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RESEARCH ARTICLE

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Synthesis and catalytic properties of tetraorganodistannoxanes containing silicon

Abstract Three tetraorganodistannoxanes containing silicon were synthesized and their catalytic properties in esterification and acetalization were observed *via* the reactions of acetic acid with isoamyl alcohol and butyraldehyde with glycol. The factors affecting the reaction, such as the catalyst dosage, reaction time and solvent, etc. were discussed. The results show that the three tetraorganodistannoxanes displayed similar good catalytic activities compared to dichlorotetrabutyldistannoxane in esterification and acetalization. When the dosage of $[ClBu_2SnOSn(CH_2SiMe_3)_2Cl]_2$ was 1.5% based on the mass of reactant, the yield of isoamyl acetate was 91.8% and the yield of butyraldehyde glycol acetal 94.2%. The different alkyl and bridging groups on Sn sites in the structure of tetraorganodistannoxanes showed some influence on the catalytic activities of these compounds.

Keywords tetraorganodistannoxane containing silicon, synthesis, catalysis, esterification, acetalization

In a conventional process of preparation of acetals (ketals) and acetates, inorganic acid catalysts were commonly used. The process often resulted in environmental pollution and equipment corrosion. As a kind of Lewis acid catalysts, organotin compounds have many advantages over inorganic acid catalysts such as low catalyst dosage, few by-products, simple workup procedure and less environment pollution. They are also non-corrosive to equipment [1,2]. Since the late 1980s, organotin oxo clusters represented by 1,1,3,3-tetraorganodistannoxane have attracted much attention owing to their outstanding catalytic activities in transesterification, esterification, acetalization, and ring-opening polymerization, etc. [3,4]. Tetraorganodistannoxanes, which consist of distannoxane monomers and have the unique dimeric ladder structure both in the solid and liquid state, as reverse-micelle type homogeneous catalysts show excellent catalytic activity and selectivity in many organic reactions [5–7]. However, organotin compounds are limited in practical application due to their toxicity. It was reported that the toxic side effects could be decreased apparently when one carbon atom is replaced by silicon atom in the molecules of some drugs. In addition, biodegradability increased [8]. Therefore, the synthesis and application of organotin compounds containing silicon may meet the requirements of green chemistry. We previously reported the study of catalytic properties of several organotin compounds containing silicon in esterification [9]. To continue the investigation on the catalytic property of organotin compounds containing silicon in other organic reactions and discover safe and efficient organotin catalysts with application prospects, we present in this article the syntheses of three tetraorganodistannoxanes containing silicon: $[Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2Cl]_2$, $ClBu_2SnOSn(CH_2SiMe_3)_2Cl]_2$, and $[(p\text{-}NO_2C_6H_4COO)Bu_2SnOSn(CH_2SiMe_3)_2(OOCC_6H_4NO_2\text{-}p)]_2$. The last two compounds are reported for the first time. The catalytic properties of these three tetraorganodistannoxanes containing silicon in esterification and acetalization are observed in comparison with $[ClBu_2SnOSnBu_2Cl]_2$.

1 Experimental

1.1 Materials and methods

All reagents including acetic acid, butyraldehyde, isoamyl alcohol, glycol, toluene, xylene, cyclohexane, *n*-hexane, chloroform, diethyl ether and petroleum ether were of C.P. or A.R. grade. Bu_2SnO was prepared by the method described in the literature [3] and obtained as white powder with a mp $>300^{\circ}C$. $(Me_3SiCH_2)_2SnCl_2$ was prepared

