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# Phosgene-free Synthesis of Carbamates Using CO<sub>2</sub> and Titanium Alkoxides

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## Abstract

A facile one-pot, phosgene-free method for the synthesis of *N*-phenylcarbamates is developed. Using this method, various aromatic carbamates could be prepared from aromatic amines, CO<sub>2</sub> and metal alkoxides. Aniline reacted with titanium methoxide (Ti(OMe)<sub>4</sub>) in the presence of CO<sub>2</sub> (5 MPa) to give methyl *N*-phenylcarbamate in 85% yield, in 20 min. Titanium residue could be regenerated by reaction with dimethyl carbonate at 220 °C for 16 h.

**Keywords:** CO<sub>2</sub>, organic carbamates, metal alkoxides

## 1. Introduction

Polyurethanes (PUs) are commonly used in various applications such as furniture, bedding, and footwear as well as in the automotive, medicine, electronics, and construction industries.<sup>1</sup> Furthermore, PUs are next-generation 3D printing materials. Various 3D printing players are exploring the PU market and offering innovative solutions, from artificial organs to fabrics or complex 3D models of machines.<sup>2</sup> PUs are manufactured via the polyaddition of a diol onto a diisocyanate. The latter is prepared on an industrial scale via the reaction of the corresponding amines with phosgene, which is a highly toxic and hazardous reagent.<sup>3</sup> Alternative synthesis strategies for PUs without the use of phosgene have been explored by many industry and academic researchers. Elimination of alcohol from carbamates via thermal decomposition is a simple and convenient method to produce isocyanates.<sup>4</sup> Another promising synthetic route to PUs is transurethanization polycondensation between a dicarbamate and a diol.<sup>5</sup> Hence, most of the studies on non-phosgene pathways to PUs have aimed at the development of efficient carbamate processes.

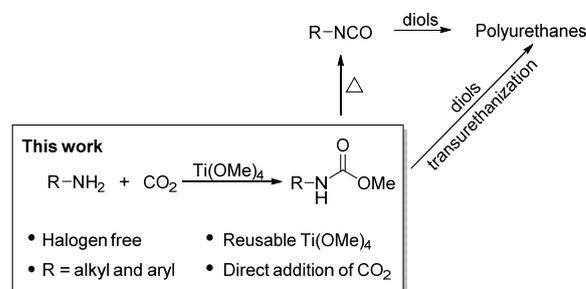
Because of the large-scale depletion of petrochemicals, renewable resources have gained much attention for sustainable polyurethane production. The use of the inexpensive and abundant CO<sub>2</sub> as the C1 synthon for synthesizing carbamates would be viewed as a promising, eco-friendly method.<sup>6</sup> Most of the approaches in this context rely on the production of the carbamic acid derivatives via the reaction of CO<sub>2</sub> and amines,

followed by the reaction with electrophiles, usually alkyl halides.<sup>7</sup> A general problem associated with the direct conversion of alcohols, amines, and CO<sub>2</sub> to carbamates is the formation of water as the by-product, which must be removed from the equilibrium reaction. We used *n*Bu<sub>2</sub>SnO or a nickel complex as the catalyst and an acetal as the dehydrating agent to obtain good yields of the amine-based carbamates.<sup>8</sup> De Vos et al.<sup>9</sup> reported that bases such as catalysts Cs<sub>2</sub>CO<sub>3</sub>, could catalyze the transformation of an amine and an alcohol into a carbamate with CO<sub>2</sub> as the carbonyl source. Moreover, Tomishige et al.<sup>10</sup> developed a method using a heterogeneous CeO<sub>2</sub> catalyst for the one-pot synthesis of organic carbamates from amines, CO<sub>2</sub>, and alcohols. However, in this case, only aliphatic amines could be activated because aromatic amines are poor nucleophiles.<sup>11</sup> Therefore, the development of a method for synthesizing aromatic carbamates from aromatic amines, CO<sub>2</sub>, and alcohols is desirable.

