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Diethylammonium iodide as catalyst for the metal-free synthesis of 5-aryl-2-oxazolidinones from aziridines and carbon dioxide†

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The catalytic potential of ammonium halide salts was explored in the coupling reaction of a model aziridine with carbon dioxide, highlighting the superior activity of $[NH_2Et_2]I$. Then, working at room temperature, atmospheric CO_2 pressure and in the absence of solvent, the $[NH_2Et_2]I$-catalyzed synthesis of a series of 5-aryl-2-oxazolidinones was accomplished in good to high yields and excellent selectivity, from 2-aryl-aziridines with *N*-methyl or *N*-ethyl groups. NMR studies and DFT calculations outlined the pivotal role of both the diethylammonium cation and the iodide anion. The proposed method represents a convenient choice for obtaining a limited number of valuable molecules for which more complex and more expensive catalytic systems have been reported even in recent years.

Introduction

The employment of carbon dioxide as a sustainable, non-toxic and largely available C_1 synthon for organic synthesis, replacing hazardous compounds, has witnessed an increasing advance in recent years.[1] In this setting, oxazolidinones are five-membered heterocyclic compounds that are key precursors for the manufacture of bioactive chemicals,[2,3] and synthetic processes exploiting CO_2 fixation routes have been intensively investigated.[2a,4] In general, the available methods require the use of a catalyst, unless high pressure of CO_2 or supercritical conditions are employed.[5] A variety of suitable unsaturated organic substrates (*e.g.* amines and amino-alcohols[6,7]) and also appropriate combinations of reactants have been evaluated for their coupling with carbon dioxide, such as epoxide/amine,[8] alkyne/amine,[9] aniline/1,2-dibromoethane,[10] alkene/amine[11] and amine/(2-bromo-1-aryl)dimethylsulfonium salts.[12] The use of aziridines for their direct coupling with CO_2 is appealing from the point of view of the atom economy,[13] but is featured by a high activation barrier;[14] therefore, pressurized conditions are often required and a catalyst is strictly necessary, either metal based[15,16] or not.[17,18]

In fact, the catalyst-free synthesis of 5-aryl-2-oxazolidinones from aziridines has been forced at temperatures above 100 °C and at 3.5–10.0 MPa CO_2 pressure, affording products in 30–90% yields;[19] in the absence of a catalyst, drastic conditions are avoided only using a special apparatus (high-speed ball milling).[20]

Most of the metal-catalysed reactions, and even some organocatalytic systems,[18,21] require a Lewis base additive to facilitate the aziridine ring opening, and tetrabutylammonium halides have been widely employed in this regard.[16] The direct catalytic effect of simple halide salts has been sparingly investigated, and in some cases (tetraalkyl)ammonium halides alone have revealed some potential to promote the aziridine/CO_2 coupling. Working at ambient conditions, 2-methyl-aziridine was converted to 4-methyl-1,3-oxazolidin-2-one in organic solvent by means of $[NBu_4]X$ (X = Cl, Br, I), Scheme 1A, and $[NBu_4]Br$ in THF solution revealed to be the best choice (95% yield). The alternative use of lithium/sodium halides needed a considerably higher amount of salt (20% mol) to provide satisfying yields, which are increased upon addition of 18-crown-6.[22] Similarly, the carboxylation of a small series of aziridines by lithium iodide, in THF solution at room temperature and normal CO_2 pressure, required a stoichiometric amount of salt (1.5 equivalents *vs.* aziridine), Scheme 1B; the addition of hexamethylphosphoramide (HMPA) as a co-solvent improved the regioselectivity of the reaction.[23] On the other hand, relatively low amounts of LiBr efficiently operate under drastic conditions.[24–26]

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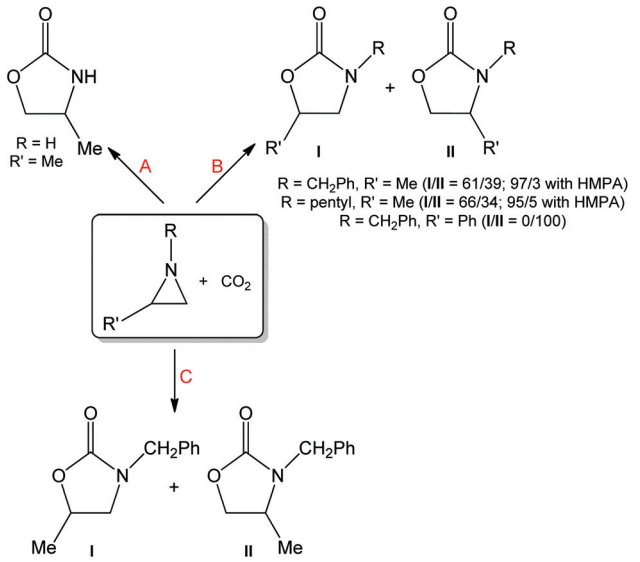
†Electronic supplementary information (ESI) available: NMR studies, DFT optimized structures, NMR spectra. Cartesian coordinates of the DFT-optimized structures are collected in a separated .xyz file. See DOI: 10.1039/d1ob00458a



