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C,N-chelated organotin(IV) compounds as catalysts for transesterification and derivatization of dialkyl carbonates

Tomáš Weidlich[a], Libor Dušek[a], Barbora Vystrčilová[a], Aleš Eisner[b], Petr Švec[c] and Aleš Růžička[c]*

The potential catalytic activity of selected *C,N*-chelated organotin(IV) compounds (e.g. halides and trifluoroacetates) for derivatization of both dimethyl carbonate (DMC) and diethyl carbonate (DEC) was investigated. Some tri-, di- and monoorganotin(IV) species ($L^{CN}(n\text{-Bu})_2SnCl$ (1), $L^{CN}(n\text{-Bu})_2SnCl.HCl$ (1a), $L^{CN}(n\text{-Bu})_2SnI$ (2), $L^{CN}Ph_2SnCl$ (3), $L^{CN}Ph_2SnI$ (4), $L^{CN}(n\text{-Bu})SnCl_2$ (5), $L^{CN}SnBr_3$ (6) and $[L^{CN}Sn(OC(O)CF_3)]_2(\mu\text{-O})(\mu\text{-OC(O)CF}_3)_2$ (7)) bearing the L^{CN} moiety (L^{CN} = 2-(*N,N*-dimethylaminomethyl)phenyl-) were assessed as catalysts for reactions of both DMC and DEC with various substituted anilines. The catalytic activities of 4 and 7 for derivatization of DMC with *p*-substituted phenols were studied for comparison with the standard base K_2CO_3/Silcarbon K835 catalyst (catalyst 8). The composition of resulting reaction mixtures was monitored by multinuclear NMR spectroscopy, GC and GC-MS techniques. In general, catalysts 1, 3 and 7 exhibited the highest catalytic activity for all reactions studied, while some of them yielded selectively carbonates, carbamates, lactam or substituted urea. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: organotin(IV) compounds; *C,N*-chelating ligand; dialkyl carbonates; catalysis

Introduction

Dialkyl carbonates are attractive compounds for the preparation of carbamates since they offer genuine green advantages over classical alkylating reagents:[1] (i) they are non-toxic; (ii) their alkylation mediated reactions are always catalytic processes, with no by-products except for alcohols recyclable to the synthesis of dialkyl carbonates, and CO_2 which does not involve disposal problems; (iii) very often, (light) organic carbonates can be used not only as reactants, but also as reaction solvents. Moreover, their alkylation reactivity can be tuned for a variety of nucleophiles. This behavior has been extensively investigated by Selva's research group in the past 15 years.[2]

Organic carbamates represent an important class of compounds, largely employed in pharmacology (medical drugs), agriculture (pesticides, fungicides, herbicides), and chemical industry (intermediates of synthesis).[3] Aryl-alkyl carbamates are important intermediates for the preparation of pharmaceuticals (e.g. kinase inhibitors)[4] and can be also used as raw materials for synthesizing polyurethanes using a phosgene-free route: carbamate → isocyanate → polyurethane.[5] Cyclic carbamates are useful as chemical technology intermediates for the production of remedies for treating of pain and inflammation,[6] novel inhibitors of *S*-nitroisoglutathione reductase,[7] and for the preparation of azepino[1,2-*b*]isoquinolines.[8]

Aryl-alkyl carbamates are generally prepared from phosgene,[9] phosgene derivatives[10] or isocyanates[11] by reactions with alcohols, in the case of carbamates, and amines in the case of ureas. Nevertheless, none of these methods are environmentally benign because of the necessary use of toxic reagents and the generation of by-products.

The synthesis of aryl-alkyl carbamates from diethyl carbonate (DEC) or dimethyl carbonate (DMC) (e.g. synthesis of methyl phenyl carbamate (MPC) from aniline and dimethyl carbonate) has been investigated thoroughly. Thus Gurgiolo prepared MPC over zinc acetate catalyst, the selectivity of MPC to aniline being 99.8% under the conditions of 140°C and 0.88 MPa.[12] Fu and Ono have obtained high aniline conversion and MPC yield over $Pb(OAc)_2$ catalyst, too. At a temperature of 400 K for 1 h, the conversion of aniline was 96.7%, yielding 95.1% of MPC.[13] It can be inferred from the above that metal acetates possess excellent catalytic activity. However, they bring about troublesome problems such as product separation and recovery of the homogeneous metal acetate catalyst.