a) Classic synthetic routes to polyurethanes



b) Phosgene free pathway to polyurethanes



**Scheme 1.** Synthetic routes to polyurethanes.

Our group has reported the synthesis of a series of *N*-phenylcarbamates from aromatic amines, and, CO<sub>2</sub> using dibutyltin dialkoxides or titanium alkoxides.<sup>12</sup> However, because

of the low boiling point of MeOH, it is difficult to regenerate dibutyltin dimethoxide or titanium tetramethoxide from the residues and MeOH. For this reason, we chose the butylated carbamate as the final product. However, the decomposition and transurethanization of methylated dicarbamate were easier than those of butylated carbamate because MeOH is easily eliminated by distillation during dealcoholysis.<sup>4b-d,5b</sup> Synthesis of a carbamate from an amine, CO<sub>2</sub>, and silicate ester has also been reported.<sup>13</sup> Herein, we describe an efficient synthesis of carbamates directly from an amine, CO<sub>2</sub>, and Ti(OMe)<sub>4</sub>. Both aliphatic and aromatic amines could be transformed to the corresponding carbamates in good yields within 30 min. Ti(OMe)<sub>4</sub> could be regenerated via the reaction between Ti-containing residues and dimethyl carbonate (DMC) at 220 °C.

## 2. Experimental

### Materials

The starting compounds NaOMe, Mg(OMe)<sub>2</sub>, Al(OMe)<sub>3</sub>, *n*Bu<sub>2</sub>Sn(OMe)<sub>2</sub>, Ti(OMe)<sub>4</sub>, and Ta(OMe)<sub>5</sub> were purchased from Sigma-Aldrich. Si(OMe)<sub>4</sub>, Ca(OMe)<sub>2</sub>, and Ge(OMe)<sub>4</sub> were purchased from Wako Chemicals Co. Cu(OMe)<sub>2</sub> and Zn(OMe)<sub>2</sub> were purchased from Tokyo Chemical Industry. CO<sub>2</sub> was purchased from Showa Tansan (purity > 99.99%). All the chemicals were used without further purification.

### Instruments

The catalytic reactions were performed in a 10-mL stainless-steel autoclave with a gas-pressure monitor (max. 25 MPa). All the moisture-free operations were carried out in a glovebox. The reaction mixtures were heated in a Sibata Chem-300 Synthesizer. The product mixtures were analyzed by NMR, HPLC, and GC-MS. <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were measured on a Bruker AVANCE-III high resolution spectrometer (400 MHz for <sup>1</sup>H). HPLC analyses were conducted using Shim-pack VP-ODS columns (GL Science) mounted on a Shimadzu prominence HPLC system equipped with a refractive index detector (RID). Carbamates were isolated by a Yamazen AI-580 single channel automated flash chromatography system using ethyl acetate and *n*-hexane as eluents. All volatile products were characterized by GC-MS using a Shimadzu GC-2010 gas chromatograph connected to a GCMS-QP 2010 plus mass spectrometer.

### Typical reaction procedure

Under N<sub>2</sub> protection, aniline (75 mg, 0.8 mmol), metal methoxide (0.8 mmol), and CH<sub>3</sub>CN (3 mL) were added to an autoclave equipped with a stir bar. The autoclave was sealed tightly and filled with CO<sub>2</sub> up to a pressure of 3 MPa. The autoclave was heated to 150 °C, and the pressure of CO<sub>2</sub> was adjusted to 5 MPa. After 20 min, the autoclave was cooled in an ice bath, and CO<sub>2</sub> was released slowly. Toluene (85.3 mg, 0.1 mL) as an internal standard was added to the mixture. A small amount of the mixture was filtered for HPLC or <sup>1</sup>H NMR analysis. The isolated material was purified by automated flash chromatography with ethyl acetate and *n*-hexane as eluents. All the isolated products listed in Table 4 were characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, as well as GC-MS. The data were consistent with those for authentic materials and literature values.<sup>7g,14</sup>

### Recycling of Ti(OMe)<sub>4</sub> for carbamates synthesis

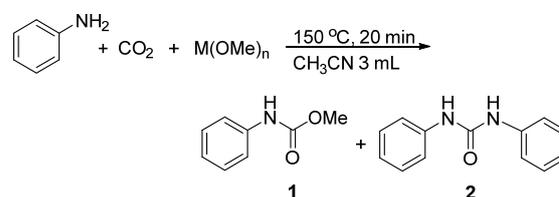
Under N<sub>2</sub> protection, aniline (75 mg, 0.8 mmol), Ti(OMe)<sub>4</sub> (138 mg, 0.8 mmol), and CH<sub>3</sub>CN (3 mL) were added to an autoclave with a stir bar. The autoclave was sealed tightly and

filled with CO<sub>2</sub> to 3 MPa. The autoclave was heated to 150 °C, and the pressure of CO<sub>2</sub> was adjusted to 5 MPa. After 20 min, the autoclave was cooled in an ice bath, and CO<sub>2</sub> was released slowly. Toluene (85.3 mg, 0.1 mL) as an internal standard was added to the mixture. A small amount of the mixture was filtered for HPLC analysis. The products were separated from the reaction mixture by vacuum sublimation at 100 °C.

