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Experimental and theoretical investigations for the regio and stereoselective transformation of *trans* 1,2,3-trisubstituted aziridines into *trans* oxazolidin-2-ones

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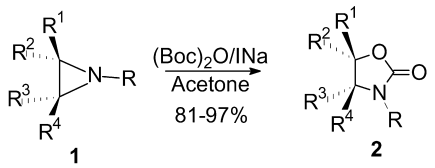
Abstract—The regio and stereoselective transformation of *trans* 1,2,3-trisubstituted aziridines into *trans* oxazolidin-2-ones takes place in good yield. However, the *cis* configuration at C2 and C3 in monocyclic aziridines is a limiting factor for this transformation. Ab initio calculations show that while the ring-opening process assisted by iodide is regioselective, the subsequent ring-closure is responsible for the retention of the configuration at the *trans* oxazolidin-2-one. The larger energy found for the ring-closure process for the *cis* aziridines accounts for the non-formation of the *cis* oxazolidin-2-ones.

The reaction of *N*-alkylaziridines **1** with di-*tert*-butyl dicarbonate (Boc_2O) and sodium iodide in acetone was previously reported as a new synthetic procedure for the stereoselective preparation of oxazolidin-2-ones **2** (see Scheme 1).[1] Further work on this topic has shown that the *cis* configuration of C2 and C3 in 1,2,3-trisubstituted monocyclic aziridines is a limiting factor for the transformation of **1** into **2**. The substrates used for this study were the *trans* aziridines **1a**,**b** and the *cis* aziridines **1c**,**d**. They were prepared from (1*R*,2*S*) (−)-ephedrine (**3a**), (1*S*,2*S*) (+)-pseudoephedrine (**4a**), and the racemic 3-methylamino-2-butanols[2] **5b** and **6b** (see Scheme 2).



1 **2**

Scheme 1. R=3-oxocyclohexyl or 3-oxocyclobutyl, $R^1=R^2=R^3=R^4=H$; R=3-oxocyclohexyl or 3-oxocyclobutyl, $R^1=R^3=R^4=H$, $R^2=CH_3$; R=3-oxocyclohexyl or 3-oxocyclobutyl $R^1=R^4=H$, $R^2=R^3=(CH_2)_3$; R=3-oxocyclohexyl or benzyl, $R^1=R^4=H$, $R^2=R^3=(CH_2)_4$; R=methyl, $R^1=H$, $R^2=C_6H_5$, $R^3=H$, $R^4=CH_2OTBDMS$.

The reaction of **3a** with triphenylphosphine–diethyl azodicarboxylate yielded *trans* (1*S*,2*S*)-1,2-dimethyl-3-phenylaziridine (**1a**),[3] and the reaction of **3a** with thionyl chloride–sodium hydroxide gave *cis* (1*S*,2*R*)-1,2-dimethyl-3-phenylaziridine (**1c**). The *trans* aziridine **1a** was converted into the *trans* oxazolidin-2-one[4] **2a** in 84% yield, by reaction with di-*tert*-butyl dicarbonate and sodium iodide in acetone at room temperature. However, when a similar transformation was attempted on the *cis* aziridine **1c**, the expected *cis* oxazolidin-2-one **2c** was not detected in the crude mixture.

The aziridines **1a** and **1c** were also prepared using (1*S*,2*S*) (+)-pseudoephedrine **4a** as starting material (see Scheme 2). The *trans* aziridine **1a** was obtained with thionyl chloride–sodium hydroxide, while the *cis* aziridine **1c** was prepared with triphenylphosphine–diethyl azodicarboxylate. The *trans* aziridine **1a** was then transformed into the oxazolidin-2-one **2a** in 72% yield, by reaction with di-*tert*-butyl dicarbonate and sodium iodide in acetone at room temperature. However, the *cis* aziridine **1c** did not afford the *cis* oxazolidin-2-one **2c**, under the same reaction conditions.

To verify the influence of the relative configuration of the C2 and C3 carbon atoms of the trisubstituted aziridines, two new derivatives, **1b** and **1d**, were prepared (see Scheme 2). These aziridines were obtained from racemic (2*R*,3*S*) and (2*S*,3*R*) 3-methylamino-2-butanol (**5b**) as starting material.[2] The reaction of **5b** with triphenylphosphine–diethyl azodicarboxylate yielded the *trans* aziridine **1b**, while the reaction with thionyl chloride–sodium hydroxide gave the *cis* aziridine **1d**.

Keywords: aziridines; oxazolidinones; regioselectivity; stereoselectivity; molecular mechanism; ab initio calculations.