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by the method described in the literature [10]. It is a colorless transparent liquid with a bp of 100°C–102°C/100 Pa. $(Me_3SiCH_2)_2Sn(OCOPhNO_2\text{-}p)_2$ was prepared by the method described in the literature [11]. It is a light yellow acicular crystal with mp of 148.5°C. $[ClBu_2SnOSnBu_2Cl]_2$ was prepared by the method described in the literature [5] and recrystallized from diethyl ether-petroleum ether mixed solvent to give a colorless crystal with mp 111.4°C–114.2°C (literature value [5] 112°C–114°C). ^{1}H-NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer (Swiss) using Me_4Si (TMS) as the internal standard and $CDCl_3$ as the solvent. The composition of the products were determined by a SP-3420 GC set (Beijing Beifenruili Analytical instrument Co., Ltd, China) using an OV-1 capillary column. The melting points were measured by an X-5 Micro Melting Point apparatus (Guilin Optical Instrument Factory, China) and were uncorrected.

1.2 Preparation of catalysts of tetraorganodistannoxanes containing silicon

1.2.1 Preparation of $[Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2Cl]_2$

Reaction equation:

$$4(Me_3SiCH_2)_2SnCl_2 + 2H_2O \rightarrow [Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)Cl]_2 + 4HCl$$

In a 100 mL conical flask, 1.808 g (5.0 mmol) $(Me_3SiCH_2)_2SnCl_2$ and 20 mL diethyl ether were mixed and stirred uniformly. Exactly 0.505 g (5.0 mmol) triethylamine and 45 mg (2.5 mmol) water were also added under agitation. The solution was heated to about 40°C and reacted for 12 h. The solvent was evaporated under vacuum and the solid residue was recrystallized from *n*-hexane to give a 1.308 g of a white flour crystal with a mp of 192.4°C–194.6°C (literature value [12] 194°C). The yield was 78.3%.

1.2.2 Preparation of $[ClBu_2SnOSn(CH_2SiMe_3)_2Cl]_2$

Reaction equation:

$$2Bu_2SnO + 2(Me_3SiCH_2)_2SnCl_2 \rightarrow [ClBu_2SnOSn(CH_2SiMe_3)_2Cl]_2$$

In a 100 mL conical flask, 1.245 g (5 mmol) Bu_2SnO, 1.808 g (5 mmol) $(Me_3SiCH_2)_2SnCl_2$ and 30 mL acetone were mixed and stirred. The solution was heated and refluxed until it was clear. The hot solution was filtered immediately and the filtrate was concentrated under vacuum to give a light yellow solid. The solid was recrystallized from diethyl ether-petroleum ether to give 2.210 g of white crystals. The yield was 78.3%. The mp of the crystal was 156.4°C–157.8°C. ^{1}H-NMR δ: 0.190 (s, 18H, $SiCH_3$), 0.958 (s, 4H, $SiCH_2$); 0.975 (t, 6H, CH_3), 1.824 (m, 8H, CH_2CH_2), 1.428 (t, 4H, $SnCH_2$).

1.2.3 Preparation of $[(p\text{-}NO_2C_6H_4CO_2)Bu_2SnOSn(CH_2SiMe_3)_2(O_2CC_6H_4NO_2\text{-}p)]_2$

Reaction equation:

$$2Bu_2SnO + 2(Me_3SiCH_2)_2Sn(O_2CC_6H_4NO_2\text{-}p)_2 \rightarrow [(p\text{-}NO_2C_6H_4CO_2)Bu_2SnOSn(CH_2SiMe_3)_2(O_2CC_6H_4NO_2\text{-}p)]_2$$

The title compound was prepared using the same procedures as described in section 1.2.2, while the raw materials were 1.245 g(5 mmol) Bu_2SnO and 3.151 g(5 mmol) $(Me_3SiCH_2)_2Sn(OCOC_6H_4NO_2\text{-}p)_2$. The yellow solid obtained was recrystallized from acetone-petroleum ether to give 3.266 g of light yellow crystals. The yield was 74.3%. The mp of the solid was 163.2°C–164.8°C. ^{1}H-NMR δ: 0.145 (s, 18H, $SiCH_3$), 0.955 (s, 4H, $SiCH_2$); 0.965 (t, 6H, CH_3), 1.825 (m, 8H, CH_2CH_2), 0.965 (t, 4H, $SnCH_2$); 8.303(m,8H, C_6H_4).