We have published recently a study of the zwitterionic tri- and diorganostannates containing the protonated 2-(dimethylaminomethyl)phenyl- moiety prepared by reactions of *C,N*-chelated organotin(IV) chlorides with various protic acids (both inorganic and organic).[14] Results concerning the reaction of $L^{CN}(n\text{-Bu})_2SnCl$ with CF_3COOH were also described there. Latter results led us to prepare and structurally characterize some novel *C,N*-chelated organotin(IV) trifluoroacetates bearing the L^{CN} ligand(s)

* *Correspondence to: Aleš Růžička, Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic. E-mail: ales.ruzicka@upce.cz*

a *Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic*

b *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic*

c *Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic*

subsequently employed as catalysts in the direct synthesis of DMC from carbon dioxide and methanol as discussed elsewhere.[15]

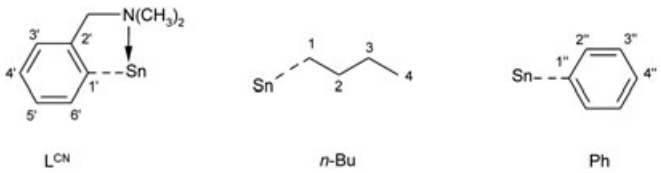
As a contribution to this field of chemistry, we report on the use of selected *C,N*-chelated organotin(IV) species (e.g. halides and trifluoroacetates) as catalysts for the derivatization of DMC and DEC. In addition, a new and easy procedure for the synthesis of $L^{CN}(n\text{-Bu})_2SnI$ (**2**) and $L^{CN}Ph_2SnI$ (**4**) is described (for general ^1H NMR numbering see Scheme 1).

Results and Discussion

General Remarks

All of the *C,N*-chelated organotin(IV) compounds used as catalysts (for numbering see Table 1) have been already prepared and structurally characterized by us and/or other authors (for details see the Experimental section).

In addition, compounds **2** and **4** were prepared by a very quick alternative procedure compared to that reported in the literature.[17,19] It is based on a modification of the Finkelstein reaction,[18] in which the corresponding triorganotin(IV) chloride reacts with an equimolar amount of sodium iodide in acetone. The insoluble sodium chloride is then simply filtered off. Evaporation of the filtrate to dryness gave desired triorganotin(IV) iodide with a very high isolated yield (96% and 85%, respectively). Owing to the excellent purity of the triorganotin(IV) iodides formed, no necessity for recrystallization of the products is another advantage of this alternative synthetic route. The ^1H and ^{119}Sn NMR spectral patterns of **2** and **4** prepared by this procedure are in excellent agreement with data found in the literature.[17,19]



Scheme 1. General ^1H NMR numbering of prepared compounds

Table 1. Compounds (catalysts) studied

Catalyst	Compound	Ref.
1	$L^{CN}(n\text{-Bu})_2SnCl$	[16]
1a	$L^{CN}(n\text{-Bu})_2SnCl.HCl$	[14]
2	$L^{CN}(n\text{-Bu})_2SnI$	[17]
3	$L^{CN}Ph_2SnCl$	[18]
4	$L^{CN}Ph_2SnI$	[19]
5	$L^{CN}(n\text{-Bu})SnCl_2$	[16,20]
6	$L^{CN}SnBr_3$	[16,21]
7	$[L^{CN}Sn(OC(O)CF_3)]_2(\mu\text{-O})(\mu\text{-OC(O)}CF_3)_2$	[15]
8	K_2CO_3/Silcarbon K835	[22]

Catalysis

Transesterification of 2-N-phenylaminoethanol with DMC

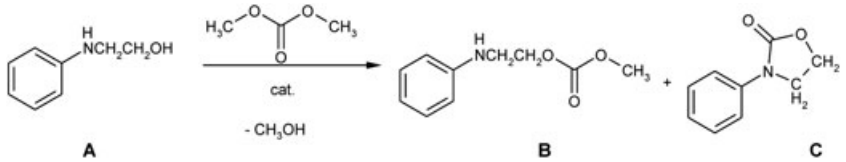
N-Phenylaminoethanol **A** was chosen as the bidentate nucleophile. The transesterification of dialkyl carbonates with *N*-phenylaminoethanol **A** represents a safe approach to the simple preparation of 3-phenyl-1,3-oxazolidin-2-one **C**. Lactam **C**, a product of the acylation of *N*-phenylaminoethanol **A** with phosgene, serves as a useful synthetic intermediate and mimics 2-phenylaziridine in the decarboxylative ring opening reaction under the action of nucleophiles. The reaction of 3-phenyl-1,3-oxazolidin-2-one **C** with cyanide produces 3-*N*-phenylaminopropanenitrile,[24] with amines produces *N*-phenylethylenediamine derivatives,[25] and with mercaptoethanol produces *N*-phenylamino-substituted thioethers.[26] In addition, 3-phenyl-1,3-oxazolidin-2-one works as an alkylamination reagent of aromatics under Friedel–Crafts alkylation.[27] Action of dialkyl carbonate on 2-*N*-benzylaminoethanol using a base was described earlier[28]; this reaction gives 3-benzyl-1,3-oxazolidin-2-one in good yield.

