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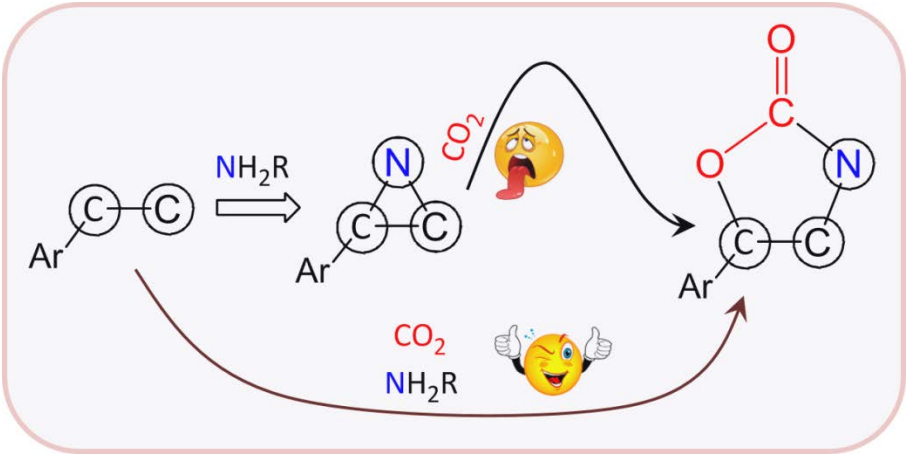
The largely investigated catalytic process affording 5-aryl-2-oxazolidinones by two-step assembly of a C_2 precursor with primary amine and carbon dioxide is replaced by the catalyst-free, direct addition of the amine/CO_2 adduct to the C_2 unit in isopropanol or water.



Bypassing the Inertness of Aziridine/CO_2 Systems to Access 5-Aryl-2-Oxazolidinones: Catalyst-Free Synthesis Under Ambient Conditions

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Abstract

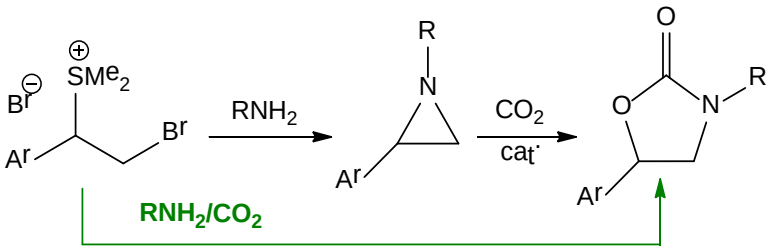
The development of sustainable synthetic routes to access valuable oxazolidinones via CO_2 fixation is currently a hot topic of research, and the aziridine/carbon dioxide coupling has aroused a considerable interest.This reaction is featured by a high activation barrier, so torequire a catalytic system, andmay present some other critical issues. Here, we describethe straightforwardgram-scale synthesis of a seriesof 5-aryl--oxazolidinonesat ambient temperature and atmospheric CO_2 pressure, in the absence of any catalyst/co-catalystand using isopropanol or water as solvent. The key to this innovative procedure consists in the direct transfer of the pre-formed amine/CO_2 adduct (carbamate) to common aziridine precursors (dimethylsulfonium salts), replacing the classical sequential addition of amine (intermediate isolation of aziridine) and then CO_2. The reaction mechanism has been elucidated by NMR studies and DFT calculations applied to model cases.

Keywords: carbon dioxide activation; sustainability; catalyst free organic synthesis; oxazolidinones; aziridines.