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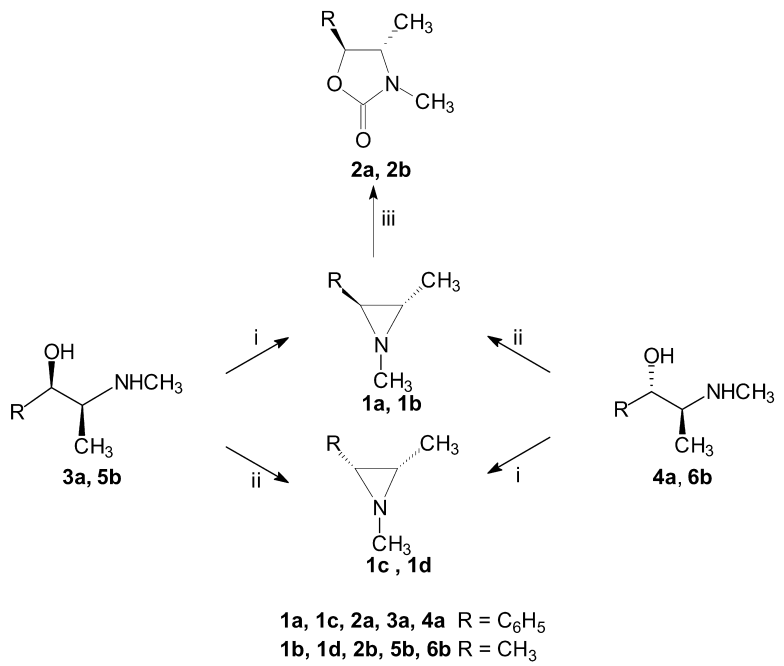


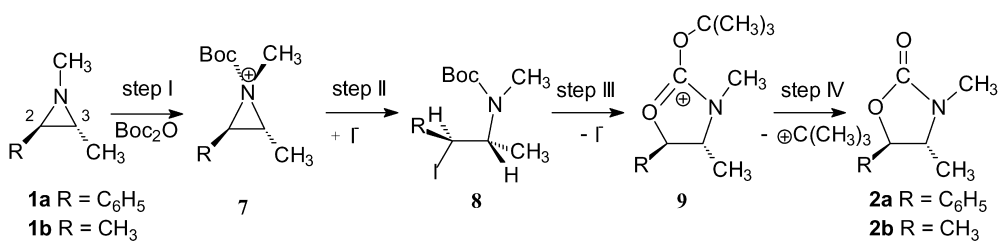
Scheme 2. (i) Ph_3P/DEAD; (ii) $SOCl_2$/NaOH; (iii) $(Boc)_2O$/INA, acetone.

The transformation of the *trans* aziridine **1b** into the *trans* oxazolidin-2-one **2b** took place by reaction with di-*tert*-butyl dicarbonate and sodium iodide in acetone at room temperature in 80% yield. However, the *cis* aziridine **1d** under the same reaction conditions did not afford the *cis* oxazolidin-2-one **2d**. The aziridines **1b** and **1d** were also prepared from racemic (2*R*,3*R*) and (2*S*,3*S*) 3-methylamino-2-butanol (**6b**). In this case the *trans* aziridine **1b** prepared with thionyl chloride–sodium hydroxide was converted into the *trans* oxazolidin-2-one **2b** in 75% yield. However, when the *cis* aziridine **1d** obtained by reaction of **6b** with triphenylphosphine–diethyl azodicarboxylate was reacted with di-*tert*-butyl dicarbonate and sodium iodide in acetone, only a complex mixture was obtained, but the *cis* oxazolidin-2-one **2d** was not detected.

