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Interaction of substrate and catalyst during the formation of oxazolidinones from 2-aminoalcohols and diethyl carbonate using recyclable 1,3-dichlorodistannoxanes

Sharon Pulla[a,1], Vineed Unnikrishnan[b,1], Punnamchandar Ramidi[a], Shane Z. Sullivan[a], Anindya Ghosh[a,*], Jerry L. Dallas[d], Pradip Munshi[c,**]

[a] Department of Chemistry, University of Arkansas at Little Rock, 2801 South University Avenue, Little Rock, AR 72204, USA
[b] Department of Applied Chemistry, Cochin University of Science and Technology, Cochin, Kerala 682022, India
[c] Research Centre, Rubamin Laboratories, Dabhasa, Vadodara, Gujarat 391323, India
[d] NMR Facility, Med Biochem, 4303 Tupper Hall, University of California, Davis, CA 95616, USA

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ABSTRACT

An efficient synthesis of oxazolidinone (OXZ) using 2-aminoalcohols (2AAs) and diethyl carbonate (DEC) as reagents in the presence of recyclable catalyst 1,3-dichloro-1,1,3,3-tetraalkyldistannoxane, $[(RR'SnCl)_2O]_2$ (**1**) is reported. 0.5 mol% (with respect to 2AA) of **1** provides OXZ quantitatively within 1 h at 80 °C with turnover frequency (TOF) of 200 h^{-1}. The observed TOF is much higher than the reported value (4 h^{-1}) of the most convenient and commercially feasible K_2CO_3 catalyst. Chiral 2AAs produce OXZs with 99% ee. Molar dependency of **1**, DEC and 2AA is found to be 1:2:2. Molar conductivities (Ω^{-1} cm^2 mol^{-1}) in DMSO at 25 °C are 6.41 for **1a** (R = R′ = Bu), 5.25 for **1b** (R = Bu, R′ = Ph), 2.87 for **1c** (R = Ph, R′ = Bu), and 2.21 for **1d** (R = R′ = Ph) which reveal the mobility of bridged Cl in **1** during reaction. The study of a broad range of substrates and reaction parameters supports a reaction pathway that begins with initial attack by –OH of the pre-formed 2-ethylcarbamato aminoalcohol (2ECA) of 2AA on Sn^b of **1** displacing the bridged Cl. Change in the reaction rates resulted due to various alkyl and aryl substituents on Sn provides better understanding of the distannoxane catalysis, which has not been attempted before for the said reaction.

1. Introduction

Oxazolidinones (OXZs) are a class of cyclic urethanes that have various important applications. One of the major applications of OXZs is as chiral auxiliaries [1] for asymmetric transformations. Utilizing the versatile properties of OXZs, several important pharmaceutical products [2], polymers [3], and significant organic molecules can be synthesized [4]. Thus, in terms of organic synthesis, OXZs belong to a very important class of chemicals. In particular, 3-substituted 2-OXZs have been reported to be useful as synthetic reagents, inhibitors, and additives, demonstrating antibacterial and fungicidal activity [5]. Thus, synthetic methods having high yields and reduction in the production costs for such an important class of molecule are a realistic goal of many research efforts.

The preparation of OXZs is well-documented in the literature using various starting materials, catalysts, and reaction conditions. For example, oxidative carbonylation is one of the commonly practiced methods known to produce OXZs with CO and oxygen as starting materials on Pd- and Cu-based catalyst systems with high efficiency [6]. However, costly palladium cannot provide the economic viability for the synthesis, and copper has considerable toxicity. OXZs have also been synthesized using carbon dioxide as the starting material either in catalytic [7] or non-catalytic pathways [8]. But inferior reaction yields and undesirable byproduct formation make the processes less interesting. Propargylamine and CO_2 produce corresponding OXZs with greater ease and with high yields in the presence of Pd [9] or Ru [10] and a heterogeneous catalyst [11]. Still, the acetylenic group holds the key for the success of the reaction and is thus applicable to only a narrow range of substrates. Use of costly palladium or ruthenium at catalyst loading of 5 mol% is another disadvantage of the process. A tosyl derivative of OXZ can be obtained in high yields from serine using a Grignard/CuX catalyst system [12]. A four-step synthetic method has been reported by Green and co-workers for a tyrosine-based OXZ

* Corresponding author.
** Corresponding author. Present address: Research Centre, Reliance Technology Group, Reliance Industries Limited, Vadodara, Gujarat 391346, India.
Tel.: +91 265 669 6049; fax: +91 265 669 63934/3937.
E-mail addresses: axghosh@ualr.edu (A. Ghosh), pradip.munshi@ril.com, pradip.munshi@gmail.com (P. Munshi).
[1] These authors contributed equal amount of work and can be indicated as '*Unnikrishnan and Pulla et al.*'.

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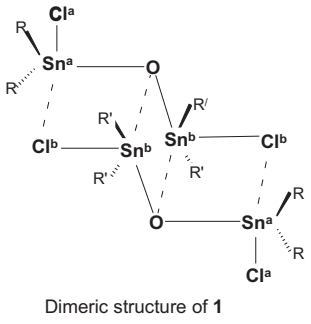


Dimeric structure of **1**

Name	R =	R′ =
1a	Bu	Bu
1b	Bu	Ph
1c	Ph	Bu
1d	Ph	Ph

Scheme 1. OXZ formation from 2AA and DEC using **1**.

that can be used as a chiral auxiliary [13]. Selective rearrangement of certain carbamates also generates OXZ [14]. The rearrangement of specific propargylic *tert*-butylcarbamates, initiated by an efficient gold catalyst, has been reported for the synthesis of OXZ [15]. N-protected alkynylamines can be converted into alkylidene 2-OXZ under mild reaction conditions [16]. Cycloaddition of aziridines with isocyanates produces imino-OXZ [17], but the specific nature of the substrate and expensive catalyst system restricts the procedure from being widely practiced. Use of microwave irradiation as an energy efficient and "green" pathway to synthesize OXZ-2-ones starting with urea and ethanolamine and assisted by a catalytic amount of nitromethane has also been reported [18]. Trichloromethylchloroformate, a very reactive reagent, has been found to form OXZ, imidazolidinone and dioxolanone catalyzed by activated charcoal [19]. However, use of microwave irradiation and toxic trichloromethylformate severely limits these processes. Therefore, from the above discussion, it is evident that the synthesis of OXZs is specific to a substrate and catalyst, and lacks a broader scope.

2-Aminoalcohols (2AAs), which can be derived from their corresponding amino acids, are very useful substrates in the context of OXZ synthesis. They provide a much wider scope, and thus they are the focus of the present work. The synthesis involves cyclilization of 2AAs with organic carbonates or equivalent molecules in the presence of catalysts. The catalyst can be alkali-based or an equivalent, Lewis acidic, or transition metal-based [20]. Alkoxide catalysts require drastic reaction conditions that may damage the chirality, if present, of the final product [21] and may also produce other undesirable byproducts. Diethyl carbonate (DEC) in the presence of K_2CO_3 as a catalyst can produce the product at satisfactory yields [22]. It is noteworthy that 2AAs can also be converted to OXZ using alkali catalyst at the expense of cyclic carbonate [23] by transesterification method. However, use of DMF as solvent, long reaction time and moderate yields are major drawbacks for this process [24].

Considering all of the above-mentioned concerns, a simple, economically viable catalytic method that can be used for synthesizing a broad range of OXZs in good yields is still a major challenge. We have tried to address these concerns by using 1,1,3,3-tetraalkyl/aryl-1,3-dichloro distannoxane (**1**, 0.5 mol%) as an efficient, robust, and recyclable catalyst that can generate OXZ from the corresponding 2-aminoalcohols (2AA) in the presence of DEC in short time (1 h), under mild reaction conditions (80 °C) and in the absence of any additional solvent (Scheme 1). Turn over frequency (TOF) of the process is as high as 200 h^{-1} and the purity of the product is more than 98%. This is a significant improvement in comparison to one of the most efficient synthetic methods of OXZ production where TOF of 4 h^{-1} is achieved using K_2CO_3 as catalyst [20].