Scheme 1 Overview of previously investigated aziridine/CO_2 coupling reactions promoted by (alkyl)ammonium halides and alkali metal halides in mild conditions. (A) Catalyst (equivalents *vs.* aziridine, yield): $[NBu_4]Cl$ (0.02, 22%), $[NBu_4]Br$ (0.02, 10–95%), $[NBu_4]I$ (0.02, 63%), LiCl (0.20, traces), LiBr (0.20, 74%), LiI (0.20, 32%), NaBr (0.20, 37%), NaBr (0.20 + 0.05 18-crown-6, 76%), KBr (0.20 + 0.05 18-crown-6, 62%); solvent: THF, MeCN or MeOH; pCO_2 = 1 atm; *T* = 0–40 °C; reaction time = 24 h.[22] (B) Catalyst (equivalents *vs.* aziridine, yield): LiI (1.5, 83–99%), LiI (1.0 + 1.0 HMPA, 88–91%); solvent: THF; pCO_2 = 1 atm; *T* = room temperature; reaction time = 4 h.[23] (C) Catalyst (equivalents *vs.* aziridine, yield): $[NH_4]Cl$ (1.0, 0%), $[NH_4]Br$ (1.0, 0%), $[NH_4]I$ (1.0, 94%), LiCl (1.0, 33%), LiBr (1.0, 76%), LiI (1.0, 85%), NaCl (1.0, 0%), NaBr (1.0, 27%), NaI (1.0, 83%); solvent: THF; pCO_2 = 3 atm; *T* = room temperature; reaction time = 4 h; the use of $[NH_4]I$ (5 mol%) at pCO_2 = 4 atm provided 98% yield of product after 2 h; I/II ratio variable between 66/34 and 99/1.[27]

A range of halide salts was explored for carrying out the carboxylation of *N*-benzyl-2-methylaziridine in THF at room temperature and 4 atm of CO_2 pressure (Scheme 1C).[27] Two regioisomers were generally obtained, and ammonium iodide performed better than lithium and sodium salts under stoichiometric conditions. Ammonium iodide was efficient also in a catalytic amount, and its favourable action was attributed to the preliminary formation of an aziridinium cation.

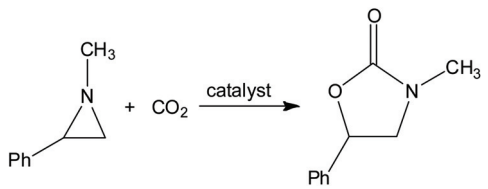
This scenario prompted us to systematically investigate the catalytic potential of alkylammonium halides in the synthesis of oxazolidinones from aziridines *via* CO_2 fixation, with a particular focus on partially alkylated ammonium species, which, to the best of our knowledge, have never been evaluated heretofore. No solvent, room temperature and atmospheric pressure of carbon dioxide were adopted as fixed experimental conditions, due to sustainability issues. Note that working under 1 atm CO_2 pressure is an added value also for safety reasons, allowing to conduct the synthesis using common laboratory glassware and a simple, safe and cheap balloon technique, without the needing of any pressurized equipment.

The results of this work will be presented, including DFT calculations giving insight into the higher performance provided by the use of a dialkylammonium halide as catalyst.

Results and discussion

We studied the coupling between 1-methyl-2-phenylaziridine and carbon dioxide as a model reaction, and several ammonium salts were evaluated as possible catalysts by ^1H NMR spectroscopy. The results of this study are compiled in Table 1. The reaction was conducted in the absence of solvent at ambient temperature and atmospheric pressure of CO_2 from a balloon. Fixing the catalyst concentration to 2 mol%, 3-methyl-5-phenyloxazolidin-2-one was produced in variable yields after 24 hours. Tetramethylammonium iodide and tetrahexylammonium bromide revealed totally inactive, while other tetraalkylammonium iodides and $[NBu_4]Br$ led to the formation of the desired product in 15–29% yields. This fact suggests that a balance between steric and electronic factors related to the nitrogen substituents is crucial to provide activity. Moreover, iodide salts manifested higher efficiency than the homologous chlorides and bromides (compare runs 3–5 and 12–14). Overall, ammonium iodides performed as the best catalysts of the series with $[NH_2Et_2]I$ leading to the highest yield of product (78%, run 14).

Table 1 Synthesis of 3-methyl-5-phenyloxazolidin-2-one from 1-methyl-2-phenylaziridine and carbon dioxide



Run	Aziridine (mg, mmol)	Catalyst	Catalyst, mol% (mg)	*t* (° C)	Yield[a] (%)
1	(133, 1.00)	$[NMe_4]I$	2 (4.0)	21	0
2	(135, 1.01)	$[NEt_4]I$	2 (5.2)	21	15
3	(130, 0.98)	$[NBu_4]Cl$	2 (5.4)	21	5
4	(133, 1.00)	$[NBu_4]Br$	2 (6.4)	21	20
5	(136, 1.02)	$[NBu_4]I$	1 (3.8)	21	30
6	(130, 0.98)	$[NBu_4]I$	2 (7.2)	21	29
7	(133, 1.00)	$[NBu_4]I$	5 (15)	21	65
8	(135, 1.01)	$[NHex_4]Br$	2 (8.8)	21	Traces
9	(136, 1.02)	$[NMe_3Bn]I$	2 (5.6)	21	26
10	(133, 1.00)	$[NHEt_3]I$	2 (4.6)	21	74
11	(136, 1.02)	$[NH_2Me_2]I$	2 (3.5)	21	70
12	(133, 1.00)	$[NH_2Et_2]Cl$	2 (2.2)	21	0
13	(130, 0.98)	$[NH_2Et_2]Br$	2 (3.0)	21	25
14	(130, 0.98)	$[NH_2Et_2]I$	2 (3.9)	21	78
15	(135, 1.01)	$[NH_2Et_2]I$	1 (2.0)	21	66
16	(133, 1.00)	$[NH_2Et_2]I$	5 (10)	21	82
17	(133, 1.00)	$[NH_2Et_2]I$	5 (10)	0	50
18	(130, 0.98)	$[NH_2Et_2]I$	5 (9.8)	35	53
19	(136, 1.02)	$[NH_2Et_2]I$	10 (20)	21	75
20	(133, 1.00)	$[NH_2{}^iPr_2]I$	2 (4.6)	21	72
21	(136, 1.02)	$[NH_3Me]I$	2 (3.2)	21	58
22	(130, 0.98)	$[NH_3Et]I$	2 (3.4)	21	67
23	(136, 1.02)	$[NH_3Cy]I$	2 (4.6)	21	68
24	(136, 1.02)	$[NH_4]I$	2 (2.9)	21	73

Experimental conditions: no solvent; pCO_2 = 1 atm; *t* = 24 hours
[a] Calculated as integral ratio between the ^1H NMR signals of ring CH (product) and 1,1,2,2-tetrachloroethane as standard

Different concentrations of diethylammonium iodide and tetrabutylammonium iodide were then tested: the best result was obtained by using $[NH_2Et_2]I$ in a concentration of 5 mol% (yield = 82%, run 16). An appreciable influence of the temperature was observed, and working at room temperature (*ca.* 21 °C) resulted to be the most favourable choice, presumably representing a compromise between slow kinetics (low temperature) and side reactions (high temperature).

