Organocatalytic Regioselective Synthesis of Sulfur-Containing *N*-Alkyl Carbamates from Alkyne-Derived Cyclic Carbonates

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A highly regioselective synthesis of sulfur-containing *N*-alkyl carbamate from propargyl alcohol, carbon dioxide (CO₂) and amine via metal-free catalysis is described. The regioselective ring-opening addition of tri-substituted cyclic carbonate with amine was investigated in detail. A key feature of this system is the ability to afford tertiary β -hydroxyl *N*-alkyl carbamate with 100% selectivity by using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst in a wide range of reaction temperatures. The steric hindrance of amine and the use of ethanol favored the regioselective ring-opening addition reaction. A proposed mechanism for the ring-opening addition elaborated the underlying reason for the regioselective synthesis of sulfur-containing *N*-alkyl carbamate. This study provides a new alternative synthetic route to sulfur-containing *N*-alkyl carbamates from alkyne and CO₂ and may offer an attractive scaffold for further synthesis.

Keywords organocatalyst, sulfur-containing *N*-alkyl carbamate, tri-substituted cyclic carbonate, regioselective ring-opening, 1,5,7-triazabicyclo[4.4.0]dec-5-ene

Introduction

It is of great significance to utilize alkyne as a synthon because alkyne can be produced from coal or calcium carbide that is very rich in nature. Indeed, alkyne and its derivatives represent one of the most fundamental building blocks for organic synthesis.^[1-3] Concurrently, carbon dioxide (CO₂), as a safe, cheap, plentiful, renewable, environmentally benign and nontoxic one-carbon (C1) resource, has already been transformed efficiently into various fine chemicals^[4,5] and polymers.^[6] Consequently, it is promising to combine alkyne or its derivatives with CO₂ to produce useful compounds and materials, which can also reduce the CO₂ emission and our dependency on the petroleum resources.^[7,8]

As an inert C1 compound, CO₂ is usually converted to the five-membered cyclic carbonate via the coupling reaction with alkyne derivatives or epoxides that are high-energy compounds.^[9-12] Followed by ring-opening addition reaction with amines, these cyclic carbonates can be effectively converted to the urethane compounds. This reaction is the basic chemistry of the non-isocyanate route for making polyurethanes (PUs).^[13,14] Compared with the traditional isocyanate route, the ring-opening addition of cyclic carbonate with amines avoids the use of toxic di- or polyisocyanates that are originated from toxic phosgene.^[15,16] The coupling reaction of CO₂ with various epoxides has been extensively studied for producing cyclic carbonates.^[17-19] However, most of the epoxides are derived from raw oils and often high-cost. Moreover, because of non-regioselective reaction of the cyclic carbonate with amine, two isomeric products are often produced, which caused the difficulty of separation and further preparation for well-defined PUs.^[20-24] The main reason is that the epoxide-derived cyclic carbonates are often mono- or di-substituted and less steric.

In addition, sulfur is a widely distributed element in the earth and was of tremendous importance to the development of chemistry and organic synthesis, such as the vulcanization of rubber and thiol-ene click reaction. Lots of sulfur-containing compounds are widely employed in various branches of industry because of their specific properties, *i.e.*, high refractive indices, thermal and flame resistance, strong adhesion to various materials, *etc.*^[25-27] Therefore, the introduction of sulfur can improve the properties of small molecules or polymers.

Herein, we report the synthesis and regioselective ring-opening reaction of a sulfur-containing five-membered cyclic carbonate using 4,4-dimethyl-5-methylene-2-oxo-1,3-dioxolane (DMOD) as the starting material. DMOD can be synthesized from the coupling reaction of CO₂ and propargyl alcohol, which is an inexpensive acetylene derivative, by using various catalytic systems such as metal,^[28-30] metal complexes^[31,32], Lewis base^[33] and phosphines.^[34,35] Note that propargyl alcohol can be synthesized from the addition of acetylene and acetone,^[36,37] and acetone can also be prepared from the direct reaction of acetylene with water.^[38] Therefore, DMOD can be regarded as the product of the reaction of CO₂, acetylene and water, without loss of any atom. It is thus a non-petroleum approach for making new chemicals. Previously investigations^[39,37,40] on the reaction of DMOD with amines disclosed that the intermolecular cyclization to produce oxazolidones depended on whether the catalyst exists and the types of catalysts and amines. Detrembleur *et al.*^[41] confirmed that the cyclization occurred quickly in the absence of catalyst. We thus considered that the modification of the double bond of DMOD could not only prevent the abovementioned cyclization, but also increase the steric hindrance that might be beneficial to the regioselective reaction, as shown in Scheme 1. Such proposed synthetic route to produce *N*-substituted carbamates with sulfur element has yet not been reported. During our