Catalysts **1** have been used in a number of places in organic syntheses: namely, in polyester synthesis [25], urethane [26] and polyurethane [27] synthesis, ring opening polymerization [28], esterification and transesterification [29] reactions, etc. They (**1**) show unique advantages in terms of reaction rate, product and catalyst separation, and high reaction yields when compared to the conventional Lewis acid-base catalysts like metal alkoxides or trihalides [29]. We have also demonstrated an efficient green process of transesterification reaction of polyhydric alcohol by varying lipophilicity of **1** [30]. Very recently, for the first time, we have established a synthetic method of producing biodiesel from triglycerides using **1** in supercritical CO_2 [31]. One of the major features of **1** is that it possesses multi-active catalytic centers with controllable Lewis acidity, offering several advantages over other catalysts [29,32]. This unique feature and versatility of **1** have encouraged us to study several unexplored areas such as OXZs synthesis.

In this report, we have studied a series of 2AAs, both chiral and achiral, in order to understand the structure-reactivity relationship (Scheme 1). Interestingly, recovered catalyst (**1**) shows efficiency in producing OXZ similar to that of the original one. Additionally, the reaction kinetics and the possible mechanism of the catalytic pathway have been discussed. The present work also addresses for the first time the effect of substituents on Sn to understand the mechanistic route of OXZ formation using **1**. The proposed mechanistic route is different compared to other literature reported distannoxane catalyzed [27,29,33] reactions where mostly alkyl and bridging groups of the catalyst are varied. As diethyl carbonate, a congener of carbon dioxide, is considered as a green solvent/reagent, the present findings will also contribute to the field of sustainable development for OXZ synthesis.

2. Experimental

2.1. General

Chemicals are purchased from Aldrich Chemical Company, USA and used without further purification unless otherwise specified. Solvents are purified by standard purification procedures before use in the reactions [34]. Reaction products are analyzed by Gas Chromatography (Shimadzu, GC 2010) using a DB-5 column (J&W Scientific). ^{1}H NMR spectra are obtained with a 300 MHz Varian FT spectrometer using deuterated solvent as the lock. The spectra are collected at 25 °C and chemical shifts (δ, ppm) are referenced to residual solvent peak ($CDCl_3$ δ, ^{1}H, 7.26 ppm). ^{119}Sn NMR has been recorded using a Bruker AV500 in $CDCl_3$. Electrospray ionization mass spectra (ESI-MS) are recorded using a Micromass Q-TOF mass spectrometer. Infra Red (IR) spectra are recorded using a Perkin Elmer, Spectrum 100 instrument. The elemental analyses (C, H) are carried out with a Perkin-Elmer 2400 C elemental analyzer (accuracy ±0.3%). Amount of tin was estimated using inductively coupled plasma optical emission spectroscopy (ICP-OES), Perkin Elmer, model 4300 DV (detection limit 1 ppm). Chloride is estimated using an Ion Chromatography (Metrohm) method (detection limit 1 ppb). Enantiomeric excess is measured in Shimadzu LC 2010 HPLC using Daicel's CHIRALPAK® AD-H column.

Catalysts are synthesized according to an established procedure [30]. Chlorine and Sn are determined according to published methods [35].

2.2. Preparation of oxazolidinone

In a typical reaction, 257 g (2.18 mol) of DEC, 73.3 g (0.49 mol) (S)-phenylalaninol and 1.2 g (0.001 mol) catalyst **1a** are combined in a three-necked round bottom flask equipped with a 12″ Vigreux condenser and heated at 80 °C for 1 h. The initial heterogeneous solution slowly becomes homogenous within 10 min. The progress

of the reaction is monitored by a Shimadzu 2010 gas chromatograph equipped with a DB-5 column while comparing the reaction mixture with the authentic sample. After 1 h, the flask is cooled to room temperature. The excess of DEC and ethanol produced are distilled. The resultant concentrated mass is diluted with dichloromethane and analyzed using GC. During the cooling of the reaction mixture, the catalyst also settles down at the bottom of the flask, which is easily collected by filtration. The recovered catalyst and DEC are used in the next reaction to test for recyclability. The procedure also works for 2-aminophenol and 2-aminophenylethanol.

Other OXZs are synthesized following the similar procedure except the purification method, which is performed according to the nature of substrates and products. For example, in case of the substrates 2-aminobutanol and ethanolamine **1a** does not separate from the reaction mixtures. So at the end of the reaction, mixture is loaded on a 6″ silica gel column for the separation of the catalyst. OXZ and the catalyst are then eluted with ethylacetate–hexane mixture with 3:1 and 1:1 ratio, respectively.

The recovered catalyst is dried under vacuum oven for 4 h at 80 °C and characterized by ^{1}H NMR and ^{119}Sn, ESI-MS and the elemental analysis. The recovered catalyst is used for further experiments. Generally solvent extraction methods are employed for catalyst recovery. In cases where solvent recovery cannot be used due to solubility issue, separation using silica-gel column chromatography is pursued.

2.3. N-(2-hydroxyethyl)ethylcarbamate

Ethanolamine (100 mg, 1.64 mmol), and DEC (871 mg, 7.37 mmol) are taken in a round bottom flask and heated at 80 °C for 1 h. The reaction is monitored by GC where no formation of oxazolidinone is noticed at this reaction condition. Formation of carbamate is confirmed by indentifying the corresponding m/z (M^+ 132) of the desired product in the GC–MS. The reaction mixture is concentrated under reduced pressure and purified by silica gel column chromatography. N-ethylcarbamatoethanolamine is eluted with 1:5 ethyl acetate–hexane mixture. The solvent eluted from the column is concentrated at the reduced pressure to get the desired product. Yield 65%. ^{1}H NMR; δ 1.24 (3H, t, J = 7.1), 4.23 (2H, q, J = 7.1), 3.49 (2H, t, J = 6.6), 3.48 (2H, t, J = 6.6).

Other carbamates are prepared using the same procedure with the appropriate amount of reactants. The carbamate of 2-ethoxyethylamine is prepared in a similar manner.

N-(methyl)(2-hydroxyethyl)ethylcarbamate: ^{1}H NMR: δ 1.24 (3H, t, J = 6.9), 2.74 (3H), 4.24 (2H, q, J = 7.1), 3.50 (2H, t, J = 6.1), 3.53 (2H, t, J = 6.1).

N-(2-ethoxyethyl)ethylcarbamate: ^{1}H NMR: δ 1.25 (3H, t, J = 6.9), 1.24 (3H, t, J = 6.9), 3.40 (2H, q, J = 6.9), 4.28 (2H, q, J = 6.9), 3.46 (2H, t, J = 6.7), 3.45 (2H, t, J = 6.7).

2.4. Oxazolidinone from N-(2-hydroxyethyl)ethylcarbamate

N-(2-hydroxyethyl)ethylcarbamate (175 mg, 2.0 mmol) is taken with 20 mL toluene in a round bottom flask and heated at 80 °C for 1 h. The reaction is monitored by GC. The peak at 8.95 min of the chromatogram which is different from the N-(2-hydroxyethyl)ethylcarbamate peak at 10.11 min indicates the formation of oxazolidinone. Concentrated mass obtained after evaporation of toluene from the reaction mixture is separated through a 10 in. silica gel column and oxazolidinone is eluted by 1:3 ethylacetate–hexane. ^{1}H NMR: δ 3.49 (2, 1H, ddd, J = 8.0, J = 4.3, J = 0.0), 3.491 (2, 1H, ddd, J = 8.0, J = 4.3, J = 0.0), 4.44 (3, 1H, ddd, J = 8.0, J = 4.3, J = 0.0), 4.44 (3, 1H, ddd, J = 8.0, J = 4.3, J = 0.0). mp 87 °C.