Using the optimal reaction parameters found for the model reaction, we extended the catalytic study to the carboxylation of a series of 2-arylaziridines (Table 2). In general, variable yields were recognized, mainly depending on the nature of the nitrogen substituent. More precisely, the carboxylation of 1-*H*-2-arylaziridines did not work or provided low yields of the corresponding cyclic products after 24 hours (runs 1–4). This result is probably ascribable to the prevalent occurrence of side aziridine polymerization.[28] On the other hand, the reactions involving 1-methyl-2-arylaziridines led to the formation of the oxazolidinones in 76–85% yields, including the first synthesis of 3-methyl-5-(4-fluorophenyl)oxazolidin-2-one *via* the aziridine/CO_2 route (runs 5–8). The Me/Et replacement at nitrogen leads to a lower conversion, and the products were detected in 28–66% yields, including the unprecedented 3-ethyl-5-(4-fluorophenyl)oxazolidin-2-one (runs 9–12). ^{1}H NMR analyses outlined the formation of aziridine oligomerization species and piperazines as by-products, consistently to previous findings.[29]

On further increasing the steric hindrance of the aziridine *N*-substituent (isopropyl, *n*-butyl, cyclohexyl, tosyl), no reaction took place. Moreover, the results shown in Table 2 evidence some role of the aryl *para*-substituent, although a clear correlation between its electronic and steric properties and the yield values seems hard to be rationalized.

The synthesis, from the respective aziridine, of the products indicated in Table 2 is not a trivial task, since more expensive/elaborated catalytic systems and eventually drastic experimental conditions have been reported, even recently, for the same reactions. Note that ammonium halides are often employed as co-catalysts, in a range of concentrations comparable to that adopted here for $[NH_2Et_2]I$.

In order to figure out possible differences in the mechanism of action of different catalysts, the interaction between equimolar amounts of 1-methyl-2-phenylaziridine and two selected ammonium iodides was NMR investigated. Thus, solutions of the aziridine in CD_3CN were treated with $[NBu_4]I$ and $[NH_2Et_2]I$, respectively. The addition of $[NBu_4]I$ did not determine any appreciable change in the ^{1}H NMR resonances of the two mixed species over 4 days (Fig. S1†). Then, the expected formation of 3-methyl-5-phenyloxazolidin-2-one was cleanly observed upon bubbling CO_2 to the solution (no additional information was achieved by carrying out the reaction directly under CO_2 atmosphere). Conversely, mixing diethylammonium iodide and 1-methyl-2-phenylaziridine resulted in a downfield shift (from 3.15 to 2.98 ppm) and an increase of the intensity of the signal due to the ammonium protons (Fig. S2†). This variation is ascribable to the occur-

Table 2 Carboxylation of aziridines to 5-aryl-2-oxazolidinones catalysed by $[NH_2Et_2]I$ under solventless and ambient conditions

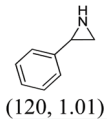
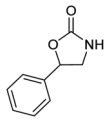
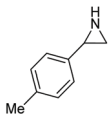
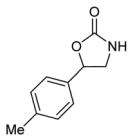
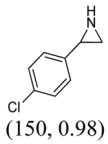
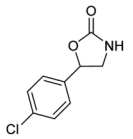
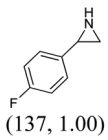
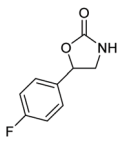
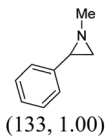
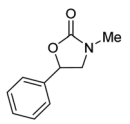
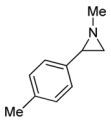
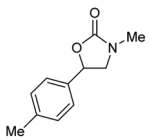
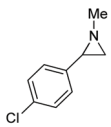
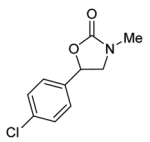
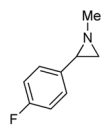
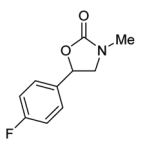
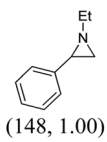
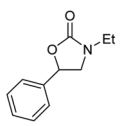
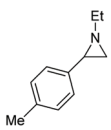
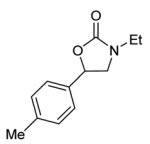
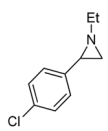
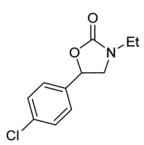
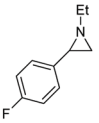
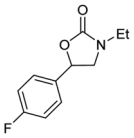
Run	Aziridine (mg, mmol)	Oxazolidinone	Yield[a] (%)
1	 (120, 1.01)		0
2	 (136, 1.02)		20
3	 (150, 0.98)		0
4	 (137, 1.00)		17
5	 (133, 1.00)		82
6	 (150, 1.02)		76
7	 (165, 0.98)		85
8	 (150, 0.99)		81
9	 (148, 1.00)		28
10	 (165, 1.02)		50
11	 (183, 1.01)		52

Table 2 *(Contd.)*

Run	Aziridine (mg, mmol)	Oxazolidinone	Yield[a] (%)
12	 (163, 0.987)		66

Experimental conditions: aziridine *ca.* 1 mmol (no solvent); catalyst: $[NH_2Et_2]I$, 5 mol%; pCO_2 = 1 atm; t = 24 hours. [a] Calculated as integral ratio between the ^1H NMR signals of ring CH (product) and 1,1,2,2-tetrachloroethane as standard.

rence of N–H···N hydrogen bonding between the diethylammonium cation and the aziridine nitrogen, as previously described for analogous systems.[30] After 15 hours in the absence of CO_2, a complicated mixture of products was detected, presumably derived from oligomerization and cyclization processes;[29a] this fact highlights the major activating power towards the aziridine of $[NH_2Et_2]I$ compared to $[NBu_4]I$.

