TBSP catalytic systems

Catalyst	Temperature (°C)	Time (min)	Yield (%)
Bu_4NF[a]	Ambient	5	98
Bu_4NCl	Ambient	5	94
$(Hex)_4NBr$	60	20	86
Bu_4NBr	Ambient	7	93
KF[b]	Ambient	20	98
$PhNMe_3Br$	80	30	94
Bu_4NI	80	10	96
$PhCH_2NEt_3Cl$[c]	Ambient	7	98
Me_4NCl	80	15	98

[a] The same result was obtained in the absence of 2-TBSP
[b] KF-catalysed reaction has been introduced because of the extremely low catalytic activity observed in the absence of cocatalyst[6]
[c] Benzyltriethylammonium chloride (TEBAC)



Scheme 1 Proposed mechanism for catalysis by the 2-TBSP/$R_4N^+X^-$ system

Typical results are summarized in *Table 1*. Trimerizations were first examined under similar reaction conditions to the above-mentioned fluoride-catalysed reactions (2 mol% catalyst)[6]. Apart from TBAF, ammonium salts do not present any intrinsic catalytic activity, even on heating, while addition of some catalytic amount of organotin alcohol promotes the polymerization. Best results were obtained under the experimental conditions depicted in *Table 1*, without the appearance of any unfavourable side reaction ($R_4N^+X^-$/2-TBSP: 0.1/0.1 mol%). Although similar results have been obtained by changing some substituents, R or R′ in $Bu_3SnC(R)(R')OH$, 2-TBSP is the more interesting cocatalyst from a practical and synthetic point of view.

For comparison, we investigated the $Bu_4N^+Br^-$/2-TBSP-catalysed trimerization of 3-chlorophenyl and 1-naphthyl isocyanates at ambient temperature. As expected, corresponding isocyanurates were obtained in high yields (93% in 5 min and 95% in 40 min, respectively).

It should be mentioned that TBAF and the TBAF/2-TBSP system have the same catalytic activity. While F^--catalysed trimerization of phenyl isocyanate has been suggested to proceed because of the high nucleophilicity of the fluoride anion, allowing direct addition on the hard heterophilic isocyanate[6], such behaviour does not take place with other halides. It could be predicted that organotin alcohol cocatalysts generate an O^- anion playing the same role as the fluoride one. A likely mechanism of the reaction is represented by *Scheme 1*.

Conclusions

The data presented in this work demonstrate the catalytic efficiency of the proposed quaternary ammonium salt/organotin alcohol combination for isocyanate trimerization. For the first time, tin chemicals could play an important role as cocatalysts in isocyanurate chemistry. In our opinion, two major advantages would result, in comparison to F^--catalysed trimerization processes. First, a much smaller amount of catalyst is needed (0.1 mol% compared to 2 mol%), and secondly, it allows the use of ammonium salts with extremely low prices as starting materials (ammonium salts in *Table 1* are listed in order of decreasing cost in the Aldrich catalogue).

Acknowledgements

The authors are indebted to Schering for their generous gift of organotin compounds and to the CNRS and to the Conseil Régional d'Aquitaine for financial support.

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