preliminary studies, Kleij *et al.*^[42] presented an elegant study demonstrating a highly regioselective catalytic route towards carbamates from di-substituted cyclic carbonates with amine. Thereof, the cyclic carbonate was originated from 4,4-dimethyl epoxide.^[42]

Scheme 1 The synthetic route of the tertiary β -hydroxyl *N*-alkyl carbamates via the ring-opening addition of tri-substituted cyclic carbonates with amines by using organocatalyst.^a

^a R_1 and R_2 refer to alkyl chains.

In present work, we provided a new alternative pathway to synthesize sulfur-containing carbamates derived from alkyne and CO_2 . A regioselective ring-opening addition of substituted DMOD with amines to access tertiary β -hydroxyl *N*-alkyl carbamate (**A**) with 100% selectivity via metal-free catalytic route is presented and discussed (Scheme 1).

Experimental

Materials and methods

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) (98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (99%), 4-dimethylaminopyridine (DMAP) (99%), butylamine (99.5%), methyl thioglycolate (95%), 3-mercaptopropionic acid (99%), 1,2-ethanedithiol (98%), 1,6-hexanedithiol (97%), 4-methylpiperidine (99%) and 2-methyl-3-butyn-2-ol (98%) were purchased from Aldrich and used as received. Phosphine (95%), 1-propanethiol (99.5%), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (99%), cetyltrimethyl ammonium bromide (CTAB) (98%, Aladdin), ethanol (99.8%), chloroform (99.8%), dodecylamine (**1**) (99%), ethanolamine (**2**) (99%), ethylenediamine (**3**) (99%), 1,6-hexane-diamine (**4**) (99%), isophorondiamine (**5**) (99%), 1,2-diaminocyclohexane (**6**) (99%), tris(2-aminoethyl)amine (**7**) (97%), furfurylamine (**8**) (99%), *p*-xylylenediamine (**9**) (99%), aniline (**10**) (99%), acetoguanamine (**11**) (98%), 4-methylpiperidine (**12**) (99%), 4-hydroxypiperidine (**13**) (98%), 2-(methylamino)ethanol (**14**) (99%) and piperazine (**15**) (99%) were purchased from Aladdin and used as received. ^1H NMR, ^{13}C NMR and ^{13}C -DEPT 135 NMR spectra of all the products were obtained on a Bruker Advance DMX 400 MHz and 101 MHz spectrometer using TMS as the internal reference, respectively. Infrared spectrum was measured using a Bruker Vector 22 FT-IR spectrophotometer. GC-MS spectra were taken on a GC/MS-QP2010 chromatograph.

Synthesis of 4,4-dimethyl-5-methylene-2-oxo-1,3-dioxolane (DMOD)

The reaction of 2-methyl-3-butyn-2-ol and CO_2 was performed in the autoclave (80 mL) equipped with mechanical stirrer and barometer. 2-Methyl-3-butyn-2-ol (20 mL, 205.8 mmol) and phosphine (4.2 mL, 16.8 mmol) were transferred into the autoclave. Then the autoclave was filled with CO_2 until its pressure up to 3.0 MPa under stir-

ring. The pressure and temperature were kept at 5.0 MPa and 100 °C, respectively, and stirred for 8 h. Afterwards, the autoclave was cooled in an ice-water bath and the pressure was slowly vented. The resulting crude product was purified by vacuum distillation at 120 °C. Yield 90%. ^1H NMR (400 MHz, CDCl_3) δ : 4.76 (d, J = 3.9 Hz, 1H), 4.31 (d, J = 4.0 Hz, 1H), 1.61 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ : 158.66, 151.22, 85.28, 84.68, 27.47.