Introduction

Carbon dioxide is a nontoxic and ubiquitous substance associated to environmental issues, and its utilization as a C_1 synthon for organic synthesis, replacing hazardous compounds, is an ultimate goal of research, in theperspective of a sustainable world.[1] In particular, oxazolidinones are five-membered heterocyclic compounds that find important applications for their biological activity[2] and as synthetic precursors to various natural and bioactive compounds.[3] The recent years have witnessed an intense investigation aimed to develop new straightforward synthetic processes to access such fine chemicals exploiting CO_2 fixation routes.1[b,f,]2[a,4]All of the reported methods require the use of a catalyst unless high CO_2 pressure or supercritical carbon dioxide is employed.[5]Thus, unsaturated amines,[6,7] haloamines[8]and amino-alcohols6[d,9] have been investigated for their cyclization reactions with CO_2 to afford 2-oxazolidinones; even three-component systems may be effective, and in this regard,several epoxide/amine,[10] alkyne/amine,[11] and alkene/amine [12] combinations have been considered. Repo and co-workers demonstrated that a series of N-aryl-2-oxazolidinones are accessible from the one-pot carboxylation of aniline/1,2-dibromoethane in organic solvents under mild conditions.[13]In this scenario, the coupling of CO_2 with aziridinesremainsan intriguing andintensively investigated approach.1[b,g,]6[d,14]However, this reaction is featured by a high activation barrier,[15]thereforeboth metal[16] and organocatalysts[17] have been explored to the purpose. It should be remarked that the engagement of pressurized carbon dioxide is usually necessary, insteadexamples of efficient aziridine/CO_2 coupling atambienttemperature and pressure are rare andinevitablyassociated to either a catalyst,[18]specialized

equipment[19]or limited substrate scope.[20]Furthermore, the catalytic systems may present some critical issuesin terms of catalyst loadingand the need for a halide co-catalyst (Lewis base) and toxic solvents.[14]It is quite common in the literature that aziridines employed for the cyclization reaction with $CO_2$are prepared witha convenient procedure whereby a sulfonium bromide salt, derived fromstyrene or related ring-substituted species, provides the C_2 unit of the three membered heterocycle (Scheme 1).[16a-b,17a-c,21] This protocol allows to access a variety of 2-aryl-aziridinesusing an excess of amine, and conversion into the corresponding aryl-oxazolidinones follows. In principle,two possible regioisomers can be finally obtained, bearing the substituted ring carbon bound to either oxygen (5-aryl-2-oxazolidinone) or nitrogen (4-aryl-2-oxazolidinone), and full regioselectivity is not oftenrealisable.[14,16a-b,22] Looking at the synthetic route in Scheme 1 and at variance to the literature, we wondered whether the two-step incorporation of the carbamato unit $\{OC(=O)NR\}$[23] (from RNH_2 and CO_2) within the final five-membered ring could occur in one pot, avoiding the intermediate aziridine step. Our idea stemmed from the largely documented evidence that carbon dioxide and amines easily form carbamato adducts.[24]Thus, the present work describes a novel and simple CO_2-fixation strategy to synthesize 5-aryl-2-oxazolidinones bypassing the inertness of the aziridine/carbon dioxide system: exceptional simplicity and increased sustainable valuerespect to existing procedures is guaranteed by operating at ambient conditions (ambient temperature, atmospheric CO_2 pressure) and the complete absence of any catalyst/co-catalyst.



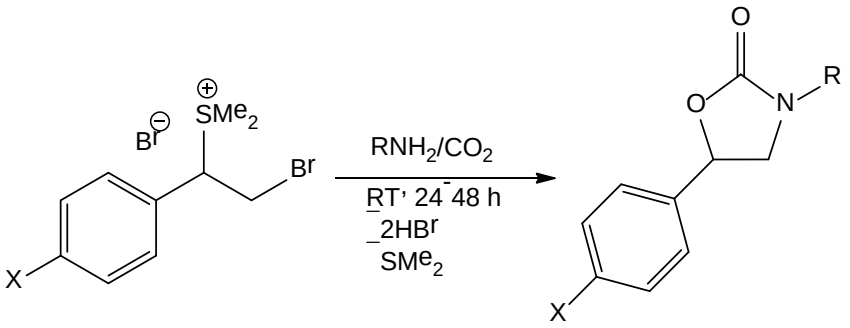
Scheme 1. Black: widely investigated synthetic pathway to 5-aryl-2-oxazolidinones via aziridine/CO_2 coupling using a variety of catalytic systems and operating at variable reaction conditions; Green: unprecedentedstrategy described in this work (ambient temperature and CO_2 pressure; solvent = isopropanol or water; absence of metal/catalyst/nucleophile; full regioselectivity).