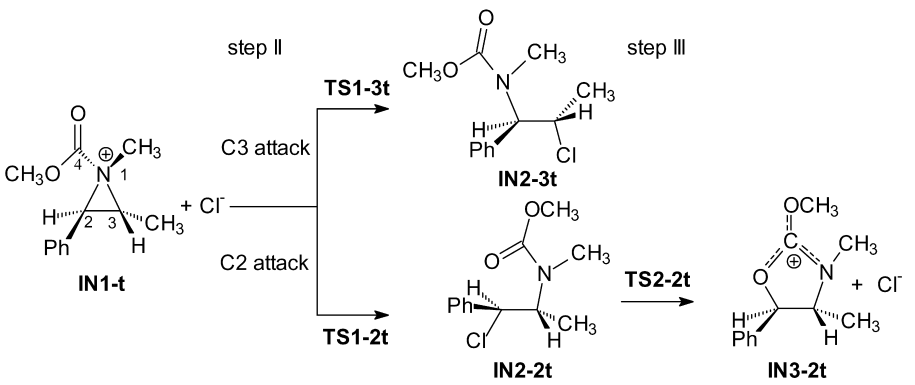
1. Theoretical studies on the mechanism

In order to explain the unlike behaviour of the *trans* and *cis* 1,2,3-trisubstituted aziridines **1a–d** a theoretical study was carried out. For the stereoselective conversion of the *trans* trisubstituted aziridines **1a** and **1b** into the *trans* oxazolidin-2-ones **2a** and **2b**, respectively, a stepwise mechanism was proposed (see Scheme 3). The first step is the nucleophilic attack of the nitrogen atom of the *trans* aziridines **1a** and **1b** to a carbonyl group of di-*tert*-butyl dicarbonate with formation of an aziridinium cation intermediate **7**. The ring-opening of the aziridinium **7** promoted by the nucleophilic attack of the iodide anion to the C2 carbon atom affords the urethane iodide **8**. The subsequent displacement of iodide in compound **8** through the intramolecular nucleophilic attack of the carbonyl oxygen atom of the urethane framework of **7** affords the cationic *O*-alkylated oxazolidin-2-one intermediate **9**. This intermediate yields the final *trans* oxazolidin-2-ones **2a** and **2b** through the extrusion of the *tert*-butyl group (see Scheme 3).

At this stepwise mechanism, while the second step is responsible for the regioselectivity observed at the *trans* aziridine **1a**, the formation of the iodide intermediates **8** and the subsequent intramolecular displacement of iodide are responsible for the observed retention of the C2 configuration on the *trans* oxazolidin-2-ones **2a** and **2b**. The formation of the intermediate **8** could take place also through a stepwise process in which the ring-opening of the aziridinium intermediate **7** could be done without the participation of the iodide anion to give a carbocationic intermediate. However, this path was discarded because of the stereospecificity of the reaction excludes the formation of a planar carbocation, and the fact that when the reaction was made experimentally in presence of chloride instead of iodide the formation of the oxazolidin-2-ones did not take place.[1]



Scheme 3.



Scheme 4.

In order to give light for the proposed mechanism, the steps II and III, which are responsible for the regio and *trans* stereoselection, were theoretically studied. A preliminary AM1 semi-empirical[5] study of the potential energy surface (PES) for complete models that included the bulky Boc framework and the iodide anion allowed to locate the corresponding intermediates **7**–**9**. However, all attempts to locate the corresponding transition structures (TS) at this semi-empirical level were unsuccessful. Therefore, ab initio calculations at the HF/6-31G*[6] computational level were necessary in order to perform a complete characterization of the PES. A reduced model where the bulky *tert*-butyl group of the Boc was replaced by a methyl group and the iodine atom by the chlorine atom was used in order to do feasible the ab initio calculations. A schematic representation of the steps II and III, including the atom numbering, for the *trans* 3-methyl-2-phenylaziridine is given in Scheme 4, while the total and relative energies are in Table 1. In Figure 1 the energy profiles for the stationary points corresponding to the ring-opening and ring-closure steps for the *cis* and *trans* aziridines are shown. The geometries of the TSs are displayed in Figure 2.

Table 1. HF/6-31G* total energies (au) and SCRF relative energies (kcal/mol, in parentheses, ε=20.7) for the stationary points corresponding to the ring-opening and ring-closure steps for the aziridinium intermediates **IN1-t** and **IN1-c**

	In vacuo	In acetone	
trans Aziridines			
IN1-t	−667.678662	−667.739785	
TS1-2t	−1127.334849	−1127.370939	(0.8)
TS1-3t	−1127.331575	−1127.364290	(5.0)
IN2-2t	−1127.417058	−1127.422165	(−31.3)
IN2-3t	−1127.414800	−1127.420780	(−30.5)
TS2-2t	−1127.359572	−1127.386235	(−8.8)
IN3-2t	−1127.396539	−1127.415944	(−27.4)
cis Aziridines			
IN1-c	−667.670849	−667.733198	
TS1-2c	−1127.330453	−1127.364600	(0.7)
IN2-2c	−1127.414800	−1127.420799	(−34.6)
TS2-2c	−1127.354008	−1127.375799	(−6.4)
IN3-2c	−1127.394177	−1127.414038	(−30.4)

Relative to **IN1-t**+Cl^- or **IN1-c**+Cl^-. The total energy of Cl^- in acetone is −459.632432 a.u.