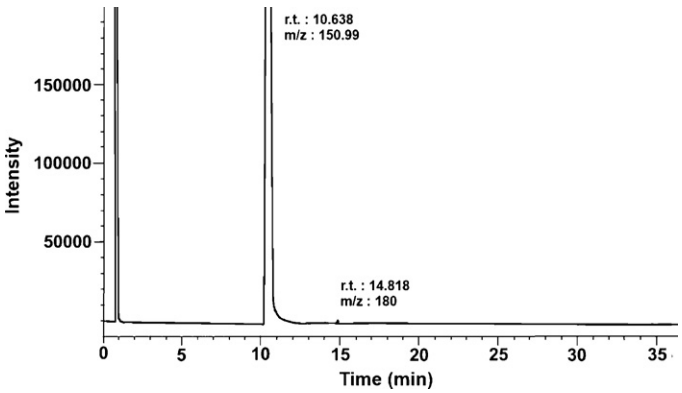


Fig. 1. GC chromatogram of (S)-2-benzyloxazolidinone. Phenylalaninol 0.25 mmol, DEC 1.08 mol, **1a** 1.0 mmol, 80 °C, 1 h.

2.5. Determination of rate constants (k)

Rate constants are measured for various oxazolidinone formations as shown by Eq. (1). As observed the reaction is considered first order with respect to 2AA. Concentration of DEC is kept high enough in order to maintain a pseudo first order nature of the reaction. For each reaction following the above-mentioned procedure, concentration of the components including the product varied during the course of the reaction is measured by GC. Variation of 2AA are noted in 10 min time interval and plotted against time following the equation

$$[2AA] = [2AA]_0 - kt \quad (1)$$

where [2AA] denotes concentration of 2AA at time t while $[2AA]_0$ denotes the initial concentration of 2AA and k denotes the rate constant. Finally k is obtained from the slope of the plot.

2.6. Estimation of Cl^- and Sn

A representative method for the estimation of Cl^- and Sn during 4-benzyl-2-oxazolidinone synthesis using catalyst **1a** is described here. 150 mg (0.99 mmol) of 4-benzyl-2-oxazolidinone is digested with equivalent amount of concentrated HNO_3 (69%) in a porcelain crucible for 5 h. The resultant digested mass is then evaporated to dryness. The solid obtained after evaporation is dissolved in 10 mL water and acidified with dilute HNO_3 (6.9%) until solution turned clear. After filtering the solution, the filtrate is transferred into a 100 mL volumetric flask and made up the volume with water. The solution is then analyzed to estimate Cl^- by using a Metrohm column in ion chromatography method (limit of detection 1 ppb). The same solution is used to determine Sn content by ICP-OES.

3. Results and discussion

3.1. Synthesis of oxazolidiones

All the catalysts are synthesized according to our previously reported procedures [30]. For the synthesis of OXZ, typically DEC, 2AA and a catalyst (0.5 mol% with respect to 2AA) are combined in a round bottom flask while the progress of the reaction is monitored using a GC equipped with a DB-5 column, following the diminishing peak of 2AA and growing peak of OXZ. As an example, Fig. 1 shows a typical chromatogram obtained during the formation of (S)-4-benzyl-2-oxazolidinone (retention time 10.6 min) using (S)-phenylalaninol (retention time 14.2 min) as the starting compound. The purified (S)-4-benzyl-2-oxazolidinone from the reaction mixture is characterized using ^{1}H NMR, electrospray ionization mass spectroscopy (ESI-MS) and elemental analysis. (S)-

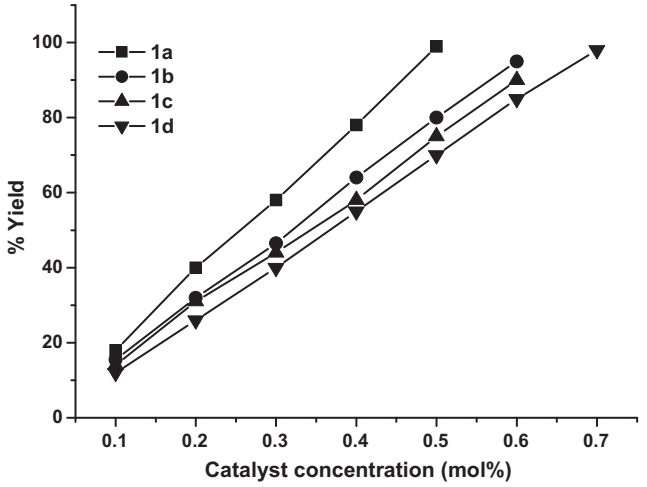


Fig. 2. Variation in yield of formation of (S)-2-benzyloxazolidinone with respect to catalyst concentration. Temperature 80 °C, DEC 1.07 mol, phenylalaniol 0.25 mol, time 1 h.

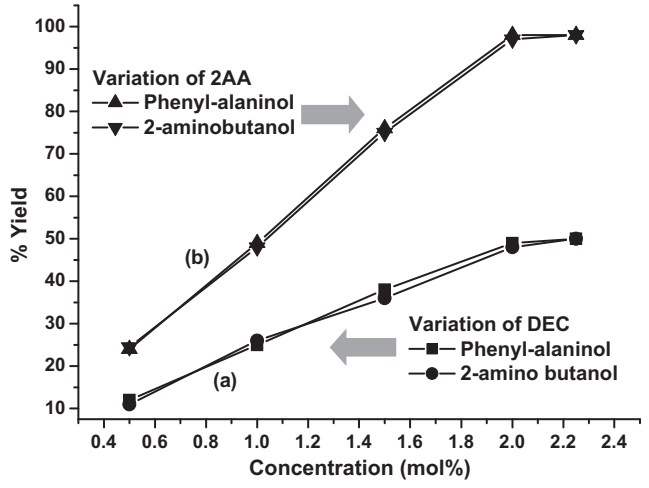


Fig. 3. Variation of (a) 2AA and (b) DEC. 1 h, 80 °C. (a) **1a** 0.004 mol, 2AA 1.09 mol and (b) **1a** 0.004 mmol, DEC 1.13 mol.

4-benzyl-2-oxazolidinone shows *m*/*z* 150.99, which is in complete agreement with the literature-reported values [36]. The yield of OXZ is calculated based on external standard method using in-house produced authentic OXZ samples. In the GC (Fig. 1), there is an extra peak at 14.8 min which vanishes with time and is also different from the product and reactant. The new peak shows mass spectrum at *m*/*z* 180 which corresponds to ethyl carbamate of 2AA, a possible intermediate of the reaction.

Results indicate that almost 100% yield is obtained within 1 h at 80 °C using 0.5 mol% of **1a**, while maintaining concentrations of DEC and 2AA of 5:1 (Table 1). The role of **1** is critical for OXZ formation as no product formation is observed when reactions are performed under similar conditions without adding any catalyst. **1** and OXZ can be separated using short column chromatography, depending upon the nature of the 2AAs. We have studied ICP-OES and ion chromatography analyses for detecting Sn and Cl^- [35] in order to check if they have leached from the catalyst during the reaction. The result indicates that tin or chlorine residues are present at lower than the detection limit in the product.

A series of 2AAs along with different catalysts have been studied in order to understand the reactivity patterns and mechanism. It has been found that the nature of both 2AAs and **1** affects the efficiency of the reaction, which is addressed in details here.