Ti(OMe)<sub>4</sub> was regenerated by a method similar to the preparation of Ti(OEt)<sub>4</sub> from TiO<sub>2</sub>·*x*H<sub>2</sub>O and diethyl carbonate (DEC).<sup>15</sup> Under N<sub>2</sub> protection, a mixture of Ti-containing residue (121 mg) and DMC (5 mL) was introduced into an autoclave with a stir bar. The autoclave was heated to 220 °C for 16 h. After the reaction, the mixture was transferred into a flask under N<sub>2</sub> atmosphere. DMC and methanol were removed under reduced pressure to obtain the recovered Ti(OMe)<sub>4</sub> (136 mg, 99%).

The reaction was conducted in a similar manner using the recovered Ti(OMe)<sub>4</sub> to synthesize carbamates.

## 3. Results and Discussion



**Table 1.** Synthesis of carbamates from aniline, CO<sub>2</sub> and various methoxy sources.<sup>a</sup>

Entry	Reagent	Conv. (%) <sup>b</sup>	Yield of 1 (%) <sup>b</sup>	Yield of 2 (%) <sup>b</sup>
1	MeOH	3	< 1	< 1
2	NaOMe	34	< 1	< 1
3	Mg(OMe) <sub>2</sub>	50	< 1	< 1
4	Al(OMe) <sub>3</sub>	2	< 1	< 1
5	Si(OMe) <sub>4</sub>	8	1	2
6	Ca(OMe) <sub>2</sub>	33	< 1	< 1
7	Ti(OMe) <sub>4</sub>	62	59	1
8	Cu(OMe) <sub>2</sub>	4	< 1	< 1
9	Zn(OMe) <sub>2</sub>	52	3	< 1
10	Ge(OMe) <sub>4</sub>	1	< 1	< 1
11 <sup>c</sup>	<i>n</i> Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	47	41	4
12	Ta(OMe) <sub>5</sub>	30	12	< 1

<sup>a</sup> Reaction conditions: M(OMe)<sub>n</sub> (0.8 mmol), aniline (0.8 mmol), CH<sub>3</sub>CN (3 mL), CO<sub>2</sub> (5 MPa), 150 °C. <sup>b</sup> Determined by HPLC. <sup>c</sup> ref. 12a.

In a previous work, *n*Bu<sub>2</sub>SnO was shown to be very active for the catalytic activation of CO<sub>2</sub>, alcohols and aliphatic amines, giving the corresponding carbamates in good yields and with high selectivity. Tin alkoxide was the key compound in the catalytic cycle.<sup>8a</sup> Therefore, we decided to investigate the activity of metal alkoxides especially tin alkoxide for the synthesis of carbamates from amines and CO<sub>2</sub>. A series of metal

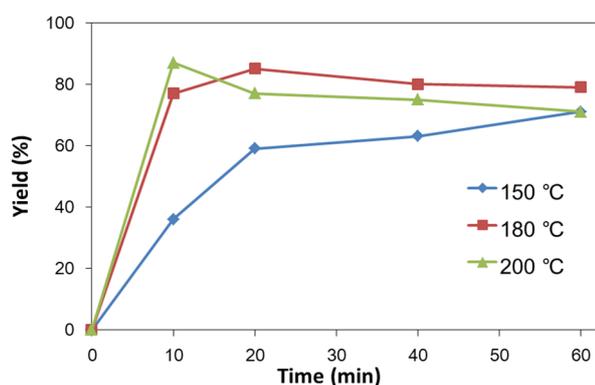
alkoxides were screened for use in the synthesis of carbamates (Table 1). In the absence of metal alkoxides, no carbamates formed when MeOH was used as the methoxy-source; this was because of thermodynamic limitations and the poor nucleophilic properties of aromatic amines (Table 1, entry 1). Among the metal alkoxides tested, Ti(OMe)<sub>4</sub> and *n*Bu<sub>2</sub>Sn(OMe)<sub>2</sub> exhibited relatively higher activity for carbamate synthesis. In the presence of Ti(OMe)<sub>4</sub>, the desired product methyl *N*-phenylcarbamate **1** was obtained in modest yield (59%) and 1% *N,N'*-diphenylurea **2** was formed as the minor product (Table 1, entry 7).