The reaction of the 2-*N*-aminoethanol **A** with an excess of boiling DMC gave linear aminocarbonate **B** and/or the lactam **C** (Scheme 2 and Table 2). When the reaction is conducted without a catalyst, no conversion of the starting 2-*N*-aminoethanol is observed. On the other hand, the specific formation of carbonate **B** is observed when catalysts **1**, **3**, **5** and **7** are used under boiling DMC reflux for 17 h. The lowest catalytic activity among all catalysts used was observed for catalyst **1a** because only traces of aminocarbonate **B** were formed. The highest yield is found for triorganotin(IV) species **1** and **3** with lower Lewis acidity (Table 2, entries 2 and 4) of the tin atom. Within these two catalysts, the *n*-butyl-substituted one (**1**) seems to be slightly more efficient, probably because of the higher tendency of *n*-butyl-substituted triorganotin compounds to form stannylium cations.[29] Catalysts **5** and **7** reveal much lower activity, but the selectivity towards the carbonate **B** is again satisfactory. To complete the reaction catalyzed by **3** (entry 5) a much longer reaction time is necessary, but the reaction is no more selective,

Table 2. Results of transesterification of 2-*N*-phenylaminoethanol (**A**) with DMC (reflux), reaction time 17 h

Entry	Catalyst (% mol.)	Conversion of **A** (% mol.)	Conversion to **B** (mol. %)	Conversion to **C** (mol. %)
1	—	0	0	0
2	**1** (10%)	100	100	0
3	**1a** (10%)	0	0	0
4	**3** (10%)	56	56	0
5[a]	**3** (10%)	95	78	17
6[b]	**3** (10%)	100	0	100
7	**5** (10%)	20	20	0
8	**7** (5%)	34	34	0
9[b]	**7** (5%)	100	9	91

[a]Reaction time 72 h.
[b]Removal of methanol by azeotropic distillation.



Scheme 2. Transesterification of 2-*N*-phenylaminoethanol (**A**) with DMC catalyzed by **1**, **1a**, **3**, **5** and **7**

and lactam **C** is observed with about 17% yield. However, the lactam **C** is the only product obtained under prolonged heating of an excess of DMC and 2-*N*-aminoethanol **A** in the presence of **3** as a catalyst with subsequent removal of methanol (entry 6). Under the same conditions, the lactam is also formed in the case of catalyst **7**, but the selectivity is lower. The identity of the lactam **C** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and the single crystals obtained from the chloroform solution gave essentially the same unit cell parameters as published elsewhere.[30] The main advantage of catalyst **3** over catalysts **7** and **1** is the possibility of simple recycling of non-destroyed catalyst **3** by filtration of the precipitated **3** obtained by cooling of the reaction mixture.

*Reaction of 4-t-*butylaniline with DEC

The carbamate **E** produced by the acylation of 4-*tert*-butylaniline **D** with dialkyl carbonates is the starting material for a new synthetic route for heterocycles, e.g. tryptamines.[31]

The carbamate **E** is the major product of the reaction of 4-*t*-butylaniline (**D**) with an excess of boiling DEC when catalyzed by **1**, **3**, and **7** (Scheme 3 and Table 3). When the catalyst **1** protonated by HCl, **1a** and triorganotin(IV) iodide **2** is used, only traces of desired products were obtained. The catalytic activity of di-*n*-butyl-substituted chloride **1** is slightly higher than of monoorganotin(IV) trifluoroacetate **7**, but a major decrease in yield is observed upon switching from di-*n*-butyl to diphenyl chloride **3**. On the other hand, a non-identified by-product is formed in the reaction catalyzed by **1** (entry 2) in 4% yield (as determined by ^{1}H NMR).

*Reaction of 4-bromoaniline (**F**) with excess DEC*

The products prepared by the acylation of 4-bromoaniline **F** using DEC (carbamate **G** or urea **H**) are versatile synthetic intermediates. Bis(4-bromophenyl)urea **H** forms 4-bromophenylisocyanate under acylation with acetanhydride[32]; 1,3,5-triphenylimidazolidine-2,4-diones and 1,3,5-triphenyl-2-thioxoimidazolidin-4-ones (new CB1 cannabinoid receptor inverse agonists/antagonists) are simply available by the reaction of bis(4-bromophenyl)urea with phenylglyoxal.[33]

Ethyl *N*-bromophenylcarbamate **G** serves as bromoaromatic compound for C-C or C-heteroatom cross-coupling reactions[34] or on the other hand as a weak *N*-nucleophile.[35]

The catalyzed reaction of 4-bromoaniline (**F**) with boiling DEC yields carbamate **G** and urea **H** (Scheme 4 and Table 4). The conversion of starting 4-bromoaniline is nearly quantitative in the cases of reactions catalyzed by **1**, **2** and **7**. While the reactions catalyzed by **1** and **7** gave essentially quantitatively urea **H**, the reaction catalyzed by iodide **2** is non-specific, yielding a mixture of carbamate **G** and urea **H**. The specific formation of only carbamate **G** in about 17% yield is observed in the case of the reaction catalyzed by monoorganotin(IV) tribromide **6**.