1.3 Synthesis of isoamyl acetate

In a 100 mL three-neck flask equipped with a thermometer, a reflux condenser and a water separator, acetic acid, isoamyl alcohol, catalyst and water entrainer were added in a certain proportion. The solution was stirred and refluxed while heating. The results of esterification were obtained by sampling at certain intervals and analyzing the samples by GC.

1.4 Synthesis of butyraldehyde glycol acetal

In a 100 mL three-neck flask equipped with a thermometer, a reflux condenser and a water separator, butyraldehyde, glycol, water entrainer and catalyst were added in a certain proportion. The solution was stirred and refluxed while heating. The results of acetalization were obtained by sampling at certain intervals and analyzing the samples by GC.

2 Results and discussion

2.1 Catalytic activity of different tetraorganodistannoxanes

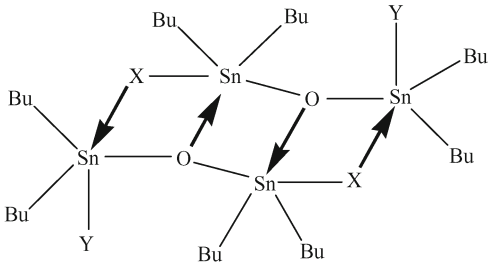
$[ClBu_2SnOSnBu_2Cl]_2$ (catalyst 1) was used as the reference, and the catalytic properties of the three tetraorganodistannoxanes containing silicon, $[ClBu_2SnOSn(CH_2SiMe_3)_2Cl]_2$ (catalyst 2), $[Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2Cl]_2$ (catalyst 3), and $[(p\text{-}NO_2C_6H_4CO_2)$-

$Bu_2SnOSn(CH_2SiMe_3)_2(O_2CC_6H_4NO_2\text{-}p)]_2$ (catalyst 4) were studied *via* the catalytic synthesis of isoamyl acetate and butyraldehyde glycol acetal. In the esterification, 0.1 mol acetic acid was used. The molar ratio of of acetic acid to isoamyl alcohol was 1:1. In the acetalization, 0.1 mol butyraldehyde was used and the molar ratio of butyraldehyde to glycol was 1:1. For all the reactions, the dosage of catalyst was 1.5% based on the mass of the reactant, the volume of the water entrainer was 10 mL and the reaction time was 10 h. The experimental data are given in Table 1.

Table 1 The catalytic activity of the tetraorganodistannoxanes

catalyst	esterification		acetalization	
	water entrainer	yield/%	water entrainer	yield/%
catalyst 1	toluene	94.2	cyclohexane	95.2
catalyst 2	toluene	91.8	cyclohexane	94.2
catalyst 3	toluene	82.6	cyclohexane	86.3
catalyst 4	toluene	89.3	cyclohexane	91.1

The results in Table 1 show that, under the same reaction conditions, the four tetraorganodistannoxanes can be written in order of decreasing catalytic activity as catalyst 1, catalyst 2, catalyst 4 and finally, catalyst 3. This order is observed in both the esterification and acetalization reactions. According to literature [3,5], tetraorganodistannoxanes have dimeric ladder structures (Scheme 1) and the three rings are nearly coplanar. There are two kinds of five-coordinated tin atoms in the structure of tetraorganodistannoxanes. Each *endo*-cyclic tin atom is connected by two alkyl groups R, two oxygen atoms and one bridging group X. Each *exo*–cyclic tin atom is connected by two alkyl groups R, one oxygen atom and two bridging groups X and Y.