The step II is the ring-opening of the aziridinium intermediate **IN1-t** to give the corresponding urethane chloride **IN2-2t**, while the step III corresponds with the ring-closure of **IN2-2t** to give the cationic *O*-alkylated oxazolidin-2-one intermediate **IN3-2t**. For the ring-opening process two regioisomeric path are possible depending on the nucleophilic attack of the chloride anion to the C2 or C3 carbon atoms of the aziridinium intermediate **IN1-t** (see Scheme 4). Due to the ionic character of some species, the relative energies were obtained in acetone (see Section 3.1). The ring-opening process is thermodynamically very favourable, ca. −31 kcal/mol, because of the formation of the neutral urethane chlorides **IN2-2t** and **IN2-3t**. In addition, this step presents a very low activation barrier. The relative energies of **TS1-2t** and **TS1-3t** relative to the aziridinium intermediate **IN1-t** plus chloride anion are 0.8

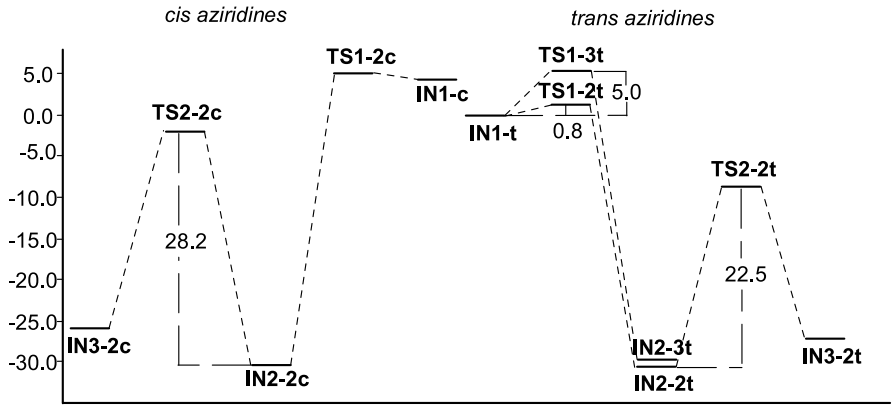


Figure 1. Energy profiles (in kcal/mol, acetone) for the stationary points corresponding to the ring-opening and ring-closure steps for the aziridinium intermediates **IN1-t** and **IN1-c**.

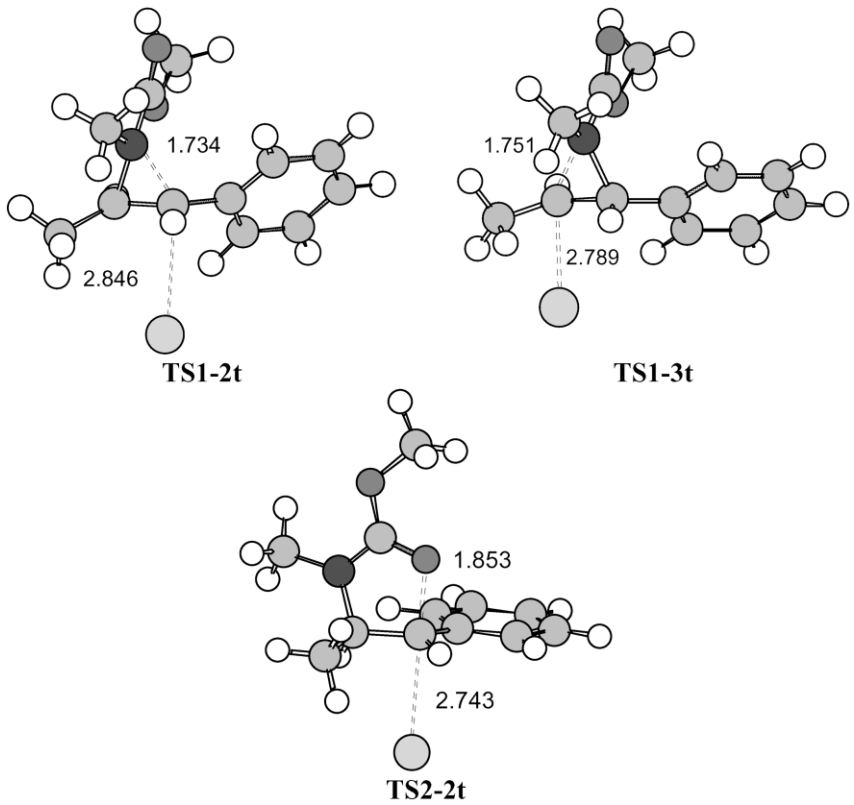
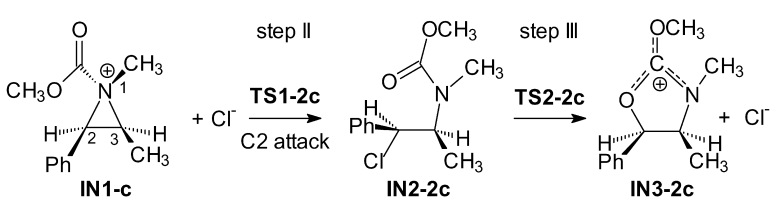


