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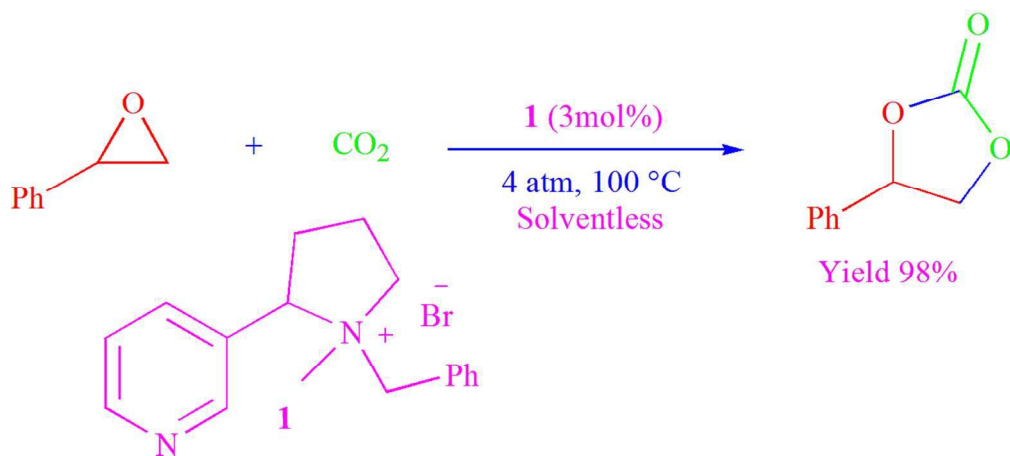


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ARTICLE

Nicotine-derived ammonium salts as highly efficient catalysts for chemical fixation of carbon dioxide into cyclic carbonates under solvent-free conditions

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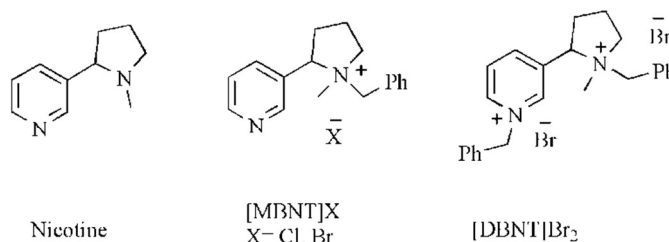
A series of easily prepared nicotine-derived ammonium salts were applied for the first time as recyclable and efficient catalysts for the coupling of carbon dioxide and epoxides to form cyclic carbonates at low pressure without using additional organic solvents and co-catalysts. Remarkably, excellent yields and selectivity were achieved when 1-Benzyl-1-methyl-2-pyridin-3-yl-pyrrolidinium bromide [MBNT]Br was used as the catalyst. Furthermore, the catalyst can be easily recovered and reused without a significant loss of activity. The influences of the catalyst structure and various reaction parameters on the catalytic activity were also investigated in detail.

Introduction

Carbon dioxide is an attractive C₁ feedstock gas in organic synthesis as it is extremely practical, inexpensive, abundant, non-toxic, and non-flammable. As petroleum treasuries are exhausted, the development of efficient catalytic systems for CO₂ fixation is consequently a significant and challenging theme.¹⁻³ In this regard, the synthesis of cyclic carbonates from epoxides and CO₂ has attracted widespread attention owing to the 100% atom efficiency of the reaction and the wide range of applications of cyclic carbonates such as polar aprotic solvents in organic and polymeric synthesis, electrolyte components for lithium batteries and intermediates in the syntheses of pharmaceuticals.⁴⁻⁶

In the past decades, a wide variety of homogeneous and heterogeneous catalysts have been developed for this reaction, such as alkali metal salts,^{7,8} metal oxides,⁹ Cs-loaded zeolite and alumina,¹⁰ transition metal salen complexes,¹¹ zeolite,¹² quaternary ammonium and phosphonium salts,¹³⁻¹⁸ and various ionic liquids (ILs).¹⁹⁻²³ However, most of these catalysts suffer one or more of the following drawbacks: low catalyst activity, the need of higher CO₂ pressure and/ or longer reaction time, the presence of expensive transition metal additives, and water or air sensitivity. Hence, the design of easily prepared, metal-free catalysts with enhanced catalytic activity for the conversion of CO₂ to cyclic carbonate still remains a challenge. In this study, a series of ammonium salts derived from nicotine (scheme 1) are considered for the first time as catalysts towards the cycloaddition reaction of carbon dioxide with epoxide. These salts have advantages such as the facile preparation of various structures^{24,25} from nicotine and benzyl or alkyl halides, gratifyingly thermal behaviour, air/water stability. More