Various solvents were applied for this reaction; the results are shown in Table 2. Similar results were obtained when using 1,4-dioxane, tetrahydrofuran (THF), CH<sub>2</sub>Cl<sub>2</sub>, or ethyl ether as the solvent (entries 1-4). No carbamate was obtained when using alcohol as the solvent, because of the formation of DMC as the main product. With acetonitrile as the solvent, the conversion was 65% and the yield of carbamate reached 61% (entry 5).

**Table 2.** Synthesis of carbamates from aniline, CO<sub>2</sub>, and Ti(OMe)<sub>4</sub> in various solvents.<sup>a</sup>

Entry	Solvent	Conv. (%) <sup>b</sup>	Yield of <b>1</b> (%) <sup>b</sup>	Yield of <b>2</b> (%) <sup>b</sup>
1	THF	48	47	< 1
2	1,4-dioxane	50	50	< 1
3	CH <sub>2</sub> Cl <sub>2</sub>	48	46	1
4	ethyl ether	51	47	1
5	CH <sub>3</sub> CN	65	61	1
6	MeOH	< 1	< 1	< 1

<sup>a</sup> Reaction conditions: aniline (0.8 mmol), Ti(OMe)<sub>4</sub> (0.8 mmol), CO<sub>2</sub> (5 MPa), solvent (3 mL), 150 °C, 20 min. <sup>b</sup> Determined by HPLC.

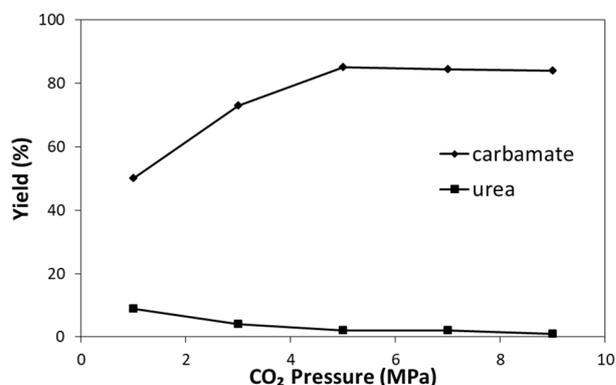


**Figure 1.** Effect of temperature on carbamate synthesis from aniline, CO<sub>2</sub>, and Ti(OMe)<sub>4</sub>. Reaction conditions: aniline (0.8 mmol), Ti(OMe)<sub>4</sub> (0.8 mmol), CO<sub>2</sub> (5 MPa), CH<sub>3</sub>CN (3 mL). The yield of carbamate was determined by HPLC. The yield of urea is omitted for clarity.

Figure 1 illustrates the effect of temperature on the yield of carbamate. High temperatures (>100 °C) are necessary for carbamate synthesis directly from aniline, CO<sub>2</sub>, and Ti(OMe)<sub>4</sub>. At 150 °C, the yield of carbamate increased upon prolonging the reaction, and reached 71% at 60 min. The formation of carbamate at 180 °C was rapid in the initial stage and reached the maximum at 20 min. The yield of carbamate could not be

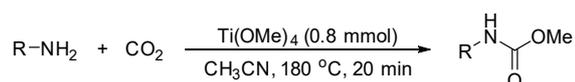
increased even after 60 min of reaction at 180 °C. The reaction conducted at a higher temperature of 200 °C for 10 min gave 87% carbamate yield, which was similar to the yield obtained at 180 °C. However, a lower carbamate yield was observed upon increasing the reaction time beyond 20 min because of the reaction of aniline and carbamate to give urea as the side product (See Supporting Information Scheme S2). The optimal reaction temperature was determined to be 180 °C for a reaction time of 20 min.

CO<sub>2</sub> pressure-dependent plots of carbamate synthesis from aniline, CO<sub>2</sub>, and Ti(OMe)<sub>4</sub> are shown in Figure 2. The yield of carbamate increased with increasing CO<sub>2</sub> pressure from 1 MPa to 5 MPa, and remained almost unchanged, above 5 MPa. CO<sub>2</sub> insertion into a M-O bond is reported to occur very easily even under low CO<sub>2</sub> pressure at room temperature.<sup>16</sup> Because metal carbonates, which are products of CO<sub>2</sub> insertion, are thermolabile, high CO<sub>2</sub> pressures are required to shift the reaction equilibrium to the product side at the given reaction temperature. The formation of urea depends on the aniline concentration and carbamate concentration in the reaction mixture. Thus, the low aniline conversion at 1 MPa CO<sub>2</sub> pressure leads to a higher yield of urea (9%). When the CO<sub>2</sub> pressure was raised to 9 MPa, the yield of urea decreased to 1%.