Figure 2. Transition structures corresponding to the ring-opening, **TS1-2t** and **TS1-3t**, and ring-closure, **TS2-2t**, steps for the *trans* aziridinium intermediate **IN1-t**. The values of the bond lengths directly involved in the process are given in angstroms.

and 5.0 kcal/mol, respectively. In consequence, in acetone **TS1-2t** is 4.2 kcal/mol less energetic than **TS1-3t**. This energetic result, which is in reasonable agreement with the experiments, allows us to explain the formation of the 5-phenyl-oxazolidin-2-one **2a**. Therefore, the larger stabilization of the TS corresponding to the nucleophilic attack of the chloride anion to the benzylic C2 position of aziridinium intermediate **IN1-t** accounts for the observed regioselectivity.

The step III corresponds with the formation of the oxazolidin-2-one ring through the internal nucleophilic attack of the carbonylic oxygen atom of the urethane to the chloride substituted C2 carbon atom of **IN2-2t**. Due to the large regioselectivity found at the step II, the ring-closure for the intermediate **IN2-3t** was not studied. The activation energy for the ring-closure via **TS2-2t** is 22.5 kcal/mol. Although the process is slightly endothermic, 2.9 kcal/mol, the subsequent extrusion of the *tert*-butyl cation framework on **9**, and its posterior conversion in isopropene turn on this step as irreversible. The presence of one α nitrogen atom and two α oxygen atoms at the carbocationic C4 center of the cationic *O*-alkylated oxazolidin-2-one intermediate **IN3-2t** accounts for the large stability of this intermediate (see **IN3-2t** in Scheme 4); **IN3-2t** is 27.4 kcal/mol less energetic than the isomeric aziridinium **IN1-t** (see Fig. 1).

In order to explain the unlike reactivity of the *trans* and *cis* 1,2,3-trisubstituted aziridines, the ring-opening and ring-closure steps for the *cis* aziridinium intermediate **IN1-c** were also studied (see Scheme 5). Assuming a similar regioselectivity than that observed at the *trans* aziridinium **IN1-t**, we considered only the attack of the chloride anion to the benzylic C2 position of **IN1-c**. The barrier for this nucleophilic attack via **TS1-c2** is 0.7 kcal/mol. Therefore, this barrier is similar to that found for the ring-opening of the *trans* aziridinium intermediate **IN1-t** via **TS1-2c**. These results are in agreement with the disappearing of both *trans* and *cis* disubstituted aziridines at the experimental conditions. However, a different result was found for the ring-closure step. The activation energy for this step via **TS2-2c** is 28.2 kcal/mol. Therefore, this barrier is 5.7 kcal/mol larger than that found for the *trans* isomer via **TS2-2t**. These energetic results allow us to explain the unlike



Scheme 5.

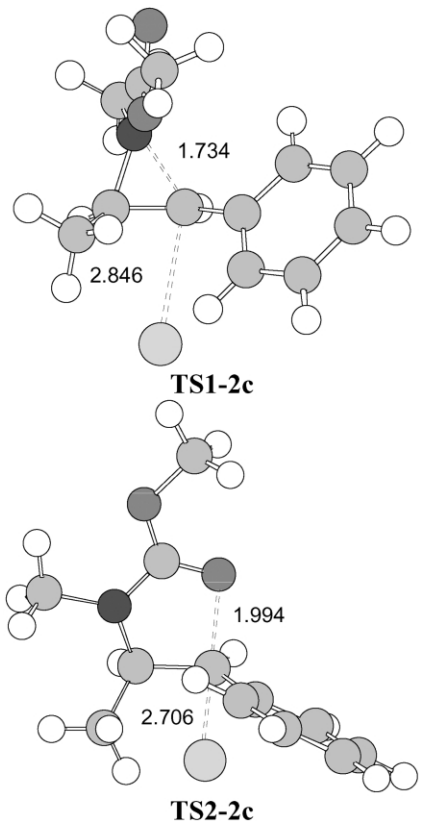


Figure 3. Transition structures corresponding to the ring-opening, **TS1-2c**, and ring-closure, **TS2-2c**, steps for the *cis* aziridinium intermediate **IN1-c**. The values of the bond lengths directly involved in the process are given in angstroms.

reactivity for the *trans* and *cis* 1,2,3-trisubstituted aziridines. While the *trans* aziridines **1a** and **1b** afford directly the *trans* oxazolidin-2-one **2a** and **2b** through an intramolecular iodide displacement, for the *cis* aziridines **1c** and **1d** other competitive channels associated with the intermolecular substitution of iodide can be operative as a consequence of the large energy for the intramolecular ring-closure.