Results and discussion

1. Synthesis and characterization of compounds.

In order to obtain 5-aryl-2-oxazolidinones(gram-scale synthesis), deaeratedisopropanol saturated with carbon dioxide was left reacting with the primary amine up to completion. Following addition of the sulfonium salt (**1-7**)in an optimal 1:4 molar ratio respect to the amine, the mixture was stirred for 24-48 hours at ambient temperature under CO_2 atmosphere from a balloon.The desired products**8-14**, except **8g**, **8h** and **10g**, were generally isolated after work-up in good to excellent yields(Scheme 2).In comparison, the use of water as solvent required 6 equivalents of the amine and longer reaction times to achieve satisfying yields (see Table S1

in the Supporting Information for details). Nonetheless, water revealed to be the appropriate choice to incorporate hydrazine and ethylenediamine, since the carbamates of these aminesare not soluble in isopropanol, andthus **8g**, **8h** and **10g** were obtained. The reaction leading to **8b** was selected as a model one to test further reaction solvents, and isopropanol resulted to be the best option (see SI, page S32). A comparative view of yields after variable times (Table S1) suggeststhat electronic and steric factors associated tothe amine R substituent are influencing, and the best results are achieved with a compromise of electron donor properties and bulkiness. For instance, R = Me is beneficial compared to R = H, while lower yields have been achieved with R = Cy, and our attempts to obtain oxazolidinones from tert-butylamine and aniline were not successful.



	X	*R*		*Time (h)*	*Yield%*[a]
1	H	H	**8a**	48	62
		CH_3	**8b**	24	96
		CH_2CH_3	**8c**	48	91
		$CH(CH_3)_2$	**8d**	48	65
		Cy	**8e**	48	60
		CH_2Ph	**8f**	48	74
		NH_2	**8g**	48	87[b]
		$CH_2CH_2NH_2$	**8h**	48	71[b]
		CH_2CH_2OH	**8i**	48	95
2	CH_3	H	**9a**	48	58
		CH_3	**9b**	24	68
		CH_2CH_3	**9c**	48	84
		$CH(CH_3)_2$	**9d**	48	50
		Cy	**9e**	48	44
		CH_2Ph	**9f**	48	68
3	Cl	H	**10a**	48	67
		CH_3	**10b**	24	92
		CH_2CH_3	**10c**	48	87
		$CH(CH_3)_2$	**10d**	48	79
		Cy	**10e**	48	69

		CH_2Ph	**10f**	48	87
		NH_2	**10g**	48	88[b]
		$CH(CH_2)_2CH_3$	**10h**	48	88
4	F	H	**11a**	48	65
		CH_3	**11b**	24	92
		$CH(CH_3)_2$	**11d**	48	72
		$CH(CH_2)_2CH_3$	**11h**	48	82
5	OMe	CH_3	**12b**	24	98
		CH_2CH_3	**12c**	48	92
6	NO_2	CH_3	**13b**	24	98
		CH_2CH_3	**13c**	48	92
7	CO_2Me	CH_3	**14b**	24	89
		CH_2CH_3	**14c**	48	67

Scheme 2. One pot synthesis of 5-aryl-2-oxazolidinones from (2-bromo-1-arylethyl)dimethylsulfonium bromide, primary amines (4 eq. respect to **1-7**; Cy = cyclohexyl, C_6H_{11}) and CO_2 in isopropanol. T = 298 K, pCO_2 = 1 atm. [a]Yields referred to isolated products.[b]Solvent H_2O, 6 eq. of amines respect to **1**,**3**.

All thecompounds**8-14**were fully characterized by elemental analysis, IR and multinuclear NMR spectroscopy. According to the respective ^{1}H NMR spectra, **8-14**are exclusively obtained as a single regioisomer (no traces of 4-aryl-2-oxazolidinones). In addition, the molecular structures of **10a** and **10e** were elucidated by single-crystal X-ray diffraction studies; the representative structure of **10e** is shown in Figure 1, while a view of **10a** is supplied as Supporting Information (Figure S1).