Table 1 shows the results obtained upon variation of substrates, catalysts and other reaction parameters. The yield increases with time and reaches the maximum within 1 h (Table 1, entries 3–8). Similarly the temperature (Table 1, entries 19–21) is optimized at 80 °C. A rise in temperature is required to obtain similar efficiencies in the case of a less efficient catalyst. However, very high temperature lowers the reaction yield (Table 1, entries 19–24).

3.2. Dependence of catalyst, DEC and 2AA

When the amount of **1** is varied (in terms of mol%) in the formation of OXZ using (S)-phenylalaninol as substrate, it is shown in Fig. 2 that yield is directly proportional to the concentration of **1**. This indicates a first order dependency on the catalyst. However, when different catalysts are used, depending on the substitution on the catalysts, the yield of the reaction varies too. As Fig. 2 shows, **1a** is much superior in comparison to other catalysts, namely **1b**–**1d**. In fact, **1d** is found to be the least active among the series. It can be concluded from Fig. 2 that the introduction of aromatic substituents in the catalyst structure causes a reduction of activity. An optimum amount of catalyst of 0.5 mol% with respect to 2AA is chosen for most of the reactions.

We have checked the dependency of DEC for OXZ formation using catalyst **1a** and (S)-phenylalaninol as a substrate. Hexane is used as an inert solvent during this investigation. It is presumed that the use of hexane is just limited as a medium in order to perform the reaction at very low concentration of DEC. Fig. 3 shows the effect of DEC concentration on OXZ formation using catalyst **1a**. It is evident from the plot that a 1st order dependency exists on DEC when the concentration of DEC is low and reactivity reaches a maximum when the molar ratio of DEC to catalyst reaches 2:1. Further increase in the DEC concentration does not effectively improve the yield. The result has been verified for different 2AAs too.

A similar observation is encountered when percent yields are determined using different concentrations of 2AAs namely, (S)-phenylalaninol and 2-aminobutanol. In these cases, addition of hexane is not necessary. It is evident from Fig. 3 that there is a linear relationship between yield (%) and concentrations of 2AA when catalyst (**1a**) concentration is kept constant. This is a different observation when compared to those of other reported reactions, like esterification reaction catalyzed by **1** where saturation of the reaction yields is observed [27,37]. Therefore, it can be presumed that the change in Gibbs free energy (ΔG) for the reaction is highly negative and this is true at least for the rate determining step (RDS) of the overall reaction [38]. Stoichiometrically, the present reaction (Eq. (1)) has positive entropy change ($\Delta S = 1$ eu), whereas esterification and other reported reactions have $\Delta S = 0$ eu. As a result, in accord with the formula $\Delta G = \Delta H - T\Delta S$, assuming ΔH is small, ΔG comes out to be negative, resembling a spontaneous reaction [39].

The linear relationship is found to be maintained even under the low concentrations of 2AAs. With increasing 2AA concentration, the yield reaches a maximum when 2AA and **1a** have a ratio of 2:1. Thus, it can be concluded that for obtaining an optimum product yield, maintaining a ratio of **1**, DEC and 2AA of 1:2:2, respectively is extremely important. The fact that **1** has two active Lewis acid centers and taking into consideration the above-mentioned ratio of reactants to **1** for obtaining the optimum yield, it can be concluded that two nonequivalent Sn (Sn^a and Sn^b) atoms of **1** interact with both DEC and 2AA during the product formation. The yield obtained in the case of DEC variation (Fig. 3a) is lower than that of 2AA variation (Fig. 3b). This is due to the dilution by hexane which lowers the effective concentration of **1**. However, the slopes of the two different plots indicate that the strength of interaction of catalyst with 2AA is higher than with DEC [40]. This can be explained

Table 1
Reactivity of **1a** with 2AA.[a]

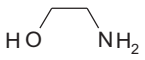
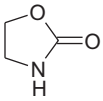
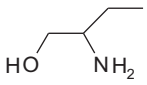
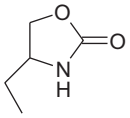
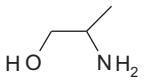
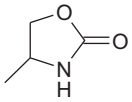
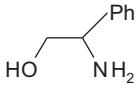
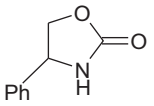
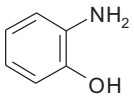
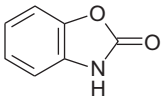
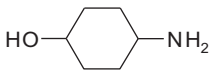
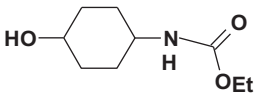
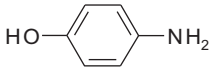
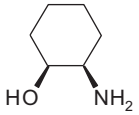
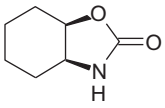
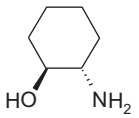
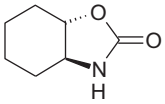
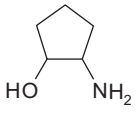
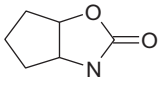
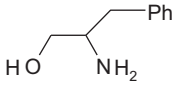
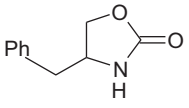
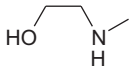
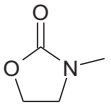
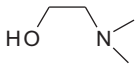
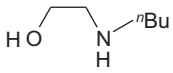
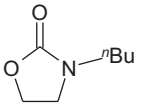
Entry	Substrate	Catalyst[b]	Temperature (°C)	Time (min)	Product	% Yield[c]	% ee[d]
1		**1a**	80	60		97	
	Ethanolamine						
2		**1a**	80	60		98.5	99
	(S)-2-Aminobutanol						
3		**1a**	80	50		30	
4		**1a**	80	40		<5	
5		**1b**	80	60		80	
6		**1c**	80	60		76	
7		**1d**	80	60		67	
8		**1a**	80	60		99	99.2
	(S)-2-Aminopropanol						
9		**1a**	80	60		100	99.5
	(S)-2-Aminophenylethanol						
10		**1a**	80	60		80	
	2-Aminophenol						
11		**1b**	80	60		60	
12		**1c**	80	60		40	
13		**1d**	80	60		10	
14		**1a**	80	60		70	99.2
	cis-4-Aminocyclohexanol						
15		**1a**	80	60	No reaction	-	
	4-Aminophenol						
16		**1a**	80	60		71.4	98.9
17		**1a**	80	60		98.2	99.4
18		**1a**	80	60		98.8	99.5
	2-Aminocyclopentanol						
19		**1a**	80	60		99	99.8

Table 1 (*Continued*)

Entry	Substrate	Catalyst[b]	Temperature (°C)	Time (min)	Product	% Yield[c]	% ee[d]
	(S)-phenylalaninol						
20		**1a**	60	60		52	99.5
21		**1a**	40	60		20	99
22		**1a**	100	60		95	95
23		**1a**	110	60		80	95
24		**1a**	120	60		70	93
25		**1a**	80	60		93	
26		**1a**	80	60	No reaction		
27		**1a**	80	60		86	

[a] DEC is used in all cases.
[b] In all the cases 0.5 mol% catalyst is used with respect to substrate 0.5 mol, unless the value mentioned in parentheses.
[c] Yields are measured in GC by external standard method using authentic samples.
[d] ee is determined by % area obtained in chiral HPLC chromatogram.

by considering the nucleophilicity of the reagents. 2AA is actually a stronger nucleophile than DEC. So it is expected that 2AA will be the first to attack the most active Lewis acidic site of **1**.