1-Methyl-2-phenylaziridine was selected as a model substrate for the computational investigation of the coupling reaction with carbon dioxide leading to 3-methyl-5-phenyloxazolidin-2-one, catalysed by ammonium halides. Preliminary calculations indicate that the three-membered cycle is not opened by the direct attack of iodide or bromide on the phenyl-substituted carbon. Therefore, the presence of an acidic species able to interact with the nitrogen atom appears of paramount importance for the subsequent coupling with CO_2.[24,31] Carbon dioxide itself is a possible acid, and in fact, the transition state for the aziridine ring-opening reaction by iodide in the presence of one CO_2 molecule was found (N-CO_2 bond length = 1.497 Å). This transition state is 36.5 kcal mol^{-1} higher than the free reactants and presumably involved in the case of the reaction promoted by $[NBu_4]I$, being the tetrabutylammonium cation unable to interact with the aziridine/iodide system, in agreement with NMR studies (see above).

Much lower energy barriers were obtained on considering $[NH_2Et_2]^+$ as Brønsted acid. The computed reaction profiles for the formation of 3-methyl-5-phenyloxazolidin-2-one by $[NH_2Et_2]X$ (X = Br, I) are shown in Fig. 1. Coherently with NMR experiments (see above), the cation gives hydrogen bond interaction with the aziridine, with modest Gibbs energy variation with respect to the reactants (step **a**, Fig. S3†). The nucleophilic

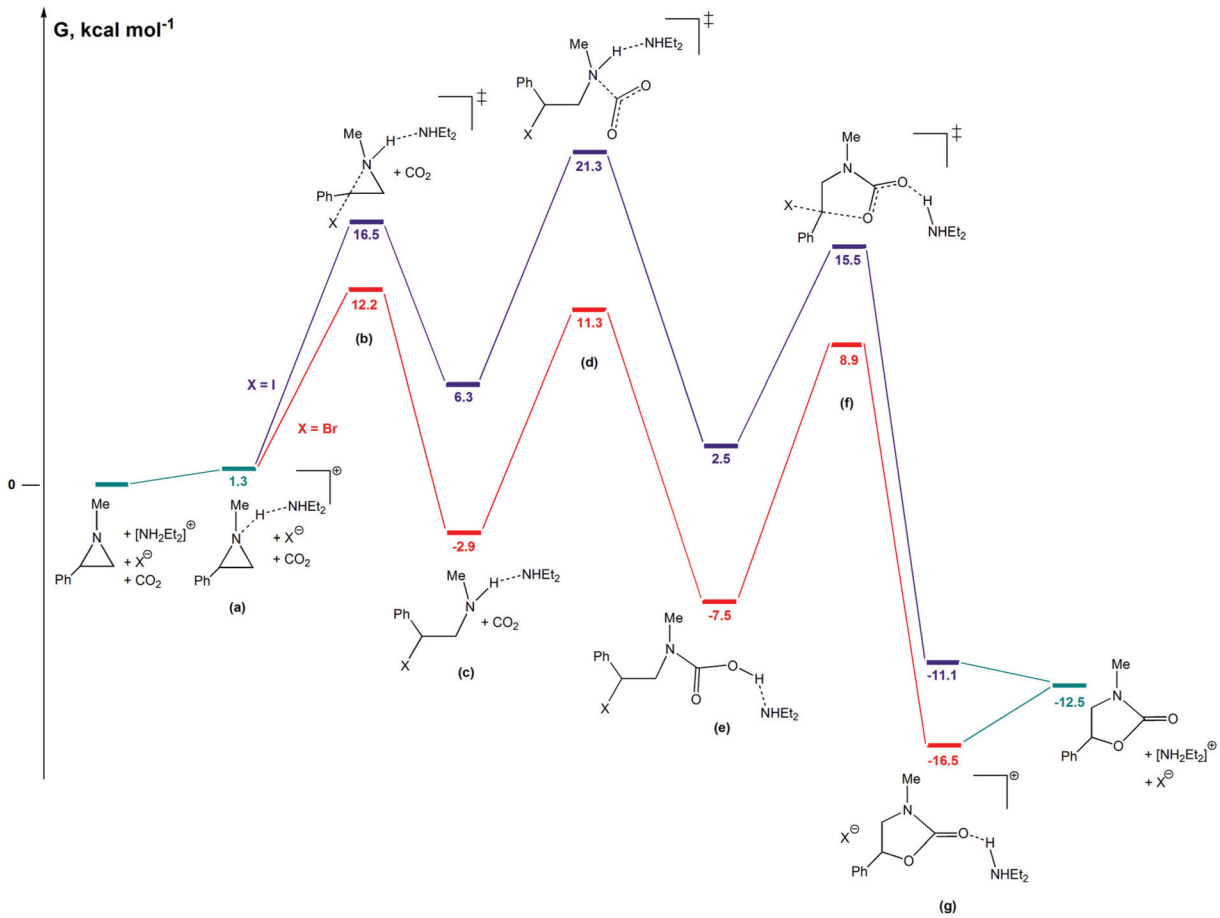


Fig. 1 Computed reaction profiles for the conversion of 1-methyl-2-phenylaziridine and carbon dioxide to 3-methyl-5-phenyloxazolidin-2-one, catalysed by $[NH_2Et_2]X$ (X = Br, red; X = I, violet). C-PCM/ωB97X/def-SVP calculations, ε = 8.9. Gibbs energy values (kcal mol^{-1}) are referred to the free reactants.