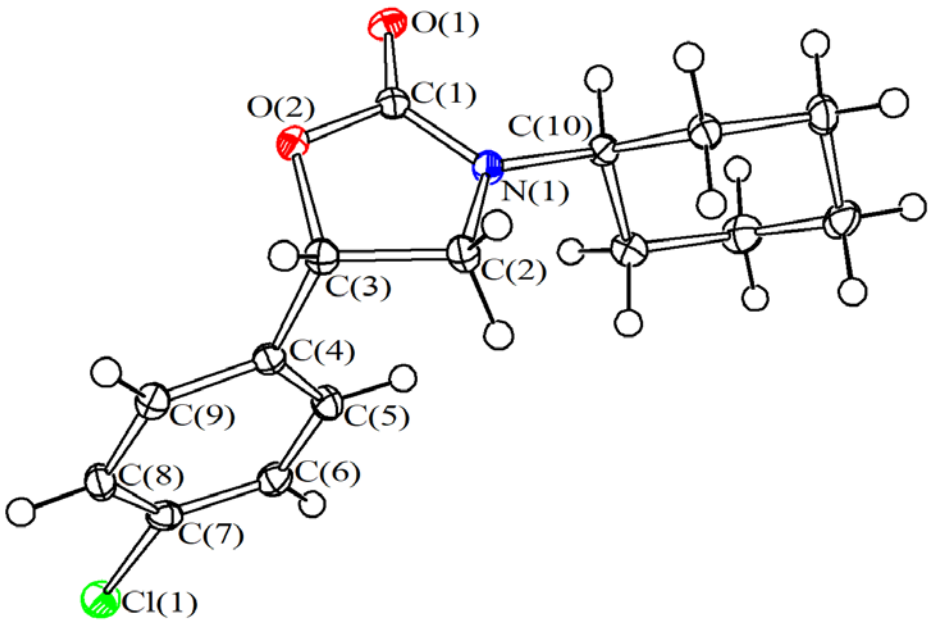
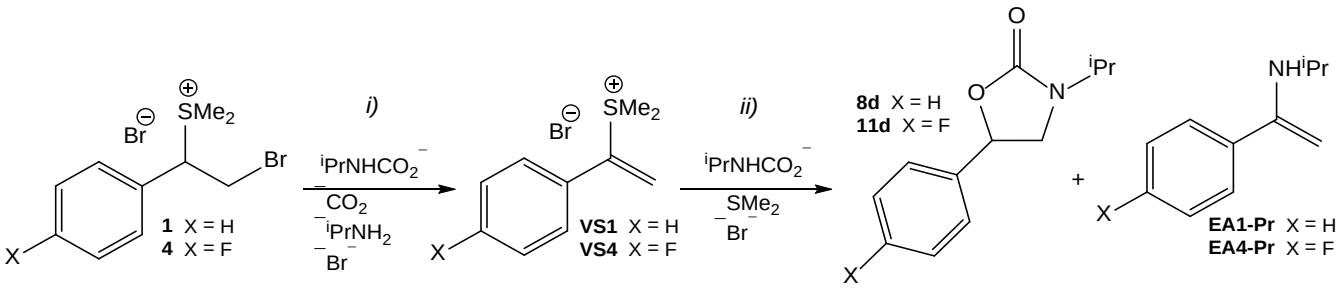


Figure 1. Molecular structure of **10e**, with labelling. Displacement ellipsoids are at the 50% probability level. H-atoms have been omitted for clarity. Main bond distances (Å) and angles (°): C(1)-O(1) 1.2124(19), C(1)-O(2) 1.3663(18), C(1)-N(1) 1.3465(19), N(1)-C(2) 1.4522(18), C(3)-O(2) 1.4695(18), C(2)-C(3) 1.534(2), C(3)-C(4) 1.507(2), C(7)-Cl(1) 1.7429(15), N(1)-C(10) 1.4633(19), O(2)-C(1)-N(1) 121.39(13), C(1)-N(1)-C(2) 112.21(12), N(1)-C(2)-C(3) 101.24(12), C(2)-C(3)-O(2) 103.56(11), C(3)-O(2)-C(1) 109.09(11), C(2)-C(3)-C(4) 116.07(13).