3.3. Effect of nature of substrates and proximity of substituent

Results listed in Table 1 reveal that catalyst **1** is highly efficient in promoting the reaction of 2AA and DEC to form OXZs. However, the nature of the substrate has a significant effect on the reaction yield. In order to understand such an effect a detailed study using various substrates is performed. Proximity of –OH and $–NH_2$ groups in 2AAs is an important factor in governing the yield of the reaction, as it is directly related to the feasibility of the OXZ ring formation. Thus, no products are obtained when *p*-aminophenol and *p*-aminocyclohexanol are combined, as the amine and alcohol groups are too far apart in these molecules making the ring formation difficult. Only ethylcarbamic ester forms in the case of *p*-aminocyclohexanol; *p*-aminophenol does not even form any carbamate ester due to its low nucleophilicity (Table 1, entries 14 and 15).

Subsequently, the rate of formation of OXZ from *cis*-2-aminocyclohexanol is lower than that of the *trans* isomer (Fig. 4). According to Paizs's calculation, the *trans* isomer remains in the low energy conformation where both –OH and $–NH_2$ are in equatorial positions due to internal hydrogen bonding [41]. As both groups are locked into equatorial positions they are in close proximity to each other and can interact with **1** and subsequently form the OXZ ring very easily. However, this is not the case for the *cis* isomer, making the reaction rate low. In the *cis* isomer the axial hydrogen comes within close proximity of the axial chlorine, Cl[a], of **1** making the relevant transition state (TS) unstable. In the case of S_N2 attack on the Sn[b] for replacing Cl from Cl–Sn[b]–O moiety, the angle of attack named 'deviation angle', is too narrow to allow the axial hydrogen of the *cis* isomer to be accommodated in the intermediate structure and thus explaining the slower reaction rate. As described in Fig. 5, deviation angle of Cl[b]–Sn[b]–O in **1a** is 38° and it is shortened to 29° in **1d**. The value for **1a** is actually the value of tetraethyldichlorodistannoxane. This, we have approximated based upon the fact that they are structurally similar, also ^{119}Sn NMR and Mössbauer isomeric shift almost do not change while changing from ethyl group to butyl group in **1** [42].

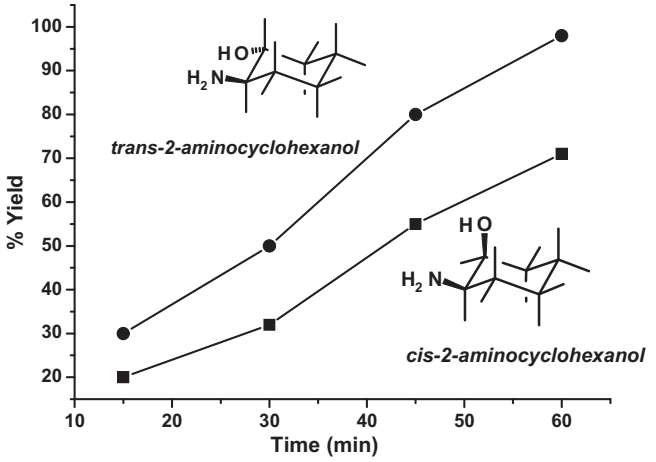


Fig. 4. Relative rate of *cis* and *trans* 2-aminocyclohexanols towards formation of OXZ. 2AA 0.25 mol, DEC 1.15 mol, 80 °C, **1a** 0.001 mol. H is omitted from the bonds for clarity.

Substituents on the nitrogen atom of 2AA can also influence the reaction yield. Results indicate that a 1° amine reacts more efficiently than a 2° amine even though the basicity and nucleophilicity of a 2° amine is higher than that of a 1° amine [43]. The lowered reactivity of a 2° amine can be attributed to its steric bulk [44]. Thus, 2-aminoethanol (a 1° amine) provided a higher yield of OXZ than N-

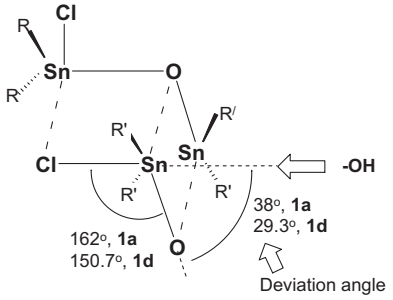


Fig. 5. 'Deviation angle', the angle of deviation from linearity, showing availability of bigger room for **1a** than **1d** for S_N2 displacement of Cl by incoming –OH of 2AA.

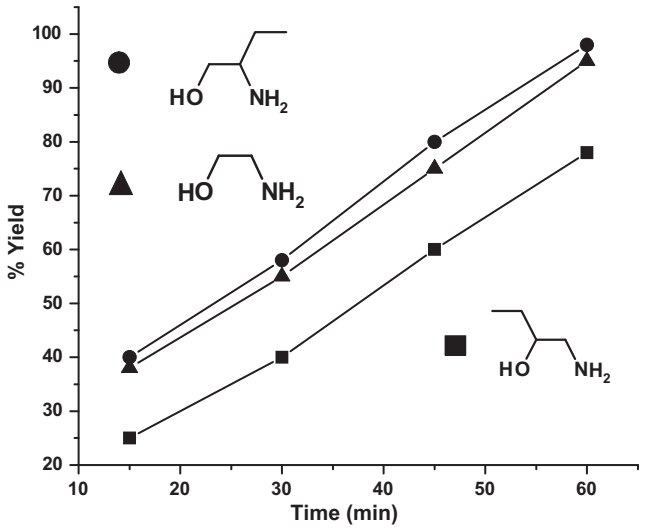


Fig. 6. Effect of substituents in **1** and **2** positions in 2AA. 2AA 0.23 mol, DEC 1.06 mol, **1a** 0.001 mol, 80 °C, 1 h.

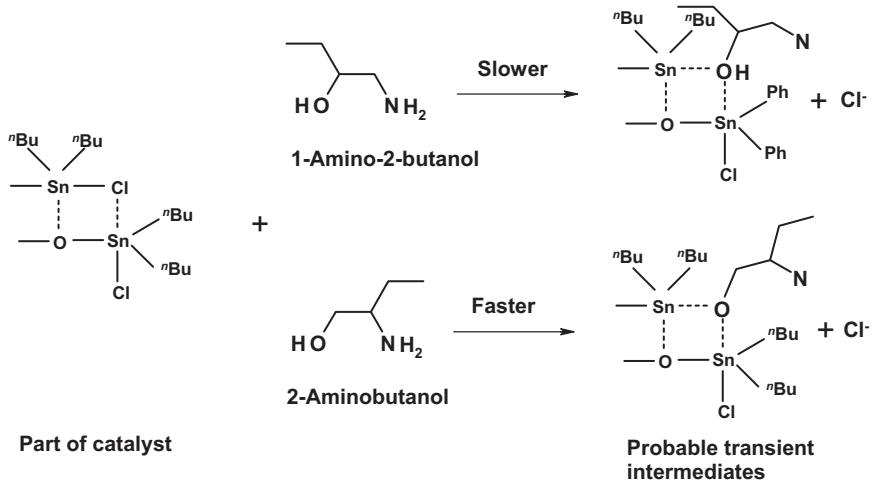
ethyl-2-aminoethanol (a 2° amine) (Table 1, entries 1 and 25). This observation is further verified when N-butyl-aminoethanol, a more sterically hindered 2° amine, yielded much less OXZ (Table 1 entry 27). Basically, substituents on nitrogen do not allow the intermediate or TS to be accommodated in the deviation angle for displacing Cl^b.