Table 3. Results of reaction of 4-*t*-butylaniline (**D**) with DEC (reflux), reaction time 17 h

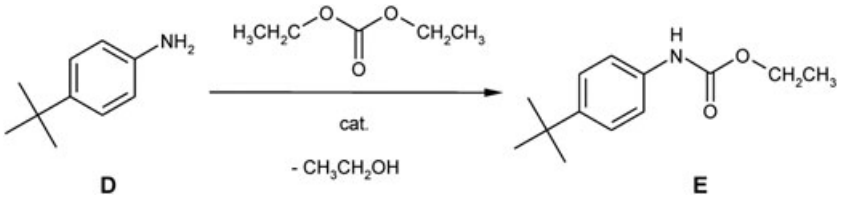
Entry	Catalyst (% mol)	Conversion of **D** (% mol)	Conversion to **E** (% mol)
1	—	0	0
2	**1** (10%)	99	95
3	**1a** (10%)	0	0
4	**2** (10%)	0	0
5	**3** (10%)	38	38
6	**7** (10%)	91	91

*Reactions of p-*substituted phenols with DMC

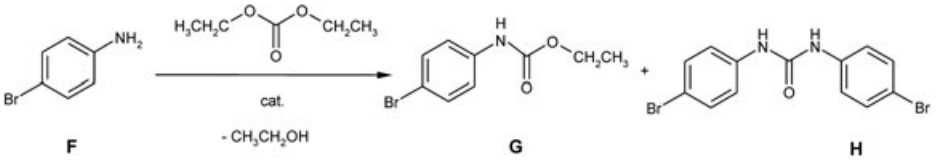
Different phenols are chosen as the model nucleophilic substrates for the testing the above-mentioned *C,N*-chelated organotin(IV) catalysts. Both anisoles and aryl methyl carbonates as the possible products of the reaction of phenols with DMC are industrially important solvents and/or synthetic building blocks for the preparation of polycarbonates,[36] plasticizing agents for epoxide resins,[37] pharmaceuticals and dyestuffs.[38]

Reactions of *p*-substituted phenols (**I**) with an excess of DMC catalyzed by **4**, **7** and **8** (Scheme 5) provided corresponding anisoles (**J**, method I) and mixed alkyl-aryl carbonates (**K**, method II) (together with other by-products, analyzed by GC-MS; see Tables 5–7). Despite the amounts of catalysts **4** and **7** involved in the reactions studied being 120 times lower when compared to the amount of base catalyst **8** used, the yields of corresponding products were still satisfactory and, in some cases, even higher. Formation of the corresponding diaryl carbonates was not observed. In general, higher temperature (200°C) and short reaction times (6 h) promoted the formation of anisoles **J**, which is a consequence of the thermodynamic driving of the reaction (Table 6). On the other hand, the kinetic driving of the reaction at lower temperatures (100°C) and prolonged reaction times (15 h) provided slightly higher yields of the respective alkyl-aryl carbonates **K** (Table 5) when compared with yields of **K** by thermodynamically driven reactions. When catalyst **4** was used in kinetically driven reactions (Table 5) the overall yields of by-products were distinctly higher when compared to yields observed for the same reactions catalyzed by **8**, but this trend vanished when higher temperatures and long reaction times were applied (Table 6).

The nature of the X substituent attached to the phenols influenced the transesterification of DMC independently of temperature. Phenols bearing electron-donating substituents reacted with DMC more readily while electron-withdrawing substituents clearly decreased their reactivity towards the DMC, as demonstrated in Tables 5–7.



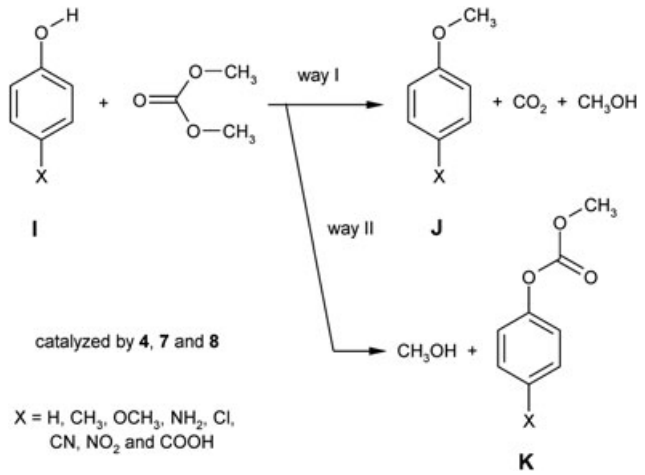
Scheme 3. Reaction of 4-*t*-butylaniline (**D**) with excess of DEC catalyzed by **1**, **1a**, **2**, **3** and **7**