**Figure 2.** Effect of CO<sub>2</sub> pressure on carbamate synthesis from aniline, CO<sub>2</sub>, and Ti(OMe)<sub>4</sub>. Reaction conditions: aniline (0.8 mmol), Ti(OMe)<sub>4</sub> (0.8 mmol), CO<sub>2</sub>, CH<sub>3</sub>CN (3 mL), 180 °C, 20 min.

With the optimized reaction conditions (0.8 mmol amine, 0.8 mmol Ti(OMe)<sub>4</sub>, 5 MPa CO<sub>2</sub>, 3 mL CH<sub>3</sub>CN at 150 °C for 30 min) in hand, we next investigated the substrate scope. <sup>1</sup>H NMR spectra and GC-MS studies showed that various substituted aryl and alkyl carbamates could be obtained from the corresponding amines (Table 3) by this method. Aromatic amines with an electron-donating group (Table 3, entries 2 and 7) gave higher yields of the corresponding carbamates than those with an electron-withdrawing group (Table 3, entries 3-6). The effect of electron-donating groups on the electrophilic aromatic substitution can result in a negative charge to the nitrogen atom of the -NH<sub>2</sub> group, thus promoting carbamate formation. The reactivity of the substituted aromatic amines employed in this reaction decreased in the order *para* > *meta* > *ortho*, which was ascribed to the increased steric hindrance. Only the amino group was activated, while other functional groups such as methoxy, methyl, halo, nitro, and cyano were unreactive; this made our protocol a chemoselective method for carbamate synthesis. Electron-enriched aliphatic amines also gave good yield of the corresponding carbamates. After 20 min, cyclohexylamine and *tert*-butylamine were converted to the corresponding carbamates in 88% and 81% yields, respectively.



**Table 3.** Carbamate synthesis using various amines.<sup>a</sup>

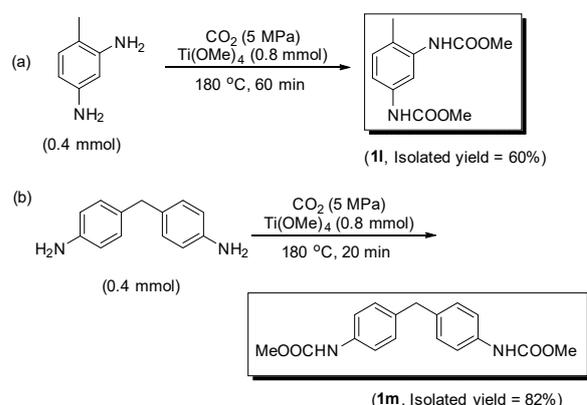
Entry	amine	Conv. (%) <sup>b</sup>	Yield (%) <sup>b</sup>
1		86	85 (83)
2		97	95 (92)
3		84	82 (77)
4		55	54 (50)
5		66	62 (60)
6		64	61 (55)
7		99	99 (98)
8		88	85 (81)
9		65	65 (61)
10		95	93 (88)
11		99	90 (81)

<sup>a</sup> Reaction conditions: amine (0.8 mmol), Ti(OMe)<sub>4</sub> (0.8 mmol), CO<sub>2</sub> (5 MPa), CH<sub>3</sub>CN (3 mL), 180 °C, 20 min. <sup>b</sup> Determined by <sup>1</sup>H NMR, isolated yields are given in parentheses.

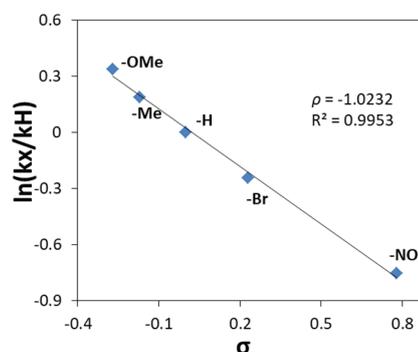
Our research highlights the activation of 2,4-diaminotoluene (DAT) and 4,4'-methylenedianiline (MDA) to produce a dicarbamate required for the polyurethane industry. In the case of 2,4-DAT (Scheme 2a), we achieved a high conversion of 2,4-DAT (93%) with a modest yield of the desired product **II** (60%), and a significant amount of monocarbamoylated products (33%) was formed after 1 h of reaction at 180 °C. In this case of 4,4'-MDA (Scheme 2b), **1m** was obtained in 82% yield after 20 min, along with trace amounts of the monocarbamoylated product.