As seen in Fig. 6 the rates of OXZ formation using 2-aminobutanol and 1-amino-2-butanol are significantly different. A lower reaction yield is obtained in case of the latter. Substituent effects at the **2** and **1** positions of 2AA may imply a possible influence in the transition state. In this case too, the deviation angle can help to explain the effect. Interestingly, Fig. 6 also reveals that aminoethanol has a similar reaction rate to that of 2-aminobutanol, proving that the substituents next to $-NH_2$ in 2AA have little effect. This may be due to the fact that substituents at the **1** position of 2AA, which is next to the –OH, cause more steric hindrance (Scheme 2) in the TS. On the other hand, substituents at the **2** position in 2AA, next to $-NH_2$, are too far away to create an obstacle for product formation, resulting in a higher reaction rate and yield. It can be surmised from this information that the involvement of the –OH group in the TS during product formation has more influence on the RDS. The presence of a IR band at 582 cm^{-1} and the absence of Sn–N stretching at 428 cm^{-1} [45] confirm the formation of Sn–OR [46] and precludes the interaction of $-NH_2$ with **1** (Scheme 2). Absence of –OH stretching at 3400 cm^{-1} also supports the transformation [47]. Following the previously reported mechanism using **1** as a catalyst [29,30,33] for various reactions, it can be argued that 2AA attacks **1** by displacing the bridged Cl, which we also have demonstrated and described later. So it can be concluded that –OH of 2AA interacts with **1** displacing Cl [33]. Minor lower yield encountered in case of aminoethanol than 2-aminobutanol is probably due to higher nucleophilicity of 2-aminobutanol.

3.4. Nature of the catalyst

The crystal structures of distannoxanes reported by a number of authors [42,48,49] reveal that **1** has a stable dimeric ladder type structure in a distorted trigonal bipyramidal environment. This makes two Sn atoms non equivalent which is also reflected in ^{119}Sn NMR studies [50]. Our observation, as mentioned above (Fig. 2) also supports the non equivalency of Sn^a and Sn^b. The unique features of the catalysts, which differ from conventional single site Lewis acidic catalysts, are due to two dissymmetric Sn centers (Sn^a and Sn^b) in **1**. In order to study the effect and role of Sn centers of **1** on reactivity, substituents on Sn are varied. Alkyl and aromatic substituents further control the varying electronic and steric environment and, in turn, the different activity of **1**. The catalysts with all the butyl groups (**1a**) are found to be the most superior and progressively show lower activity when substituted with phenyl groups (**1b**–**1d**) as shown in Fig. 7. Position of the phenyl substituent on Sn is one of the deciding factors on the reactivity of **1** too. This is noticed in the variation of activities between **1b** and **1c**, once again proving the non-degeneracy of Sn. This is in agreement with our earlier observation regarding the formation of glycerol carbonate from DEC and showing **1a** and **1d** are most and least reactive catalysts, respectively [30].

Studies on distannoxanes by a number of groups imply that its reactivity lies in the displacement of bridged Cl [42,48,49,51,52]. Due to the dimeric structure of distannoxanes the bridged Sn–Cl bond is longer than the axial bond, making it more susceptible to displacement. This is shown in many other crystal structures of distannoxanes as well [53–55]. According to the theoretical calculations proposed by Wakamatsu and co-workers, additional stabilization of **1** is gained upon dimerization through the bridging of Cl with another molecule [56]. This makes the Sn–Cl bond long enough to be partially ionic in nature. For example, distances of Sn^a–Cl^b and Sn^b–Cl^b are 2.697 Å and 2.43 Å, respectively in **1d** [49]. This difference in distances is even more promi-



Scheme 2. Effect of the position of substituents in 2AA.

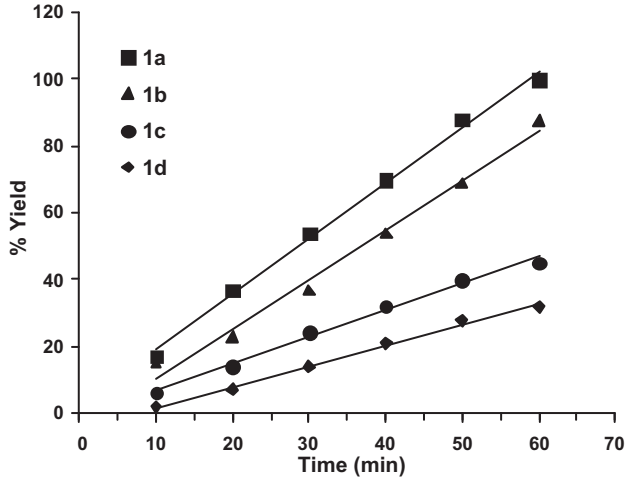
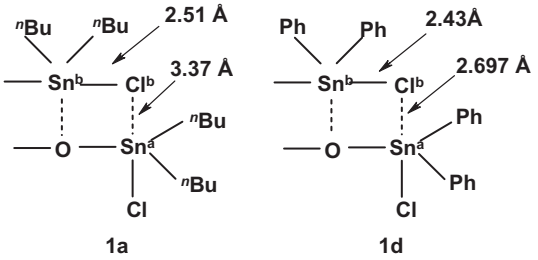


Fig. 7. Relative efficiencies of **1**. Phenylalaninol 0.5 mol, **1** 1.1 mmol, DEC 1.08 mol, 80 °C.



Scheme 3. Longer Sn^b–Cl^b and Sn^a–Cl^b distances caused by ^{n}Bu substituents in **1a** for Cl displacement with greater ease in comparison to Ph substituted **1d**. Data for **1a** is taken from dichlorotetraethyldistannoxane assuming that Et and Bu has no effect in structural change as confirmed by Mossbauer and ^{119}Sn NMR.

nent in the case of **1a**, which are 3.37 Å and 2.51 Å, respectively (Scheme 3) [42]. In this case too, the data mentioned for **1a** is actually of tetraethyldichlorodistannoxane, due to the same reason spelled in Section 2.3 [51]. Measurements of the molar conductivity (Ω^{-1} cm^2 mol^{-1}) of the catalysts in DMSO (Table 2) show a similar downward trend: 6.41 for **1a**, 5.25 for **1b**, 2.87 for **1c** and 2.21 for **1d**. The value for **1a** is in accordance with the literature reported value of 6.36 Ω^{-1} cm^2 mol^{-1} [57]. Therefore, the more ionic character of bridged chlorine would be favorable for producing the reaction with more ease. The distance of the Sn^a–Cl^b bond is 3.37 Å for **1a** and 2.697 Å (Scheme 3) for **1d**. This clearly indicates more lability of Cl in **1a**. The longer bond length in **1a** can be explained by isomeric shift (IS) values, in Mössbauer spectrum as reported by Harrison and co-workers, 1.46 (mm/s) and 1.26 (mm/s) for **1a** and **1d**, respectively. Due to the –I effect of the phenyl group, the IS value of **1d** is as close as a methyl derivative (1.28). As indicated by a large IS, a higher electron density on Sn in **1a** is responsible for making a weaker bridged chlorine, rendering more lability to the Cl atom. As the Ph on Sn^a shortens the Sn^a–Cl^b bond distance, **1b** should be more active than **1c**. In other words, a Ph on Sn^a has a stronger influence than on Sn^b. It is apparent that the displacement of bridged chloride from terminal Sn is of prime importance in governing catalytic activity. Although there is not much information available for **1b** and **1c**, the sudden drop in molar conductivity from 5.25 (**1b**) to 2.87 (**1c**) clearly demonstrates the mobility difference in bridged chlorines between these two catalysts. The conclusion drawn above is valid as it has been found that the rate constants measured for the four catalysts (Table 2) show the same trend as that of the conductivity.

Table 2
Characteristics of **1** that influence reactivity.

Catalyst	Sn^a–Cl^b (Å)	Sn^b–Cl^b (Å)	Λ_m (s cm^2 mol^{-1})	$k \times 10^{-3}$ (s^{-1})	
				2-AB[a]	Phal[b]
1a	2.697	2.43	6.41	51.9333	49.721
1b			5.25	41.4217	40.003
1c			2.87	18.930	12.232
1d	3.37	2.51	2.21	6.9943	5.890

[a] 2AB = 2-aminobutanol.
[b] Phal = (S)-phenylalaninol, 80 °C, 1 h.