Synthesis of 4,4-dimethyl-5-[(propylthio)methyl]-2-oxo-1,3-dioxolane (DPMOD)

DMOD (8.0 mL, 69.3 mmol), 1-propanethiol (6.28 mL, 69.3 mmol) and DMPA (532.8 mg, 2,079 mmol) were transferred into the flask with a magnetic stirrer under nitrogen atmosphere and irradiated for 1 h by 365 nm UV lamp at room temperature. The crude product was purified by chromatography on a silica gel column with mixed solvent of THF/hexane=1/20. Yield 95%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.59 (t, J = 6.6 Hz, 1H), 2.85 (d, J = 6.6 Hz, 2H), 2.58 (td, J = 7.2, 0.8 Hz, 2H), 1.62–1.51 (m, 2H), 1.49 (s, 3H), 1.35 (s, 3H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ : 153.09, 84.12, 83.80, 54.81, 39.48, 33.82, 29.83, 25.82, 22.29, 20.70, 13.10.

The ring-opening addition of DPMOD with amines

Take the reaction of DPMOD with butylamine as an example, the reaction was carried out in a Schlenk flask under a nitrogen atmosphere at given temperature, ethanol or TCM were used the solvents. After the reaction, the solvent was removed by vacuum distillation at 30 °C. The conversion of DPMOD was determined by the ^1H NMR spectra of the crude product. The regioselectivity of DPMOD with butylamine was determined by ^1H (^{13}C) NMR and ^{13}C -DEPT 135 spectra. Yield 95%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 4.62 (dd, J = 10.5, 2.1 Hz, 1H), 3.02–2.94 (m, 2H), 2.89 (dd, J = 14.0, 2.1 Hz, 1H), 2.55–2.39 (m, 3H), 1.52 (dd, J = 7.3, 2.2 Hz, 2H), 1.43–1.33 (m, 2H), 1.33–1.24 (m, 2H), 1.05 (d, J = 10.6 Hz, 6H), 0.92 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ : 156.21, 77.16, 70.71, 39.03, 33.22, 31.55, 31.27, 27.21, 24.06, 22.12, 19.26, 13.59, 13.16. IR ν_{max} : 3460, 3348, 2958, 2926, 2868, 1700, 1518, 1248, 1062 cm^{-1} . The reaction data of DPMOD with various amines (**1**–**15**) can be found in the supporting information part.

Results and Discussion

Initially, DMOD was synthesized from the direct coupling reaction of propargyl alcohol with CO_2 using tributylphosphine as the catalyst [Scheme 2, step (i)].^[34,43] The reaction was carried out with a CO_2 pressure of 5.0 MPa at 100 °C for 8 h. The crude product was then purified by vacuum distillation at 120 °C to obtain a crystal with a purity of >99%, revealed by GC-MS spectra (Figure S1). The molecular structure of DMOD was also confirmed by the ^1H NMR spectrum with the characteristic chemical shifts of the double bond at 4.31 and 4.76 ppm (Figure S2). Afterwards, the ultraviolet (UV) light-induced thiol-ene click reaction^[44–51] of DMOD with 1-propanethiol was performed using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a free radical generator at room temperature, afforded 4,4-dimethyl-5-[(propylthio)methyl]-2-oxo-1,3-dioxolane (DPMOD) within 1.0 h. After the purification through a silica gel column chromatography eluted by the mixed THF/hexane (volume ratio: 1/20) solution, a pure DPMOD was obtained. The molecular structure of DPMOD was confirmed by the

^1H NMR and ^{13}C NMR spectra (Figure S3). The integral area ratio of the protons d (2.85 ppm) to c (4.59 ppm) was 2.01/1.00 (see curve 1 in Figure S3), suggesting that 1-propanethiol was exclusively added to the terminated CH_2 site of DMOD,^[46] which was a completely regioselective reaction.

Scheme 2 The regioselective synthesis of *N*-alkyl carbamates. (i) Synthesis of DMOD, (ii) thiol-ene click reaction, and (iii) ring-opening addition of DPMOD with butylamine.