For the TSs associated with the ring-opening process of the *trans* aziridinium **IN1-t** the lengths of the Cl–C forming and C–N breaking bonds are 2.846 and 1.734 Å at **TS1-2t** and 2.789 and 1.751 Å at **TS1-2c**, respectively (see Fig. 2). A similar lengths are found at the reaction of the *cis* isomer **IN1-c**, 2.846 and 1.734 Å at **TS1-2c**, respectively (see Fig. 3). For the TSs associated with the ring-closure processes, the lengths of the O–C forming bond and Cl–C breaking bond are 1.853 and 2.743 Å at **TS2-2t**, and 1.994 and 2.706 Å at **TS2-2c**, respectively. These lengths indicate that for the ring-closure processes the more favourable *trans* reactive channel is more advanced.

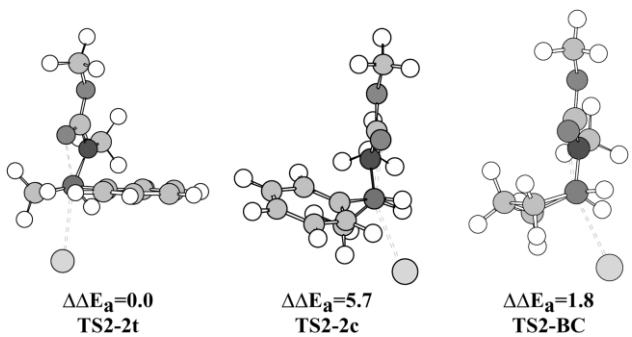


Figure 4. *anti* and eclipsed arrangements of the C2 phenyl and C3 methyl substituents at the antiperiplanar TSs **TS2-2t** and **TS2-2c**. The TS corresponding with the ring-closure, **TS2-BC**, for the 5-membered bicyclic aziridine is also included. $\Delta\Delta E_a$, in kcal/mol, are relative to the ΔE_a for **TS2-2t**.

A conformational analysis along the C2–C3 bond for the TSs associated with the ring-closure step, **TS2-2t** and **TS2-2c**, shows that whereas the former has the C2 phenyl and C3 methyl substituents in an *anti* arrangement in the latter these substituents are in an eclipsed arrangement (see Fig. 4). Therefore, the hindrance that appears between the methyl and phenyl substituents at the eclipsed arrangement, is responsible for the larger energy of **TS2-2c**; the *cis* **TS2-2c** is ca. 6.2 kcal/mol more energetic than *trans* **TS2-2t**. In consequence, intermediates as **IN2-2c** can try other competitive intermolecular nucleophilic substitutions of iodide, for instance the attack of the $BocO^-$ anion generated in the first step, allowing to explain the non-formation of the *cis* oxazolidin-2-one intermediate **IN3-2c**. However, the presence of the 5 or 6-membered-ring at the *cis* bicyclic aziridines prevents the C2–C3 bond-rotation allowing, in consequence, the formation of the *cis* bicyclic oxazolidin-2-ones by an intramolecular iodide displacement (see **TS2-BC** in Fig. 4).[1,7]

The values of the unique imaginary frequency of the TSs associated with the ring-opening process are 334 cm^{-1} at **TS1-2t**, 366 cm^{-1} at **TS1-3t** and 307 cm^{-1} at **TS1-2c**; while these values for the TSs associated with the ring-closure are 402 cm^{-1} at **TS2-2t** and 324 cm^{-1} at **TS2-2c**. Analysis of the atomic motion along these vibrational frequencies indicates that these TSs are mainly associated with the motion of the N and C atoms along the C–N bond-breaking for the TSs associated with the step II, and the C and O atoms along the C–O bond-formation for the TSs associated with the step III; the motion of the Cl atom is negligible at these TSs.

