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Highly efficient chemical fixations of carbon dioxide and carbon disulfide by cycloaddition to aziridine under atmospheric pressure

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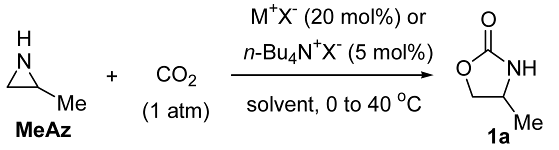
Abstract—Cycloaddition of aziridine with carbon dioxide was successfully catalyzed by alkali metal halide or tetraalkylammonium halide to give the corresponding 5-membered cyclic urethane, 1,3-oxazolidin-2-one, selectively. The reaction can be performed at ambient temperature under atmospheric pressure. Analoguous reaction of aziridine with carbon disulfide also successfully gave the corresponding 5-membered cyclic dithiourethane, 1,3-thioxazolidine-2-thione.

Development of highly efficient methods for chemical fixation of CO_2 and its efficient utilization as a C1 building block is one of the most urgent subjects to solve the recent problems of earth pollution and depletion of fossil fuels. In order to minimize the energy consumption for utilization of CO_2 as a chemical resource, the ideal systems will be operated at ambient temperature under atmospheric pressure. Among the various approaches studied so far,[1–4] the reaction of CO_2 with epoxide has emerged as an efficient one.[5–10]

Aziridine, a nitrogen analogue of epoxide, has also high ring strain, and is a hopeful candidate as a highly reactive compound that can react with relatively inert CO_2 without its intensive activation. On the analogy from the cycloaddition reaction of CO_2 with epoxides that gives cyclic carbonates, the reaction of aziridine with CO_2 would lead to formation of the corresponding 5-membered cyclic urethane, 1,3-oxazolidin-2-one. Several reports on this reaction have been reported,[11–15] however, they suffer from requirements of high pressure, high temperature, employment of toxic compound as a catalyst, and contamination by the corresponding polyurethane.

In this paper, we report the first selective synthesis of 2-oxazolidinone by cycloaddition of CO_2 with aziridine at ambient temperature under atmospheric pressure. As the catalysts, alkali metal halides or tetraalkyl ammonium salts were employed, which have been found to be highly effective catalysts for cycloaddition of atmospheric CO_2 with epoxide by our previous studies.[10] A similar cycloaddition of CS_2, which is a sulfur analogue of CO_2, is also reported herein.

The reaction of commercially available 2-methylaziridine (MeAz) with CO_2 was performed in the presence of alkali metal halide as a catalyst (Scheme 1). CO_2 was supplied to the reaction vessel from the equipped balloon without pressuring. At first, lithium bromide, which is one of the most effective catalysts for the cycloaddition of CO_2 with epoxide, was employed as a catalyst (Table 1, run 3). After the reaction for 24 h, we found that 4-methyl-1,3-oxazolidin-2-one (**1a**)



Scheme 1.

Keywords: aziridine; cycloaddition; carbon dioxide; atmospheric pressure; carbon disulfide.

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Table 1. Cycloaddition of CO_2 with 2-methylaziridine (MeAz) catalyzed by alkali metal halide (M^+X^-) in THF[a]

Run	Catalyst	Yield (%)[b]
1	None	0
2	LiCl	Trace
3	LiBr	74
4	LiI	32
5	NaBr	37
6[c]	NaBr	76
7[c]	KBr	62

[a] Conditions: $[MeAz]_0=0.875$ M, $[MeAz]_0/[M^+X^-]=5.0$, at room temperature, for 24 h.

[b] Isolated by bulb-to-bulb distillation.

[c] The reaction was carried out in the presence of 5 mol% 18-crown-6.

was given as a sole product. The corresponding regioisomer, 5-methyl-1,3-oxazolidin-2-one, was not detected at all by GC or by 300 MHz ^1H NMR analysis of the crude mixture. Thus, bulb-to-bulb distillation of the mixture gave pure **1a** in 74% yield. Other alkali metal halides also catalyzed the reaction. A series of reactions using lithium salts showed the superiority of bromide as a counter anion (runs 2–4). Sodium bromide and potassium bromide were also effective catalysts when they were solvated in THF by addition of 18-crown-6. It is noteworthy that the reaction smoothly proceeds at room temperature under atmospheric pressure, while the analogous reaction of epoxide requires elevation of temperature to 100°C to achieve sufficient reaction rate.[10]

Quaternary ammonium salt was also an effective catalyst for the reaction (Table 2). Tetrabutylammonium bromide (TBAB) most efficiently catalyzed the reaction to obtain **1a** in excellent yield (run 2). The catalyst efficiency largely depended on the counter anion (runs 1, 2 and 7), and its order was Br>I>Cl, which is same as found in the aforementioned lithium halide-catalyzed reaction. In addition, as can be seen from the results of runs 2–6, THF and room temperature were the best choice for the optimum conditions.

