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New organotin catalysts in urethane and polyurethane technology

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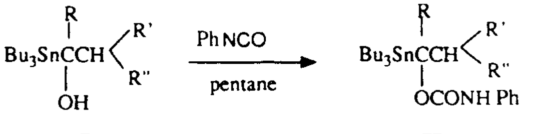
The use of organotin α-substituted alcohols and carbamates as catalysts has been investigated in urethane and polyurethane preparations. These compounds have been shown to be new and very active catalysts. The mechanism of the reaction has been studied.

Keywords: Organotin catalysts, organotin α-substituted alcohols, organotin α-substituted carbamates, isocyanate, urethane, polyurethane

INTRODUCTION

The catalysis of the alcohol–isocyanate reaction is a topic which has led to extensive studies. A number of nucleophilic or electrophilic active catalysts have been reported to increase the rate of addition and inhibit undesirable side elimination processes.[1–6] In particular, organometallic compounds[7] such as tin chemicals[8–10] were found to be powerful electrophilic catalysts. In the polyurethane industry, the widely-used dibutyltin diacetate and stannous acetate are often associated with tertiary amines for better efficiency due to a synergistic effect.[11] Owing to the industrial importance of the catalytic aspects of the reaction,[12, 13] the search of new catalysts continues to draw the attention of numerous research groups. Recently, convenient synthetic procedures have been reported with copper(I) chloride[14] or hydrogen chloride[15] activation.

In a programme to prepare various organotin α-substituted esters as precursors of vinyltins in flash-pyrolysis experiments, we have proposed[16] a direct synthesis of stannyl *N*-phenylcarbamates from tertiary cyclic or acyclic organotin α-substituted alcohols and phenyl isocyanate (Eqn [1]).



$$Bu_3SnC(R)(OH)CH\langle^{R'}_{R''} \xrightarrow[\text{pentane}]{PhNCO} Bu_3SnC(R)(OCONHPh)CH\langle^{R'}_{R''} \quad [1]$$

I → II

It is noteworthy that catalysts are not apparently necessary in the formation of stannyl carbamate. This behaviour can be considered as general since similar results were obtained in related systems by varying the steric environment of the alcohol. These data, which are indicative of a self-catalytic process, prompted us to investigate the activity of these compounds in urethane and polyurethane areas. The mechanistic aspect of the reaction has been rationalized by a catalytic scheme.

RESULTS

Using 2-tributylstannylpropanol (**I**, $R = CH_3$, $R' = R'' = H$) as model compound, we have investigated the catalysed addition of thermally sensitive tertiary alcohols to phenyl isocyanate.

Catalytic efficiency of 2-tributylstannylpropanol

In a typical procedure, equimolecular amounts of various alcohols and phenyl isocyanate were allowed to react in the presence of 1% of catalyst under the experimental conditions depicted in Table 1. Indicated yields correspond to isolated carbamates after recrystallization from petroleum ether.

The reaction was found to proceed directly at ambient temperature with acceptable yields. Nevertheless, the best results were obtained by heating mixtures for a few minutes in the 40–60 °C temperature range. In all cases the only products detected were the carbamates, free from

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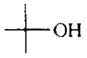
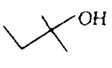
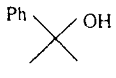
Table 1 Catalytic efficiency of $Bu_3SnC(CH_3)_2OH$

Alcohol	Temp. (°C)	Time (min)	Yield (%)
	25	10	50
	25	25	75
	25	45	92
	40	3	91
	60	2	92
	25	720	80
	40	39	75
	60	8	93
	25	720	81
	40	17	72
	60	10	73
	25	30	68
	40	10	92
	60	5	93

elimination products. As a general rule, 2-tributylstannylpropanol has proved to have best efficiency at 60 °C. Comparison with the uncatalysed thermal reaction and the best current literature procedures is given in Table 2 (in the absence of catalyst, the reaction produces poor yields of the expected carbamates and gives olefins on heating).

Effect of catalyst structure on activity

In order to check the generality of the method, the phenyl isocyanate/t-butyl alcohol reaction was carried out with various catalysts obtained by changing the substituents R and R′ in $Bu_3SnC(R)(R')OH$. Good results were also obtained for $R = H$ and with cyclic systems. Although the results given in Table 3 have not been optimized, they confirm clearly the catalytic efficiency of organotin α-substituted alcohols. Similar data were obtained with the alcohols listed in Table 1.

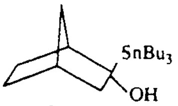
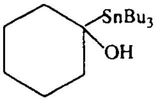
Table 2 Catalytic activity of 2-tributylstannylpropanol compared with other catalysts [phenyl isocyanate/t-butyl(amyl) alcohol reaction]

Alcohol	Catalyst	Time (min)	Temp. (°C)	Yield (%)
tBuOH	None	1440	25	27
	$Bu_2Sn(OAc)_2$	14	32–60	42[a]
	LiOR	10	37	82[a]
	$Bu_3SnC(CH_3)_2OH$	2	60	93[b]
tAmylOH	None	145	25	15
	$Bu_2Sn(OAc)_2$	145	25–40	60[a]
	LiOR	25	37	81[a]
	$Bu_3SnC(CH_3)_2OH$	8	60	92[b]

[a] See Ref. 8.

[b] After recrystallization.