Scheme 1 Ladder structure of the tetrabutyldistannoxanes

The catalytic mechanism of tetraorganodistannoxanes in the esterification and acetalization is considered to be a typical catalytic mechanism of metal coordination [3]. The process of coordination-substitution happens mainly on the sites of bridging ligand X. Hence, the catalytic activity of tetraorganodistannoxanes is closely related to the alkyl group R or the bridging ligand X. The catalytic activities in tetraorganodistannoxanes are slightly lower in Table 1 when R is Me_3SiCH_2 possibly because the bulky alkyl group hinders the access of reaction substrate to the catalytic reaction center in the Sn-O ring and delays the progress of the reaction. As a result, a sequence of catalytic activity of catalyst 1 $[ClR_2SnOSnBu_2Cl]_2$ > catalyst 2 $[ClBu_2SnOSn(CH_2SiMe_3)_2Cl]_2$ > catalyst 3 $[Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2Cl]_2$ is established. The influences of different bridging ligands on the catalytic activity of tetraorganodistannoxane are said to be decided by the feasibility of the bridging ligand X being substituted, that is, by the coordinating ability of the bridging ligand X to the Sn atom. For the bridging ligands Cl and $p\text{-}NO_2C_6H_4CO_2$, the former has a strong ability to coordinate with Sn and the latter can be substituted readily by a reaction substrate. As a result, in both the catalytic reactions of esterification and acetalization, the catalytic activity of $[(p\text{-}NO_2C_6H_4CO_2)Bu_2SnOSn(CH_2SiMe_3)_2(O_2CC_6H_4NO_2\text{-}p)]_2$ (catalyst 4) is higher than that of $[Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2Cl]_2$ (catalyst 3). This further proves the metal coordination mechanism in tetraorganodistannoxane-catalyzed reactions.

2.2 Influence of water entrainers

Catalyst 2 was selected for the discussion of the influence of water entrainers in the catalytic reactions. In the catalytic synthesis of isoamyl acetate, the catalyst dosage was 1.8% and reaction time was 12 h. All other reaction conditions were unchanged. Toluene, cyclohexane and chloroform were selected as the water entrainer. In the catalytic synthesis of butyraldehyde glycol acetal, the reaction time was 10 h but all other reaction conditions were the same as in the esterification. Cyclohexane, toluene and xylene were selected as the water entrainer. The experimental data are listed in Table 2. Results show that, in esterification, when toluene was used as the water entrainer, relatively higher catalytic efficiency was obtained and the yield reached 92.5%. In the acetalization reaction, when cyclohexane was used as the water entrainer, the yield was as high as 94.2%.

Table 2 Effect of the water entrainer on the reaction yield

esterification			acetalization		
water entrainer	*t*/°C	yield/%	water entrainer	*t*/°C	yield/%
cyclohexane	87–108	80.2	toluene	116–130	80.3
toluene	116–130	92.5	cyclohexane	87–108	94.6
chloroform	70–90	78.7	xylene	138–146	75.8

2.3 Influence of catalyst dosage

Catalyst 2 was used in the discussion of the influence of catalyst dosage on the catalytic reactions. In the reaction of acetic acid with isoamyl alcohol, the molar ratio of acetic acid to isoamyl alcohol was kept at 1:1. Ten mL of toluene was used as the water entrainer and the

reaction time was 12 h. In the reaction of butyraldehyde with glycol, the molar ratio of butyraldehyde to glycol was kept at 1:1. Ten mL of cyclohexane was used as the water entrainer and the reaction time was 12 h. The experimental values are listed in Table 3. The results indicate that the increase of catalyst dosage was good for the yield of both reactions. In the esterification reaction, when the catalyst dosage was above 2.0% based on the mass of reactant, the increase in yield was not notable. Hence 2.0% was chosen as the appropriate catalyst dosage. In the acetalization reaction, when the catalyst dosage was above 1.8%, the increase in yield was not notable and hence, 1.8% was chosen as the appropriate catalyst dosage.