Relative chlorine replacement strength of a substrate can be observed from the fact that 2-aminophenol exhibits lower activity than 2-aminocyclohexanol when catalyzed by **1a** (Table 1, entries 10, 16 and 17). Thus apart from the ionic character, Sn^b–Cl^b bond distance of bridged Cl is equally important that differs for all the catalysts. Activity can be simply correlated to the nucleophilic strength of –OH groups, which is less in 2-aminophenol [58]. Thus, the rate of reaction varies depending on both substituents on the catalyst and the substrate.

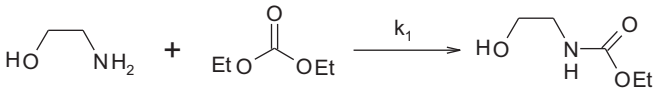
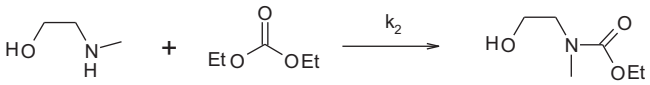
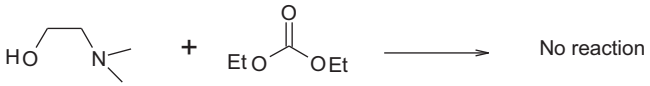
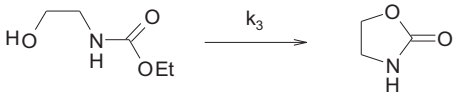
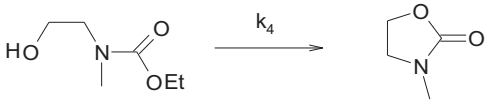
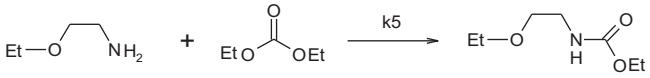
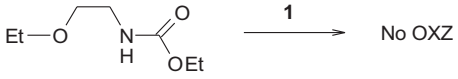
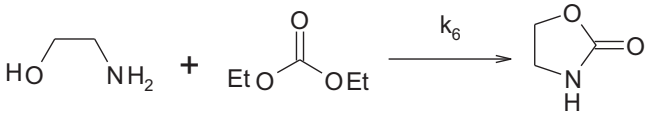
3.5. Mechanism

Few attempts have already been made by various groups in describing distannoxane catalysis. But in our case bifunctionality of 2AA presents complications, which made us to look into the mode of interaction of 2AA (through –NH_2 or –OH) with the specific catalyst active site, Sn^a or Sn^b.

As explained earlier (Scheme 2), FTIR band at 582 cm^{-1} (**1a**) indicates that it is –OH functionality, and not the –NH_2 group, most likely interacts with **1**. This also points out that the –OH of 2AA interacts with Sn^a not Sn^b, otherwise the peak would have appeared at 605 cm^{-1} [46]. Findings of past studies involving transesterification reaction catalyzed by **1** resulted in the displacement of bridged Cl by alcohol –OH [33]. The chloride replacement perhaps occurs in our case as well. Addition of $AgNO_3$ to the water extract of reaction mixture of 2-aminobutanol and DEC in the presence of **1a** at 30 min (incomplete reaction) produced immediate precipitate of AgCl, indicating the presence of free chloride (Cl^-). Similar test on **1d** does not produce AgCl at all. Only a faint white coloration is observed in case of **1b** and **1c**. Above results dictate that **1a** has got highest and **1d** has got least ability to displace Cl.

External treatment of DEC with ethanolamine (Table 3, entry 1) and N-methylethanolamine (Table 3, entry 2) at 100 °C (higher than the OXZ reaction temperature) provides the corresponding carbamic esters, namely ethyl-2-ethanolcarbamate (EEC) and ethyl-2-ethanol-N-methylcarbamate (EENMC). But when N,N-dimethylaminoethanol is treated with DEC, no carbamic ester can be isolated (Table 3, entry 3), perhaps due to the reason of unavailability of nitrogen proton that hinders in OXZ ring formation. EEC and EENMC when heated with **1** form a stoichiometric amount of the corresponding OXZs (Table 3, entries 4 and 5), evidencing carbamate formation as one of the intermediate steps. Mentioned earlier, the peak at *m/z* 180 (Fig. 1) detected due to ethyl-4-benzylcarbamate strongly support aforesaid statement. 2-Ethoxyethylamine produces corresponding carbamic ester ethyl-2-ethoxyethylcarbamate when reacted with DEC (Table 3, entry 6), but no OXZ formation is observed, even when heated separately with **1** and an excess DEC (Table 3, entry 7). Therefore the presence of free OH group is necessary for the formation of OXZ which is protected in the case of 2-ethoxyethylamine. DEC is known to be more susceptible to attack by -NH_2 than by –OH group [40,59]. Hence, only the –OH (from 2AA) group is involved in interacting with **1** as free amine groups have already reacted with DEC to form the carbamate. It is examined that the carbamate formation is much faster

Table 3
Rate constants of the reactions studied to evaluate the mechanism.

Entry	Reactions	Catalyst
1		No
2		No
3		No
4		**1a**
5		**1a**
6		No
7		**1a**
8		**1a**

than the corresponding OXZ formation (Table 3, entries 1 and 4), indicating the formation of carbamate prior to OXZ ring.

On the other side, the effect of the concentration of DEC on yield (Fig. 3b) designate the activation of the ester group of carbamate occurs by **1**. Most likely Sn^b of **1** is responsible for this activation, as Sn^a is in interaction with –OH. Therefore, it can be concluded that Sn^a activates –OH and Sn^b activates the ester (EtO–CO–) groups of the preformed 2-ethyl carbamato alcohol.

We may now be in a better position to explain the lower activity of **1c** for OXZ formation when compared to **1b**. Degeneracy in the

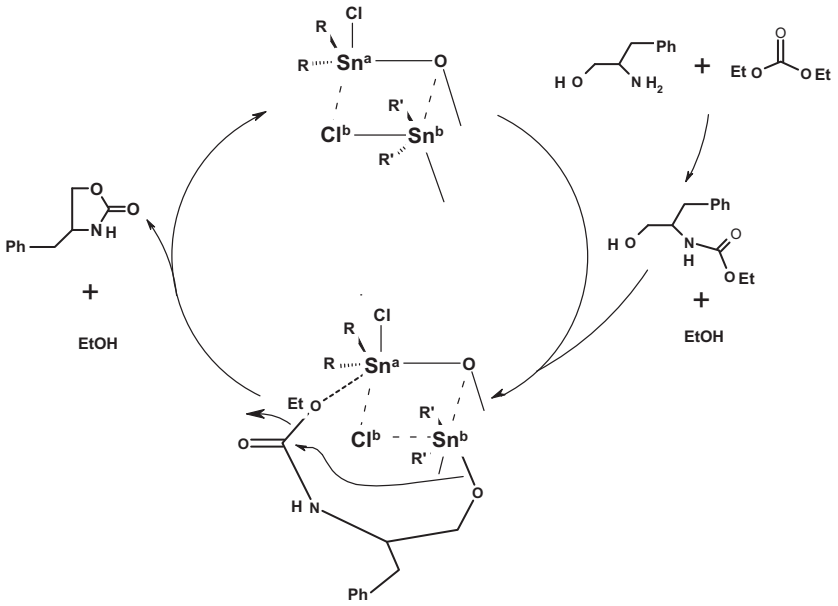


Fig. 8. Possible mechanism is shown by presenting one half of the catalyst.