importantly, Suzuki et al.²⁶ reported the solubility of nicotine in carbon dioxide and also the presence of the tertiary nitrogen in the cation has the potential to react with CO₂ to form the carbamate species, assumed to be an activated form of CO₂.²⁷ Indeed, the ammonium salt [MBNT]Br displayed high catalytic activity for conversion of CO₂ and epoxide to cyclic carbonate and respectable yield together with excellent selectivity obtained without utilization any organic solvents or additives.



Scheme 1. Nicotine and ammonium salts based on nicotine used in this study

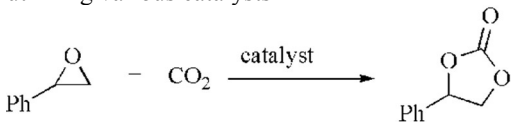
Results and Discussion

At the initial study, a series of ammonium salts based on nicotine have been applied to catalyse the cycloaddition reaction of styrene oxide (SO) and CO₂. The results are summarized in Table 1. It can be seen that nicotine which contains basic active sites afforded styrene carbonate (SC) in 40% yield (Table 1, entry 1), while after the quaternization, monobenzylnicotinium salts showed higher catalytic activities (table 1, entries 2, 3), indicating that without any anions the presence of only nicotine could not afford highly active centers

for this reaction. Hence, the effects of halogen anions such as Cl⁻ and Br⁻ on the catalytic activity were examined, and it was found that [MBNT]Br showed much higher activity than [MBNT]Cl (entry 3 vs 2) probably being ascribed to the nucleophilicity and leaving ability of the anion in the corresponding ammonium salt.²⁸⁻³⁰

To obtain more information for the effects of tertiary amine group in the cation part on the reaction, dibenzylnicotinium bromide [DBNT]Br which has no basic active sites was investigated. [DBNT]Br was found to be inactive probably due to loss of basic active sites and consequently loss of its CO₂ activation effect²⁷ (Table 1, entries 4). This result indicated that the effect of tertiary amine group was a significant factor in promoting the reaction. Therefore, [MBNT]Br was selected as the benchmark structure for further studies on the reaction parameters.

Table 1. Reaction of styrene oxide with CO₂ utilizing various catalysts^a



Entry	Catalyst	Catalyst (mol%)	Yield (%) ^b	Selectivity ^b (%)
1	Nicotine	3	40	81
2	[MBNT]Cl	3	86	93
3	[MBNT]Br	3	98	99
4	[DBNT] Br	3	2	3
5	[MBNT] Br	5	98	99
6	[MBNT]Br	2	81	91

^a Reaction conditions: SO (10 mmol), CO₂ (5 atm), 24 h, 120°C, solventless

^b Determined by GC using an internal standard technique.

Subsequently, the effects of the catalyst loading on the SC synthesis were investigated. It can be observed that the SC yield decreased from 98% to around 81% with catalyst loading decreasing from 3 to 2 mol% (Table 1, entry 6), while the SC yield remained almost constant when the catalyst loading was increased to 5 mol% (Table 1, entry 5). As a consequence, 3 mol% was chosen as the most suitable catalyst loading.

As shown in Fig. 1, the temperature had a pronounced positive influence on the cycloaddition reaction when it varied from 80 to 100°C. The SC yield was increased from about 71% to above 98% correspondingly, whereas it remained almost unchanged in the temperature range from 100 to 120°C. Conclusively, 100°C could be the optimal temperature for SC synthesis.

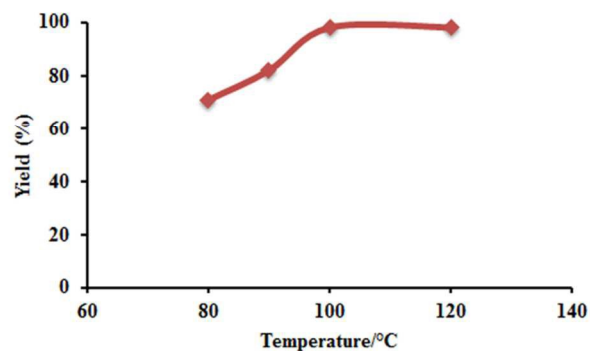


Fig. 1. Influence of temperature on SC yield Reaction conditions: SO (10 mmol), [MBNT]Br (3 mol%), CO₂ (5 atm), 24 h.