With DPMOD in hand, the ring-opening addition of DPMOD with butylamine was investigated. For this reaction, two regioisomers, *i.e.*, 3-hydroxy-3-methyl-1-(propylthio)butan-2-yl butylcarbamate (**A**) and 3-hydroxy-2-methyl-4-(propylthio)butan-2-yl butylcarbamate (**B**) would be produced, as depicted in Scheme 2.^[13,52,23] In order to elaborate the regioselectivity of this reaction clearly, we defined firstly the method for calculating the regioselectivity based on the NMR results of the final products, using the product of Entry 1 in Table 1 as an example, as shown in Figures S4 and S5. Two kinds of protons (**a** and **b**) linked to the tertiary carbon were clearly observed at 3.82 and 4.52–4.70 ppm that are two separated peaks (see curve 1 in Figure S4), represented the isomers **A** and **B**, respectively. The **A/B** molar ratio was estimated to be 74:26 based on the integral area ratio of two peaks. Correspondingly, two sets of the resonance peaks at 77.1 (70.7) and 80.6 (74.7) ppm, which could be ascribed to the isomers **A** and **B**, respectively, were accurately located by combining ^{13}C NMR and ^{13}C -DEPT 135 techniques (Figures S5 and S8). Thus, the regioselectivity of the DPMOD/amine reaction could be calculated based on the ^1H NMR spectra.

The effect of the types of organocatalysts on the ring-opening addition of DPMOD with butylamine with the molar ratio of 1.0 was studied, as summarized in Table 1 (Entries 1–5). In the absence of the catalyst, such ring-opening addition presented low regioselectivity even that DPMOD had three substituents (Entry 1 in Table 1). The use of DMAP and CTAB as the catalysts resulted in slightly improved conversion of DPMOD (33.5 and 27.5% respectively) but similar **A/B** molar ratios with that of the products of entry 1 in Table 1. When DBU was used for the reaction, the conversion of DPMOD and the **A/B** molar ratio were sharply improved to 78.8% and 82/18, respectively (Entry 4, Table 1). The employment of TBD led to a higher regioselectivity for producing **A** (**A/B** molar ratio: 94/6) but a slightly low conversion of DPMOD (73.3%, Entry 5 in Table 1). Clearly, strong organic bases had higher activity and selectivity towards the ring-opening addition of DPMOD with butylamine.

The DPMOD conversion and the selectivity to produce

A could be dramatically improved by either using the ethanol or increasing the amounts of butylamine. For example, when TCM was replaced by ethanol, the DPMOD conversion increased from 73.3% to 87.8%, and the **A/B** molar ratio increased from 94:6 to 97:3 in the presence of 5 mol% TBD (Entries 5–6 in Table 1). Owing to the high reactive activity of butylamine unlike aniline, 5 mol% TBD is enough for the ring-opening reaction. Increasing the feeding ratio of butylamine/DPMOD to 1.5 in ethanol led to a dramatic improvement of the DPMOD conversion to 100% at 30 °C within a shorter reaction time (12 h), and the selectivity of producing **A** reached to >99% (100%) determined by ^1H NMR [^{13}C (^{13}C -DEPT 135)] NMR spectra, as shown in Entry 7 (Table 1, Figure S9). Under the circumstance of excess butylamine in ethanol, increasing the reaction temperatures to 50, 70 and 100 °C, DPMOD could be completely consumed within a shorter reaction time (4–8 h, Figures S4–S5 and S7–S8), while the regioselectivity for producing **A** was nearly unvaried, as Entries 8–10 in Table 1, only a small portion of **B** (3%) was produced at 70 and 100 °C. Of interest, even TCM used as the solvent, DPMOD could also be completely consumed with 100% selectivity to **A** at 50 °C within 8 h (Entry 11, Table 1). Thus, it is the key to improving the DPMOD conversion and **A/B** selectivity using excess of butylamine in the presence of TBD. When DBU was used as the catalyst, the DPMOD/butylamine addition reaction in ethanol (Entries 12–15, Table 1) showed slight lower DPMOD and **A/B** selectivity than those of the TBD catalysis under the same reaction conditions. Based on the above results, we can conclude that the use of TBD, excess of butylamine and ethanol are favorable to achieve selective production of tertiary β -hydroxyl *N*-alkyl carbamates (**A**) with 100% conversion of DPMOD.

Unlike what was seen for the regioselective aminolysis of epoxide-derived disubstituted cyclic carbonates using 20 mol% of TBD and excess amounts of amine (2.0–6.0 equiv.),^[42] small quantity of organocatalyst (5 mol%) and 1.0–1.5 equiv. amine were used in our system. Moreover, the use of ethanol could assist the regioselective reaction of DPMOD with butylamine under the low reaction temperature of 30 °C (Entries 5–6 in Table 1).