Note that **8a-g**, **9a-c**, **9e**, **10a-c**, **10e, 10h** and **11a-b**, **12b-c** and **14b** were all previously synthesizedby means of a catalytic system, often under not mild conditions. Instead, **8h-i**,**9d**, **9f**, **10d**, **10f-g**,**11d-h, 13b-c**and **14c** are reported here for the first time.In particular, the classical procedure to access**8h-i**may be challenging due to elaborated protocols required for the preparation of the respective aziridine precursors,[25]or polymerization side-reactions favoured by the presence of the alcohol function.[26]

The route depicted in Scheme 2 consists in the preliminary formation of a CO_2/amine adduct (carbamate), followed by assembly of the latter with the C_2 unit supplied by the (2-bromo-1-aryl)dimethylsulfonium bromide reagent.[27]For sake of comparison, a series of 5-aryl-oxazolidin-2-ones (including **8c,d,f** and **10h**) has been recently prepared by North and co-workers[16b] via the metal-catalysed reaction at 50 °C of CO_2 with aryl-aziridines, the latter being preliminarily obtained and isolated from (2-bromo-1-arylethyl)dimethylsulfonium bromidesalts and an excess (up to 5 equivalents) of amine.[21b,28]Calculated E factors related to the synthesis of **8c** from **1** and NH_2Et were approximately 2.2 and 2.5, respectively for the one pot procedure presented herein (procedure A in the SI) and the two-step one by North and co-workers[16b] (solvent wastes were not considered).

In order to investigate mechanistic and kinetic aspects, the reactions leadingto**8d** and **11d** weremonitored by NMR spectroscopy (see NMR studies in the SI). Thus, an excess of carbamate (from $NH_2{}^iPr/CO_2$) in aqueous solution was added to the precursor (**1** and **4**, respectively) in D_2O in an NMR tube. ^1H and 2D-HMBC experiments revealed the progressive formation of (1-arylvinyl)dimethylsulfonium salts(**VS1**, **VS4**),[29]promoted by the basicity of the carbamate(Scheme 3, step *i*). This finding is in alignment with previous reports on the reactivity of **1** with Brönsted bases.[30]



Scheme 3. NMR-detected steps of the reaction of (2-bromo-1-aryl)dimethylsulfonium bromide with *N*-isopropyl carbamate in D_2O or DMSO-d_6. In D_2O, **EA** are not detected and**8d**/**11d**separate as an oily phase.

Due to severe resonance broadening determined by the separation of an organic phase containing the oxazolidinone product from the aqueous medium,[31] we repeated the NMR study in DMSO-d_6, where **8d**and **11d** are soluble.Thus, the reaction of **1/4**with$NH_2{}^iPr/CO_2$proceededmuch faster than in D_2O, affording almost immediately**VS1/VS4** (Figures S2-S5), which then slowly converted into two different species(Scheme 3, step *ii*): one correspondedto**8d**/**11d**, while the second species was identified as an enamine (**EA1-Pr**/**EA4-Pr)**.Such enamines are featured by two diagnostic ^1H NMR signals(*e.g.* for **EA4-Pr** at 5.49 and 4.98 ppm)correlatingwith the same carbon in the ^{13}C spectrum (107.4 ppm); in addition,a 2D HMBC experimenthighlighted that the amino-substituent is geminal respect to the phenyl ring, without any other long-range contact (Figures S6-S10). The kinetic profile for the reaction leading to **11d**(in DMSO-d_6) could be elucidated by ^{19}F NMR spectroscopy in the 297-319 K temperature range. The trend of [**11d**] and [**EA4-Pr**] concentrations as a function of time is fitted as an exponential growth (R^2> 0.920 in every case; Figures 2A and S11a-d), providing the values of the reaction kinetic constants at different temperatures (Table 1). Fitting the data with the Eyring equation, the linearity is quite good (R^2> 0.958; Figure 2B), and the activation enthalpies and entropies are comparable for the two products (**11d**: $\Delta H^{\ddagger}$ = 10.4 ± 1.1 kcal mol^{-1}, $\Delta S^{\ddagger}$ = –38 ± 6 cal mol^{-1} K^{-1}; **EA4-Pr**: $\Delta H^{\ddagger}$ = 10.2 ± 1.0 kcal mol^{-1}, $\Delta S^{\ddagger}$ = –40 ± 7 cal mol^{-1} K^{-1}).