2-Phenylaziridine (**PhAz**) also can be used as a substrate for the present reaction system (Scheme 2). In this case, the reaction did not proceed at room temperature. Thus we used *N*-methylpyrrolidone (NMP) as a less volatile solvent and carried out the reaction at 100°C. Under the conditions, lithium bromide efficiently catalyzed the reaction to give 4-phenyloxazolidin-2-one (**1b**) in 70% yield as a sole product.

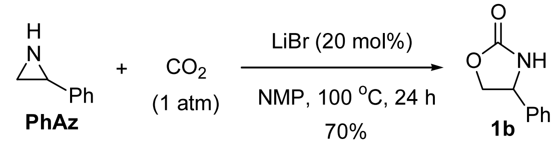
Encouraged by the successful results of CO_2-fixation using the aziridines as a substrate, we next targeted an analogous CS_2-fixation (Scheme 3). CS_2 is a sulfur analogue of CO_2, and is also an attractive C_1 building block to synthesize sulfur-containing functional molecules. We have already reported the cycloaddition of CS_2 with epoxide catalyzed by alkali metal halide.[16] The corresponding product is 5-membered cyclic dithiocarbonate, which can be applied as a versatile monomer to syntheses of various sulfur-containing polymers.[17,18]

Table 2. Cycloaddition of CO_2 with 2-methylaziridine (MeAz) catalyzed by tetrabutylammonium halide (n-$Bu_4N^+X^-$)[a]

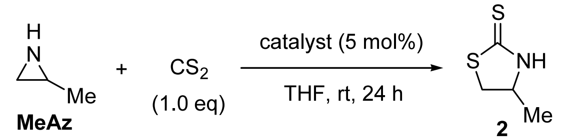
Run	X	Solvent	Temperature	Yield (%)[b]
1	Cl	THF	rt	22
2	Br	THF	rt	95
3	Br	CH_3CN	rt	72
4	Br	MeOH	rt	10
5	Br	THF	0°C	52
6	Br	THF	40°C	67
7	I	THF	rt	63

[a] Conditions: $[MeAz]_0=0.875$ M, $[MeAz]_0/[n\text{-}Bu_4N^+X^-]=20$, for 24 h.

[b] Isolated by bulb-to-bulb distillation.



Scheme 2.



Scheme 3.

There have been a few examples of the reaction of CS_2 with aziridine to obtain the corresponding 5-membered cyclic dithiourethane, 1,3-thioxazolidine-2-thione, however these suffer from requirement of using excess amount of CS_2 and of high operation temperature.[14,19–21] Since the product is hopeful as a precursor for bioactive compounds and chiral auxiliaries, development of highly efficient catalytic system still remains a significant challenge.

Table 3 shows the conditions employed for the equimolar reaction of CS_2 with MeAZ and the corresponding results. All alkali metal halides used and TBAB cata-

Table 3. Cycloaddition of CS_2 with 2-methylaziridine (MeAz) in THF[a]

Run	Catalyst	Yield (%)[b]
1	None	0
2	LiCl	76
3	LiBr	92
4	LiI	65
5	NaBr	91
6	NaI	73
7	KBr	82
8	TBAB	94

[a] Conditions: $[MeAz]_0=0.875$ M, $[MeAz]_0/[catalyst]=20$, at room temperature, for 24 h.

[b] Determined by GC.

lyzed the reaction at room temperature to give the corresponding 5-membered cyclic dithiourethane, 4-methyl-1,3-thiazolidine-2-thione (**2**). No regioisomer was detected by GC or by 300 MHz ^{1}H NMR analysis of the crude mixture. Similarly to the CO_2-fixation, bromide was found to be a suitable anionic component of catalysts for the present reaction. The reaction was found to be much faster than the CO_2-fixation. Actually, it does not take 24 h for complete conversion of MeAz at room temperature when lithium bromide was used as a catalyst: We found that it was completely converted to **2** by GC analysis of the reaction mixture at 30 min. Furthermore, the reaction proceeded smoothly even at −40°C to give **2** quantitatively within 30 min. Further study on kinetics of the reaction is needed.

In summary, cycloadditions of CO_2 and its sulfur analogue, CS_2, with aziridine were found to be hopeful candidates as methods for their chemical fixation. The fixations can be operated under atmospheric pressure at room temperature by employing alkali metal halide or quaternary ammonium salt as a catalyst, which are stable and easily handled. The present systems will be further improved to be ideally environmentally friendly ones by more detailed studies on reaction mechanism and further optimization of the conditions. Similar reactions of aziridines having various substituents are under investigation to clarify the scope and limitation of the present system.

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