The results of substrate scope indicated a relationship between the carbamate yield and the electronic properties of the substituent on aniline. The relevant Hammett plot is shown in Figure 3. Several competing reactions involving methoxy-,

methyl-, bromo-, and nitro-substituted aniline were conducted for the Hammett studies. A linear relationship and a negative slope ( $\rho = -1.0232$ ) were obtained, indicating the electrophilic nature of the titanium carbonate species attacked by the nucleophilic amines.



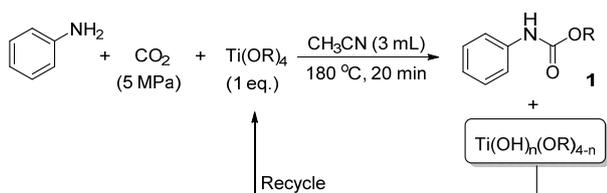
**Scheme 2.** Synthesis of dicarbamate (polyurethane precursor) with industrial application.



**Figure 3.** Hammett analysis of carbamate synthesis from *para*-substituted aniline. Reaction conditions: *para*-substituted aniline (OMe, Me, H, Cl, CN) (0.8 mmol), Ti(OMe)<sub>4</sub> (0.8 mmol), CH<sub>3</sub>CN (3 mL), CO<sub>2</sub> (5 MPa), 120 °C, 20 min.

We have reported that it is easy to regenerate Ti(*On*Bu)<sub>4</sub> by reaction with *n*BuOH during the removal of water by azeotropic distillation (Table 4, entry 2).<sup>12b</sup> However, it is difficult to regenerate Ti(OMe)<sub>4</sub> in this manner because the boiling point of MeOH is much lower than that of water, which leads to difficulties in the removal of water from the reaction mixture. Ono and coworkers reported a very useful method to obtain titanium tetraalkoxides in almost quantitative yields by the reaction of aqueous titanium dioxide with dialkyl carbonates.<sup>15</sup>

After the carbamate synthesis, aniline, carbamate, urea, and acetonitrile were distilled out from the reaction mixture, leaving behind Ti-containing residues. The Ti-containing residues were then converted into Ti(OMe)<sub>4</sub> in the presence of DMC and excess methanol at 220 °C for 16 h. After regeneration, all the volatiles were distilled out, leaving behind a colorless oil identified as Ti(OMe)<sub>4</sub>. Then, aniline was added to the recovered Ti(OMe)<sub>4</sub>, and the autoclave was pressurized with CO<sub>2</sub>. The yield of carbamate obtained using the recovered Ti(OMe)<sub>4</sub> was 86% after 20 min, which was the same as that obtained using fresh Ti(OMe)<sub>4</sub>. Ti(OMe)<sub>4</sub> showed the same level of recyclability as Ti(*On*Bu)<sub>4</sub>. This result indicates that Ti(OMe)<sub>4</sub> can be reused without loss of activity and hence finds potential application in industrial processes.

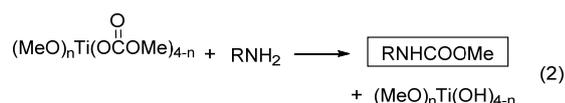


**Table 4.** Recycling of  $\text{Ti}(\text{OR})_4$  for carbamate synthesis.<sup>a</sup>

Entr y	$\text{Ti}(\text{OR})_4$	Yield of <b>1</b> (%) <sup>a</sup>	
		Fresh	Recycled
1	$\text{Ti}(\text{OMe})_4$	85	86
2 <sup>b</sup>	$\text{Ti}(\text{OnBu})_4$	84	84

<sup>a</sup> Reaction conditions: aniline (0.8 mmol),  $\text{Ti}(\text{OMe})_4$  (0.8 mmol),  $\text{CO}_2$  (5 MPa),  $\text{CH}_3\text{CN}$  (3 mL), 180 °C, 20 min. <sup>b</sup> ref. 12b.