attack of X^- to the *C*(Ph) carbon atom affords the first transition state of the reaction (step **b**, Fig. S4†), then the ammonium acidic hydrogen is transferred to the aziridine. The consequent ring-opening species (step **c**, Fig. S5†) is best described as a secondary amine with hydrogen bond interaction with diethylamine. The bromide-derivative is about 9.2 kcal mol^{-1} more stable than the corresponding iodide-one, due to the higher stability of the C–Br bond with respect to C–I. The nitrogen atom of the amino group is able to attack CO_2, assisted by hydrogen bond interaction with diethylamine. The non-protonated oxygen atom can give intramolecular nucleophilic attack to the halido-substituted carbon (step **f**, Fig. S8†). This is followed by generation of the oxazolidinone ring with strong negative Gibbs energy variation, the $[NH_2Et_2]^+$ cation binding the carbonyl moiety *via* hydrogen bond (step **g**, Fig. S9†).

In summary, DFT outcomes point out multiple roles played by the diethylammonium cation in the catalytic reaction, and in particular: (1) the initial protonation of the aziridine nitrogen to trigger the ring-opening and stabilize the intermediate amine species; (2) the hydrogen bond interaction with the amine, facilitating the nucleophilic attack towards CO_2; (3) the protonation of the carbamate formed after interaction with CO_2; (4) the deprotonation of the O–H moiety during the final cyclization step. The convenience in the use of $[NH_2Et_2]^+$ probably relies on a compromise between the good Brønsted acidic character (otherwise absent in $[NBu_4]^+$), favouring the protonation steps, and the satisfying basicity of the conjugated base provided by the two ethyl substituents, favouring the hydrogen bond formation and deprotonation steps.

Concerning the halide counteranion, the comparison of the two reaction profiles in Fig. 1 can be rationalized based on the two different carbon–halogen bond strengths: it is worth reminding that too stable intermediates are as detrimental to catalysis as too high energy intermediates. Thus, the greater stability of the C–Br bond lowers the energy barrier of the first step, and the carbamic acid (step **e**) is much more stable for X = Br (rather than X = I) compared to the reactants (ΔG = −7.5 kcal mol^{-1}). The stability of such an intermediate presumably slows down the final cyclization step, requiring C–Br bond cleavage, and this feature represents a possible explanation for the lower catalytic activity exhibited by $[NH_2Et_2]$Br with respect to $[NH_2Et_2]$I.

Conclusions

The development of sustainable synthetic routes to access 2-oxazolidones exploiting CO_2 fixation is currently of large interest. In particular, the aziridine/CO_2 coupling reaction is an atom economic process but possessing a high activation barrier, whereby a wide range of catalysts has been proposed. Nonambient temperature and/or pressure are often required and elaborated catalytic systems have been reported, including the use of tetrabutylammonium halides as co-catalysts, when working under mild conditions. In this context, the catalytic potential of ammonium halides alone has been barely explored, despite the easy availability and relatively low toxicity of these species. Here, we have carried out a screening study evidencing diethylammonium iodide as a convenient catalyst for the regiospecific conversion of 2-arylaziridines, bearing small *N*-alkyl substituents, to the corresponding 5-aryl-2-oxazolidinones under environmentally benign conditions (room temperature and atmospheric CO_2 pressure). Combined, NMR and DFT results suggest that the optimal activity provided by $[NH_2Et_2]$I arises from its nature of Brønsted acid associated with a satisfying strength of the conjugate base, and the relative weakness of the carbon-iodine bond, favouring the final cyclization step of the reaction.

Although the applicability of the present method is not broad and has not been extended to 2-alkyl-aziridines, it provides a clear advance, in terms of simplicity and sustainability, for the synthesis of a series of valuable molecules with respect to existing literature procedures.

Experimental section

General details

Operations were conducted in air. CO_2 (99.99%) was purchased from Rivoira, while other reactants and solvents were commercial products (Merck, TCI Europe or Strem) of the highest purity available, and stored under N_2 as received. Solvents (Merck) were distilled before use over appropriate drying agents. 2-Arylaziridines[17b] and $[NH_3Cy]I$[32] were prepared according to the respective literature procedures. NMR spectra were recorded at 298 K with a Bruker Avance II DRX 400 instrument equipped with a BBFO broadband probe. ^1H and ^{13}C chemical shifts were referenced to the non-deuterated aliquot of the solvent,[33] while ^{19}F chemical shifts were referenced to an external standard ($CFCl_3$). Elemental analyses were performed on a Vario MICRO cube instrument (Elementar).

Synthesis and characterization of $[NH_2{}^iPr_2]I$

An excess of hydrogen iodide (*ca.* 20 mmol from a 57% aqueous solution) was added dropwise to diisopropylamine (1.00 mL, 7.14 mmol) in a Schlenk tube. The mixture was stirred for 30 minutes, then ethanol (5 mL) was added. The liquid phase was removed, and the precipitate was washed with diethyl ether (3 × 10 mL) and then dried under vacuum. A second crop of product was recovered from the initial solution by re-crystallization using diethyl ether as non-solvent (15 mL) at −30 °C. Total yield 1.55 g, 95%. Anal. calcd for $C_6H_{16}NI$: C, 31.46; H, 7.04; N, 6.11. Found C, 31.61; H, 7.09; N, 6.04. ^1H NMR ($CDCl_3$): δ/ppm = 8.29 (br, 2H, NH_2), 3.66 (m, 1H, CH), 1.61 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH_3).