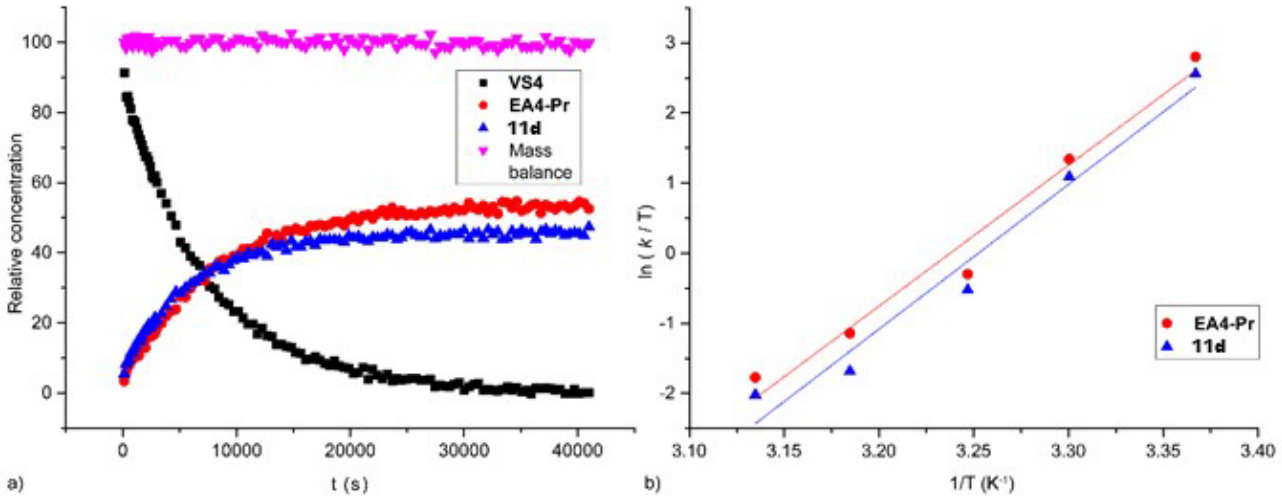


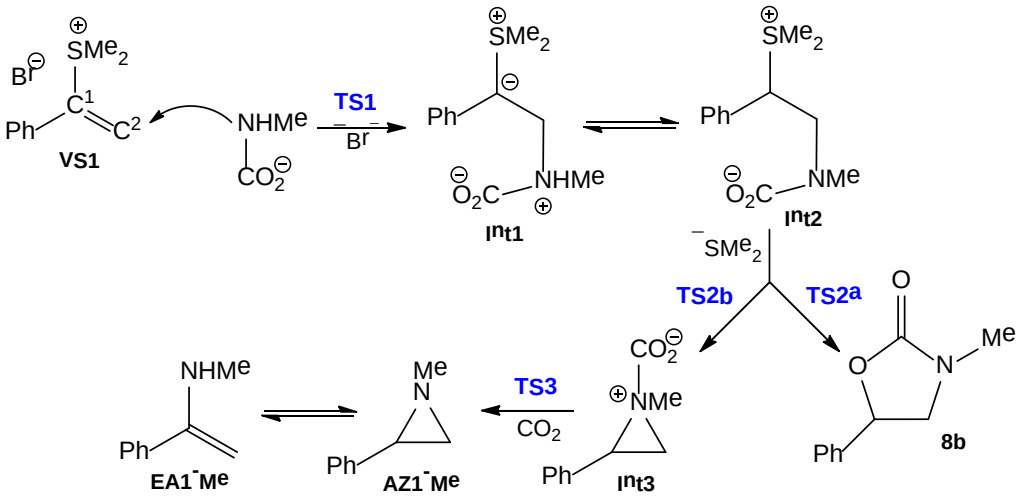
Figure 2. a) Concentration of intermediate (**VS4**) and products (**11d** and **EA4-Pr**) along the reaction of **4** with $NH_2{}^iPr/CO_2$ in DMSO-d_6, as a function of time (T = 297 K); b) Eyring plot related to **11d** and **EA4-Pr**(R^2 = 0.964 and 0.959, respectively).