Scheme 4. Reaction of 4-bromoaniline (**F**) with excess of boiling DEC catalyzed by **1**, **1a**, **2**, **5**, **6** and **7**

Table 4. Results of reaction of 4-bromoaniline (**F**) with DEC (reflux), reaction time 17 h

Entry	Catalyst (% mol)	Conversion of **F** (% mol)	Conversion to **G** (% mol)	Conversion to **H** (% mol)
1	—	0	0	0
2	**1** (10%)	94	0	94
3	**1a** (10%)	0	0	0
4	**2** (10%)	100	32	68
5	**5** (10%)	0	0	0
6	**6** (10%)	17	17	0
7	**7** (10%)	100	0	100



Scheme 5. Derivatization of DMC with *p*-substituted phenols catalyzed by **4** (0.1 mmol), **7** (0.1 mmol) and **8** (12.0 mmol) leading to formation of *p*-substituted anisoles (**J**, method I) and mixed alkyl-aryl carbonates (**K**, method II)

Experimental

NMR Spectroscopy

The multinuclear NMR spectra were recorded from solutions of reaction mixture residues in DMSO-d6 or in $CDCl_3$ on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5 mm probe) at frequencies ^{1}H (500.13 MHz), $^{13}C\{^{1}H\}$ (125.76 MHz) and $^{119}Sn\{^{1}H\}$ (186.50 MHz) at 295 K. The solutions were obtained by dissolving approximately 20 mg of each reaction mixture residue in 0.6 ml deuterated solvent. The values of the ^{1}H chemical shifts were calibrated to the residual signal of $CDCl_3$ ($\delta(^{1}H) = 7.27$ ppm) and DMSO-d6 ($\delta(^{1}H) = 2.50$ ppm). ^{13}C chemical shift values were calibrated to the signal of DMSO-d6 ($\delta(^{13}C) = 39.5$ ppm). ^{119}Sn chemical shift values are referred to external neat tetramethyltin ($\delta(^{119}Sn) = 0.0$ ppm). ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. ^{1}H NMR spectroscopy in $CDCl_3$ was also used for evaluation of some reaction products as well as to monitor the conversion of some of the reactants. Multinuclear NMR spectra of **2** and **4** were recorded only in $CDCl_3$. The identity of the catalysts was assessed by ^{119}Sn NMR after completion of the reactions.

GC and GC-MS Techniques

All the standard solutions were prepared and analyzed using GC and GC-MS techniques. The first gas chromatograph used, model GC-72FT (Labio, Czech Republic), equipped with flame ionization detector (FID) and thermal conductivity detector with a double-channel arrangement integrator (CSW Data Apex), was employed for all quantitative analyses of major products of reaction mixtures. Commercially available *p*-substituted phenols, anisole and phenyl carbonates were used as internal standards (Sigma-Aldrich). The GC-72FT system was equipped with a capillary column SUPELCO Equity®-5 L, length 30 m, 0.32 mm internal diameter, 0.25 μm film (Supelco, Bellefonte, PA, USA). Nitrogen 5.0 (Linde Gas, a.s., Pardubice, Czech Republic) was used as a carrier gas at a constant flow of 20 ml min^{-1} at an excess pressure of 100 kPa. The injection volume was 1 μl in split mode 1:100. The column temperature was programmed as follows: the initial temperature was 40°C (3 min), Δ10°C min^{-1} to 180°C (20 min). FID temperature was 280°C.

The second gas chromatograph used, model GC-2010, coupled with a mass selective detector (QP 2010plus, Shimadzu, Tokyo, Japan) with quadrupole mass analyzer and AOC-20i auto-sampler (Shimadzu), was employed for all analyses of by-products. The GC-MS system was equipped with a capillary column MDN-5, length 30 m, 0.25 mm internal diameter, 0.25 mm film (Supelco). Helium 5.3 (Linde Werk. Tech. Gase, Düsseldorf, Germany) was used as a carrier gas at a constant linear velocity of 30 cm s^{-1}. The composition of reaction mixtures was determined using the following conditions: the injector temperature was maintained at 220°C, and the injection volume was 1 μl in split mode 1:100. Interface and ion source temperatures were maintained at 200 and 220°C, respectively. The column temperature was programmed as follows: the initial temperature was 40°C (3 min) Δ20°C min^{-1} to 280°C (3 min). Electron energy was set at 70 eV. Initially, mass spectra were obtained in full-scan mode (*m/z* 10–600) to obtain a set of masses of the corresponding compounds. To improve the sensitivity of the measurement, selected ion monitoring (SIM) mode was employed for the masses acquired from full-scan mode. The identity of each compound was confirmed using the NIST 27 and NIST 147 mass spectra libraries.