Table 3 Effect of catalyst structure on activity

R	R′	Temp. (°C)	Time (min)	Yield (%)[a]
Me	Me	60	2	92
Et	Et	25	8	41
		25	60	96
		40	3	90
Me	Pr	25	50	90
Me	H	25	180	82
		25	105	71
		25	120	69
		40	6	77

[a] After recrystallization.

Effect of the amount of catalyst

We investigated the formation of urethane from phenyl isocyanate and t-butyl alcohol in the presence of various amounts of catalyst (2-tributylstannylpropanol), under the previously optimized temperature conditions (mixtures were set at 60 °C until the solid state was reached). Results depicted in Table 4 show that an optimization of the amount of catalyst led to a nearly quantitative yield of carbamate.

Mechanism of urethane formation catalysed by organotin α-substituted alcohols

The most likely mechanism involves the generation of an intermediate organotin α-substituted carbamate as active species, and can be described by the catalytic scheme shown in Fig. 1.

Table 4 Effect of the amount of catalyst

Catalyst (mol)	Time (s)	Yield (%)[a]
2×10^{-5}	205	73
5×10^{-5}	190	84
1.5×10^{-4}	145	85
2.8×10^{-4}	120	92
3.4×10^{-4}	65	97

[a] After recrystallization.

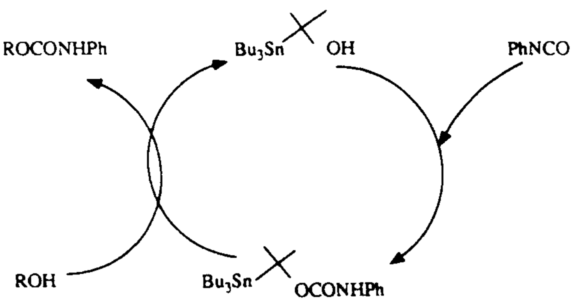


Figure 1 Proposed mechanism for catalysis by organotin α-substituted alcohols.

Such a catalysis involves a greater rate of reaction between the phenyl isocyanate and the organotin alcohol rather than with the organic alcohol. This rate enhancement could be rationalized in terms of an intermolecular acid–base complex between the catalyst and the phenyl isocyanate, resulting from the occurrence of coordination between the electron-rich nitrogen atom and the tin, and between the oxygen atom of the catalyst and the electrophilic isocyanate carbon atom. If this explanation is correct, it could be predicted that the postulated intermediate tin α-substituted carbamates would promote urethane formation as do corresponding alcohols. We have indeed observed such behaviour. Comparison with the results of the tin α-substituted alcohol catalysed reactions reveals that under the same experimental conditions, tin α-substituted carbamate catalysts are superior to the corresponding alcohols. The results in Table 5 are illustrative.

Application of 2-tributylstannylpropanol as catalyst in polyurethane preparations

The tests for polyurethane preparations were conducted on mixtures composed of 1,4-butanediol, poly(ethylene glycol), 5-isocyanato-1-isocyanato-1,3,3-trimethylcyclohexane (isophorone diisocyanate) and catalyst (content 0.09%).

Table 5 Tin-substituted carbamate catalysis of the phenyl isocyanate/t-butyl alcohol reaction at 40 °C

		Alcohols		Carbamates	
R	R′	Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]
Me	Me	3	91	3	97
Et	Et	3	90	3	98
cycloC_6H_{10}-		6	77	6	94

[a] After recrystallization.

Table 6 Polyurethane preparation

Temp. (°C)	Gel time (s)[a]
25	1860
43	1020
53	600
100	240
120	240

[a] Time necessary to reach the gel state at the given temperature.

Mixtures were heated and the gel times (given in Table 6) measured to compare the activity of 2-tributylstannylpropanol with that of dibutyltin diacetate.[12, 13]

CONCLUSION

Organotin α-substituted alcohols and carbamates have been shown to be excellent catalysts for urethane preparations. Preliminary attempts confirm the efficiency of the 2-tributylstannylpropanol in the polyurethane field.

EXPERIMENTAL

Organotin α-substituted alcohols and carbamates were synthesized according to a previous report.[16]

Preparation of urethanes

In a typical procedure, 0.0002 mol of catalyst (2-tributylstannylpropanol) was added to a mixture of t-butyl alcohol (2 g; 0.027 mol) and phenyl isocyanate (3.2 g; 0.027 mol). The mixture was stirred at 60 °C for 2 min and the reacting mass suddenly solidified. The solid was recrystallized from petroleum ether to yield 3.9 g (92%) of *t*-butyl *N*-phenylcarbamate, m.p. 136 °C (lit.[8-10] m.p. 135–136 °C).

Preparation of polyurethanes

The method described for experiments catalysed by dibutyltin diacetate[12, 13] has been followed: 0.8 g (0.009 mol) of 1,4-butanediol, 5.26 g of poly(ethylene glycol) (average MW 1000) and 1 cm^3 of a 0.0075 mol dm^{-3} solution of 2-tributylstannylpropanol in dry ether were placed in a

Schlenk tube. The ether was removed by evaporation and 4 g (0.018 mol) of 5-isocyanato-1-isocyanatomethyl-1,3,3-trimethylcyclohexane was added. The mixture was heated at the given temperatures (Table 6) until the gel state was reached.

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