Table 1. Kinetic reaction constants at different temperatures (solvent: DMSO-d_6).

T (K)	$k_{\mathbf{8c}}(s^{-1})$	$k_{\mathbf{EA4\text{-}Pr}}(s^{-1})$
297	4900 ± 230	3800 ±150
303	1160 ± 25	900 ± 25
308	228 ± 24	182 ± 7
313	100 ± 5	58 ± 2
319	54 ± 4	42 ± 3

DFT calculations.

The reaction affording **8b**, via the preliminary formation of **VS1**,[32] was chosen as a model for detailed DFT calculations, and the overall, proposed pathway is shown in Scheme 4.



Scheme 4.Proposed DFT mechanism for the reaction of dimethyl(1-phenylvinyl)sulfonium salt **VS1**(from **1**, see Scheme 3) with NH_2Me/CO_2; relevant transition states in blue; water as solvent (conductor-like polarisable continuum model).

According to the DFT-computed energies (Figure 3), the rate determining step is the initialnucleophilic addition of the carbamato nitrogen to the less hindered alkenic carbon of **VS1** (C^2), featured by anactivation enthalpy of 9.6 kcalmol^{-1}. Limited to this key step, the calculation was repeated on the reaction of **VS4** with $^{i}PrNHCO_2^-$ (DMSO as solvent, Scheme 3): the activation enthalpy resulted12.9 kcal mol^{-1},i.e.in reasonable agreement with the experimental value (10.4 ± 1.1 kcal mol^{-1}, see above).[33]While anyalternative attack to C^1 is prohibitive ($\Delta G^{\ddagger}$ = 35 kcal mol^{-1}),C^2-O coupling involving one carbamatooxygen is theoreticallypossible ($\Delta H^{\ddagger}$= 9.1 kcal mol^{-1}), but the resulting species seemsunable to evolve to any product. The intramolecular proton transfer converting **Int1** into **Int2**occurs through a high-energy transition state ($\Delta G^{\ddagger}$ = 40.3 kcal mol^{-1}), therefore it is presumably assisted by the excess of carbamate in the solution. The subsequent C-O bond forming cyclization(**TS2a**) yields**8b**and resembles a previously proposed cyclization step for the formation of oxazolidinones from alkenes, chloramine-T and CO_2;[34]the competitive, presumableformation of the enamine**EA1-Me** from **Int2**parallels the experimentally observed formation of **EA1-Pr** and **EA4-Pr**in DMSO (Scheme 3), and may be explained with a ring closure by the nitrogen atom (**TS2b**). The resulting aziridine **AZ1-Me**canrearrange to **EA1-Me**($\Delta G^{\ddagger}$ = 22 kcal mol^{-1}). In general, the route via **TS2b**in water is probably disfavouredsince the various equilibria are shifted toward the oxazolidinone product, precipitating from the aqueous reaction medium where instead enamines of the typeCH_2=C(Ar)(NHR) are expected to be soluble.[35]According to ^{1}H NMR analyses of the crude mixtures, a minor amount of the relevant aziridine(<5%) is generally aside-product of the formation of **8-14**, however this fact might be most properly related to the direct reaction of the amine with **1-7**.