X-Ray Crystallography

Data for colorless crystal of lactam **C** were collected on a Nonius KappaCCD diffractometer using MoK_{α} radiation ($\lambda = 0.71073$ Å) and a graphite monochromator at 150 K.

Table 5. Results of reactions of 4-X-phenols (**I**) with DMC in the presence of catalyst **4** (0.1 mmol) and **8** (12.0 mmol), reaction time 15 h, temperature 100°C

Entry	Cat.	**I** X	Conversion of **I** (% mol.)	Conversion to **J** (% mol.)	Conversion to **K** (% mol.)	By-products (% mol.)	Specification of by-products
1	**4**	H	20	75	1	24	1-Methoxy-4-methylbenzene 4-Methylphenol 1,2-Dimethoxybenzene 1-Methoxy-4-phenoxybenzene
2	**8**	H	19	69	27	4	1-Methoxy-4-methylbenzene
3	**4**	CH_3	5	45	19	36	Methoxybenzene 1-Methoxy-4-methoxybenzene
4	**8**	CH_3	7	43	55	2	4-Methoxybenzene
5	**4**	OCH_3	8	34	28	38	Not identified
6	**8**	OCH_3	14	21	74	5	4-Methoxyphenol
7	**4**	NH_2	27	10	—	90	4-Hydroxybenzonitrile 4-Methoxyaniline 4-Methoxybenzonitrile 4-Methoxy-*n*-methylaniline
8	**8**	NH_2	23	9	6	67	4-Hydroxybenzonitrile 4-Methoxyaniline 4-Methoxybenzonitrile 4-Methoxy-*n*-methylaniline
9	**4**	Cl	18	11	11	78	Phenol 4-Methylphenol 4-Methoxyphenol
10	**8**	Cl	29	97	—	3	Phenol 4-Methylphenol 4-Methoxyphenol
11	**4**	CN	84	87	—	13	Methoxybenzene 1-Methoxy-4-methylbenzene
12	**8**	CN	77	99	—	1	Methoxybenzene 1-Methoxy-4-methylbenzene
13	**4**	NO_2	10	83	—	17	Methoxybenzene 4-Methoxybenzonitrile
14	**8**	NO_2	7	92	—	8	4-Methoxyaniline 4-Methoxybenzonitrile
15	**4**	COOH	1	11	—	89	Phenol Methyl-4-hydroxybenzoate Methyl-4-methoxybenzoate
16	**8**	COOH	2	17	—	83	Phenol Methyl-4-hydroxybenzoate Methyl-4-methoxybenzoate

Synthesis

$L^{CN}(n\text{-Bu})_2SnCl$ (**1**),[16] $L^{CN}(n\text{-Bu})_2SnCl.HCl$ (**1a**),[14] $L^{CN}(n\text{-Bu})_2SnI$ (**2**),[17] $L^{CN}Ph_2SnCl$ (**3**),[18] $L^{CN}Ph_2SnI$ (**4**),[19] $L^{CN}(n\text{-Bu})SnCl_2$ (**5**),[16,20] $L^{CN}SnBr_3$ (**6**)[16,21] as well as $[L^{CN}Sn(OC(O)CF_3)]_2(\mu\text{-O})(\mu\text{-OC(O)CF}_3)_2$ (**7**),[15] were prepared according to published procedures. Acetone and sodium iodide for alternative preparation of **2** and **4**, as well as K_2CO_3, were purchased from Sigma-Aldrich and used as received. Silcarbon K835 was obtaining from Silcarbon Aktivkohle GmbH, Kirchhundem, Germany.

*Alternative preparation of **2***

To begin, compound **1** (1000 mg, 2.48 mmol) was dissolved in acetone (40 ml) and a solution of sodium iodide (372 mg, 2.48 mmol) in acetone (10 ml) was added. The reaction mixture was stirred for 1 h while sodium chloride precipitated. The precipitate was filtered off and the filtrate was evaporated to dryness, giving 1178 mg of pure oily **2**. Yield 96%. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 8.35 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.9$ Hz, $^3J(^{119}Sn, ^1H) = 64.8$ Hz); 7.36 (m, 2H, H(4′, 5′)); 7.15 (d, 1H, H(3′), $^3J(^1H(4'), ^1H(3')) = 6.6$ Hz); 3.67 (s, 2H, NCH_2); 2.42 (s, 6H, $N(CH_3)_2$); 1.71 (m, 4H, H(1)); 1.50 (m, 4H, H(2)); 1.41 (m, 4H, H(3)); 0.93 (t, 6H, H(4)). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −34.0.