Commonly, a significant issue connected with utilizing CO₂ as a reaction medium is the potential hazards of working at high pressure. Fig. 2 shows the effect of CO₂ pressure on the yield of SC for the [MBNT]Br catalyst at 100°C for 24 h. As easily seen, the SC yield significantly increased from 79% to 98% when the initial CO₂ pressure increased from 1 to 4 atm. Such a positive effect of CO₂ pressure on the synthesis of cyclic carbonates from CO₂ and epoxides has been reported in earlier studies.³¹⁻³³ However, a further increase in pressure did not yield more reaction products. Therefore, 4 atm was considered as the optimal pressure for the reaction.

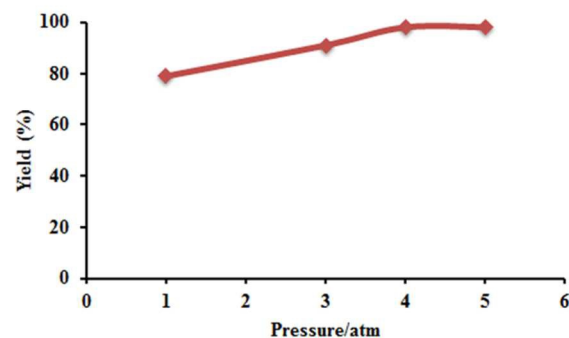


Fig. 2. Influence of the CO₂ pressure on the yield of SC. SO (10 mmol), cat. amount (3 mol%), 100°C, 24 h.

The dependence of SC yield on reaction time was also evaluated. It was observed that reaction time had a remarkable effect on the reaction. As shown in Fig. 3, the reaction proceeded rapidly within the first 4 h, and almost quantitative yield (98%) could be achieved, while the reaction rate remained almost invariant after 4 h. Therefore, a reaction time of 4 h was appropriate for the synthesis of cyclic carbonate in this study.

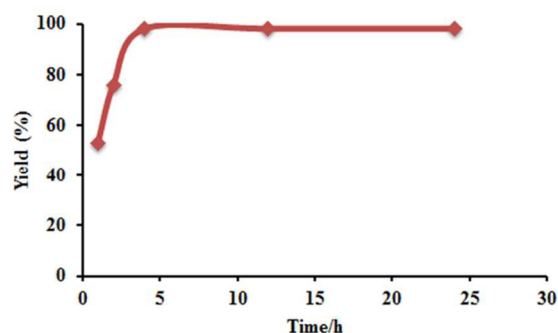


Fig. 3. Influence of the reaction time on the yield of SC for [MBNT]Br (3 mol%), at 100°C and CO₂ pressure of 4 atm.

Experiments were performed to test the reusability of the [MBNT]Br catalyst under the optimum conditions. The catalyst was recovered after separation of product from the reaction mixture by distillation under reduced pressure and then used for the next run under the identical conditions.^{27i,34} As shown in Fig. 4, there was no significant drop in SC yield after four runs, which indicated a high stability and reusability of the catalyst.

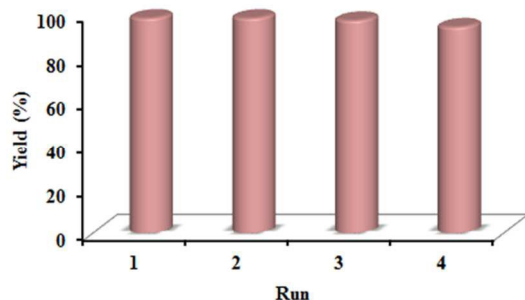
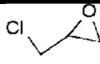
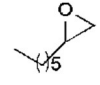
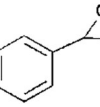
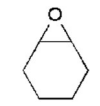
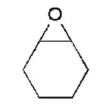
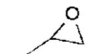


Fig. 4. The reusability results of the [MBNT]Br catalyst Reaction condition: SO (10 mmol), catalyst (3 mol%), 100°C, 4 h, CO₂ (4 atm).