Synthesis, isolation and NMR characterizaion of 2-aryl-aziridines

General procedure.[17b] Under N_2 flux, a 250 mL round bottom flask containing a solution of Me_2S (*ca.* 65 mmol) in dry CH_3CN (15 mL) was cooled to 0 °C. To this solution, Br_2 (*ca.* 40 mmol) in dry CH_2Cl_2 (35 mL) was added dropwise over 15 minutes, thus $[Me_2SBr]$Br formed as orange precipitate.[12]

The system was stirred for further 30 minutes, then the appropriate alkene (*ca.* 80 mmol) was added dropwise and the resulting mixture was stirred for 2 hours at 0 °C. White solid $[BrCH_2C(SMe_2)(4\text{-}C_6H_4R)]Br$ was recovered by filtration, washed with Et_2O (3 × 15 mL) and dried under vacuum. A portion of this solid (*ca.* 6 mmol) was dissolved in water (30 mL) and the selected amine (6 eq.) was added dropwise. The mixture was stirred overnight at room temperature, extracted with Et_2O (3 × 20 mL) and dried over Na_2SO_4. The volatiles were removed under vacuum and the residue was chromatographed on a silica column; a mixture of ethyl acetate and petroleum ether (40–60 °C) (from 1 : 10 to 1 : 6 v/v), added of triethylamine (5% v/v), as eluent allowed to isolate the aziridine product.

2-Phenylaziridine.[17b] From (2-bromo-1-phenylethyl)dimethylsulfonium bromide (6.10 mmol) and NH_3 (30% aqueous solution). Colourless liquid. Yield 363 mg, 50% ^{1}H NMR ($CDCl_3$): δ/ppm = 7.37–7.23 (m, 5H, Ph); 3.05 (m, 1H, CH); 2.29 (d, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2); 1.77 (d, $^3J_{HH}$ = 2.9 Hz, 1H, CH_2).

1-Methyl-2-phenylaziridine.[17b] From (2-bromo-1-phenylethyl)dimethylsulfonium bromide (6.25 mmol) and NH_2Me (40% aqueous solution). Colourless liquid. Yield 599 mg, 72%. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.37–7.21 (m, 5H, Ph); 2.50 (s, 3H, NMe); 2.28 (m, 1H, CH); 1.91 (d, $^3J_{HH}$ = 3.2 Hz, 1H, CH_2); 1.63 (d, $^3J_{HH}$ = 6.7 Hz, 1H, CH_2).

1-Ethyl-2-phenylaziridine.[17b] From (2-bromo-1-phenylethyl) dimethylsulfonium bromide (6.00 mmol) and NH_2Et (2 M tetrahydrofuran solution). Colourless liquid. Yield 600 mg, 68%. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.40–7.24 (m, 5H, Ph); 2.53–2.44 (m, 2H, NCH_2); 2.34 (m, 1H, CH); 1.94 (d, $^3J_{HH}$ = 3.2 Hz, 1H, CH_2); 1.68 (d, $^3J_{HH}$ = 6.7 Hz, 1H, CH_2); 1.26 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3).

2-(*p*-Tolyl)aziridine.[34] From (2-bromo-1-(*p*-tolyl)ethyl)dimethylsulfonium bromide (6.00 mmol) and NH_3 (30% aqueous solution). Colourless liquid. Yield 344 mg, 43%. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.14 (m, 4H, C_6H_4); 3.00 (m, 1H, CH); 2.35 (s, 3H, C_6H_4Me); 2.18 (m, 1H, CH_2); 1.81 (m, 1H, CH_2); 1.68 (br, 1H, NH) ppm.

1-Methyl-2-(*p*-tolyl)aziridine.[35] From (2-bromo-1-(*p*-tolyl) ethyl)dimethylsulfonium bromide (5.95 mmol) and NH_2Me (40% aqueous solution). Colourless liquid. Yield 613 mg, 70% ^{1}H NMR ($CDCl_3$): δ/ppm = 7.16 (m, 4H, C_6H_4); 2.52 (s, 3H, NMe); 2.37 (s, 3H, C_6H_4Me); 2.28 (m, 1H, CH); 1.92 (d, $^3J_{HH}$ = 3.2 Hz, 1H, CH_2); 1.64 (d, $^3J_{HH}$ = 6.7 Hz, 1H, CH_2).

1-Ethyl-2-(*p*-tolyl)aziridine.[17b] From (2-bromo-1-(*p*-tolyl) ethyl)dimethylsulfonium bromide (6.30 mmol) and NH_2Et (2 M tetrahydrofuran solution). Colourless liquid. Yield 660 mg, 65%. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.13 (m, 4H, C_6H_4); 2.52–2.36 (m, 2H, NCH_2); 2.33 (s, 3H, C_6H_4Me); 2.28 (m, 1H, CH); 1.89 (m, 1H, CH_2); 1.64 (d, $^3J_{HH}$ = 6.7 Hz, 1H, CH_2); 1.20 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3).

2-(4-Chlorophenyl)aziridine.[36] From (2-bromo-1-(4-chlorophenyl)ethyl)dimethylsulfonium bromide (6.06 mmol) and NH_3 (30% aqueous solution). Colourless liquid. Yield 539 mg, 58% ^{1}H NMR ($CDCl_3$): δ/ppm = 7.23–7.10 (m, 4H, C_6H_4); 2.92 (m, 1H, CH); 2.14 (d, 1H, CH_2, $^3J_{HH}$ = 6.2); 1.63 (d, 1H, CH_2, $^3J_{HH}$ = 3.1); 1.06 (br, 1H, NH).