Table 3 Effect of the catalyst dosage on the reaction yield

esterification		acetalization	
ω(catalyst)/%	yield/%	ω(catalyst)/%	yield/%
0.8	78.5	0.8	78.7
1.2	88.7	1.2	91.2
1.5	90.3	1.5	93.4
1.8	92.5	1.8	94.6
2.0	93.2	2.0	94.8
2.2	93.4	2.2	94.9

2.4 Influence of reaction time on the yield

The catalytic activities of tetraorganodistannoxanes were studied at various reaction times while all other reaction conditions were unchanged in the catalytic syntheses of isoamyl acetate and butyraldehyde glycol acetal. Samples taken at 2-hour intervals were subjected to GC analysis. The experimental data is given in Table 4 and the results show that the yields of the esterification and acetalization reactions increased rapidly with an increase in reaction time. For all the four catalysts, the initial reaction rate in acetalization was faster than that in esterification. A slowing down of the increase in yield was observed when reacted for 8–10 h. Further increase of reaction time caused the increase of by-products and the darkening of products but did not cause a notable increase of the yield. Considering all the various factors, 8–10 h was chosen as the appropriate reaction time.

2.5 Recycling of the catalysts

Catalyst 2 was used in the stability test of the catalytic activity of tetraorganodistannoxanes in the catalytic synthesis of isoamyl acetate and butyraldehyde glycol acetal. The reaction conditions were not changed during the test. After reacting for 2 h, the sample was dried by concentration under vacuum and new solvent and reactants were added to the remaining catalyst to repeat the reaction. Each sample was analyzed by GC. The experimental data are given in Table 5. The results in Table 5 indicate that with an increase in the number of reaction cycles, both the yields of isoamyl acetate and butyraldehyde glycol acetal practically did not decrease. The catalytic activities of tetraorganodistannoxane containing-silicon in esterification and acetalization reactions are relatively constant and the catalysts could be recycled a certain number of times.

In this article, a comparative investigation on the catalytic properties of tetraorganodistannoxanes containing silicon is carried out *via* the catalyzing synthesis of isoamyl acetate and butyraldehyde glycol acetal. The factors affecting the reactions are also discussed. The results show that the three tetraorganodistannoxanes containing silicon display good catalytic activities in the reaction of acetic acid with isoamyl alcohol and of butyraldehyde with glycol. Typically, when the dosage of $[ClBu_2SnOSn(CH_2SiMe_3)_2Cl]_2$ is 1.5% based on the mass of reactant, the yield of isoamyl acetate is 91.8%; the yield of butyraldehyde glycol acetal reaches 94.2%.

The use of safe and efficient catalysts in organic synthesis is one of the hot trends in green chemistry. Compared to $[ClBu_2SnOSnBu_2Cl]_2$, the catalytic activities of the three tetraorganodistannoxanes containing silicon prepared herein are slightly inferior to the former in esterification and acetalization reactions possibly due to the difference in the alkyl groups connected to the tin atoms. Since organotin compounds containing silicon have lower toxic side effects, they are less harmful to people and the environment. Therefore, tetraorganodistannoxanes containing

Table 4 Effect of the reaction time on the yield

time/h	yield of esterification/%				yield of acetalization/%			
	catalyst1	catalyst2	catalyst3	catalyst4	catalyst1	catalyst2	catalyst3	catalyst4
2	48.6	46.8	41.3	49.4	68.7	65.6	58.3	65.1
4	67.8	75.4	67.2	74.5	84.4	83.3	76.4	76.9
6	79.5	84.2	76.5	81.6	90.7	87.4	82.2	85.2
8	88.7	88.5	79.5	85.2	93.6	92.5	85.7	89.4
10	94.2	91.8	82.6	89.3	95.2	94.2	86.3	91.1
12	95.3	92.5	84.7	91.8	96.7	94.6	87.5	92.5

Table 5 Recycling of the catalysts

esterification		acetalization	
cycle	yield/%	cycle	yield/%
1	46.8	1	65.6
2	48.2	2	67.5
3	47.3	3	65.8
4	46.6	4	65.4
5	45.5	5	65.3

silicon have certain application prospects in organic synthesis.

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