Under the optimal reaction conditions, a series of epoxides were explored for the cyclic carbonates synthesis in the presence of [MBNT]Br. and the results are depicted in Table 2. The catalyst was found to be applicable to various terminal epoxides to provide the corresponding cyclic carbonates in high yields with excellent selectivity (up to 98%), while internal cyclohexene oxide exhibits the lowest activity (Table 2, entry 4) even at elevated pressure and prolonged reaction time (Table 2, entry 5) probably due to steric hindrance as also illustrated by other authors.³⁵⁻³⁷

Table 2. Coupling of CO₂ with various epoxides catalyzed by [MBNT]Br^a

Entry	Epoxide	Yield (%) ^b	Selectivity (%)
1		96	98
2		93	97
3		98	99
4		12	71
5 ^c		17	79
6		95	99

^aReaction conditions: SO (10 mmol), catalyst (3 mol%), 100°C, CO₂ (4 atm) 4 h, solventless.

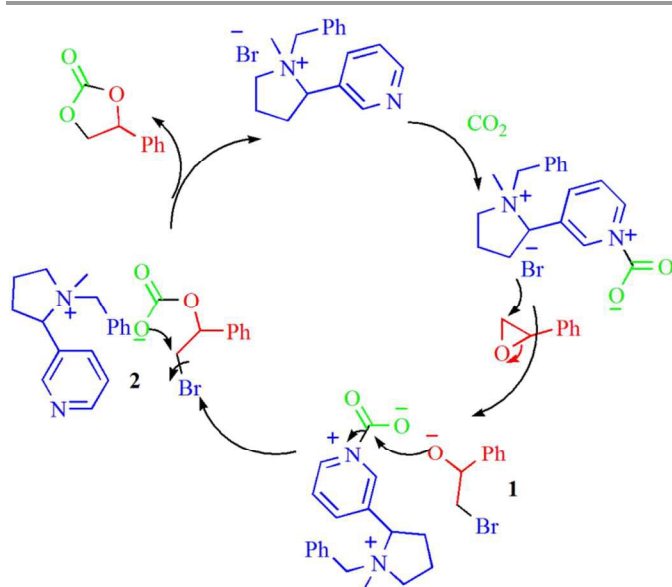
^b Isolated Yield

^c Reaction conditions: SO (10 mmol), catalyst (3 mol%), 100°C, CO₂ (5 atm) 24 h, solventless.

Based on previous reports³⁸⁻⁴⁰ and the obtained results, We proposed a plausible mechanism for the coupling of epoxides with CO₂ using the [MBNT](Br) as a catalyst, as shown in Scheme 3. Firstly, the tertiary nitrogen atom coordinates reversibly with CO₂ to afford the carbamate salt,^{41, 42} which could be an activated form of CO₂. In parallel, the nucleophilic attack of bromide anion on the less sterically hindered carbon atom of the epoxide produces the ring-opened intermediate **1**. Then, nucleophilic attack of the intermediate **1** on the carbamate salt furnishes the alkyl carbonate anion **2**. Finally, subsequent intramolecular ring-closure would form the cyclic carbonate and regenerate the [MBNT](Br) catalyst.

Conclusions

ammonium salts based on nicotine proved to be highly efficient and recyclable catalysts for the synthesis of cyclic carbonates from epoxides and CO₂ without utilizing any co-catalyst and co-solvent. It was found that monobenzylnicotinium salts showed much better catalytic performance, which could activate CO₂ through the tertiary nitrogen in the cation part. In addition, the catalyst can be recovered and reused four times without any significant loss of its initial activity.



Scheme 2 The proposed mechanism for coupling reaction catalyzed by [MBNT]Br.

Experimental

General

Commercial reagents were purchased from Merck Company and used without further purification. CO₂ of a purity of 99.99% was commercially available. ¹H NMR spectra were recorded on a Bruker 250 and 400 spectrometers using TMS as an internal standard in CDCl₃ or DMSO. Elemental analyses were performed by using a Leco, CHNS-932 elemental analyzer. Mass spectra were recorded on a Shimadzu QP 1100 BX Mass Spectrometer and FT-IR spectra were obtained as KBr pellets on a JASCO 680-Plus spectrophotometer. Melting points were measured with a Gallenkamp melting apparatus. Thermal analysis comprising TG and DSC for samples were obtained using STA system, model 409 PC Luxx under a flow of nitrogen at a rate of heating of 10°C min⁻¹ up to 600°C. Gas chromatography (GC) (BEIFIN 3420 gas chromatograph equipped with a flame ionization detector and a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 mm) were used for consideration of reactions conversions and yields.