The hydrogen bonding interaction among butylamine, TBD and DPMOD and the proton migration^[53,54] are proposed to be responsible for the highly regioselective reaction, similar to Kleij's proposal^[42,53] and as depicted in Scheme 3. Firstly, the possible intermediates **1A/1B** and **2A/2B** existed because of appearance of a tetrahedral geometry after butylamine attacked the quaternary carbon of the carbonate and N–H $\cdots$ N hydrogen bond was formed. Secondly, considering the energy barrier and the inversion from **2A** to **3B**, the route from **2A** to **3A** is easier and more reasonable. Thirdly, owing to the stronger ability of electron donating for the two methyl groups, the oxygen atom next to the two methyl groups have stronger electronegativity to combine with N–H of the TBD to produce the **3A** rather than **3B**. Finally, the oxygen anion of **4A** is more unstable so that it can capture proton easily, which was strongly supported by the fact that the protic solvent favored the selective production of **A**.

We also examined the ring-opening addition of DPMOD with various amines, including aliphatic primary and secondary amines, aromatic primary amines and guanamine in ethanol at 50 °C for 8 h in the presence of TBD (5.0 mol%), as collected in Table 2. When the aliphatic primary amines (**1**–**3**, Table 2) were used,

Table 1 Organocatalyzed ring-opening addition of DPMOD with butylamine in various reaction conditions^a

Entry	DPMOD:butylamine	T/°C	Solv.	t/h	Cat.	Conv./% ^b	A:B ^c
1	1:1	30	TCM	30	None	23.4	74:26
2	1:1	30	TCM	30	DMAP	33.5	74:26
3	1:1	30	TCM	30	CTAB	27.5	70:30
4	1:1	30	TCM	30	DBU	78.8	82:18
5	1:1	30	TCM	30	TBD	73.3	94:6
6	1:1	30	EtOH	30	TBD	87.8	97:3
7	1:1.5	30	EtOH	12	TBD	100	> 99(100) ^e
8	1:1.5	50	EtOH	8	TBD	100	> 99(100) ^e
9	1:1.5	70	EtOH	4	TBD	100	97:3
10 ^d	1:1.5	100	EtOH	4	TBD	100	97:3
11	1:1.5	50	TCM	8	TBD	100	> 99(100) ^e
12	1:1.5	30	EtOH	24	DBU	98.8	83:17
13	1:1.5	50	EtOH	8	DBU	98.5	88:12
14	1:1.5	70	EtOH	4	DBU	99	94:6
15 ^d	1:1.5	100	EtOH	4	DBU	99	97:3

^a Reaction conditions: DPMOD (0.1 mL, 0.588 mmol), catalyst loading: 5 mol% related to DPMOD, solvent: 0.2 mL, N₂ atmosphere. TCM: chloroform, EtOH: ethanol. ^b Determined by ¹H NMR spectra of the crude product, Conv. = [(A_{4.70-4.52} - A_{2.58/2})/A_{4.70-4.52}]*100%. ^c Determined by ¹H NMR of the crude product, product ratio A:B = (A_{4.70-4.52} - A_{2.58/2}):A_{3.82}. ^d In the pressure glass bottle. ^e The value of 100 was from ¹³C-DEPT 135 and ¹³C NMR spectra.

Scheme 3 Proposed mechanism for the TBD-catalyzed ring-opening addition to produce **A** and **B**.

DPMOD was completely consumed and the **A/B** molar ratios were 97:3 for **1** and **3**, and >99 for **2**. Of special, the reaction of **2** with DPMOD afforded 29.6% of 2-oxazolidone, which was derived from the back-biting reaction of **A** (Scheme 4).^[55] As compared **4** with **3**, long alkyl chain between two amino groups caused relatively low DPMOD conversion (83.4%) and **A/B** selectivity (95:5). Furthermore, isophorondiamine (**5**) has two amino groups with unequal reactivity, presented a further decreased conversion of DPMOD (71%) and **A/B** selectivity (85:15). However, 1,2-diamino-cyclo-hexane (**6**) with two amino groups with equal reactivity, had excellent **A/B** selectivity of >99, but the DPMOD conversion was 70% and similar to that of the reaction of DPMOD with **5**. As a result, big steric hindrance of the primary amine was beneficial to the selective