Table 4
Recovery and recycle test of **1** in OXZ formation.[a]

Sub	Cycl	**1a** (g)		DEC[b] (g)		**1d** (g)		DEC[c] (g)	
		U[d]	R[e]	U	R	U	R	U	R
2AB	1	1.2	1.15	257.25	250.2	1.22	1.20	257	256.1
	2		1.14		247.8		1.19		255
	3		1.12		240.9		1.18		252.1
Phal	1	1.16	1.16	260	254.2	1.20	1.18	259	250.9
	2				247.3		1.18		243.8
	3				240.4		1.17		236.4
2AB[f]	1	1.2	0.7	258.5	251.7	1.17	1.16	258	251.8
	2		0.4		244.2		1.14		247.4
	3		0.0		237.3		1.13		241.2

[a] 2AA 2.1 mol, **1** 2.16 mmol, temperature 80 °C, time 1 h.
[b] DEC used with **1a**.
[c] DEC used with **1b**.
[d] U = used amount. Amount recovered from last cycle.
[e] R = recovered amount, 2AB = 2-aminobutanol, PhAl = phenyl alaninol.
[f] Recovery was performed by silica gel chromatography.

catalyst's structure implies that Sn^a has more positive influence over the reaction parameter than Sn^b. Although the presence of butyl groups on Sn^a in **1b** helps the Cl replacement, phenyl attachment on Sn^b trims down the strength needed to activate ester group, subsequently making the catalyst comparatively inefficient. On the other hand, in the case of **1c**, the presence of Ph on Sn^a greatly reduces the activity such that it is not possible to compensate by the butyl group on Sn^b. Ph groups on both Sn^a and Sn^b in **1d** have accelerated neither Cl replacement nor the activation of the ester group, performing with least efficiency. We have tried to accumulate all the information needed to elucidate the possible reaction pathway as shown in Fig. 8. The mechanism described above in view to explicate the specific interactions of 2AA and different Sn centers in **1** is however, as a whole in agreement with the mechanism of transesterification proposed in literature [33]. The proposed mechanism holds the reason for retention of chirality of chiral substrates.

3.6. Recovery and recycling of *1* and DEC

Generally, simplicity of separation depends on the differences in the polarity of the components present in any reaction mixture. Components can be separated even by simple solvent treatment using hexane if polarity differs greatly. The reaction mixture obtained from the reactions carried out with the substrates 2-aminophenol and phenyl alaninol using catalyst **1a** is one of these situations. On the other hand, substrates like ethanolamine, 2-aminobutanol and 2-aminocyclopentanol require column chromatography to separate the components. It is noteworthy that **1c** and **1d** can be separated from the substrates ethanolamine, 2-aminobutanol and 2-aminocyclopentanol once diluted with hexane.

Solvent extraction does not work if the polarity difference between the two components is small. Silica gel chromatography is then the general method of recovering the catalyst with acceptable amount of loss. Table 4 lists the results obtained during recovery of **1** and DEC when hexane extraction is employed in the recovery process of oxazolidinone formations using 2-aminobutanol and phenyl alaninol, respectively.

The polarity difference between **1a** and phenyl alaninol or 2-aminophenol is large enough to separate them efficiently. Addition of hexane further facilitates the separation. But substrates like ethanolamine, 2-aminobutanol and 2-aminocyclopentanol have polarities closer to that of **1a** and thus need column chromatography for separation. **1c** and **1d** are sufficiently polar with respect to the reaction medium itself which facilitates easy separation.

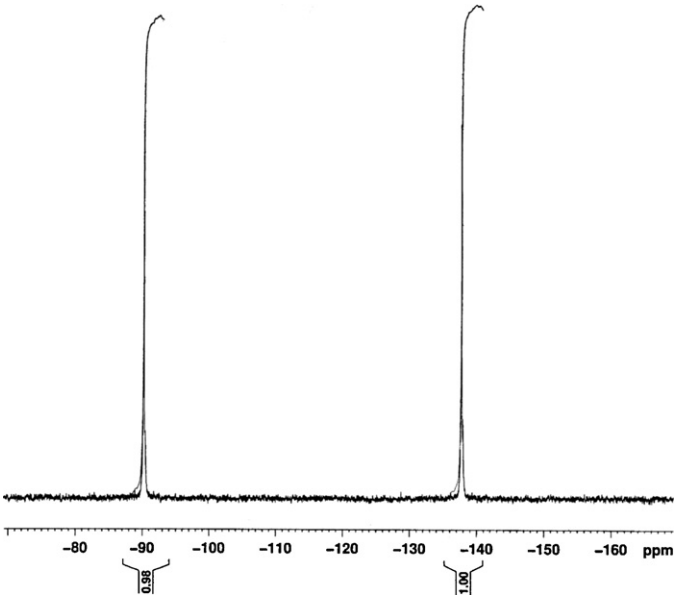


Fig. 9. ^{119}Sn NMR ($CDCl_3$) of recovered **1a**.

Although Table 4 shows up to 90% catalyst recovery, depending on the nature of the catalysts, short silica gel (12″) column chromatography can be employed as a general way of separating the catalyst.

The recovered catalyst is found to be identical to the initial catalyst and this is confirmed by elemental (C, H) analysis, mass spectrometry and ^1H NMR. Identity of the recovered catalyst is also manifested in the activity (Table 4) to produce OXZ. To confirm the retention of Sn core after reaction, we have checked ^{119}Sn NMR of the recovered catalyst. A representative ^{119}Sn spectrum is given for **1a** (Fig. 9). The distinct peaks (δ, ppm) at −90.2 corresponding to exocyclic (Sn^a) and at −137.8 corresponding to endocyclic (Sn^b) Sn atoms match very well with the literature values of −92.0 and −139.8, respectively [50]. The identity of **1a** in ^{119}Sn NMR is indicative to support the proposed mechanism [60,61]. Almost no loss in the catalytic efficiency is observed after three recycles. The catalyst is stable under reaction conditions as reflected by its activity in the recovered material, proving the finding of past studies in regard to retention of identity [62]. Tests indicate that free chloride or Sn may be present at lower than the detection limit in the product, confirming the robustness of the catalyst. The above findings show that it may be suitable to use **1** in continuous batch reactions thus making it economically feasible to produce OXZ.

4. Conclusions

In conclusion, we have shown that dichlorodistannoxanes are very effective catalysts for synthesizing oxazolidinone from 2AA and DEC within 1 h quantitatively. The recyclable catalyst is used with a variety of chiral and achiral substrates. No chirality loss is encountered during catalytic reaction. The recovered catalyst is found to be identical to the original and showed similar catalytic efficiency. The ratio of catalyst, DEC and 2AA is required to be maintained at 1:2:2 for optimum yield. Both –OH and $–NH_2$ groups within reasonable proximity are necessary to form an oxazolidinone ring. The effect of substituents in the **1** position (next to –OH) compared to **2** position in 2AA had more influence on the reaction rate. The catalysts are dimeric and contain two dissymmetric Sn centers, namely Sn^a and Sn^b, with varying reactivity. The reaction proceeds with carbamate formation as a prior step through amino group followed by chloride replacement in the cat-

alyst by –OH. The mechanistic study indicates that Sn^a activates –OH and Sn^b activate –O–CO– of a preformed ethylcarbamate from 2AA and DEC. Phenyl substituents reduce the catalytic activity by shortening the Sn–Cl bond and the influence is most prominent when attached to the terminal Sn^a atom of the catalyst. Polarity differences between substrate and catalyst facilitate an easy separation and recovery for further recycling. As the catalyst is almost fully recoverable and preparation of the catalyst is quantitative with respect to their starting materials, contamination of the product and the environment is merely negligible. Nevertheless, while triorganotin compounds are known to be toxic, there is no such toxicity is reported so far for tetraorganodistannoxane compounds. The findings as a whole provide a broad way of synthesizing OXZs while retaining their chirality. Depending upon the need, one can design the process for practical feasibility without separating the catalyst. Consequently, overall the process has promise to contribute economically as well as environmentally.

Acknowledgements

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