Catalysts Preparation and Characterization

[MBNT](Br): 5 mmol of benzyl bromide was added to a solution of (±)-nicotine (5 mmol) in MeCN (5 mL). the reaction mixture was heated at 70°C for 12 h under reflux. The precipitate was filtered off, washed with ether and dried. [MBNT](Br) was obtained in quantitative yield. [MBNT](Cl) was also synthesized using benzyl chloride by a similar procedure. [MBNT](Br): Mp: 220-222°C ¹HNMR(400MHz, CDCl₃) δ 9.34 (d, J=6 Hz, 1H), 9.28 (s, 1H), 8.2 (d, J=7.6Hz, 1H), 7.4-7.47 (m, 1H), 6.97-7.07 (m, 5H), 5.92 (s, 2H), 4.69 (t, J=12Hz, 1H), 3.01 (s, 3H), 2.05-2.14 (m, 2H), 1.85-1.88 (m, 2H), 1.45-1.65(m, 1H) ppm. ¹³CNMR (100 MHz, CDCl₃) δ 143.83, 143.67, 143.39, 132.47, 129.52, 129.28, 129.22, 129.18, 66.53, 63.74, 56.22, 40.12, 35.61, 26.23 ppm. Anal.

Calcd for C₁₇H₂₁BrN₂; C, 61.27; H, 6.33; N, 8.41. Found (%): C, 61.39; H, 6.67; N, 8.23.

[DBNT](Br₂): Amounts of 5 mmol of (±)-nicotine with an excess of benzyl bromide were mixed under solvent-free conditions and the reaction mixture was heated at 70°C for 12 h, and the precipitate was filtered off, washed with ether and dried. Mp: 211-213°C ¹HNMR(400MHz, DMSO) δ 9.60 (s, 1H), 9.38 (d, J = 6 Hz, 1H), 9.03 (d, J = 8 Hz, 1H), 8.43 (dd, J₁=8 Hz, J₂ = 6 Hz, 1H), 7.47-7.63 (m, 10H), 5.96 (s, 2H), 5.35 (t, J=10.8 Hz, 1H), 4.69 (d, J = 12 Hz, 1H), 4.35 (d, J = 12 Hz, 1H), 3.36 (s, 3H), 2.50-2.74 (m, 2H), 2.15-2.30 (m, 2H), 1.27-1.32 (m, 2H) ppm. ¹³CNMR (100 MHz, DMSO) δ 148.20, 147.56, 146.15, 133.82, 132.91, 132.47, 130.30, 129.48, 129.22, 128.96, 128.37, 74.57, 65.16, 63.77, 62.94, 41.23, 25.58, 18.69 ppm. Anal. Calcd for C₂₄H₂₈Br₂N₂; C, 57.16; H, 5.6; N, 5.55. Found (%): C, 57.10; H, 5.35; N, 5.63.

General procedure for the cycloaddition reaction

All the cycloadditions were conducted in a 100 mL stainless-steel reactor equipped with a magnetic stirrer under a CO₂ atmosphere and the reactor was put into a bath of 100°C and then pressurized to the appropriate pressure with CO₂. In the typical procedure, [MBNT]Br (3 mol%), 1,2-dichlorobenzene (internal standard of GC) and 10 mmol of styrene oxide (SO) were added into the reactor. Then, the atmosphere inside the reactor was replaced with CO₂ and the pressure was adjusted to 4 atm at 100°C and the stirrer was started. After 4 h, the reactor was cooled to room temperature, and the excess of CO₂ was gradually released, and the mixture was evaporated in vacuum. The residuals were purified by silica gel column chromatography (eluent: ethyl acetate) to give the corresponding cyclic carbonate. The cycloaddition products are known compounds and were characterized by comparing their IR, ESI-mass, ¹H and ¹³C NMR spectra with those found in the literature.⁴³⁻⁴⁵

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Graphical abstract

Ammonium salts based on nicotine proved to be highly efficient and recyclable catalysts for the synthesis of cyclic carbonates from epoxides and CO₂ without the utilization of any organic solvent and any additives.