1-Methyl-2-(4-chlorophenyl)aziridine.[35] From (2-bromo-1-(4-chlorophenyl)ethyl)dimethylsulfonium bromide (6.18 mmol) and NH_2Me (40% aqueous solution). Colourless liquid. Yield 746 mg, 72% ^{1}H NMR ($CDCl_3$): δ/ppm = 7.27–7.14 (m, 4H, C_6H_4); 2.48 (s, 3H, NMe); 2.24 (m, 1H, CH); 1.85 (d, 1H, CH_2, $^3J_{HH}$ = 3.0); 1.63 (d, 1H, CH_2, $^3J_{HH}$ = 6.7).

1-Ethyl-2-(4-chlorophenyl)aziridine.[17b] From (2-bromo-1-(4-chlorophenyl)ethyl)dimethylsulfonium bromide (5.92 mmol) and NH_2Et (2 M tetrahydrofuran solution). Colourless liquid. Yield 742 mg, 69%. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.38–7.22 (m, 4H, C_6H_4); 2.44 (m, 2H, NCH_2); 2.25 (m, 1H, CH); 1.82 (d, $^3J_{HH}$ = 3.2, 1H, CH_2); 1.64 (d, $^3J_{HH}$ = 6.7 Hz, 1H, CH_2,); 1.18 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3).

2-(4-Fluorophenyl)aziridine.[34] From (2-bromo-1-(4-fluorophenyl)ethyl)dimethylsulfonium bromide (6.15 mmol) and NH_3 (30% aqueous solution). Colourless liquid. Yield 388 mg, 46%. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.39–7.24 (m, 4H, C_6H_4); 3.07 (m, 1H, CH); 2.30 (d, $^3J_{HH}$ = 6.3 Hz, 1H, CH_2); 1.78 (d, $^3J_{HH}$ = 3.1 Hz, 1H, CH_2); 1.23 (br, 1H, NH).

1-Methyl-2-(4-fluorophenyl)aziridine. From (2-bromo-1-(4-fluorophenyl)ethyl)dimethylsulfonium bromide (6.28 mmol) and NH_2Me (40% aqueous solution). Colourless liquid. Yield 475 mg, 50%. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.17, 6.97 (m, 4H, C_6H_4); 2.47 (s, 3H, NMe); 2.24 (m, 1H, CH); 1.84 (d, 1H, CH_2, $^3J_{HH}$ = 3.4); 1.60 (d, 1H, CH_2, $^3J_{HH}$ = 6.6). ^{13}C NMR ($CDCl_3$): δ/ppm = 162.0 (d, $^1J_{CF}$ = 244.5 Hz, *C*F); 136.0 (d), 127.6 (d), 115.1 (d) (C_6H_4); 47.9 (NCH_3); 41.7 (CH); 39.3 (CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = −116.2. Anal. Calcd for $C_9H_{10}FN$: C, 71.50; H, 6.67; N, 9.26. Found: C, 71.43; H, 6.75; N, 9.23.

1-Ethyl-2-(4-fluorophenyl)aziridine. From (2-bromo-1-(4-fluorophenyl)ethyl)dimethylsulfonium bromide (5.96 mmol) and NH_2Et (2 M tetrahydrofuran solution). Colourless liquid. Yield 581 mg, 59%. Colourless liquid. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.38–7.22 (m, 4H, C_6H_4); 2.44 (q, $^3J_{HH}$ = 7.2 Hz, 2H, NCH_2); 2.29 (m, 1H, CH); 1.86 (d, 1H, CH_2, $^3J_{HH}$ = 3.2); 1.65 (d, 1H, CH_2, $^3J_{HH}$ = 6.7); 1.20 (t, 3H, CH_3, $^3J_{HH}$ = 7.2); ^{13}C NMR ($CDCl_3$): δ/ppm = 161.9 (d, $^1J_{CF}$ = 244.6 Hz, *C*F); 136.3 (d), 127.8 (d), 115.1 (d) (C_6H_4); 55.8 (NCH_2), 40.5 (CH); 37.5 (CH_2); 14.5 (CH_3). ^{19}F NMR ($CDCl_3$): δ/ppm = −116.3. Anal. Calcd for $C_{10}H_{12}FN$: C, 72.70; H, 7.32; N, 8.48. Found: C, 72.75; H, 7.37; N, 8.43.

Synthesis and NMR characterization of 5-aryloxazolidin-2-ones

General procedure. The appropriate amount of ammonium salt (according to Table 1) was introduced into a Schlenk tube, which was evacuated by a vacuum pump and then filled with CO_2. The vacuum/CO_2 sequence was repeated twice. Under a stream of carbon dioxide, the selected aziridine (*ca.* 1 mmol) was added, and the resulting mixture was stirred for 24 hours at room temperature under atmospheric pressure of carbon dioxide from a balloon. A precise amount of 1,1,2,2-tetrachloroethane (*ca.* 0.2 mL) was added as internal standard, then an aliquot (*ca.* 0.1 mL) of the mixture was mixed with $CDCl_3$ (0.5 mL) in an NMR tube. Yield values were determined by ^{1}H

NMR spectroscopy and are referenced to 1,1,2,2-tetrachloroethane.

5-Phenyloxazolidin-2-one.[17b] From 2-phenylaziridine (120 mg, 1.01 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43–7.34 (m, 5H, Ph); 6.54 (br, 1H, NH); 5.61 (t, $^3J_{HH}$ = 8.4 Hz, 1H, CH); 3.97, 3.54 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2).

3-Methyl-5-phenyloxazolidin-2-one.[17b,12] From 1-methyl-2-phenylaziridine (133 mg, 1.00 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.41–7.26 (m, 5H, Ph); 5.48 (t, $^3J_{HH}$ = 8.6 Hz, 1H, CH); 3.91, 3.44 (t, $^3J_{HH}$ = 8.6 Hz, 2H, CH_2); 2.92 (s, 3H, CH_3).