The extent of bond-formation and bond-breaking along a reaction pathway is provided by the concept of bond order (BO). This theoretical tool has been used to study the molecular mechanism of chemical reactions.[8] To follow the nature of these processes, the Wiberg bond indices[9] have been computed using the natural bond orbital analysis[10] as is implemented in Gaussian 98.[11] The BO values for the N–C breaking bond at the TSs associated with the ring-opening process are ca. 0.5, while the BO values for the Cl–C forming bond are 0.1. These BO values, which are in agreement with the vibrational frequencies, indicate that these TSs are associated with high asynchronous processes where the N–C breaking bonds are more advanced than the Cl–C forming-bonds. Finally, the BO values for the O–C forming bond at the TSs associated with the ring-closure process are 0.4, while the BO values for the Cl–C breaking bond are ca. 0.2. Therefore, these TSs correspond also with asynchronous processes where the Cl–C bond-breaking is more advanced than the O–C bond-formation.

2. Conclusions

The reaction of *N*-alkylaziridines with di-*tert*-butyl dicarbonate and sodium iodide in acetone was reported in previous works as a new synthetic procedure for the stereoselective preparation of oxazolidin-2-ones. In the present work we found that while *trans* 1,2,3-trisubstituted aziridines give *trans* oxazolidin-2-ones in good yield, the *cis* disposition of the substituents at C2 and C3 in monocyclic aziridines is a limiting factor for the ring expansion. Ab initio theoretical calculations for these reactions show that while the ring-opening process assisted by the chloride anion is regioselective and takes place with inversion of the carbon atom involved on the nucleophilic attack, the subsequent ring-closure is responsible for the retention of the configuration at the final *trans* oxazolidin-2-ones. On the other hand, the hindrance that appears between the substituents at the C2 and C3 positions of the *cis* monocyclic aziridines along the intramolecular ring-closure prevents the formation of the corresponding *cis* oxazolidin-2-ones.

3. Experimental

3.1. Computational details

All calculations were carried out with the Gaussian 98 suite of programs.[11] An extensive characterization of the PES was carried out at the HF/6-31G*[6] level to ensure that all relevant stationary points were located and properly characterized. The optimizations were carried out using the Berny analytical gradient optimization method.[12] The stationary points were characterized by frequency calculations in order to verify that the TSs have one and only one imaginary frequency.

Since the mechanism involves ionic species, the inclusion of solvent effects is necessary in order to obtain accurate energies. The solvent effects, acetone, was considered by HF/6-31G* single point calculations at stationary points involved on the reaction using a relatively simple self-consistent reaction field (SCRF)[13] based on the polarizable continuum model (PCM)[14] of the Tomasi's group. The solvent used in the experimental work is acetone. Therefore, we have used its dielectric constant at 298.0 K, ε=20.7.

3.2. General procedures

Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography was performed on Merck silica gel (60 F_{254}) plates and flash column chromatography was accomplished on Merck Kieselgel 60 (230–240 mesh). Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured at room temperature in a Perkin Elmer 241 polarimeter. IR spectra were recorded for KBr discs using a FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-300 spectrometer. Chemical shifts (δ) are reported in ppm with TMS as a internal standard. High-resolution mass spectra were obtained using a VG Autospec, TRIO 1000 (Fisons) instrument. The ionisation mode used in mass spectra were electron impact (EI) at 70 eV or chemical ionisation (CI).

3.2.1. (2*R*,3*S*) and (2*S*,3*R*) 3-Methylamino-2-butanol (5b).[2] A solution of *trans* 2,3-dimethyloxirane (20 mmol) in methanol (30 ml) and a solution of aqueous methylamine (40%) (3 ml) was heated in a pressure reactor at 100°C for 8 h. After cooling, the mixture was concentrated in vacuo affording the 3-methylamino-2-butanol (**5b**)[2] (97%). Colourless oil. ν_{max} (cm^{-1}) 3351 and 2979; δ_H ($CDCl_3$) 0.69 (3H, d, *J*=6.6 Hz), 0.81 (3H, d, *J*=6.4 Hz), 2.11 (3H, s), 2.20 (1H, dq, *J*=6.6, 3.0 Hz), 3.54 (1H, dq, *J*=6.6, 3.0 Hz) and 4.60 (2H, bs); δ_C ($CDCl_3$) 13.4 (q), 17.9 (q), 33.8 (q), 59.6 (d) and 67.1 (d). HRMS [EI], found: M$^+$ 103.1000. $C_5H_{13}NO$ requires M 103.0997.