Several reaction mechanisms for carbamate formation from  $\text{RNH}_2 + \text{CO}_2 + \text{MOR}'$  have been proposed.<sup>12,16a</sup> When  $\text{Ti}(\text{OnBu})_4$  is used, it typically reacts with  $\text{CO}_2$  to produce a titanium carbonate complex as the reaction intermediate. In our case,  $\text{CO}_2$  insertion into a Ti-O bond of  $\text{Ti}(\text{OMe})_4$  occurs in the same manner (eq. 1).



The results of Hammett analysis indicate that the nucleophilic attack of the amine nitrogen on the carbon atom derived from  $\text{CO}_2$  insertion generates the carbamate (eq. 2).

#### 4. Conclusion

In summary, we have developed an efficient method for the direct synthesis of carbamates from amines,  $\text{CO}_2$ , and  $\text{Ti}(\text{OMe})_4$ . Notably, this reaction is chemoselective toward amine activation.  $\text{Ti}(\text{OMe})_4$  can be regenerated by a reaction with DMC at 220 °C. This methodology opens up a new route for the production of organic carbamates, especially aromatic carbamates, which are important precursors for PUs. A tentative mechanism for this reaction is proposed, and the negative  $\rho$  value determined by Hammett analysis indicates nucleophilic attack of the amine onto the Ti carbonyl species derived from  $\text{Ti}(\text{OMe})_4$  and  $\text{CO}_2$ .

#### Acknowledgement

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#### Supporting Information

Analytical data, NMR and MS data for compounds **1a-1m**. This material is available on <http://dx.doi.org/10.1246/bcsj.xxx>.

#### References

- (a) T. Thomson, in *polyurethanes as specialty chemicals: Principles and applications*, CRC Press, Boca Raton, FL, 2004. (b) R. J. Zdrahala, I. J. Zdrahala, *J. Biomater. Appl.* **1999**, *14*, 67. (c) Z. S. Petrovic, *Polym. Rev.* **2008**, *48*, 109. (d) O. Kreye, H. Mutlu, M. A. R. Meier, *Green Chem.* **2013**, *15*, 1431.