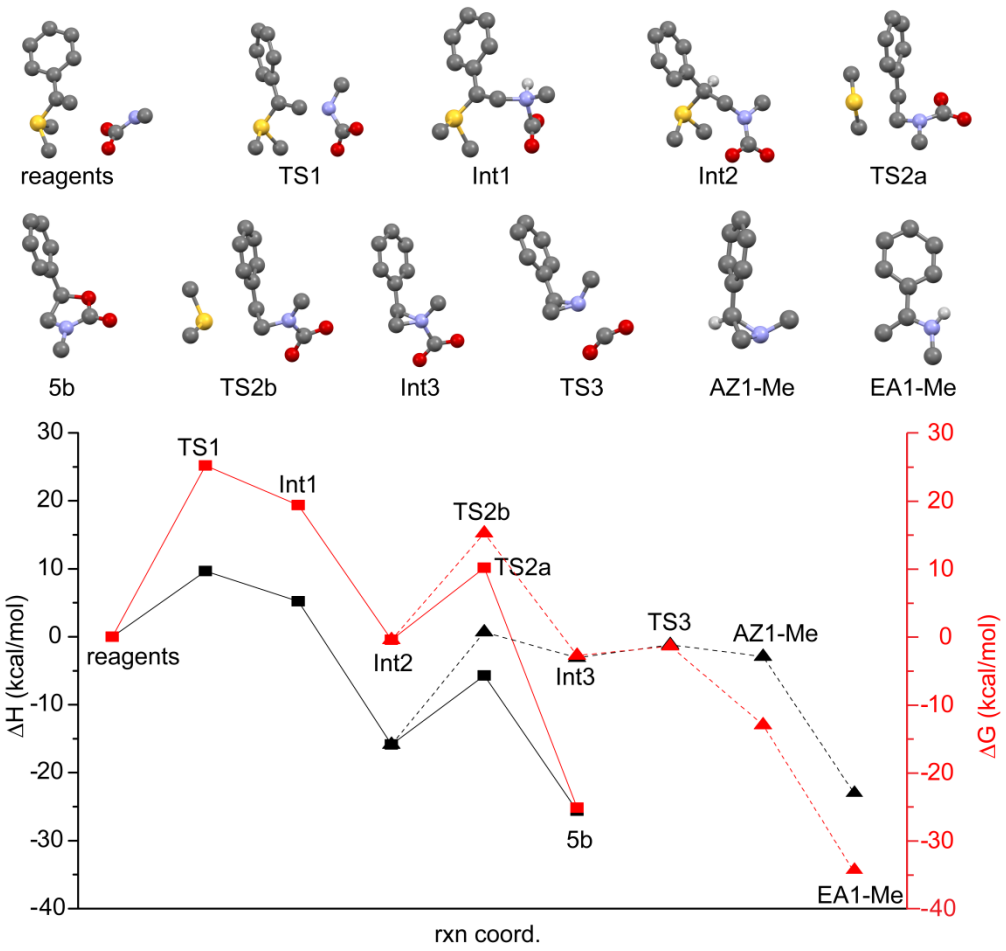


Figure 3. (Down) DFT-computed energy paths for the formation of **8b** and **EA1-Me** from **VS1** and NH_2Me/CO_2. (Up) DFT-optimized geometries of the species involved in the mechanism; for the sake of clarity, most of hydrogen atoms are omitted.

Alternative, hypothetical reaction pathways were carefully examined by DFT calculations (Scheme S1): all of them exhibit higher activation barriers and are thus ruled out at ambient temperature (Figures S12-S14).

Conclusions

The synthesis of valuable oxazolidinones from the coupling of aziridines with CO_2 has aroused a notable interest:the use of a catalytic system has been usually taken for granted, often associated to high CO_2 pressure and/or high temperature, and many efforts have been addressed to develop suitable metal catalysts pointing towards a more sustainable process. Herein, we have reported a novel method to access thirty-three 5-aryl-oxazolidinones (twelve reported for the first time) in a gram-scale, consisting in the preliminary facile fixation of CO_2 with NH_2R, and subsequent reaction of the resulting carbamate with a C_2 synthon. The latter is widely employed in the literature to obtain aryl-oxazolidinones, but through a two-step route with the intermediate

isolation of 2-aryl-aziridines. Our innovative method overcomes the inertness of the aziridine/CO_2 system, and therefore does not require any type of promoter (catalyst or ring-opening nucleophile) and allows to operate under ambient temperature and atmospheric CO_2pressure. Moreover, avoiding the aziridine-forming step is beneficial even considering that aziridines are toxic, potentially carcinogenic chemicals.[14,36]

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Supporting Information Available

Experimental procedures and characterizationof products; X-ray studies;NMR studies; DFT calculations; NMR and IR spectra of products. Cartesian coordinates of the DFT structures are collected in a separated .xyz file. CCDC reference numbers 1967793 (**10a**) and 1967794 (**10e**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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