Table 2 TBD-catalyzed reaction of DPMOD with various amines for producing sulfur-containing *N*-alkyl carbamates^a

1 100% (97:3) ^b	2 100% (>99) ^c	3 100% (97:3)	4 83.4% (95:5)
5 71% (85:15)	6 70% (>99)	7 100% (97:3)	8 78% (>99)
9 71% (95:5)	10 No reaction ^e	11 No reaction ^e	12 100% (>99)
13 72% (>99)	14 93% (>99) ^d	15 93% (>99)	

^a Reaction conditions: DPMOD (0.1 mL, 0.588 mmol), the molar ratio of the amino group (N-H) to DPMOD was 1.5, TBD: 5 mol% related to DPMOD, ethanol: 0.2 mL, N₂ atmosphere. The DPMOD conversion and regioselectivity were determined by ¹H (¹³C) NMR spectra of the crude products. ^b "1" refers to the serial number of amine, "100% (97:3)" refers to the conversion of DPMOD (the molar ratio of **A/B**). ^c 29.6% 2-oxazolidone was produced. ^d 52.6% 3-methyl-2-oxazolidone produced. ^e TBD: 30 mol% related to DPMOD, 75 °C, 24 h.

Scheme 4 The back-biting reaction of **A** to produce the by-product of oxazolidone.

production of **A**, while the DPMOD conversion was weakened. In addition, tris(2-aminoethyl)amine (**7**) presented the same DPMOD conversion and **A/B** selectivity with **3**. Therefore, both **3** and **7** could be potentially applied for regioselective synthesis of PUs.

Aryl-substituted aliphatic primary amines showed low reactivity towards the DPMOD/amine reaction. When furfurylamine (**8**) and *p*-xylylenediamine (**9**) were employed, the DPMOD conversions reached to 78% and 71%, respectively. However, the regioselectivity to produce **A** was >99% and 95%, respectively. Aniline (**10**) and acetoguanamine (**11**), which were aromatic, could not react with DPMOD under the same reaction conditions.

The results of the ring-opening addition of DPMOD with secondary amines **12–15** are listed in Table 2. All the reactions showed >99% production of regioisomer **A**, which indicated that the steric hindrance of these secondary amines is favourable to the regioselective ring-opening of DPMOD. Compared with 4-methylpiperidine (**12**), the use of **13** caused lower conversion of DPMOD (72%), while **12** led to a 100% conversion of DPMOD. It is reasonable that the methyl group of **12** was more electron-donating than the hydroxyl group of **13** and thus improved the reactivity of **12** towards DPMOD. 2-(Methylamino)ethanol (**14**) with less steric hindrance than **13**, could also react with DPMOD with 99% regioselectivity for producing **A**. However, 52.6% of 3-methyl-2-oxazolidone was produced via the same route as the reaction of DPMOD with **2**, as shown in Scheme 4. Obviously, the reaction of the aminoethanol with DPMOD produced oxazolidone inevitably, which is conversely a useful method to synthesize heterocyclic compound from CO₂.^[55–57] In addition, piperazine (**15**) could react with DPMOD with 93% DPMOD conversion and >99% regioselectivity, which could be potentially migrated to the synthesis of PUs.

Conclusions

In summary, we reported a highly efficient and regioselective synthesis of sulfur-containing *N*-alkyl carbamate that was originated from propargyl alcohol, CO₂ and amine. Ring-opening addition of DPMOD with various amines were carried out using the organocatalysts, afforded tertiary β -hydroxyl *N*-alkyl carbamates (**A**) with DPMOD conversion of up to 100% and regioselectivity of 100%. TBD was shown to be a very active organocatalyst for the regioselective formation of β -hydroxyl *N*-alkyl carbamate. Due to abundant mercapto compounds and amines, considerable amounts of sulfur-containing *N*-alkyl carbamates could be synthesized by this method, greatly broadening their practical applications. Of importance, propargyl alcohol and CO₂ were used as the basic substrates during the synthetic process, which is petroleum-independent, eco-friendly and sustainable. Such regioselective product, β -hydroxyl *N*-alkyl carbamate could be used as a platform compound for potential synthesis.

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Supporting Information

Supporting information for this article is available on the WWW under www.genchemistry.org/EN/10.21127/yaoyigc20180007.

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