- (a) A. Pfister, R. Landers, A. Laib, U. Hübner, R. Schmelzeisen, R. Mülhaupt, *J. Polym. Sci. A. Polym. Chem.* **2004**, *42*, 624. (b) K.-C. Hung, C.-S. Tseng, S.-H. Hsu., *Adv. Healthc. Mater.* **2014**, *3*, 1578. (c) K.-C. Hung, C.-S. Tseng, L.-G. Dai, S.-H. Hsu, *Biomaterials* **2016**, *83*, 156.
- (a) R. L. Shriner, W. H. Horne, R. F. B. Cox, *Org. Synth.* **1943**, *2*, 453. (b) R. J. Slocombe, E. E. Hardy, J. H. Saunders, R. L. Jenkins, *J. Am. Chem. Soc.* **1950**, *72*, 1888.
- (a) O. Bayer, *Angew. Chem.* **1947**, *59*, 257. (b) E. Dyer, G. C. Wright, *J. Am. Chem. Soc.* **1958**, *81*, 2138. (c) E. Dyer, G. E. Newborn, *J. Am. Chem. Soc.* **1958**, *80*, 5495. (d) P. Uriz, M. Serra, P. Salagre, S. Castillon, C. Claver, E. Fernandez, *Tetrahedron Lett.* **2002**, *43*, 1673. (e) D. C. D. Butler, H. Alper, *Chem. Commun.* **1998**, 2575.
- (a) L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Gramail, *Chem. Rev.* **2015**, *115*, 12407. (b) H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Gramail, J. L. Hedrick, *Macromolecules* **2015**, *48*, 3153.
- (a) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365. (b) D. Chaturvedi, *Tetrahedron* **2012**, *68*, 15. (c) H. Blattmann, M. Fleischer, M. Bähr, R. Mülhaupt, *Macromol. Rapid Commun.* **2014**, *35*, 1238. (d) R. H. Heyn, I. Jacobs, R. H. Carr, *Adv. Inorg. Chem.* **2014**, *66*, 83.
- (a) Y. Yoshida, S. Ishii, T. Yamashita, *Chem. Lett.* **1984**, *9*, 1571. (b) Y. Yoshida, S. Ishii, M. Watanabe, T. Yamashita, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1534. (c) W. McGhee, D. Riley, K. Christ, Y. Pan, B. Parnas, *J. Org. Chem.* **1995**, *60*, 2820. (d) M. Yoshida, N. Hara, S. Okuyama, *Chem. Commun.* **2000**, 151. (e) R. Srivastava, M. D. Manju, D. Srinivas, P. Ratnasamy, *Catal. Lett.* **2004**, *97*, 41. (f) J. M. Hooker, A. T. Reibel, S. M. Hill, M. J. Schueller, J. S. Fowler, *Angew. Chem. Int. Ed.* **2009**, *48*, 3482; (g) D. Riemer, P. Hirapara, S. Das, *ChemSusChem* **2016**, *9*, 1916.
- (a) M. Abla, J.-C. Choi, T. Sakakura, *Chem. Commun.* **2001**, 2238. (b) M. Abla, J.-C. Choi, T. Sakakura, *Green Chem.* **2004**, *6*, 524.
- A. Ion, C. V. Doorslaer, V. Parvulescu, P. Jacobs, D. D. Vos, *Green Chem.* **2008**, *10*, 111.
- (a) M. Honda, S. Sonchra, H. Yasuda, Y. Nakagawa, K. Tomishige, *Green Chem.* **2011**, *13*, 3406. (b) M. Tamura, M. Honda, K. Noro, Y. Nakagawa, K. Tomishige, *J. Catal.*, **2013**, *305*, 191. (c) M. Tamura, M. Honda, Y. Nakagawa, K. Tomishige, *J. Chem. Technol. Biotechnol.* **2014**, *89*, 19.
- (a) T. Jiang, X. Ma, Y. Zhou, S. Liang, J. Zhang, B. Han, *Green. Chem.* **2008**, *10*, 465. (b) W. Guo, J. Gonzalez-Fabra, N. A. G. Bandeira, C. Bo, A. W. Kleij, *Angew. Chem. Int. Ed.* **2015**, *54*, 11686.
- (a) H.-Y. Yuan, J.-C. Choi, S.-y. Onozawa, N. Fukaya, S. J. Choi, H. Yasuda, T. Sakakura, *J. CO<sub>2</sub> Util.* **2016**, *16*, 282. (b) J.-C. Choi, H.-Y. Yuan, N. Fukaya, S.-y. Onozawa, Q. Zhang, S. J. Choi, H. Yasuda, *Chem. Asian J.* **2017**, *12*, 1297.
- (a) Q. Zhang, H.-Y. Yuan, N. Fukaya, J.-C. Choi, *ChemSusChem* **2017**, *10*, 1501. (b) Q. Zhang, H.-Y. Yuan, N. Fukaya, H. Yasuda, J.-C. Choi, *Green Chem.* **2017**, *19*, 5614. (c) Q. Zhang, H.-Y. Yuan, N. Fukaya, J.-C. Choi, *ACS Sustainable Chem. Eng.* **2018**, *6*, 6675.
- (a) J. Holt, T. Andreassen, J.M. Bakke, A. Fiksdahl, *J. Heterocycl. Chem.* **2005**, *42*, 259. (b) Q. Yang, A. Robertson, H. Alper, *Org. Lett.* **2008**, *10*, 5079. (c) M. Hutchby, C. E. Houlden, J. G. Ford, S. N. G. Tyler, M. R.

- Gagne, G. C. Lloyd-Jones, K. I. Booker-Milburn. *Angew. Chem. Int. Ed.* **2009**, *48*, 8721. (d) X. Zhang, H. Jing, G. Zhang, *Synth. Commun.* **2010**, *40*, 1614. (e) A. Yoshimura, M. W. Luedtke, V. V. Zhdankin, *J. Org. Chem.* **2012**, *77*, 2087.
15. E. Suzuki, S. Kusano, H. Hatayama, M. Okamoto, Y. Ono, *J. Mater. Chem.* **1997**, *7*, 2049.
16. (a) A. J. Goodsel, G. J. Blyholdes, *J. Am. Chem. Soc.* **1972**, *94*, 6725. (b) T. Tsuda, S. Sanoda, K. Ueda, T. Saegusa, *Inorg. Chem.* **1976**, *15*, 2329. (c) T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1983**, *105*, 1304. (d) J.-C. Choi, T. Sakakura, T. Sako, *J. Am. Chem. Soc.* **1999**, *121*, 3793. (e) M. M. Ibrahim, K. Ichikawa, M. Shiro, *Inorg. Chem. Commun.* **2003**, *6*, 1030. (f) F. Parrino, C. Deiana, M. R. Chierotti, G. Martra, L. Palmisano, *J. CO<sub>2</sub> Util.* **2016**, *13*, 90.