3.2.2. (2*R*,3*R*) and (2*S*,3*S*) 3-Methylamino-2-butanol (6b).[2] A solution of *cis* 2,3-dimethyloxirane (20 mmol) in methanol (30 ml) and a solution of aqueous methylamine (40%) (3 ml) was heated in a pressure reactor at 100°C for 8 h. After cooling, the mixture was concentrated in vacuo affording the methylamino alcohol (**6b**) (98%). Colourless oil. ν_{max} (cm^{-1}) 3557 and 2978; δ_H ($CDCl_3$) 0.46 (3H, d, *J*=6.6 Hz), 0.64 (3H, d, *J*=6.6 Hz), 1.85 (3H, s), 2.81 (1H, m), 2.67 (1H, m) and 4.01 (2H, bs); δ_C ($CDCl_3$) 13.7 (q), 19.0 (q), 31.6 (q), 60.3 (d) and 68.53 (d). HRMS [CI] MH$^+$ 104.1070. $C_5H_{14}NO$ requires 104.1075.

3.3. Synthesis of aziridines

Method (a). To an ice-cooling and stirred solution of the appropriate amino alcohol (−)-ephedrine (**3a**), (+)-pseudoephedrine (**4a**), (2*R*,3*S*) and (2*S*,3*R*) 3-methylamino-2-butanol (**5b**) or (2*R*,3*R*) and (2*S*,3*S*) 3-methylamino-2-butanol (**6b**) (9 mmol) and triphenylphosphine (12.0 mmol) in dry ether (30 ml) under a nitrogen atmosphere, was slowly added diisopropyl azodicarboxylate (12.0 mmol) via syringe. The stirring was continued at 0°C for 24 h. A crystalline precipitate (triphenylphosphine oxide/diisopropyl hydrazinedicarboxylate complex) was filtered off and washed with hexane/ether 1:1 (30 ml). The filtrate was concentrate in vacuo and the crude products **1a**–**1d** which were used for the following reaction without further purification.

Method (b). To an ice-cooled and stirred solution of the appropriate amino alcohol (−)-ephedrine (**3a**), (+)-pseudoephedrine (**4a**), (2*R*,3*S*) and (2*S*,3*R*) 3-methylamino-2-butanol (**5b**) or (2*R*,3*R*) and (2*S*,3*S*) 3-methylamino-2-butanol (**6b**) (9 mmol) in chloroform (36 ml) was slowly added thionyl chloride (23.4 ml, 317 mmol) and heated at 60°C for 3 h. The mixture was then cooled at 0°C, treated with water (15 ml), alkalinized with aqueous NaOH 5 M, stirred at room temperature for 24 h and extracted with dichloromethane (3×100 ml). The organic extracts were dried with Na_2SO_4, filtered and concentrated to afford the crude products **1a**–**1d** which were used for the following reaction without further purification.

3.4. Synthesis of 1,3-oxazolidin-2-ones

Di-*tert*-butyl dicarbonate (9 mmol) in acetone (5 ml) was added to a mixture of the appropriate crude aziridine **1a**–**1d**

(9 mmol) and sodium iodide (9 mmol) in acetone (10 ml) and stirred at reflux temperature for 2 h. After removing the solvent, the residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (1:1) to afford **2a** or **2b**.

3.4.1. (4*S*,5*S*)-3,4-Dimethyl-5-phenyl-1,3-oxazolidin-2-one (2a).[4] White solid. From aziridine obtained by method (a), 84%. From aziridine obtained by method (b), 72%. Mp 45–46°C. $[\alpha]_D^{20}$=29.4 (*c* 3.46, $CHCl_3$). ν_{max} (cm^{-1}) 1757; δ_H ($CDCl_3$) 1.26 (d, 3H, *J*=6.2 Hz), 2.75 (3H, s), 3.45 (1H, m), 4.80 (1H, d, *J*=8.1 Hz) and 7.28 (5H, m); δ_C ($CDCl_3$) 17.1 (q), 28.5 (q), 61.1 (d), 82.2 (d), 125.7 (d), 128.6 (d), 128.7 (d), 137.4 (s) and 157.6 (s). HRMS [EI], found: M^+ 191.0941. $C_{11}H_{13}NO_2$ requires M 191.0946.

3.4.2. (4*S*,5*S*)+(4*R*,5*R*)-3,4,5-Trimethyl-1,3-oxazolan-2-one (2b). Colourless oil. From aziridine obtained by method (a) 80%. From aziridine obtained by method (b) 75%. ν_{max} (cm^{-1}) 1730; δ_H ($CDCl_3$) 1.18 (3H, d, *J*=6.2 Hz), 1.33 (1H, d, *J*=6.2 Hz), 2.70 (3H, s), 3.21 (1H, m) and 4.04 (1H, m); δ_C ($CDCl_3$) 17.6 (q), 19.5 (q), 28.9 (q), 60.5 (d), 77.8 (d) and 158.4 (s). HRMS [EI], found: M^+ 129.0788. $C_6H_{11}NO_2$ requires M 129.0789.

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