*Alternative preparation of **4***

The same procedure was used as for **2**, using **3** (1000 mg, 2.26 mmol) and sodium iodide (339 mg, 2.26 mmol). Pure **4** was isolated as a yellowish crystalline solid. Yield 1023 mg (85%). ^{1}H NMR ($CDCl_3$, 295 K, ppm): 8.56 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 6.6$Hz, $^3J(^{119}Sn, ^1H) = 71.2$ Hz); 7.68 (d, 4H, H(2″), $^3J(^1H(3''), ^1H(2'')) = 7.0$ Hz, $^3J(^{119}Sn, ^1H) = 70.2$ Hz); 7.49 (m, 1H, L^{CN}) 7.41–7.31 (m, 7H, L^{CN} and Ph groups); 7.14 (d, 1H, H(3′), $^3J(^1H(4'), ^1H(3')) = 7.4$ Hz); 3.53 (s, 2H, NCH_2); 1.87 (s, 6H, $N(CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −199.0.

Table 6. Results of reactions of 4-X-phenols (**I**) with DMC in the presence of catalyst **4** (0.1 mmol) and **8** (12.0 mmol), reaction time 6 h, temperature 200°C

Entry	Cat.	**I** X	Conversion of **I** (% mol.)	Conversion to **J** (% mol.)	Conversion to **K** (% mol.)	By-products (% mol.)	Specification of by-products
1	**4**	H	94	71	3	26	1-Methoxy-4-methylbenzene 4-Methylphenol 1,4-Dimethoxylbenzene 1-Methoxy-4-phenoxybenzene
2	**8**	H	97	72	2	26	1-Methoxy-4-methylbenzene 4-Methoxy benzoic acid methyl ester
3	**4**	CH_3	95	59	3	38	Methoxybenzene 1-Methoxy-4-methoxybenzene 1-Methyl-2-(phenylmethoxy)benzene
4	**8**	CH_3	99	69	2	29	Methoxybenzene
5	**4**	OCH_3	100	89	2	9	Not identified
6	**8**	OCH_3	93	72	4	24	Not identified
7	**4**	NH_2	98	2	—	96[a]	4-Hydroxybenzonitrile 4-Methoxyaniline 4-Methoxybenzonitrile 4-Methoxy-*N*-methylaniline
8	**8**	NH_2	97	73	—	27	4-Hydroxybenzonitrile 4-Methoxyaniline 4-Methoxybenzonitrile 4-Methoxy-*N*-methylaniline
9	**4**	Cl	100	64	—	36	Phenol 4-Methylphenol 4-Methoxyphenol
10	**8**	Cl	99	65	1	34	Phenol 4-Methylphenol 4-Methoxyphenol
11	**4**	CN	100	69	<1	30	Methoxybenzene 1-Methoxy-4-methylbenzene
12	**8**	CN	100	91	—	9	Methoxybenzene 1-Methoxy-4-methylbenzene
13	**4**	NO_2	99	95	—	3	Methoxybenzene 4-Methoxybenzonitrile 1-Nitro-4-(phenylmethoxy)benzene
14	**8**	NO_2	100	74	—	26	Methoxybenzene 4-Methoxybenzamine 4-Methoxybenzonitrile
15	**4**	COOH	100	92[b]	—	8	Phenol 2-Methylphenol 4-Methylphenol Methyl-4-hydroxybenzoate Methyl-4-methoxybenzoate
16	**8**	COOH	98	68[b]	—	32	Phenol 2-Methylphenol 4-Methylphenol Methyl-4-hydroxybenzoate Methyl-4-methoxybenzoate

[a] *p*-Hydroxybenzonitrile as the major product.
[b] Methyl ester of *p*-methoxybenzoic acid as the major product.

The standard base K_2CO_3/Silcarbon K835 catalyst (**8**) was prepared by a similar procedure to that reported in the literature[22]: solid K_2CO_3 (7.5 g, 0,05 mol) was dissolved in distilled water (200 ml). Subsequently, well-dried activated carbon Silcarbon K835 (42.5 g) was added and the resulting dark mixture was stirred overnight at ambient temperature. After evaporation of the water under reduced pressure the residue was dried for 6 h at 150°C to give solid granules of the catalyst. Total content of the potassium carbonate was 15% by weight based on the weight of the carrier: Silcarbon K835.