3-Ethyl-5-phenyloxazolidin-2-one.[12,17b] From 1-ethyl-2-phenylaziridine (148 mg, 1.00 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.29–7.20 (m, 5H, Ph); 5.33 (t, $^3J_{HH}$ = 8.7 Hz, 1H, CH); 3.80 (t, $^3J_{HH}$ = 8.7 Hz, 1H, CH_2); 3.30–3.15 (m, 3H, CH_2 + NCH_2); 1.04 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3).

5-(*p*-Tolyl)oxazolidin-2-one.[12,37] From 2-(*p*-tolyl)aziridine (136 mg, 1.02 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.31–7.22 (m, 4H, C_6H_4); 6.22 (br, 1H, NH); 5.60 (t, $^3J_{HH}$ = 8.4 Hz, 1H, CH); 3.97, 3.56 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2); 2.39 (s, 3H, CH_3).

3-Methyl-5-(4-tolyl)oxazolidin-2-one.[12,16d] From 1-methyl-2-(*p*-tolyl)aziridine (150 mg, 1.02 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.27–7.21 (m, 4H, C_6H_4); 5.46 (t, $^3J_{HH}$ = 8.4 Hz, 1H, CH); 3.90, 3.45 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2); 2.94 (s, 3H, NCH_3); 2.38 (s, 3H, $C_6H_4CH_3$).

3-Ethyl-5-(4-tolyl)oxazolidin-2-one.[12,17b] From 1-ethyl-2-(*p*-tolyl)aziridine (165 mg, 1.02 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.20–7.13 (m, 4H, C_6H_4); 5.39 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH); 3.83 (t, $^3J_{HH}$ = 8.6 Hz, 1H, CH_2); 3.38–3.25 (m, 3H, CH_2 + NCH_2), 2.30 (s, 3H, $C_6H_4CH_3$); 1.12 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3).

5-(4-Chlorophenyl)oxazolidin-2-one.[12,37] From 2-(4-chlorophenyl)aziridine (150 mg, 0.976 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.39–7.29 (m, 4H, C_6H_4); 6.49 (br, 1H, NH); 5.58 (t, $^3J_{HH}$ = 8.4 Hz, 1H, CH); 3.97, 3.49 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2).

3-Methyl-5-(4-chlorophenyl)oxazolidin-2-one.[12,38] From 1-methyl-2-(4-chlorophenyl)aziridine (165 mg, 0.984 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.38–7.28 (m, 4H, C_6H_4); 5.45 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH); 3.91, 3.40 (t, $^3J_{HH}$ = 8.3 Hz, 2H, CH_2); 2.92 (s, 3H, CH_3).

3-Ethyl-5-(4-chlorophenyl)oxazolidin-2-one.[12,15a] From 1-ethyl-2-(4-chlorophenyl)aziridine (183 mg, 1.01 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.37, 7.29 (d, $^3J_{HH}$ = 7.9 Hz, 4H, C_6H_4); 5.45 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH); 3.92 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH_2); 3.44–3.30 (m, 3H, CH_2 + NCH_2); 1.17 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3).

5-(4-Fluorophenyl)oxazolidin-2-one.[12,37] From 2-(4-fluorophenyl)aziridine (137 mg, 1.00 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.39–7.34, 7.11–7.07 (m, 4H, C_6H_4); 6.17 (br, 1H, NH); 5.60 (t, $^3J_{HH}$ = 8.4 Hz, 1H, CH); 3.97, 3.58 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2).

3-Methyl-5-(4-fluorophenyl)oxazolidin-2-one.[12] From 1-methyl-2-(4-fluorophenyl)aziridine (150 mg, 0.992 mmol) and carbon dioxide. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.36–7.32, 7.11–7.07 (m, 4H, C_6H_4); 5.46 (t, $^3J_{HH}$ = 8.1 Hz, 1H, CH); 3.90, 3.42 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2); 2.93 (s, 3H, CH_3).

3-Ethyl-5-(4-fluorophenyl)oxazolidin-2-one. From 1-ethyl-2-(4-fluorophenyl)aziridine (163 mg, 0.987 mmol) and carbon dioxide. In this case, the reaction mixture was dissolved in the minimum volume of ethyl acetate, and this solution was charged on a silica column. A mixture of ethyl acetate and petroleum ether (40–60 °C) (from 1 : 10 to 1 : 4 v/v), added of triethylamine (5% v/v), was used as eluent to collect the fraction corresponding to the product. Yield 132 mg, 64%. Anal. Calcd for $C_{11}H_{12}FNO_2$: C, 63.15; H, 5.78; N, 6.69. Found: C, 63.20; H, 5.77; N, 6.63. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.34–7.30, 7.07–7.03 (m, 4H, C_6H_4); 5.45 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH); 3.91 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH_2); 3.41–3.25 (m, 3H, CH_2 + NCH_2); 1.15 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ/ppm = 162.7 (d, $^1J_{CF}$ = 246.6 Hz, *C*F); 161.5 (C=O); 134.6 (d), 127.5 (d), 115.8 (d) (C_6H_4); 73.72 (CH); 51.5 (CH_2); 38.8 (NCH_2); 12.4 (CH_3). ^{19}F NMR ($CDCl_3$): δ/ppm = −112.9.

DFT calculations

The ground- and transition state structures were optimized using the hybrid B3PW91 DFT functional[39] in combination with Ahlrichs' split-valence-polarized basis set, with ECP on the iodine atom.[40] The C-PCM implicit solvation model was added to ωB97X calculations, considering a dielectric constant ε = 8.9.[41] The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 25 °C) were obtained. The software used was Gaussian 09.[42] Cartesian coordinates of the DFT-optimized structures are collected in a separated .xyz file.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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