Table 7. Results of reactions of 4-X-phenols (**I**) with DMC in the presence of catalyst **7** (0.1 mmol) and **8** (12.0 mmol), reaction time 6 h, temperature 200°C

Entry	Cat.	**I** X	Conversion of **I** (% mol.)	Conversion to **J** (% mol.)	Conversion to **K** (% mol.)	Byproducts (% mol.)	Specification of byproducts
1	**7**	H	99	71	1	28	1-Methoxy-4-methylbenzene 4-Methylphenol 1,2-Dimethoxylbenzene 1-Methoxy-4-phenoxybenzene
2	**8**	H	97	72	2	26	1-Methoxy-2-methylbenzene 1-Methoxy-4-methylbenzene 2-Methoxy benzoic acid methyl ester 4-Methoxy benzoic acid methyl ester
3	**7**	CH_3	100	77	3	20	Methoxybenzene 1-Methyl-2-(phenylmethoxy)benzene
4	**8**	CH_3	99	69	2	29	Methoxybenzene
5	**7**	OCH_3	95	88	5	7	Not identified
6	**8**	OCH_3	93	72	4	24	4-Methoxyphenol
7	**7**	NH_2	99	81	—	29	4-Methoxyaniline 4-Methoxybenzonitrile 4-Methoxy-*N*-methylaniline
8	**8**	NH_2	97	73	—	27	4-Methoxyaniline 4-Methoxybenzonitrile 4-Methoxy-*N*-methylaniline
9	**7**	Cl	100	87	—	13	Phenol 4-Methylphenol 4-Methoxyphenol
10	**8**	Cl	99	65	1	34	Phenol 4-Methylphenol 4-Methoxyphenol
11	**7**	CN	100	96	—	4	Methoxybenzene 1-Methoxy-4-methylbenzene
12	**8**	CN	100	91	—	9	Methoxybenzene
13	**7**	NO_2	100	82	—	18	Methoxybenzene 1-Nitro-4-(phenylmethoxy)benzene
14	**8**	NO_2	100	74	—	26	Methoxybenzene 4-Methoxyaniline 4-Methoxybenzonitrile
15	**7**	COOH	99	68	—	32	Phenol 2-Methylphenol 4-Methylphenol Methyl-4-hydroxybenzoate Methyl-4-methoxybenzoate
16	**8**	COOH	98	68	—	32	Phenol 2-Methylphenole 4-Methylphenole Methyl-4-hydroxybenzoate Methyl-4-methoxybenzoate

Catalytic Experiments

DMC, DEC and all other reactants used were obtained from commercial sources (Acros Organics) and used as received.

General procedure for experiments run in boiling DMC or DEC

The experiments were carried out in a 250 ml round-bottomed flask equipped with a condenser using a magnetic stirrer equipped with a StarFish® attachment. The outlet of the condenser was fitted to a glass tube filled with granulated charcoal. The flask was charged with the selected catalyst (0.50 or 0.25 mmol) and a dialkyl carbonate solution (50 ml) of the appropriate organic substrate (5 mmol). The resulting reaction mixture was heated to reflux for 17 h under vigorous stirring and evaporated to dryness in the next step. The final composition of the residue of the reaction mixture was monitored by ^{1}H and ^{13}C NMR and GC-MS techniques.

General procedure for experiments performed in the Berghof BTC-3000 autoclave

Starting organic substrate (10.0 mmol, various *p*-substituted phenols) and DMC (36 ml, 400 mmol) was charged into the autoclave. The appropriate catalyst (0.1 mmol of **4** or **7** and

12.0 mmol of **8**, respectively) was subsequently added. The resulting reaction mixture was heated to 100°C for 15 h or to 200°C for 6 h. The final composition of the reaction mixture after evaporation of the volatiles was monitored by GC and GC-MS.

Conclusion

First, some well-known organotin(IV) halides and one dinuclear monoorganotin(IV) trifluoroacetate bearing the *C*,*N*-chelating ligand(s) were employed as catalysts for the derivatization of DEC and DMC with 2-*N*-phenylaminoethanol, 4-*t*-butylaniline and 4-bromoaniline. These reactions, catalyzed by **1**, **3** and **7** (which exhibited the best catalytic activity in almost all reactions studied), provided corresponding substituted carbonates, carbamates, lactam or substituted urea as depicted in Schemes 2–4 in reasonable yields. When these reactions were carried out under the same conditions without the presence of the catalyst, no formation of desired products was observed, as expected. In the second part of this work we investigated the catalytic activity of **4** and **7** with the reactions of DMC with *p*-substituted phenols. Studied reactions gave corresponding anisoles and mixed alkyl-aryl carbonates in varying yields depending on the substrate, reaction time and temperature used. It was found that compounds **4** and **7** reveal promising catalytic activity when compared to the standard base K_2CO_3 catalyst, which was used at 120 times higher amounts relative to **4** and **7** in all cases. In addition, an alternative procedure for the quick preparation of **2** and **4** with excellent yields has been described.

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